

**ANKARA YILDIRIM BEYAZIT UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCE**



**ALUMINA/GLASS COMPOSITES FOR LOW TEMPERATURE CO-  
FIRED CERAMICS (LTCC) AND RADOME APPLICATIONS**

**M. Sc. Thesis by**  
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**ANKARA**

**ALUMINA/GLASS COMPOSITES FOR LOW  
TEMPERATURE CO-FIRED CERAMICS (LTCC) AND  
RADOME APPLICATIONS**

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**ANKARA**

## M.Sc. THESIS EXAMINATION RESULT FORM

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# ALUMINA/GLASS COMPOSITES FOR LOW TEMPERATURE CO-FIRED CERAMICS (LTCC) AND RADOME APPLICATIONS

## ABSTRACT

A commercial  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  based glass at 20 wt% (G-20), 40 wt% (G-40), 50 wt% (G-50), 55 wt% (G-55), and 60 wt% (G-60) was added to  $\text{Al}_2\text{O}_3$  in order to determine composite compositions for specific applications such as substrate, low temperature co-fired ceramics (LTCC) and radome. Densification, phase formation and characterization of dielectric, mechanical and thermal properties were studied. The optimum densification temperatures were determined to be  $1350^\circ\text{C}$  for the G-20,  $1200^\circ\text{C}$  for the G-40, and  $850^\circ\text{C}$  for the G-50, G-55 and G-60. The sintering mechanism was liquid phase sintering for the G-20 and G-40, and viscous sintering for the G-50 to G-60. Main crystalline phase was  $\text{Al}_2\text{O}_3$  as well as anorthite crystallized after  $825^\circ\text{C}$ . Young's modulus decreased from 231 GPa for the G-20 to 105 GPa for the G-60. Flexural strength ranged between 387 MPa for the G-20 and 213 MPa for the G-60. Hardness also decreased with increasing amount of glass; 1058 HV for the G-20 and 679 HV for the G-60. Similarly, fracture toughness was  $4.5 \text{ MPa}/\sqrt{\text{m}}$  for the G-20 and  $1.9 \text{ MPa}/\sqrt{\text{m}}$  for the G-60. Dielectric constant and dielectric loss of the composites (G-20 and G-60) at 5 MHz were 8.76-7.32 and 0.0022-0.0081, respectively. Thermal conductivity decreased with increasing glass content; 1.25 W/m.K for G-40 and 0.98 W/m.K for the G-60 at  $75^\circ\text{C}$ . Thermal expansion coefficient decreased with increasing glass such that it was  $7.72 \text{ ppm}/^\circ\text{C}$  for the G-20 and  $6.66 \text{ ppm}/^\circ\text{C}$  for the G-60. Mechanical, thermal and dielectric properties were considered together for possible applications. For substrate applications, all composites were proposed due to low dielectric constant. For LTCC applications, the G-50 to G-60 composites were proposed due to lower sintering temperature, lower dielectric properties together with moderate mechanical and thermal properties. The G-55 composite was successfully fabricated by tape casting and co-fired with silver electrode. For radome applications, the G-20 and G-40 composites were proposed due to lower density, higher sintering temperature, lower Young's modulus and thermal expansion coefficients.

**Keywords:** Glass, glass-ceramic, glass ceramic composite, sintering, liquid phase sintering, viscous sintering, LTCC, substrate, radome.

# ALÜMİNA/CAM KOMPOZİTLERİN DÜŞÜK SICAKLIKTA BERABER PİŞEN SERAMİKLER (LTCC) VE RADOM UYGULAMALARI

## ÖZ

Elektronik altlık, düşük sıcaklıkta beraber pişirilen seramikler (LTCC) ve radom uygulamalarında kullanılmak üzere, alüminaya ağırlıkça %20 (G-20), %40 (G-40), %50 (G-50), %55 (G-55) ve %60 (G-60) oranlarında ticari  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -CaO bazlı bir cam eklenerek, alümina/cam kompozitler incelenmiştir. Kompozitlerin yoğunlaşma davranışları ve faz oluşumları, dielektrik, mekanik ve ısı özellikleri incelenmiştir. Kompozitlerin optimum sinterleme sıcaklıkları G-20 için  $1350^\circ\text{C}$ , G-40 için  $1200^\circ\text{C}$ , G-50, G-55 ve G-60 için  $850^\circ\text{C}$  olarak belirlenmiştir. Sinterleme mekanizmaları G-20 ve G-40 için sıvı faz sinterleme, G-50, G-55 ve G-60 için viskoz sinterlemedir. Bütün kompozitlerde ana kristal faz  $\text{Al}_2\text{O}_3$  olmakla birlikte  $850^\circ\text{C}$ 'den sonra anortit kristalleşmesi görülmüştür. Elastik modül değeri G-20'de 231 GPa'dan G-60'da 105 GPa'a düşmüştür. Bükülme mukavemeti G-20'de 387 MPa ile G-60'da 213 MPa arasında değişmiştir. Sertlik değeri de artan cam miktarıyla düşmüştür; G-20'de 1058 HV ve G-60'da 679 HV'dir. Benzer şekilde kırılma tokluğu G-20'de  $4.5 \text{ MPa}/\sqrt{\text{m}}$  ve G-60'da  $1.9 \text{ MPa}/\sqrt{\text{m}}$ 'dir. Kompozitlerin (G-20 ve G-40) 5 MHz'deki dielektrik sabitleri 8.76 ve 7.32 ve dielektrik kayıpları 0.0022 ve 0.0081'dir. Isıl iletkenlik değeri artan cam miktarıyla düşmüştür; G-40'da  $1.25 \text{ W/m.K}$  ve G-60'da  $0.98 \text{ W/m.K}$ 'dir. Benzer şekilde  $75^\circ\text{C}$ 'de ısı genleşme katsayısı G-20'de  $7.72 \text{ ppm}/^\circ\text{C}$  ve G-60'da  $6.66 \text{ ppm}/^\circ\text{C}$ 'dir. Uygun uygulama alanları için mekanik, ısı ve dielektrik özellikler beraber göz önünde bulundurulmuştur. Elektronik altlık için düşük dielektrik sabitinden dolayı bütün kompozitler uygun bulunmuştur. LTCC uygulaması için düşük sinterleme sıcaklığı ve dielektrik sabiti ile birlikte orta derecede mekanik ve ısı özelliklerinden dolayı G-50, G-55 ve G-60 kompozitleri uygun bulunmuştur. Ayrıca G-55 kompozisyonu şerit döküm yöntemiyle başarılı bir şekilde üretilmiş ve gümüş elektrot ile birlikte pişirilmiştir. Radom uygulamaları için düşük yoğunluk, yüksek sinterleme sıcaklığı, düşük elastik modül ve ısı genleşme katsayısından dolayı G-20 ve G-40 kompozitleri uygun bulunmuştur.

**Anahtar Kelimeler:** Cam, cam-seramik, cam seramik kompozit, sinterleme, sıvı faz sinterleme, viskoz sinterleme, LTCC, elektronik altlık, radom.

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## ABBREVIATIONS

|                         |                  |
|-------------------------|------------------|
| $\mu\text{m}$           | Micrometer       |
| $\text{Al}_2\text{O}_3$ | Alumina          |
| $\text{CaO}$            | Calcium Oxide    |
| $\text{K}_2\text{O}$    | Potassium Oxide  |
| $\text{MPa}$            | Mega Pascal      |
| $\text{Na}_2\text{O}$   | Sodium Oxide     |
| rpm                     | Round per minute |
| $\text{SiO}_2$          | Silica           |
| vol%                    | Volume percent   |
| wt%                     | Weight percent   |

## Acronyms

|      |                                    |
|------|------------------------------------|
| EDS  | Energy Dispersive Spectrometry     |
| HTCC | High Temperature Co-Fired Ceramics |
| HV   | Vickers Hardness                   |
| IC   | Integrated Circuit                 |
| LPS  | Liquid Phase Sintering             |
| LTCC | Low Temperature Co-Fired Ceramics  |
| MCM  | Multi-Chip Module                  |
| MLC  | Multilayer Ceramics                |
| OM   | Optical Microscope                 |
| SEM  | Scanning Electron Microscopy       |
| SSS  | Solid State Sintering              |
| XRD  | X-ray Diffraction                  |

## LIST OF SYMBOLS

|            |                               |
|------------|-------------------------------|
| $R_t$      | Thermal shock resistance      |
| $^{\circ}$ | Degree                        |
| $\mu$      | Poisson's ratio               |
| $2\theta$  | Diffraction angle             |
| C          | Capacitance                   |
| E          | Young's modulus               |
| J          | Joule                         |
| K          | Dielectric constant           |
| m          | Meter                         |
| N          | Newton                        |
| $\eta$     | Viscosity                     |
| P          | Force                         |
| Pa         | Pascal                        |
| T          | Temperature                   |
| $T_g$      | Glass transition temperature  |
| $T_m$      | Melting temperature           |
| V          | Volume                        |
| W          | Watt                          |
| $\alpha$   | Thermal expansion coefficient |
| $\Delta$   | Difference                    |
| $\epsilon$ | Permittivity                  |
| $\rho$     | Density                       |
| $\rho$     | Density                       |
| $\sigma$   | Stress                        |

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# CHAPTER 1

## INTRODUCTION

### 1.1 Glass

Glass is a non-crystalline amorphous solid where there is no long-range order in the arrangement of its molecular constituents. The word “glass” means shiny and the word “vitreous” comes from the Latin word of glass. There is no distinction between glass and vitreous. The glass materials have great importance on both traditional and newly developed ceramics. Silicates comprise the most important part of the glasses [1]. Formation of glass materials and some of their properties will be discussed in this part.

#### 1.1.1 Glass Formation

Glasses are usually formed by supercooling from the melt. The final temperature must be adjusted such that cooling does not allow rearrangement of molecules and atoms to a more stable crystalline form (e.g., crystallization). This can be seen from the volume-temperature graph represented in Figure 1.1. When the liquid is slowly cooled, transformation from liquid to solid occurs at melting point ( $T_m$ ) with a discontinuous change in volume (Figure 1.1 (a)). However, if the liquid is supercooled, the volume of liquid decreases below the melting point until there is a decrease in expansion coefficient at a transformation range often called as glass transition temperature ( $T_g$ ). The  $T_g$  corresponds to intersection temperature between the curves of glass and super cooled liquid. Below  $T_g$ , the glass structure is not able to rearrange. Generally, the specific volume of the glass is greater than the crystal form, hence the density of the glass is lower. Besides, different cooling rates for glass formation give different configurations of glassy state as represented in Figure 1.1 (b). A faster cooling rate does not allow the structure to rearrange and results in higher  $T_g$  and lower density, while slower cooling rate gives lower  $T_g$  and higher density [2, 3].

The glass structure is simultaneously determined by the volume-temperature relation and the viscosity of the glass. The viscosity of glass is highly temperature dependent.

A solid material has a viscosity of more than  $10^{15}$  Poise (P). The viscosity at  $T_g$  is typically about  $10^{13}$  to  $10^{14}$  P and hence the sample behaves like a solid [1, 3].

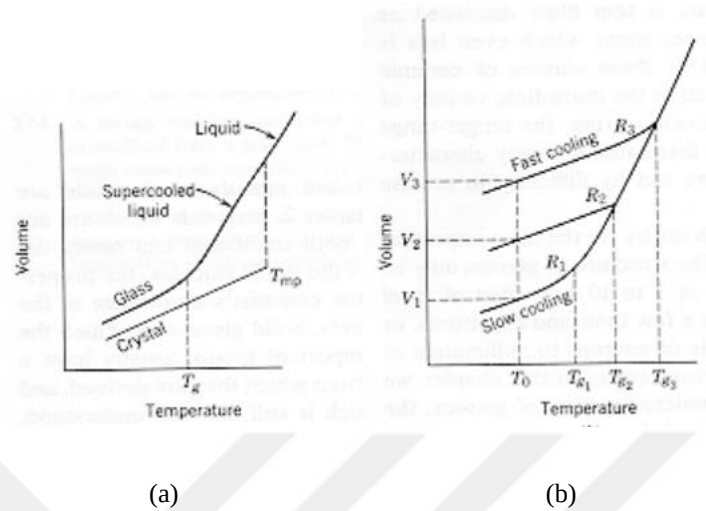


**Figure 1.1** Specific volume-temperature relations; (a) relations of liquid, glass and crystal; (b) volume of glass at different cooling rates [2].

### 1.1.2 Glass Structure

There are a lot of models to describe the glass structures. In the crystallite model, X-ray diffraction pattern of the glasses is distinguished from the crystalline ones in that glasses exhibit broad peaks and the crystalline materials have sharp and strong peaks. This observation considers glasses to be composed of very small crystals. However, this model is not supported today with its original form [2].

The random-network model considers the glasses as three-dimensional networks in which there is no symmetry and periodicity as well as the unit of the structure is not repeated at regular intervals. In oxide glasses, the network is formed by oxygen polyhedra. In Figure 1.2, crystal and glass structure of a  $A_2O_3$  oxide where A is metal atom shown in two-dimension. The crystalline structure has a continuous ordered network while the amorphous structure has a random atomic positions distributed through the structure [2, 3].

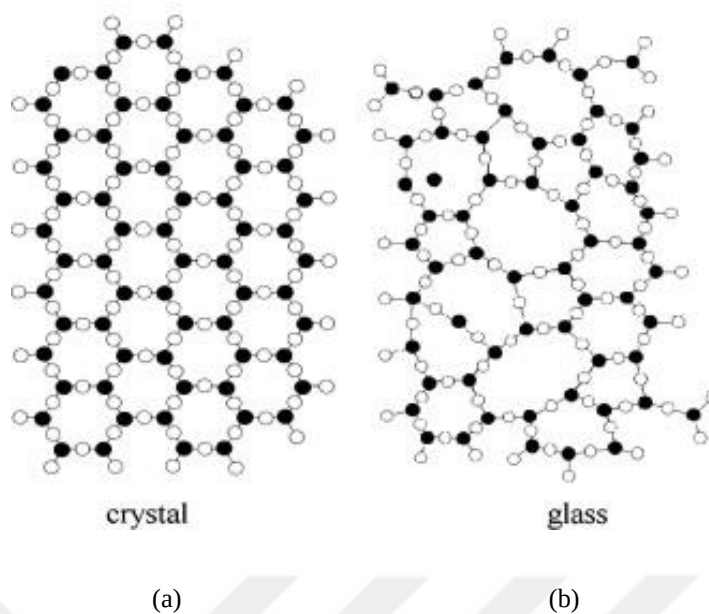


**Figure 1.2** Schematic representation of (a) ordered crystalline structure; (b) random network of glass structure [2].

Zachariasen proposed and stated four rules for glass forming tendency of oxides [4]:

1. Each oxygen atom should be linked to no more than two cations.
2. The number of oxygen atoms surrounding the cation must be small, 4 or less.
3. Oxygen polyhedra share corners rather than edges or faces.
4. At least three corners of each polyhedron should be shared.

Generally, the glass-forming oxygen polyhedra are triangle or tetrahedra and cations which form that polyhedra are referred to as network formers.  $\text{SiO}_2$  is the fundamental glass network former. Generally glasses contain additives to alter processing and properties. A schematic structure of a sodium silicate glass is represented in Figure 1.3.  $\text{Na}_2\text{O}$  molecules result in formation of nonbridging oxygens in  $\text{SiO}_2$  network, and local charge neutrality is provided by  $\text{Na}^+$  ions. Since alkali ions like  $\text{Na}^+$  provide extra oxygen ions which modify the network structure, they are called network modifiers. The modifiers reduce the processing temperature of silicate glasses.  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$  and  $\text{PbO}$  are commonly used modifiers in silicate glasses. Cations with higher valance and lower coordination number than the alkali and alkaline earth metals may contribute to network structure and are termed as intermediates such as  $\text{Al}_2\text{O}_3$ . Various cations

according to their roles as network formers, modifiers, and intermediates in oxide glasses are classified in Table 1.1 [2, 3].

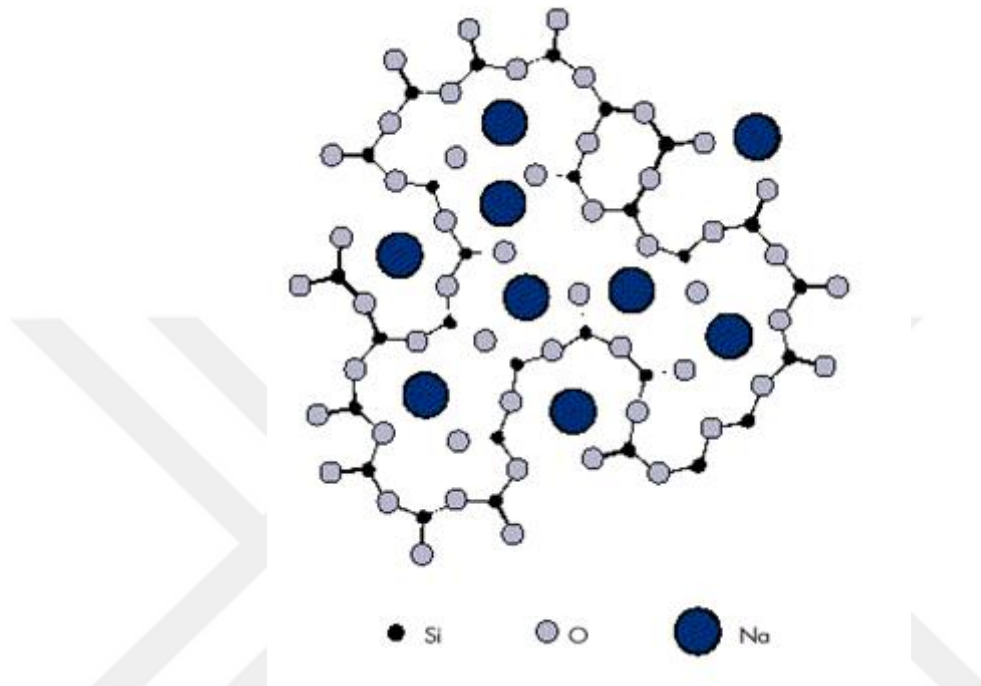


**Figure 1.3** Schematic representation of sodium silicate glass structure [2].

**Table 1.1** Cations in oxide glasses as network formers, modifiers, and intermediates [2].

| Role            | Cation | Valance | Coordination Number |
|-----------------|--------|---------|---------------------|
| Network formers | Si     | 4       | 4                   |
|                 | B      | 3       | 3                   |
|                 | Ge     | 4       | 4                   |
| Intermediates   | Ti     | 4       | 6                   |
|                 | Al     | 3       | 6                   |
|                 | Zr     | 4       | 8                   |
|                 | Be     | 2       | 4                   |
|                 | Zn     | 2       | 2                   |
| Modifiers       | Ca     | 2       | 8                   |
|                 | Na     | 1       | 6                   |
|                 | K      | 1       | 9                   |
|                 | Pb     | 2       | 6                   |
|                 | Mg     | 2       | 6                   |
|                 | Li     | 1       | 4                   |

### 1.1.3 Properties

Some common commercial glass compositions and their characteristics and applications are listed in Table 1.2.

**Table 1.2** Some common commercial glass compositions and characteristics [5].

| Glass Type            | Composition (wt%) |                   |     |                                |                               |                                              | Characteristics and Applications                                               |
|-----------------------|-------------------|-------------------|-----|--------------------------------|-------------------------------|----------------------------------------------|--------------------------------------------------------------------------------|
|                       | SiO <sub>2</sub>  | Na <sub>2</sub> O | CaO | Al <sub>2</sub> O <sub>3</sub> | B <sub>2</sub> O <sub>3</sub> | Other                                        |                                                                                |
| Fused silica          | >99.5             |                   |     |                                |                               |                                              | High melting temperature, very low coefficient of expansion (shock resistance) |
| 96% Silica (Vycor)    | 96                |                   |     |                                | 4                             |                                              | Thermally shock and chemically resistant laboratory ware                       |
| Borosilicate (Pyrex)  | 81                | 3.5               |     | 2.5                            | 13                            |                                              | Thermally shock and chemically resistant ovenware                              |
| Container (soda-lime) | 74                | 16                | 5   | 1                              |                               | 4 MgO                                        | Low melting temperature, easily worked, also durable                           |
| Fiberglass            | 55                |                   | 16  | 15                             | 10                            | 4 MgO                                        | Easily drawn into fibers-glass-resin composites                                |
| Optical flint         | 54                | 1                 |     | 18                             |                               | 37 PbO, 8 K <sub>2</sub> O                   | High density and high index of refraction optical lenses                       |
| Glass-ceramic         | 70                |                   |     |                                |                               | 4.5 TiO <sub>2</sub> , 2.5 Li <sub>2</sub> O | Easily fabricated; strong; resists thermal shock-ovenware                      |

## 1.2 Glass-Ceramics

Glass-ceramics are ceramic materials produced through controlled crystallization of a glass composition. Typically, the microstructure of glass-ceramics is 50–95 vol% crystalline and the remainder is residual glass phase. The mechanical properties of glass-ceramics are aimed to be improved with respect to the parent glass. Besides, other distinct properties can be tailored which are beneficial for particular applications. Therefore, glass-ceramic materials can be used in a wide range of applications, enabling the development of unique microstructures with specific properties [6, 7].

There are two approaches to obtain glass-ceramics; glass-ceramic route (Glass Ceramics) and glass+ceramic route (Glass Ceramic Composites) [8].

### **1.2.1 Glass-ceramic route**

In this approach, the glass ceramic is produced from original glass that is devitrified by a sequential thermal process. The main processing routes for glass ceramic production are; conventional method where volume crystallization occurs from a bulk glass, and powder method where sinter-crystallization occurs from a glass powder compact [6, 7]. In conventional method, the materials are melted to form the glass and then glass ceramic is produced by controlled crystallization of glass through two steps, namely, nucleation and crystal growth. A schematic processing cycle of crystallization of a glass for conventional method is represented in Figure 1.4. In the nucleation step, small nuclei formed in the glass and followed by crystal growth step where crystals are enlarged by heating to a higher temperature as illustrated in Figure 1.5. The nucleation of crystalline phases in glass can take place through homogeneous nucleation, when the nuclei forms in the absence of foreign boundaries, or heterogeneous nucleation, when crystalline phases form from foreign boundaries, such as impurity particles. This process is a consequence of the energy reduction where amorphous phase is transformed into a more stable phase with ordered geometry. For controlled crystallization of glass-ceramics, parent glass should be free of defects such as cracks, holes or surface roughness to obtain uniform body. Generally, growth of crystals in an amorphous phase yields a nonuniform body with large grain size. Nucleating agents are generally used to obtain small and uniform crystals in the crystallized bodies where the crystals are precipitated from their surfaces.  $\text{TiO}_2$  and  $\text{ZrO}_2$  are the most commonly used nucleating agents [2].

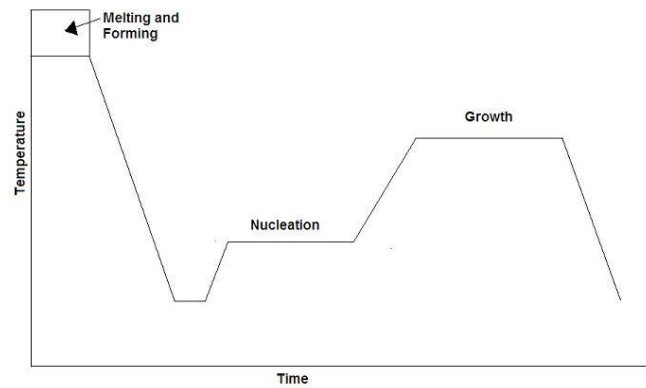


**Figure 1.4** Schematic processing cycle of crystallization of a glass for conventional method [2].

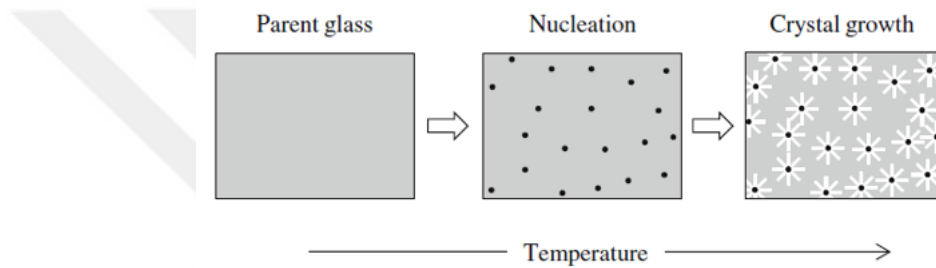


**Figure 1.5** Glass ceramic formation by conventional method [6].

In the powder method, glass powder is compacted, and then sintered via viscous flow followed by crystallization. A schematic formation process of glass ceramics by powder method is illustrated in Figure 1.6. When the glass transforms into glass ceramic, complete densification should be achieved together with the sufficient crystallization. Otherwise, high porosity and low amount of crystallinity can result in relatively poor mechanical properties. The resulting properties of glass ceramics can be adjusted by controlling the degree of crystallization [8].

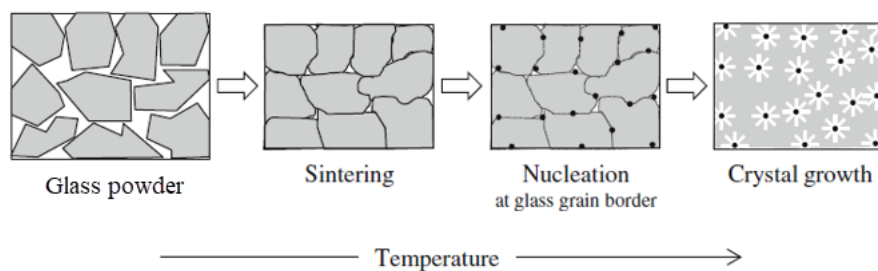


**Figure 1.6** Sintering and crystallization of glass ceramics [6].

### 1.2.2 Glass+ceramic route

In the second approach, the starting material consists of low softening point glass and crystalline ceramic powders. The densification of glass ceramic composite is attained by softening of glass and wetting ceramic powders during sintering. The volume fraction of the glass determines the sintering characteristics which take place by liquid phase sintering or viscous sintering. Depending on the reactivity between glass and ceramics, densification can be via non-reactive, partially reactive or completely reactive system. The ceramic particles dissolve slightly in glass during sintering in non-reactive systems. In the reactive systems, glass does not only serve as a bonding agent between ceramic particles but also react with them at the sintering temperature. For partially reactive systems, the dissolution of ceramic in glass is localized and limited, and no particle growth and shape accommodation are observed. The crystalline phase increases viscosity during sintering and minimize distortion, and also increases the mechanical strength of the glass ceramic composite. The glass phase connects the network and allows tailoring of properties. Thus, the properties of the final glass ceramic composites are controlled by the ratio of glass to ceramic and the individual properties of the mixtures [8].

## 1.3 Sintering

Sintering is a process of bonding particles to produce density-controlled solid structure by applying a thermal energy, during which the particles bond each other thru diffusion while improving the strength and lowering the system's total energy. General fabrication steps towards sintering are shown in Figure 1.7. Sintering is applied to instill strength to the shaped powder. Sintering is also necessary to prepare materials with desirable properties by controlling microstructure. The processing variables influence sintering conditions and the resulting microstructure. Density is the most important parameter to be considered in sintering since it is related with sintering kinetics and associated with many physical properties (e.g., mechanical, thermal, optical, etc.) of the materials. Generally, aim of sintering is to produce a body with controlled density as well as controlled microstructure for required applications [9–11].

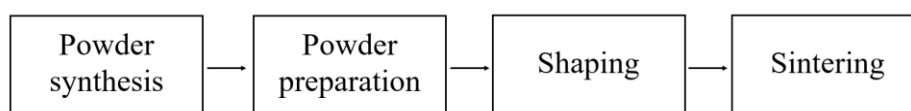


**Figure 1.7** General fabrication steps towards sintered parts.

Sintering lowers the free energy of the system by reducing surface area (solid-vapor) with the formation of interparticle bonds (solid-solid). The main driving force for sintering is the curvature of the free surfaces. Sintering is accompanied by densification and grain growth as schematically represented in Figure 1.8. At the beginning, particles are in point contact and interparticle bonds (or necks) form. Then, necks become grain boundaries to eliminate free surfaces, resulting in densification and grain growth. A dimensional shrinkage also accompanies. The kinetics of diffusion must also be considered. The driving force provides a motivation for sintering, but diffusion is required to induce sintering. In ceramics, mass transport occurs dominantly by solid-state diffusion. Alternatively, particle melting results in a solid-liquid mixture which enhances the mass transport. Another sintering technique applies pressure which enhances bonding and particle deformation. In some techniques, a chemical reaction occurs between mixed particles leading to formation of a new phase simultaneously by sintering under an exothermic reaction [9–11].

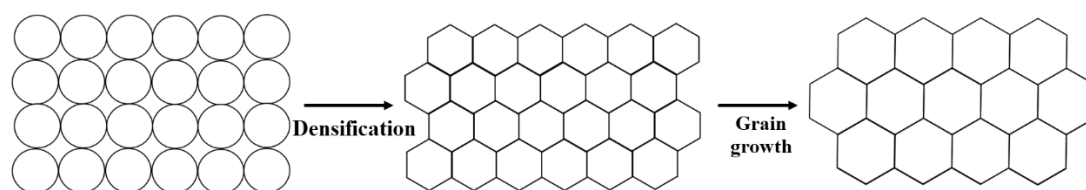


**Figure 1.8** Basic schematic representation of sintering under driving force [9].

In general, sintering temperature is nearly at temperatures higher than one-half of the melting temperature. Sinterability and the sintered microstructure can be affected by two major parameters material parameters and processing parameters. The material parameters include particle size, particle size distribution, particle shape, state of

agglomeration and chemical composition of powder. For instance, smaller particles have higher surface area and more energy per unit, which promotes faster sintering. Processing parameters include temperature, time, atmosphere, pressure, heating and cooling rate which are mostly thermodynamic variables. All of these parameters have significant effects on sintering [9, 11].

Sintering process has two basic techniques, namely, pressure assisted and pressureless sintering. Pressure assisted sintering involves application of an external pressure which increases the driving force and kinetics of densification. Hot pressing and hot isostatic pressing are used for pressure assisted sintering. However, most of the sintering processes are performed without an external pressure (pressureless sintering). Pressureless sintering processes can be basically divided into three types, solid state sintering, liquid phase sintering and viscous sintering. The densification of the particles occurs completely in solid state in the solid state sintering, while a liquid phase forms during sintering in the liquid phase sintering and viscous sintering [9–11]. A variety of sintering types are represented in a schematic phase diagram given in Figure 1.9. For an A-B powder mixture of  $X_1$  composition, solid state sintering takes place at temperature  $T_1$  while liquid phase sintering occurs at temperature  $T_3$  for the same composition. Viscous sintering occurs when the volume fraction of liquid is high enough that densification is achieved without any grain shape change during sintering. Transient liquid phase sintering is a combination of liquid phase sintering and solid state sintering where a liquid phase forms at the beginning but vanishes as sintering proceeds and densification is completed by solid state sintering. For instance, temperature  $T_2$  is above eutectic temperature so a liquid phase is formed during heating for composition  $X_1$ . However, the liquid phase disappears during sintering since the equilibrium phase is solid [9].

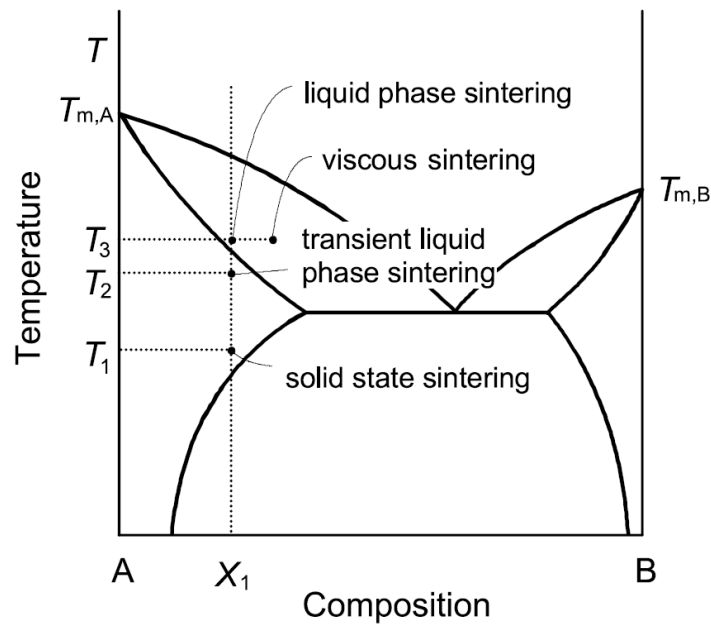


**Figure 1.9** Schematic representation of various sintering types [9].

To sum up, liquid phase sintering provides easy processing compared to the solid-state sintering and reduces the processing cost, however it degrades some physical properties like mechanical properties. Composition and amount of liquid are important parameters in controlling the properties and microstructure [9].

### 1.3.1 Solid State Sintering

Solid state sintering occurs by diffusional transport of matter from higher chemical potential regions to lower chemical potential regions. Solid state sintering has three overlapping stages; initial stage, intermediate stage, and final stage as schematically represented in Figure 1.10. There is no clear distinction between these stages [9, 11].

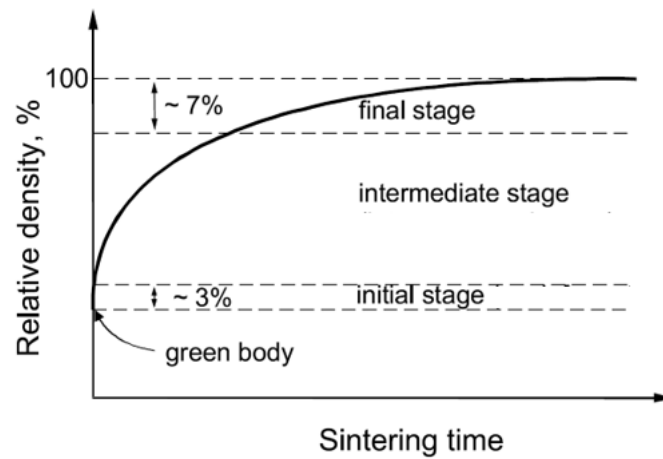


**Figure 1.10** Schematic representation of densification stages by solid state sintering [9].

**Initial Stage:** The initial stage is identified by neck formation. At the beginning, spherical particles of the same size are assumed to be in weakly point contact to each other. A simplified two sphere model is represented in Figure 1.11. Interfacial surface energy is lowered by neck growth between contacting powders where solid/vapor interfaces are replaced with solid/solid interfaces and forming grain boundary along the neck. Here  $D$  is the particle diameter and  $X$  is the neck diameter. Neck formation is defined with neck size ratio of  $X/D$  which reaches nearly 0.3 in this stage [9–11].

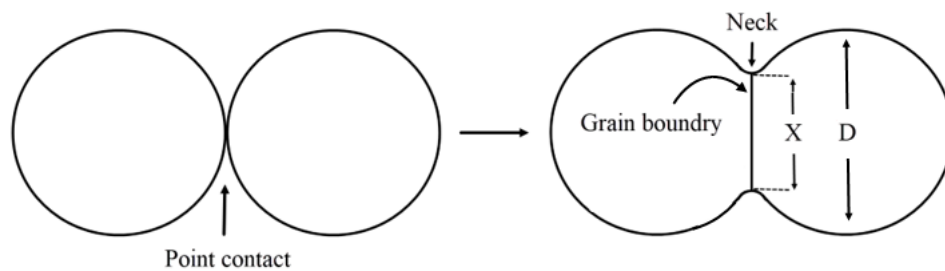


**Figure 1.11** Schematic representation of a neck formation between two particles [11].

The curvature gradient promotes the mass flow in this stage and contact surfaces are flattened. Surface area is extensively lowered with neck growth. Smaller particle size gives more curvature due to high surface area and rapid neck growth while higher temperature promotes faster mass transport. The matter transport is mainly by surface

diffusion where mass flows from surface source to surface sink so the shrinkage is low ( $\sim 3\%$ ) and densification is limited [9–11].

**Intermediate stage:** This stage is characterized by pore rounding and densification. Considerable densification up to  $\sim 93\%$  is achieved in this stage. The driving force is elimination of remaining surface area due to curvature around cylindrical pores. Figure 1.12 illustrates the pore shapes at intermediate stage on a tetrakaidecahedron (14-sided) grain that is idealized final shape of the spheres at fully density. Open cylindrical pore network is located along grain boundary edges. Generally, pores remain attached to the grain boundary through this stage. Pores located at grain boundaries are desired due to easier pore elimination. Mass transport is mainly by means of grain boundary and volume diffusion. At the same time, grain growth initiates as pores are eliminated from grain boundaries [9, 10].

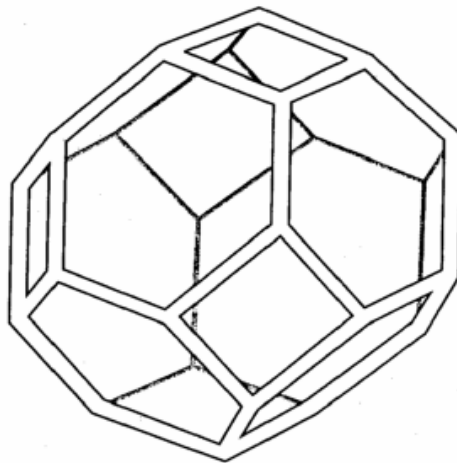


**Figure 1.12** Schematic representation of a tetrakaidecahedron grain with cylindrical pore structure [10].

**Final stage:** This stage is idealized by closed pores attached to the grain corners as represented in Figure 1.13. The cylindrical pores at intermediate stage becomes unstable and breakdown into closed pores. Pore shape depends on the pore location; spherical if not attached to the grain boundary, lenticular on grain boundary or grain edge, and rounded at grain corners. Generally, pores start to close at nearly 15% porosity and they are totally closed at 5%. Densification is slower in final stage compared to the initial and intermediate stages. Pores attached to the moving grain

boundary can shrink and disappear easily. However if pores are trapped inside the grains, it is very difficult to eliminate them since densification occurs by volume diffusion [10].

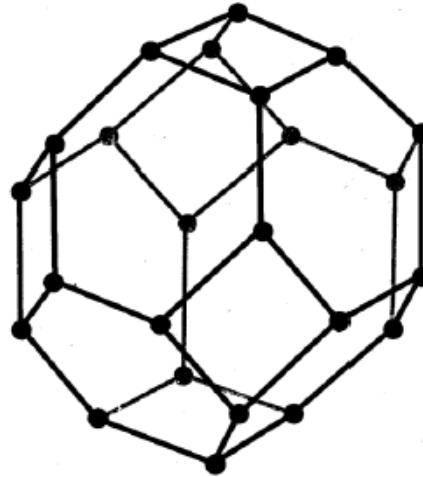


**Figure 1.13** Schematic representation of a tetrakaidecahedron grain with spherical pores at grain corners [10].

### 1.3.2 Liquid Phase Sintering

Liquid phase sintering consists of a major phase and an additive phase in which the additive phase melts over a temperature range to form a liquid. Sintering rate is accelerated due to enhanced mass transport since diffusion through a liquid is much faster than in a solid. The solubility of solid in liquid promotes wetting of solid by liquid which promotes a capillary force to penetrate liquid between solid particles. Therefore, compared to solid state sintering, sintering temperature is lowered due to formation of a liquid, yielding enhanced densification. In firing of ceramics with a glass phase, glass transforms into a viscous liquid at high temperatures. The liquid phase solidifies upon cooling and forming an amorphous phase along grain boundaries, which may alter some properties [12].

In liquid phase sintering, there are three stages for densification, namely, rearrangement, solution-precipitation and final stage (solid stage). These stages are summarized in Figure 1.14. In the heating stage, the liquid forms. Sintering is accompanied by rearrangement in the initial step, followed by solution-precipitation

and final stages. If a volume fraction of liquid content is greater than 36 vol%, full densification is achieved with only rearrangement of particles that is generally referred to as viscous sintering [11]. A schematic representation of liquid phase sintering stages is shown in Figure 1.15.

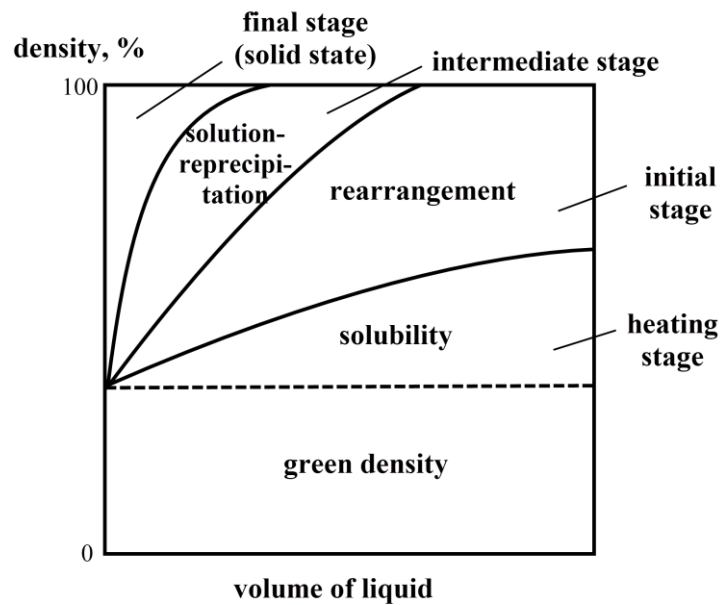


**Figure 1.14** Densification stages in liquid phase sintering as a function of liquid content [10].

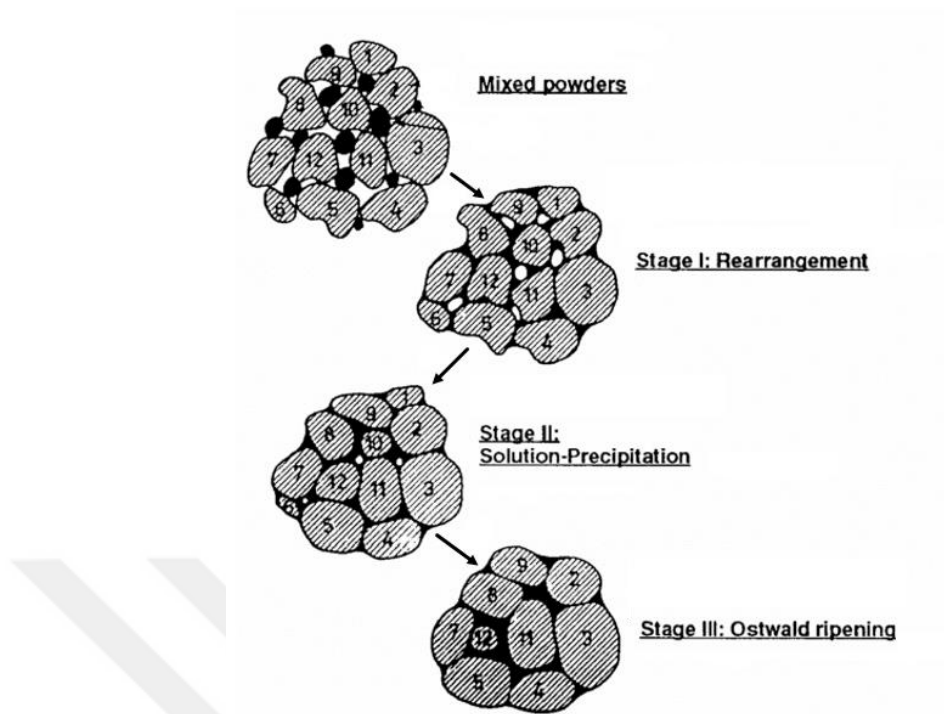


**Figure 1.15** Schematic representation of liquid phase sintering stages [11].

**Rearrangement:** Initial densification is achieved on formation of a liquid phase which wets and spreads over the solid surfaces. As a result, solid-vapor interfaces are eliminated and pores form in the liquid. Therefore, driving force in liquid phase sintering is the reduction of liquid-vapor interface. Wetting of solid by liquid promotes a capillary force to penetrate liquid between solid particles. A compressive stress is generated at particle contacts which aids the rearrangement of particles. The key parameters are low contact angle, low dihedral angle, and high solubility of the solid in the liquid. Low dihedral angle is required for liquid penetration between particles and low contact angle provides wetting and capillary force, influencing the rearrangement. Smaller particles and higher solubility of solid in liquid enhance densification in this stage [10, 11].

Volume content of liquid is important in this stage. For higher liquid content (>36 vol%), densification can be completed by only rearrangement and grains are mostly spherical in shape and separated from each other. However, for lower liquid contents, final stage sintering is dominant for densification and the grains are fairly flat. In

moderate amount of liquid, grains are a fairly rounded shape due to solution-precipitation process [10]. The microstructural changes associated with varying liquid content is illustrated in Figure 1.16. White regions corresponds to copper which forms the liquid and dark regions corresponds to cobalt that are the solid grains [13].

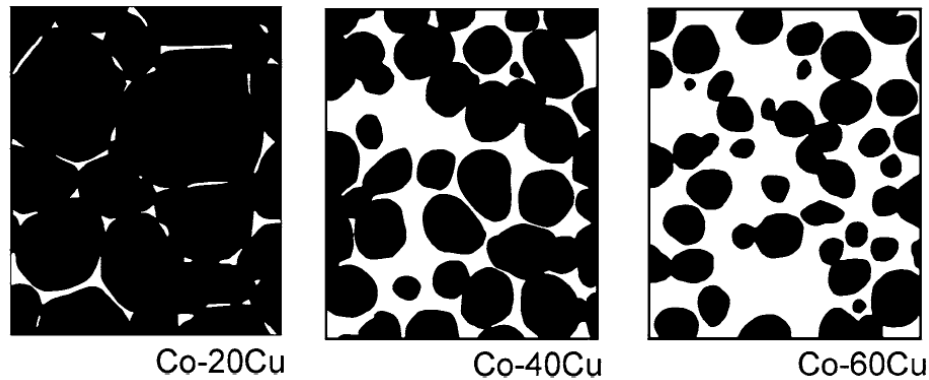


**Figure 1.16** Microstructure variations in the Cu-Co system with Cu amount [13].

**Solution-Precipitation:** Solution refers to dissolution of solid in liquid from the regions with higher chemical potential and precipitation refers to precipitation of solid from the liquid on the regions with lower chemical potential. Furthermore, dissolution of small grains, grain growth and grain shape accommodation occurs in this step [10, 11].

Densification by contact flattening was described by Kingery [14]. An idealized two sphere model is represented in Figure 1.17. As a result of the compressive capillary force of a wetting liquid, chemical potential differences at the contact point rises which leads to preferential dissolution from the contact points. Precipitation takes place away from the contact regions, resulting in low-energy flat interfaces [11].

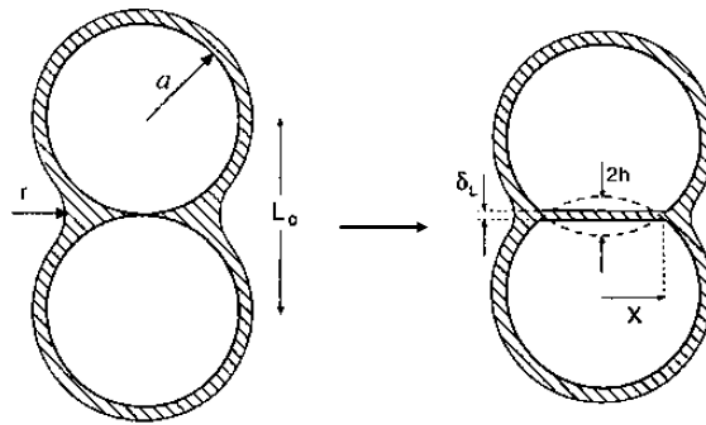


**Figure 1.17** Schematic representation of contact flattening [11].

As sintering proceeds, elimination of pores and growth of grains occur simultaneously in a liquid matrix. Densification by grain shape accommodation (also referred as Ostwald ripening) allows growing of grains and gives more efficient packaging. The energy of the system is decreased by elimination of pores, and preferential dissolution of high-energy smaller grains and reprecipitation on low-energy larger grains. Figure 1.18 shows an illustration of grain shape accommodation which is expected in low liquid contents [10, 11].

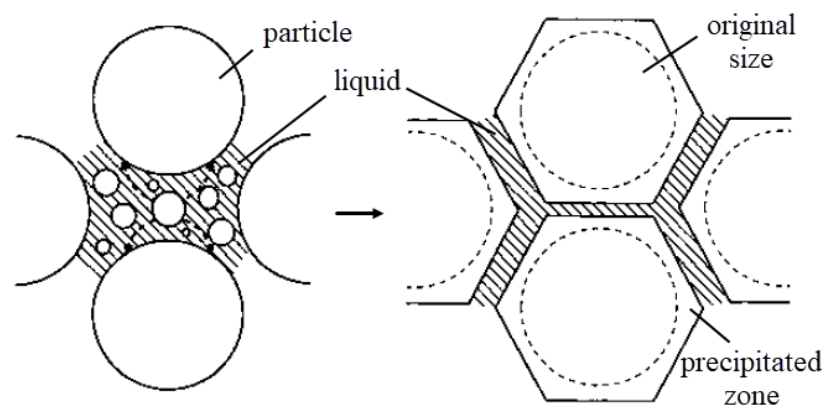


**Figure 1.18** Schematic representation of grain shape accommodation [11].

**Final Stage:** After considerable densification, a rigid solid skeleton is formed, and the final densification occurs by solid state sintering. Pores are isolated and spherical. Also, total porosity is less than 7% in the final stage. For the systems with low solid

solubility in liquid, solid-solid contacts between the grains are formed as illustrated in Figure 1.19. Neck growth between particles leads to a more rigid structure [9, 10, 11].

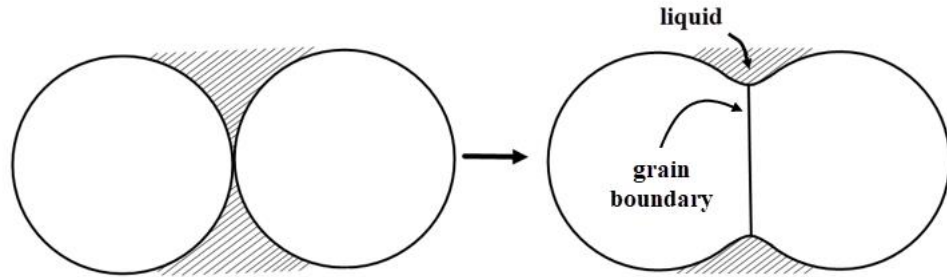


**Figure 1.19** Schematic representation of final stage [10].

### 1.3.3 Viscous Sintering

As mentioned earlier, if the liquid amount is higher than 36 vol%, densification is achieved by viscous flow, also referred to as vitrification. The sufficient amount of liquid covers the solid surfaces and densification is achieved mainly by rearrangement. In silicate systems, a viscous glass is formed at sintering temperature and aids to bond particles [2, 11].

There are two important factors, particle size and viscosity. As discussed above, decrease in particle size enhances the densification. Viscosity is another parameter which depends on temperature and composition of the glass. Arrhenius dependence of viscosity to temperature is as follows [2]:

$$\eta(T) = \eta_0 \cdot \exp\left(\frac{E}{R \cdot T}\right) \quad (1.1)$$

where  $\eta$  is viscosity (N.s/m<sup>2</sup>),  $T$  is temperature (K),  $\eta_0$  is a coefficient,  $E$  is the activation energy (J/mol) and  $R$  is the universal gas constant (J/mol.K). Viscosity decreases with increasing temperature. Also at a controlled temperature, the viscosity of the glass can be reduced by changing the composition [2].

## 1.4 Properties

### 1.4.1 Mechanical Properties

Key mechanical properties are briefly explained here. Formulations are given in the Experimental Procedures section together with the required ceramic dimensions and measurement parameters.

#### 1.4.1.1 *Young's modulus*

The elastic extension of a body under a stress corresponds to an increase in separation distance between the atoms. So, it is related with the forces between atoms. In two phase systems, the overall modulus is intermediate between two components [2].

#### 1.4.1.2 *Flexural strength*

Flexural strength is the maximum tensile strength at fracture. In glasses, fracture is non-crystallographic and they have an easy cleavage plane, while in crystalline materials, fracture occurs along a crystallographic cleavage plane. In polycrystalline ceramics, obstacles like grain boundaries can inhibit the crack propagation and prevent the fracture of the body [2].

Griffith [2] also stated that flaws can initiate the fracture at a specific applied stress in brittle solids, which explains the scattered experimental results particularly for ceramic materials.

#### 1.4.1.3 *Hardness*

Hardness is the material's resistance to localized plastic deformation (e.g. indentation). Hardness tests are performed because the hardness test is simple, inexpensive, nondestructive, and some mechanical properties can be estimated from the hardness results [5].

#### 1.4.1.4 *Fracture toughness*

Fracture toughness is a measure of materials ability to absorb energy up to fracture. Materials with high fracture toughness, the nucleated crack preferentially passes each

gain boundary to distribute energy. However, in glasses, crack tip extension has an easy cleavage plane due to lack of grain boundaries. Similarly, fracture toughness is lower in single crystals compared with the polycrystal ones. Microstructure in polycrystal materials put some obstacles such as grain boundaries to the propagating crack and reflect an irregular crack path such as intragranular or intergranular fractures. Porosity in the structure can act as stress concentrators but in some cases, pores can tend to hinder crack propagation [2].

#### 1.4.1.5 Thermal shock resistance

The thermal expansion of the ceramics can lead to undesired stress formation which can easily lead to the fracture of a component by means of thermal shock. For example, temperature gradients within the material generally lead to formation of thermal stresses between surface and interior, depending on the volume of the body. Fracture occurs when the stress is sufficient to extend a crack thru the body. Thermal shock resistance parameter (TSR) is used to define crack propagation or crack arrest under a thermal stress. For extremely rapid cooling, the critical temperature difference is defined with a TSR parameter of  $R_t$  (°C) and represented as;

$$R_t = \Delta T = \frac{\sigma_f \cdot (1 - \mu)}{\alpha \cdot E} \quad (1.2)$$

where  $\sigma_f$  is the flexural strength (Pa),  $\mu$  is the poison's ratio,  $\alpha$  is the thermal expansion coefficient (CTE) (ppm/°C) and  $E$  is the Young's modulus (Pa). However, in this formula testing geometry is not clear.  $R'_t$  (K.W/m) is defined as second parameter of TSR which includes thermal conductivity of material and represented as;

$$R'_t = \Delta T = \frac{\sigma_f \cdot k \cdot (1 - \mu)}{\alpha \cdot E} \quad (1.3)$$

where  $k$  is thermal conductivity (W/m.K). Higher TSR values gives the higher thermal shock resistance.  $E$  and CTE play important role in TSR such that lower values are preferred for higher TSR. When thermal conductivity is included,  $R_t$  and  $R'_t$  values can vary [15].

### 1.4.2 Dielectric Properties

Dielectric constant is the relative permittivity of a material with respect to permittivity of vacuum. Increase in dielectric constant increases the charge storing capacity. In an externally applied electrical field, the polarization occurs where the atomic or molecular dipole moments are aligned. There are 4 types of polarization source; electronic, ionic, orientation, and space charge. Electronic polarization is induced in all materials consisting of electron clouds. It results in displacement of negatively charged electron position relative to positive nucleus of atom. Ionic polarization occurs in only ionic materials. Lattice ions are charged under an applied electric field and increase the dipole moment of lattice ions. Orientation polarization is found in materials possessing permanent dipole moments. Rotation of the permanent moments in the direction of applied field results in polarization. Space charge polarization is because of charges blocked by interfaces and grain boundaries where they are trapped. Contribution of these polarization can be one or more of these, depending on the frequency of the electric field applied [2, 11].

Materials are polarizable with different ways. According to frequency response, dielectric constant of a material varies. Under an electrical field, the dipoles are reoriented with the field. In practice, the materials show a relaxation time for charge transport and relaxation frequency for realignment of the dipoles. Change in the polarization mechanism as a function of frequency vary the dielectric constant [2, 11] as represented in Figure 1.20.

Dielectric loss is the electrical energy absorption by the material subjected to an alternating electrical field which results in heat dissipation through the material. The origin of the dielectric loss is related with the delay between the electrical field and the electrical displacement vectors. The dielectric losses depend on crystal structure, frequency, and temperature [2, 16].

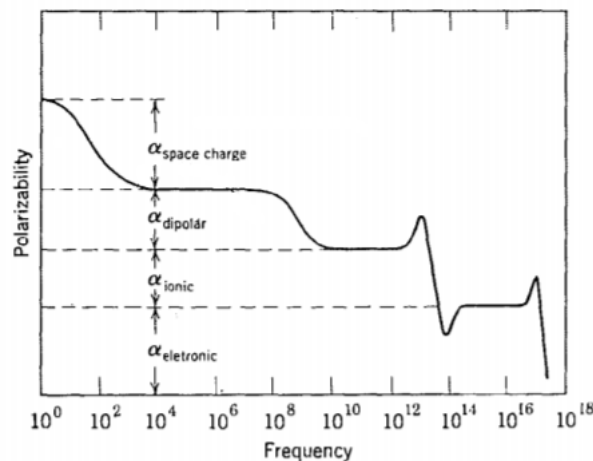


**Figure 1.20** Frequency dependence of polarization contributions to the dielectric constant [2].

### 1.4.3 Thermal Properties

#### 1.4.3.1 Thermal Conductivity

Thermal conduction is a heat energy transfer process under a temperature gradient. Thermal conductivity (W/m.K) of a material indicates the relative easiness or difficulty of energy transfer through the material. Therefore, it depends on bonding of atoms. Heat is conducted by two modes, vibration of lattice and free electrons. Free electron contribution is predominant in metals giving rise to higher thermal conductivity. In lattice vibration, energy is carried by phonons. Ceramics conduct energy by only phonons. Thermal conductivity is determined by the mean free path of the phonons which depends on the temperature, phonon-phonon interactions, and scattering from lattice defects in the solid. The mean free path of phonons is determined by phonon-phonon interactions. Phonon scattering increases with temperature resulting in short mean free path. Generally, thermal conductivity decreases with increasing temperature. Phonons are also scattered by imperfections in structure such as chemical impurities, secondary phases, dislocations, grain boundaries. Therefore, single crystals have higher conductivities compared to the polycrystal ones (e.g. 36 W/m.K in single crystalline  $\text{Al}_2\text{O}_3$  and 30 W/m.K in polycrystalline  $\text{Al}_2\text{O}_3$ ). In the same way, the random network (e.g. highly disordered and irregular) or amorphous structure of glasses limits the mean free path of the phonons. The thermal conduction in amorphous materials is mainly by atomic or molecular migration which results in very low

conductivity values. The atomic or molecular migration improves with increasing temperature, which increases thermal conductivity of the amorphous materials [2, 17, 18].

#### *1.4.3.2 Thermal Expansion*

Volume of a crystal increases with temperature due to lattice vibrations that lead to higher atomic separation and correspondingly lattice expansion. The thermal expansion coefficient (CTE,  $\alpha$ ,  $10^{-6}/K$ ) is a material property which demonstrates the material expansion upon heating. Thermal expansion coefficient is strongly related with crystal structure and bond strength. Materials with high bond strength such as diamond have low thermal expansion coefficients. Generally, CTE values for ceramics are lower than that of metals due to stronger ionic and covalent bonding. Silicate glasses normally have much lower CTE values due to the ability of absorption of vibrational energy by adjustment of bond angles in the disordered structure [2].

The CTE can be expressed in two ways that is defined at a certain temperature (true coefficient of thermal expansion,  $\bar{\alpha}$ ) or over a temperature range (mean coefficient of thermal expansion,  $\alpha$ ). The  $\alpha$  is obtained by the slope of length versus temperature plot, while the  $\bar{\alpha}$  is associated with the slope between two points on the curve. Generally,  $\bar{\alpha}$  increases with rising temperature. Hence, CTE values can vary with respect to temperature and the usage of either  $\alpha$  or  $\bar{\alpha}$  [19].

## **1.5 Applications**

### **1.5.1 Substrate**

Electronic substrates are insulating parts of the electronic components and widely used in the field of microelectronic packaging. The circuits are soldered on them, and the connections are carried out by the electrodes. Figure 1.21 shows an  $Al_2O_3$  ceramic substrate with circuit patterns. Modern electronics are based on the integrated circuits (IC) that consist of interconnected components such as transistors and resistors built up on a silicon chip. IC on a silicon chip is the central component of all logic and memory functions of electronic systems. Reliability of these circuits (microelectronic

packages) depends on insulating materials that serve as substrates. The microelectronic packaging refers to the assembly of functions that support, protect, provide power to, and transmit signals from the IC chip [20–23].

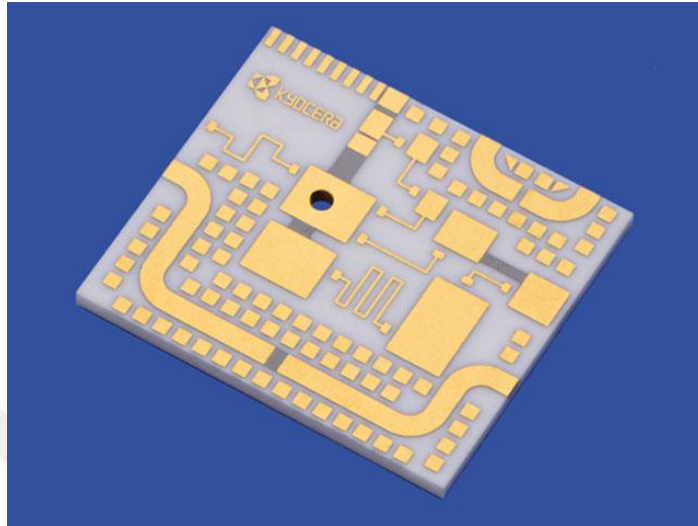


**Figure 1.21** An  $\text{Al}_2\text{O}_3$  ceramic substrate with circuit patterns [24].

There are two major types of substrates; ceramic based and polymer based. Printed circuit boards (PCB) are typically made up of organic polymer materials such as widely used FR-4. Alumina ( $\text{Al}_2\text{O}_3$ ) is the most widely used ceramic substrate material, which is sintered at nearly  $1600^\circ\text{C}$  [22]. Some of the properties of polymer and ceramic substrates are listed in Table 1.3. The main disadvantages of organic PCBs are their low thermal conductivity and high CTE values which lead to thermo-mechanical fatigue defects on chip components during thermal cycling and hence decrease the reliability of the components. Also, water absorption changes the mechanical and electrical properties of the substrates and effects the sensitive semiconductor parts [20–22].

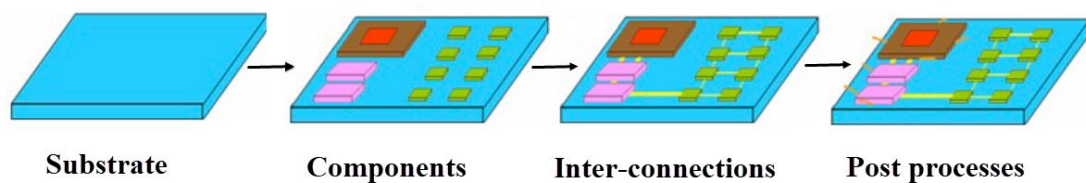
**Table 1.3** Some properties of polymer and ceramic substrates [20].

| Characteristics                             | PCB        | LTCC       | HTCC       |
|---------------------------------------------|------------|------------|------------|
| Guaranteed life time (years)                | 3          | >20        | >20        |
| Volume resistivity (ohm.m) at RT            | $>10^{11}$ | $>10^{12}$ | $>10^{12}$ |
| Thermal expansion coefficient, CTE (ppm/°C) | 16         | 6          | 7          |
| Flexural strength (MPa)                     | -          | 210        | 350        |
| Thermal conductivity (W/m.K) (RT to 400°C)  | 0.1        | 3          | 20         |
| Dielectric Constant (at 1MHz)               | 4.7        | 7.85       | 9.8        |
| Dielectric loss (at 1MHz)                   | 0.025      | 0.002      | 0.0004     |
| Integration of passive components           | L          | L, R, C    | L          |
| Hermeticity (torr)                          | $>10^{-3}$ | $<10^{-8}$ | $<10^{-8}$ |

L:inductor, R:resistor, C:capacitor

Ceramic substrates enable better thermal management due to their high thermal conductivities as compared to the polymers, and have matching thermal expansion coefficient (CTE) with integrated parts, which makes ceramic substrates attractive in microelectronic technologies. Also, they are preferred in high-performance applications where excellent thermal stability and impermeability are essential [20–22].

Production of a substrate is illustrated in Figure 1.22. The substrate provides housing for IC, other circuits and wiring patterns [23].

**Figure 1.22** A substrate processing [23].

### 1.5.2 LTCC

Rapid growth of information technology requires small, lightweight and multifunctional electronic components. Multilayer ceramics represent producing high-density electronic substrates by enabling integration of wiring into three-dimensional compact structure with highly desirable properties. Multichip Ceramic Modules (MCM) is a multilayer substrate for packaging ICs. Multilayer ceramics are an important part of MCM technology since they offer manufacturing of complex systems, allowing high density integration and packaging [8, 25].

Multilayer ceramic technology is divided into two main parts; High Temperature Co-Fired Ceramics (HTCC) and Low Temperature Co-Fired Ceramics (LTCC). HTCC are combined of a ceramic as insulating material (generally  $\text{Al}_2\text{O}_3$ ) and a metal as conductor material and co-fired at high temperatures ( $1500^\circ\text{C}$ – $1600^\circ\text{C}$ ). High sintering temperatures of ceramics allow to use only metals with high melting temperatures such as tungsten (W) and molybdenum (Mo). For high performance devices, the conductor metals should exhibit high electrical conductivity for high speed, undisturbed signal transmission and high performance. Thus, silver (Ag), gold (Au) and copper (Cu) are required in the fabrication of multilayer ceramic devices. A significant feature of these electrodes is their low melting temperature ( $T_m$ );  $961^\circ\text{C}$  for Ag,  $1063^\circ\text{C}$  for Au and  $1083^\circ\text{C}$  for Cu. Therefore, LTCC materials are developed to lower sintering temperature of ceramics. The fundamental requirement for fabrication of LTCC is “low” temperature firing which refers to a temperature that is lower than the melting temperature of the electrodes, namely, below  $950^\circ\text{C}$ . In order to obtain high sintered density with low firing temperature, glass is added to enhance sintering. The glass-ceramic route or glass+ceramic route (as discussed in Section 1.2) can be employed. Physical, thermal and electrical performance of LTCC primarily depend on the intrinsic properties and morphology of the ceramic phase, the amorphous phase, crystals formed and residual porosity [8, 25–28].

LTCC modules enable integration of active and passive electronic components such as filters, resistors (R), inductors (L) and capacitors (C) as shown in Figure 1.23. These components are embedded into layers enabling the fabrication of a monolithic

structure with increased functionality, performance and reliability. The communication between the components is provided by electrical vias, which increase wiring density and decrease signal path. Low electrical resistance metals at high frequencies and ceramics with low dielectric constant and loss makes LTCC suitable for the high frequency circuits required for high-speed data communications. Also, high integration density and miniaturizing devices enable potential application areas such as wireless communication systems, microwave products, IC packing of radars and antennas, RF devices and automotive applications [8, 23, 25, 28, 29].

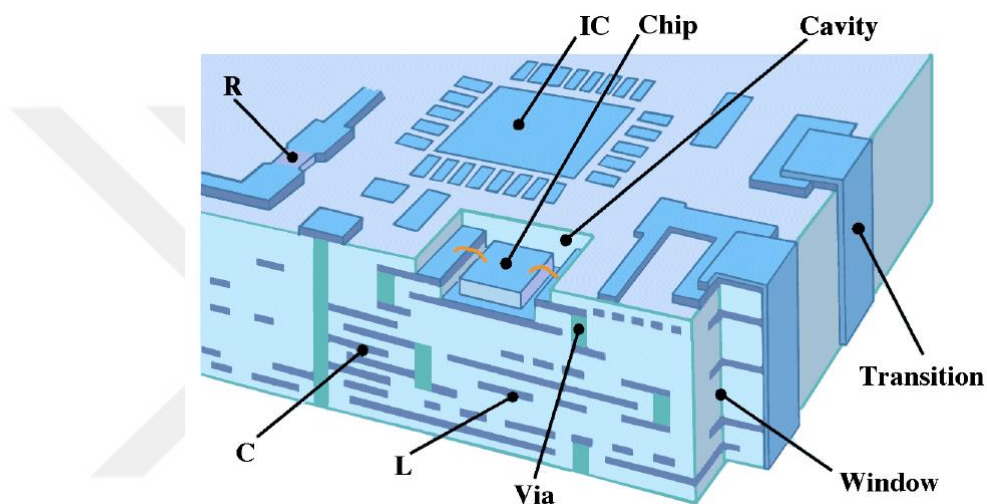


**Figure 1.23** An advanced LTCC package where the components are integrated into the module [23].

#### 1.5.2.1 Requirements

Some fundamental properties of commercial LTCC materials from leading companies are listed in Table 1.4. The general requirements for LTCC materials are as follows;

**Low Sintering Temperature:** For production of a module, the LTCC materials are cofired with an electrode. Therefore, the sintering temperature must be lower than the melting point of the electrode. Generally, Ag is used as electrode material because of its higher conductivity and chemical stability. The melting temperature of Ag is 961°C. So, the sintering temperature of the LTCC should be less than 950°C [8, 25, 30].

**Low Dielectric Constant and Dielectric Loss:** Materials with low dielectric constant (in the range of 4–12) are used for substrate layers while high dielectric constant

materials are used for mainly capacitor layers. Signal propagation delay is the one of the most important parameters in electronic packaging which is directly related with dielectric constant as follows:

$$t_d = l \cdot \sqrt{K}/c \quad (1.4)$$

where  $t_d$  is propagation delay,  $l$  is the metal line length,  $K$  is dielectric constant of the substrate and  $c$  is the speed of light. From this expression it can be seen that reduction in dielectric constant is required for high speed transmission of signals. Furthermore, dielectric loss is directly involved with the power consumption and signal quality. Consequently, low dielectric constant and loss are the key characteristic for LTCC materials [8, 22, 25, 31].

**Low Thermal Expansion and High Thermal Conductivity:** In systems based on silicon chips mounted on LTCC substrates, a thermal expansion mismatch would give rise to failure of solder connections between chip and substrate, which will affect the reliability of the whole system. So, CTE value of a substrate close to silicon ( $\sim 4$  ppm/ $^{\circ}\text{C}$ ) is highly desirable. Another important parameter is thermal conductivity of the substrate material. One main disadvantage of LTCC is low thermal conductivity which is generally between 2– 5 W/m.K. The removal of heat generated by the device is critical for a more efficient and reliable packaging. The heat removal has become even more critical with growing needs to fabricate high density and high power devices operated at high speeds [8, 22, 25].

**Chemical Compatibility with Electrode Material:** LTCC material should not react with the electrode material since formation of additional phases can degrade the performance. The conductive lines are printed on ceramics using pastes containing glass additives, instead of pure metals. In addition to conductive material, LTCC materials should not react with other additives of the conductor paste [8].

Table 1.4 Commercial LTCC products and properties.

| LTCC Supplier | Item            | Sintering Temperature | Dielectric Constant      | Dielectric Loss       | CTE (ppm/°C) | Thermal Conductivity (W/m.K) | Flexural Strength (MPa) | Young's Modulus (GPa) | Reference  |
|---------------|-----------------|-----------------------|--------------------------|-----------------------|--------------|------------------------------|-------------------------|-----------------------|------------|
| Kyocera       | GL330           |                       | 7.7 (at 2 MHz)           | 0.0005 (at 2 MHz)     | 8.2          | 4.3                          | 400                     | 178                   |            |
|               | GL952           |                       | 7.9 (at 2 MHz)           | 0.0015 (at 2 MHz)     | 8.3          | 1.8                          | 250                     | 119                   |            |
|               | GL570           | -                     | 5.7 (at 2 MHz)           | 0.0007 (at 2 MHz)     | 3.4          | 2.8                          | 200                     | 128                   | [32]       |
|               | GL771           |                       | 5.2 (at 2 MHz)           | 0.0036 (at 2 MHz)     | 12.3         | 2                            | 170                     | 74                    |            |
|               | GL773           |                       | 5.8 (at 2 MHz)           | 0.0023 (at 2 MHz)     | 11.7         | 1.9                          | 280                     | 95                    |            |
| Murata        | LFC             |                       | 7.7 (at 1 MHz)           | 0.0040 (at 6 GHz)     | 5.5          | 2.5                          | 270                     |                       |            |
|               | AWG             | 900 °C                | 8.8 (at 1 MHz)           | 0.0042 (at 6 GHz)     | 7.2          | 3.5                          | 300                     | -                     | [33]       |
|               | SWG             |                       | 8.8 (at 1 MHz)           | 0.0042 (at 6 GHz)     | 7.2          | 3.5                          | 450                     |                       |            |
| Dupont        | 951             | 850 °C                | 7.8 (at 10 GHz)          | 0.0140 (at 10 GHz)    | 5.8          | 3.3                          | 320                     | 120                   | [34]       |
|               | 9K7             |                       | 7.1 (at 10 GHz)          | 0.0010 (at 10 GHz)    | 4.4          | 6.4                          | 230                     | 145                   |            |
| Ferro         | A6-M            |                       | 5.75 - 6.05 (at 100 MHz) | 0.002 (at 100 MHz)    |              |                              | 193                     |                       |            |
|               | A6-C            | 850 °C                | 6.0 - 6.7 (at 100 MHz)   | 0.005 (at 100 MHz)    | -            | -                            | 207                     | -                     | [35]       |
| Heraeus       | X200            | 880 °C                | 8.8 – 9.5 (at 30 MHz)    | < 0.002 (at 30 MHz)   | 5.6          | 3                            |                         |                       |            |
|               | 503K08 /51555 W | -                     | 7.5 – 8.5 (at 1 MHz)     | < 0.001 (at 1 MHz)    | 5.2          |                              | -                       | -                     | [36], [37] |
|               | HL 2000         | 865 °C                | 7.3 (at 2.5 MHz)         | < 0.0026 (at 2.5 MHz) | 6.1          |                              | 200                     |                       |            |

### 1.5.2.2 Processing

The overall processing of LTCC is illustrated in Figure 1.24. In LTCC process, each layer is fabricated separately and then laminated to form a monolithic substrate. The process begins with tape casting of glass-ceramic slurry with a polymer matrix under a doctor blade at a desired thickness. The dried tape is blanked into individual layers. Then, the holes or vias are mechanically punched or laser-cut and followed by filling with a conductive paste to allow electrical connections between layers in the vertical axis of the substrate. Each layer is screen-printed to create the horizontal interconnects on the surface of the layers. Generally, each layer contains a unique set of printed electrical traces on its surface, as well as electrically conductive holes (vias). Ceramic sheets are then stacked, laminated and sintered, followed by post-firing metallization, electrical testing and final assembly. Through careful design of this combination of layers, traces, and vias, a three-dimensional block of ceramic is created with an embedded electrical circuitry [8, 23, 25].

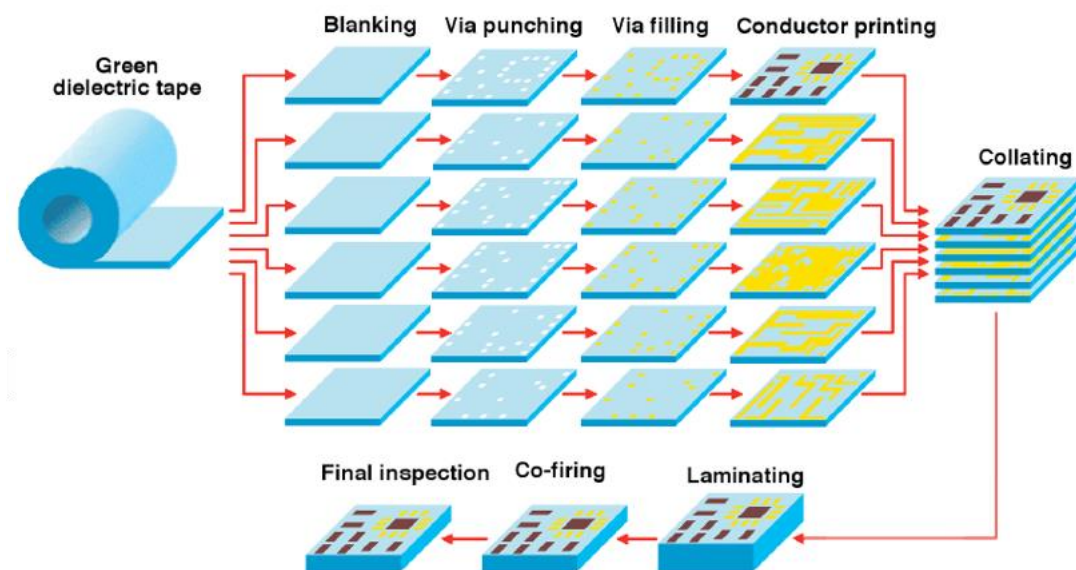


**Figure 1.24** LTCC processing [23].

### 1.5.3 Radome

A radome is an enclosure of antenna to protect it from its physical environment, while not affecting its electrical/magnetic performance. The radome wall must provide necessary structural strength and rigidity without deteriorating the electromagnetic performance (e.g., transparency) of the antenna. The electrical performance of an enclosed antenna is always altered by the radome, and hence a minimum impact of the radome on electrical performance of the antenna is required. There are two basic wall construction types; monolithic wall and multilayer (sandwich) wall. The wall configuration can change according to design and requirements (e.g. environmental and strength). In monolithic thin wall radome structures, the wall thickness should be less than  $1/20^{\text{th}}$  of a wavelength to have high electrical transmission. Thus, the radome materials should essentially meet the requirement of a low dielectric constant. Also, other important requirements are light weight, high strength, and high rain erosion resistance [38, 39].

According to the application areas there are three basic types of radomes; ground base radome, shipboard radome and airborne radome (aircraft radome and missile radome) [39] as represented in Figure 1.25.



**Figure 1.25** Radome types; (a) ground base radome, (b) shipboard radome [40], (c) airborne radome [41].

The ground base radomes are required to stand air pressures resulting from wind. Other factors to be considered are humidity, rain, snow, and moisture buildup on the outer wall. The shipboard radomes are required to counter pressure differentials and corrosion due to salty sea environment. Generally, glass-fiber reinforced polymer

materials are widely used in either monolithic or sandwich configurations for ground base and shipboard radomes. They offer low weight and relatively low production costs [38, 39, 42].

As for the airborne radomes, both thermal shocks and thermal gradients arising from high accelerations and terminal velocities have to be considered. In addition, pressure differentials and impact strength (i.e., impact loads from birds, stones, rain, etc.) are other important parameters in the selection of the suitable materials. Polymer matrix composites can be used only for lower-speed radomes; however, radomes cruising faster than Mach 2 for a long flight time experience high temperature raise. For speeds exceeding Mach 2, it is imperative to use inorganic materials based on silica, glass or ceramics. These materials should meet the requirements not only for withstanding high temperature without deterioration in performance but also for providing appropriate protection against rain erosion. Water absorption of a radome increases the dielectric constant and loss tangent and also reduces the strength of most materials [38, 39, 43].

#### *1.5.3.1 Requirements*

Some basic requirements for radome materials are as follows;

**Electrical requirements:** The radome must provide least distortion in the intrinsic antenna radiation. The dielectric constant and dielectric loss of the material decide the electrical performance of a radome. The signal propagation delay (see Equation 1.4) and transmission loss must be small as the electromagnetic wave passes through the radome, so the dielectric constant must be low. Also, radome shape and design have important impact on electrical performance. Polarization must be independent over a wide range of incident angles and antenna pointing angles. Furthermore, for high-power applications, high dielectric loss of the radome material will raise the temperature that degrades the electrical properties and increases the system noise. Therefore, dielectric loss must be low [39, 42].

**Mechanical requirements:** Mechanical requirements include structural stability, aerodynamics and the environmental conditions of the radome subjected to during operation. Mechanical stresses are produced in radomes due to airflow, acceleration

forces, and sudden thermal expansion (and thermal shock). So, the radome materials must provide necessary strength over the service temperature. In high-speed radomes, generally thermal shock causes the highest mechanical stresses. Also, radome materials must withstand vibrations or impacts. Furthermore, the design of the radome has a great importance on the mechanical properties that will determine the loads/stresses induced on the radome. The stress/load profile developed on the radome also depends on the shape, material and fabrication process [39, 42].

**High rain erosion:** Radomes are expected to have large electromagnetic transmission coefficient. However, this performance may get drastically affected by any moisture absorbed by the radome materials. Hence, any possibility of absorption of moisture in the radome wall structure must be totally avoided [39].

## 1.6 Review of the literature work

Glass-ceramic and glass+ceramic routes have been extensively studied for the LTCC applications, but their compositions are not exactly similar to our system. Therefore, similar systems are reviewed here to give an idea regarding the required physical properties.

Anorthite ( $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ , or CAS) based glass-ceramic systems has been extensively investigated for the LTCC applications. Lo *et al.* [44] studied CAS glass system with 5 and 10 wt%  $\text{TiO}_2$  addition as nucleating agent and  $\text{B}_2\text{O}_3$  to enhance densification. The glass-ceramic was sintered and crystallized at  $950^\circ\text{C}$ . Lowest dielectric constant with 5 wt%  $\text{TiO}_2$  was 8 at 10 GHz. In addition, CTE values were between 4-5 ppm/ $^\circ\text{C}$  close to that of silicon.

Luo *et al.* [28] investigated the effect of CAS glass addition to  $\text{Al}_2\text{O}_3$  and reported that 50 wt% glass was sintered at  $875^\circ\text{C}$  and anorthite phase formed. The composite had dielectric constant of 8.06, dielectric loss of 0.001 at 7 GHz, CTE of 5.47 ppm/ $^\circ\text{C}$ , and thermal conductivity of 3.1 W/m.K.

Hsiang *et al.* [45] investigated  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  glass (CMAS) crystallization into anorthite phase. Sintering temperature was  $900^\circ\text{C}$  when 10 vol%  $\text{Al}_2\text{O}_3$  was added to CMAS. Dielectric constant and dielectric loss were 7.5 and 0.005 at 1 MHz, respectively.

Induja *et al.* [46] studied a commercial glass ( $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2\text{-K}_2\text{O-P}_2\text{O}_5$ ) with 30 wt%  $\text{Al}_2\text{O}_3$  addition. The composite sintered at  $875^\circ\text{C}$  had dielectric constant and dielectric loss of 4.52 and 0.007 (at 1 MHz), respectively. CTE of composite was 4.38 ppm/ $^\circ\text{C}$  which was close to silicon, but the thermal conductivity was 1.41 W/m.K at room temperature. Low thermal conductivity is the main disadvantage of the LTCC compositions. Induja *et al.* [47] also reported a novel glass ( $\text{BiO}_3\text{-ZnO-B}_2\text{O}_3\text{-SiO}_2$ )/ $\text{Al}_2\text{O}_3$  composite with high thermal conductivity of 7.2 W/m.K. Sintered composite at  $900^\circ\text{C}$  with 40 wt%  $\text{Al}_2\text{O}_3$  addition had developed secondary phase formation of  $\text{ZnAl}_2\text{O}_4$  which improved the thermal conductivity. However, dielectric constant of the composite was very high value of 11.3 at 1 MHz.

$\text{Al}_2\text{O}_3$  based composites (glass+ceramics) are attracting much attention due to their unique electrical and physical properties [46]. Studies on borosilicate glass (BSG) systems reveals that heat treatment of BSG results in cristobalite crystallization which have high thermal expansion coefficient. However, precipitation of cristobalite can be suppressed by a small amount of  $\text{Al}_2\text{O}_3$  addition on BSG and the properties can be controlled [8].

For radome applications,  $\text{Al}_2\text{O}_3$  is used for high temperature radomes where organic materials fail. It can withstand Mach 3 speed and hence is widely used for missile radomes. Its dielectric constant is about 10 and its dielectric loss is low ( $<0.001$ ). The higher dielectric constant requires a narrow tolerance in the manufacturing compared with a lower dielectric constant material. Its relatively high density ( $3.95 \text{ g/cm}^3$ ) dictates reduction in thickness of the design. It has good mechanical properties and extremely good for rain erosion resistance [48].

Corning Pyroceram (9606) is a commercial magnesium-aluminum silicate glass ceramic which can be used in missile radomes since it has a high temperature capability of withstanding Mach 3 and above. Its dielectric constant is 5.65 at the microwave range, enabling a thickness tolerance in the design. Its density is  $2.62 \text{ gm/cm}^3$  and it is lighter than  $\text{Al}_2\text{O}_3$ . The mechanical properties are moderately lower than that of  $\text{Al}_2\text{O}_3$  because of its softening point at  $1350^\circ\text{C}$ . It also has very good rain erosion characteristics. It is generally considered to have better thermal shock resistance than  $\text{Al}_2\text{O}_3$  [48, 49].

MACOR is a commercially available glass ceramic which contains 55% fluorophlogopite mica and 45% borosilicate glass. It is stable at  $800^\circ\text{C}$  and can withstand up to  $1000^\circ\text{C}$ . It has a density of  $2.52 \text{ gm/cm}^3$ , dielectric constant of 6.01 and loss tangent of 0.004 at 1 kHz, Young's modulus of 67 GPa, and flexural strength of 94 MPa [50, 51]. Its main advantage is its machinability to the desired 3D shapes.

### 1.7 Aim of the study

In this thesis,  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{CaO}$  based glass is added to  $\text{Al}_2\text{O}_3$  system in order to vary sintering temperatures for specific applications such as substrate, LTCC and radome. Solid state, liquid phase and viscous sintering methods are applied depending on the glass content in the  $\text{Al}_2\text{O}_3$ /glass composite. The particular aim of the thesis is to determine densification behavior, investigate phase formation and characterize dielectric (dielectric constant and loss), mechanical (hardness, fracture toughness, Young's modulus and flexural strength) and thermal properties (thermal conductivity and thermal expansion coefficient) of the composites. The results will be evaluated based on the requirements of the specific applications. Furthermore, tape casting and co-firing with silver electrode will be investigated in specific  $\text{Al}_2\text{O}_3$ /glass composites for substrate and LTCC applications.

# CHAPTER 2

## EXPERIMENTAL PROCEDURE

A commercial glass frit (Gizem Frit, Turkey) and  $\text{Al}_2\text{O}_3$  (Almatis, CT 3000 SG), were used as starting materials. The properties of  $\text{Al}_2\text{O}_3$  powder are given in Table 2.1.  $\text{Al}_2\text{O}_3$  powder was used after a binder burn out process at  $600^\circ\text{C}$  for 30 min.

**Table 2.1** The properties of  $\text{Al}_2\text{O}_3$  powder [52].

| Properties                                                 | Value |
|------------------------------------------------------------|-------|
| Specific surface area ( $\text{m}^2/\text{g}$ )            | 7.5   |
| Particle size ( $\mu\text{m}$ )                            |       |
| D <sub>50</sub>                                            | 0.5   |
| D <sub>90</sub>                                            | 2     |
| <b>Chemical analysis (%)</b>                               |       |
| $\text{Al}_2\text{O}_3$                                    | 99.78 |
| $\text{Na}_2\text{O}$                                      | 0.08  |
| $\text{Fe}_2\text{O}_3$                                    | 0.02  |
| $\text{SiO}_2$                                             | 0.03  |
| $\text{CaO}$                                               | 0.02  |
| $\text{MgO}$                                               | 0.07  |
| <b>Ceramic Properties</b>                                  |       |
| Density (at 90 MPa) ( $\text{g}/\text{cm}^3$ )             | 3.9   |
| Firing temperature ( $^\circ\text{C}$ )<br>(1 h soak time) | 1540  |
| Shrinkage (%)                                              | 16.8  |

Glass frits were crushed into powder using an agate mortar and pestle, and then subjected to ball milling using yttria stabilized zirconium balls in ethanol for 48 h. The resulting ground glass powder was mixed with  $\text{Al}_2\text{O}_3$  at mass ratios of 20, 40, 50, 55, and 60 by ball milling for 24 h in ethanol with a ready-to-use vinyl-based binder solution (MSE Teknoloji, Turkey). The slurries were dried on a hot plate at  $100^\circ\text{C}$  with

continuous stirring and the dried powder mixtures were ground by mortar and pestle. The  $\text{Al}_2\text{O}_3$ /glass composites will hereafter be referred to as G-20, G-40, G-50, G-55, G-60 which corresponds to 20, 40, 50, 55, and 60 wt% of glass powder, respectively. The composites were pressed at 100 MPa into pellets using a uniaxial press and 1 cm-diameter die. The samples were sintered at various temperatures in the range of 700–1450°C, depending on the glass content, with a heating rate of 5°C/min and hold time of 1 h. All samples were furnace cooled at 5°C/min. The bulk densities of the composites sintered at different temperatures were evaluated by the Archimedes' method in water. The sintering temperature for the bulk composites were optimized based on 0% apparent porosity.

The thermal behavior of glass was determined by a heating microscope (Misura, 3 HSM). The particle size of  $\text{Al}_2\text{O}_3$  and glass powder was measured by a laser diffraction particle size analyzer (Malvern, Mastersizer 3000). Phase formation in the composites were determined using an XRD (Rigaku, Miniflex600) with  $\text{Cu K}\alpha$  radiation between 20–60° with a step size of 0.02° and scan rate of 2°/min. The microstructures and elemental analysis were analyzed by a Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) (Hitachi, TM4000 Plus), respectively. Weight loss in the samples were determined by a thermogravimetric analysis (Hitachi, STA 7300).

Samples for flexural strength and Young's modulus measurements were fabricated by dry pressing into bars at 100 MPa at nearly 3x4x50 mm dimensions using a uniaxial press. The bars were pre-sintered at temperatures determined from densification behavior of each composite and then polished to the required dimensions. The sharp edges of the samples were lightly polished before sintering to reduce sensitivity to edge damage during mechanical tests. Then, the samples were sintered at specified sintering temperatures for each composition. The samples were carefully stored and handled to avoid introduction of any flaws to the surfaces. At least 4 samples from each set were prepared. Young's modulus was measured by a resonance frequency method using a Grindo Sonic system (Grindo Sonic MK5). The specimens were struck lightly by an impulser from the center and a transducer was located at the end of the specimen. The resultant resonance frequencies were recorded, and the test was

repeated until the resonance frequencies were repeatable. Young's modulus of the composites was calculated according to ASTM standard C1259-15 from the following formulae:

$$E = 0.9465 \cdot (m \cdot f_f^2 / b) \cdot (L^3 / t^3) \cdot T_1 \quad (2.1)$$

$$T_1 = 1 + 6.585 \cdot (1 + 0.2023 \cdot \mu + 2.173 \cdot \mu^2) \cdot (t/L)^2 - 0.868 \cdot (t/L)^4 - \left[ \frac{8.34 \cdot (1 + 0.2023 \cdot \mu + 2.173 \cdot \mu^2) \cdot (t/L)^4}{1 + 6.338 \cdot (1 + 0.1408 \cdot \mu + 1.536 \cdot \mu^2) \cdot (t/L)^2} \right] \quad (2.2)$$

where E is Young's modulus (Pa), m is mass of the bar (g), b is the width of the bar (mm), L is the length of the bar (mm), t is the thickness of the bar (mm),  $f_f$  is fundamental resonant frequency of the bar (Hz),  $\mu$  is Poisson's ratio. The flexural strength was measured by a 3-point bending test (40 mm span length and 0.5 mm/min crosshead speed) using a universal tester (Instron 5569, 500 kg load cell). The flexural strength was calculated according to ASTM standard C1161-18 from the following formula:

$$S = \frac{3 \cdot P \cdot L}{2 \cdot b \cdot d^2} \quad (2.3)$$

where P is break force (N), L is support span (mm), b is specimen width (mm), and d is specimen thickness (mm). The hardness and fracture toughness of the samples were measured by Micro Vickers Hardness (Shimadzu, HVM-G) by applying 10 N for 6 seconds to glass and 20 N for 6 sec to  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ /glass composites. Vickers hardness was calculated according to ISO 6507-1:2005 standard from the following formula:

$$H = 01891 \frac{P}{a^2} \quad (2.4)$$

where H is Vickers hardness, P is test force (N) and a is average length of diagonal lines of the indentation (mm). Fracture toughness was calculated using the formula given by Lawn et al. [53]:

$$K_c = \delta \frac{\sqrt{E} \cdot P}{\sqrt{H} \cdot \sqrt{c^3}} \quad (2.5)$$

where  $K_c$  is fracture toughness (MPa/ $\sqrt{\text{m}}$ ),  $E$  is Young's modulus (MPa),  $c$  is half of the average crack length (m),  $a$  is half of the average length of indentation diagonal lines (m), and  $\delta$  is a non-dimensional constant which is primarily a function of the indenter geometry. It was given as 0.026 for the hardness tester used.

The dielectric constant at 5 MHz was calculated from capacitance measurement at room temperature using an LCR Impedance analyzer (Hioki, IM3570) according to the following formula [5]:

$$K = \frac{C \cdot d}{\epsilon_0 \cdot A} \quad (2.6)$$

where  $K$  is dielectric constant,  $C$  is capacitance (F),  $d$  is thickness of specimen (m),  $\epsilon_0$  is permittivity of vacuum (F/m) and  $A$  is area of specimen ( $\text{m}^2$ ). Parallel surfaces of the samples were first coated with Ag paste and then beaked at 600°C for 15 min. Capacitance was then measured.

The microwave dielectric properties of the G-40 was measured using a network analyzer (Keysight, N1500A high temperature probe). For preparation of this sample, the powder was granulated using 540  $\mu\text{m}$  sieve. The granules were kept at 40°C for 1 h for temperature homogenization and then uniaxially dry pressed at 100 MPa to the dimensions of 6x60x60 mm. After sintering, the sample was two side lapped.

The thermal conductivity was calculated using thermal diffusivity ( $\alpha$ ), specific heat ( $C_p$ ) and density measurements from the following formula:

$$k = \alpha \cdot \rho \cdot C_p \quad (2.7)$$

where  $k$  is thermal conductivity (W/m.K),  $\alpha$  is thermal diffusivity ( $\text{m}^2/\text{s}$ ),  $\rho$  is density ( $\text{kg}/\text{m}^3$ ) and  $C_p$  is specific heat (J/kg.K). The thermal diffusivity was measured using a laser flash apparatus (Netzsch LFA 457) and specific heat was determined by a differential scanning calorimeter (Netzsch STA 449F3A). The thermal expansion coefficient of the composites (CTE, ppm/°C) were measured using a dilatometer

(Linseis, L76 Platinum) at a heating rate of 10°C/min in the temperature range of 35–800°C for the G-20 and G40 and 35–600°C for the G-50, G-55 and G-60. Samples were prepared by dry pressing into bars at 100 MPa using a uniaxial press. The bars were pre-sintered at temperatures determined from densification behavior of each composite and then polished to the dimensions of 5x5x25 mm. Thermal expansion coefficient (CTE) of the composites was calculated from the following formula:

$$\Delta L/L_0 = \alpha \cdot \Delta T \quad (2.8)$$

where  $L_0$  (mm) is the original length of the sample,  $\Delta L$  is the length change and  $\Delta T$  is the temperature changes.

In order to evaluate the variation of bulk densities and dielectric constant of composites sintered at their determined sintering temperatures, parallel ( $E = \sum E_i \cdot V_i$ ), series ( $1/E = \sum V_i/E_i$ ) and logarithmic ( $\log E = \sum V_i \cdot \log E_i$ ) mixing models were considered [44, 54]. In these expressions,  $E$  is the material property of the composite,  $V_i$  and  $\rho_i$  represent the volume fraction and density of component  $i$ , respectively. Two phases were considered in the system;  $\text{Al}_2\text{O}_3$  and glass, so bulk density and dielectric constant were calculated from the following formula:

$$\rho = \rho_a \cdot V_a + \rho_g \cdot V_g \quad (2.9)$$

$$1/\rho = V_a/\rho_a + V_g/\rho_g \quad (2.10)$$

$$\log \rho = V_a \cdot \log \rho_a + V_g \cdot \log \rho_g \quad (2.11)$$

$$K = K_a \cdot V_a + K_g \cdot V_g \quad (2.12)$$

$$1/K = V_a/K_a + V_g/K_g \quad (2.13)$$

$$\log K = V_a \cdot \log K_a + V_g \cdot \log K_g \quad (2.14)$$

In these formulas,  $\rho$  is bulk density of the composite,  $K$  is the dielectric constant of the composite,  $V_a$  and  $V_g$  represents the volume fraction of  $\text{Al}_2\text{O}_3$  and glass,  $\rho_a$  and  $\rho_g$  represent the density of  $\text{Al}_2\text{O}_3$  and glass, and  $K_a$  and  $K_g$  represent the dielectric constant of  $\text{Al}_2\text{O}_3$  and glass, respectively.

Tape casting was performed for the  $\text{Al}_2\text{O}_3$  and G-55 composition. The powders were mixed with a vinyl-based binder solution in 60 wt% solid loading for both systems. The slurries were mixed with a speed mixer (FlackTek, DAC 150.1 FVZ) at 3500 rpm for 10 min and casted on a silicon coated Mylar film using a tape casting machine (MSE Teknoloji, Turkey) at a casting rate of 5 cm/sec with a blade gap of 250  $\mu\text{m}$ . Drying was performed in a closed system at room temperature. Green tapes were cut into desired dimensions. Ag paste was screen printed on single green sheets and then they were laminated at alternating layers for the Low Temperature Co-Fired Ceramic (LTTC) applications. A manual screen printer (LPKF ProtoPrint S RP) with 120 silk mesh was used for Ag printing. The green tapes with/out electrodes were hot laminated at 70°C applying 20 MPa for 10 min for each side. The laminated tapes were binder burnt-out at 600°C for 1 h, with a slow heating rate of 2°C/min and then temperature was increased to required sintering temperatures (and co-firing of LTTC tapes) at 825°C and 850°C for the G-55 and 1540°C for  $\text{Al}_2\text{O}_3$  for 1 h with a 5°C/min heating and cooling rates. As for the substrate applications, Ag paste was applied on laminated and sintered ceramics and then baked at 600°C for 15 min. Samples were sintered between porous  $\text{Al}_2\text{O}_3$  plates to avoid warping. Microstructure of the tapes was observed with an optical microscope (Nikon Eclipse MA-100). Electrical leakage for co-fired composite between layers was simply examined by a multimeter.

# CHAPTER 3

## RESULTS AND DISCUSSION

### 3.1 Powder characterization

A commercially available glass frit was used as starting material. Glass frit was first crushed by mortar and pestle and then subjected to ball milling for 48 h to obtain fine glass powder. The chemical analysis, phase analysis, SEM picture and particle size analysis results are given in Figure 3.1. Figure 3.1(a) shows the EDS spectrum. Au peaks were from Au coating and C peak was from carbon tape. Hence, they were not included in the composition calculation. The elements in the glass composition obtained from the EDS analysis are given in Table 3.1. Stable oxide composition for each element was then calculated and given in Table 3.2. The main constituents in the glass powder were  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$ . Therefore, the crystallization was expected to be in anorthite phase ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  or  $(\text{Ca}, \text{Na})(\text{Si}_2\text{Al})_4\text{O}_8$ ).  $\text{SiO}_2$  was the network former,  $\text{Al}_2\text{O}_3$  was the intermediate and  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  were the modifiers in the glass [2]. Figure 3.1 (b) shows the SEM image of the particles having angular shapes. XRD pattern given in Figure 3.1 (c) indicates that glass powder was amorphous in nature except for a small peak corresponding to quartz phase (Card number: 00-009-0466). Figure 3.1 (d) shows a unimodal particle size distribution with a  $d_{50}=2.13 \mu\text{m}$  and  $d_{90}=3.91 \mu\text{m}$  after milling.

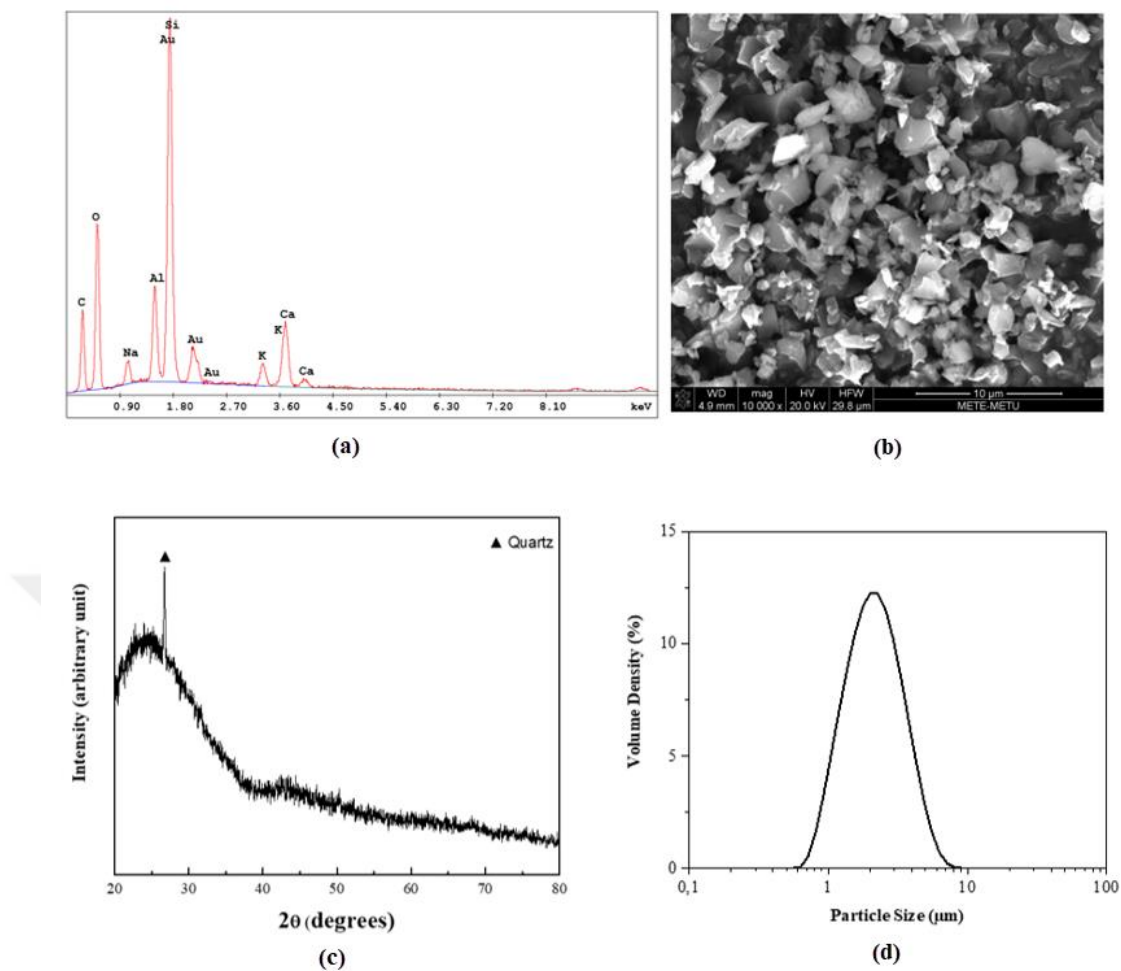


**Figure 3.1** (a) EDS analysis; (b) SEM photograph; (c) XRD pattern; (d) Particle size result after ball milling for 48 hours.

**Table 3.1** The elemental analysis of the glass powder.

| Element | Si   | Al  | Ca  | Na  | K   | O    |
|---------|------|-----|-----|-----|-----|------|
| wt%     | 31.5 | 8.5 | 7.9 | 3.6 | 2.7 | 45.8 |

**Table 3.2** Stable oxide composition of the glass powder.

| Composition | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O |
|-------------|------------------|--------------------------------|------|-------------------|------------------|
| wt%         | 65.8             | 15.1                           | 11.7 | 4.0               | 3.4              |

Figure 3.2 shows heating microscope result of the glass pellets prepared from ground glass powder. Sintering, softening and melting temperatures were determined as

726°C, 852°C, and 1180°C, respectively. These characteristic temperatures were obtained from an automatic software evaluation which were basically determined from shape change of the samples with temperature. Glass pellets heated at 750°C and 825°C showed similar behavior with heating microscope results, as presented in Figure 3.2 (a) and (b) as inset.

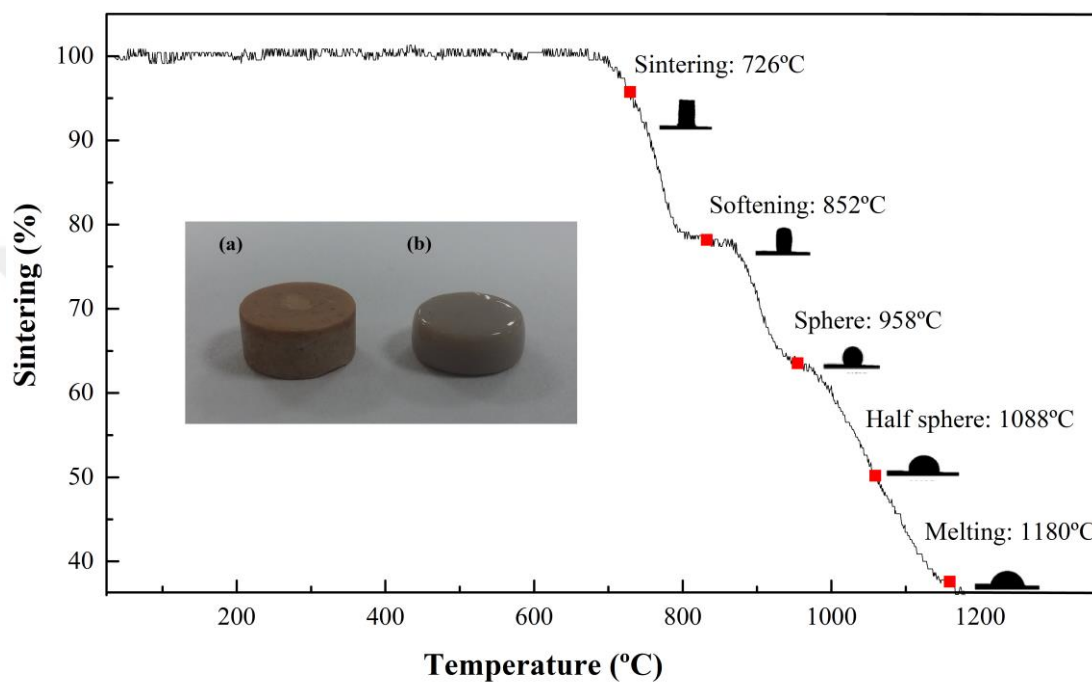


**Figure 3.2** Heating Microscope result of glass powder. Glass pellets heated at; (a) 750°C and (b) 825°C are shown as inset.

Backscattered SEM images of the polished surfaces of the glasses heated at 750°C and 825°C are shown in Figure 3.3. The irregular pore shapes in Figure 3.3 (a) shows that densification was not completed. The spherical pore shapes in the Figure 3.3 (b), however, indicates that sintering was completed.

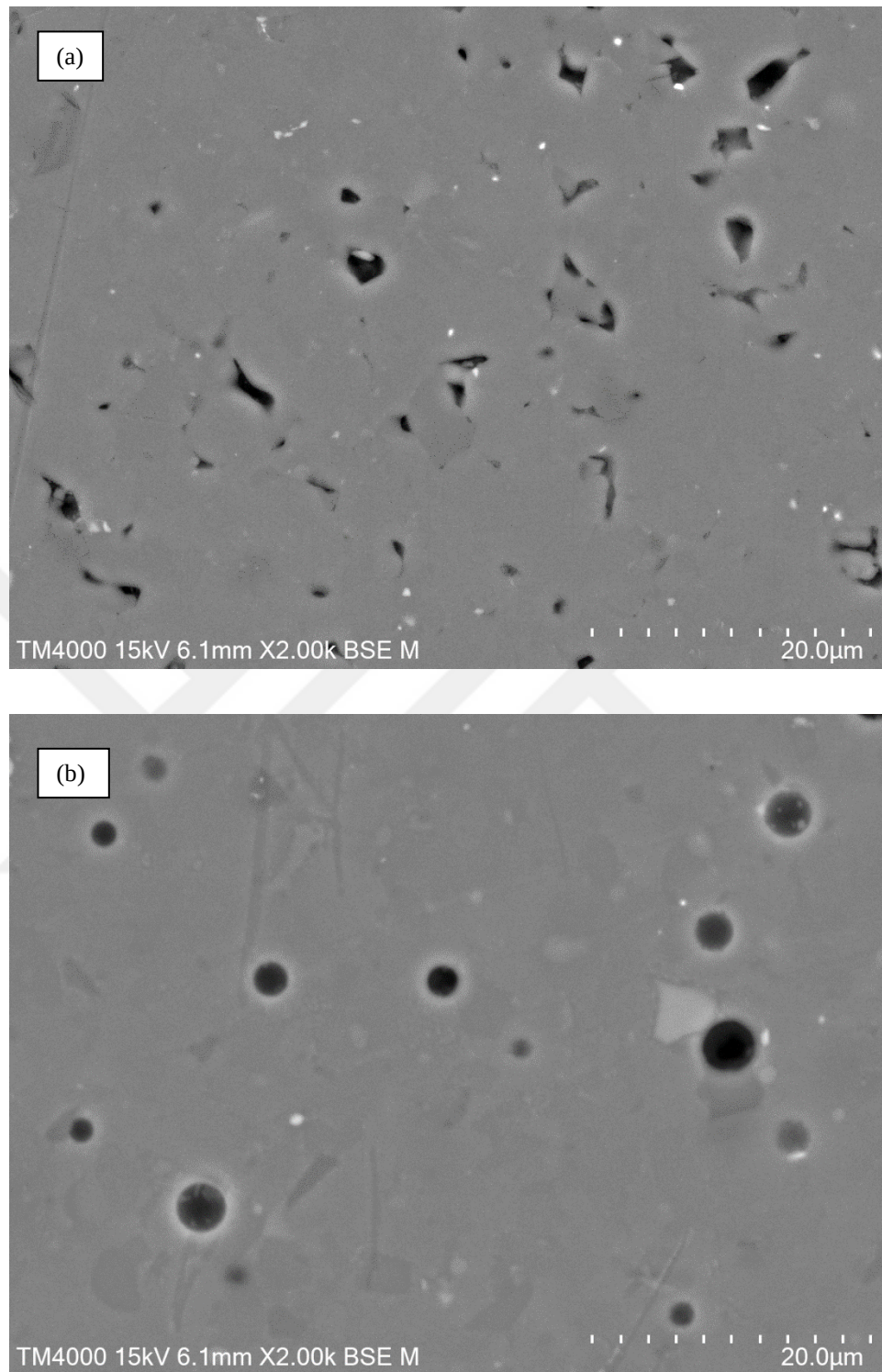


**Figure 3.3** Backscattered SEM images of the polished glass surfaces; heated at (a) 750°C and (b) 825°C.

The commercial  $\text{Al}_2\text{O}_3$  powder was in granule form and mixed with glass in ball milling. In order to understand particle size reduction during ball milling, only  $\text{Al}_2\text{O}_3$

powder was ball milled separately. The particle size distribution of the ground  $\text{Al}_2\text{O}_3$  powder was slightly bimodal as shown in Figure 3.4. The particle size of  $\text{Al}_2\text{O}_3$  decreased from  $d_{50}=0.5 \mu\text{m}$  to  $0.44 \mu\text{m}$  and from  $d_{90}=2.0 \mu\text{m}$  to  $1.17 \mu\text{m}$  when compared with the datasheet of  $\text{Al}_2\text{O}_3$  given in Table 2.1.

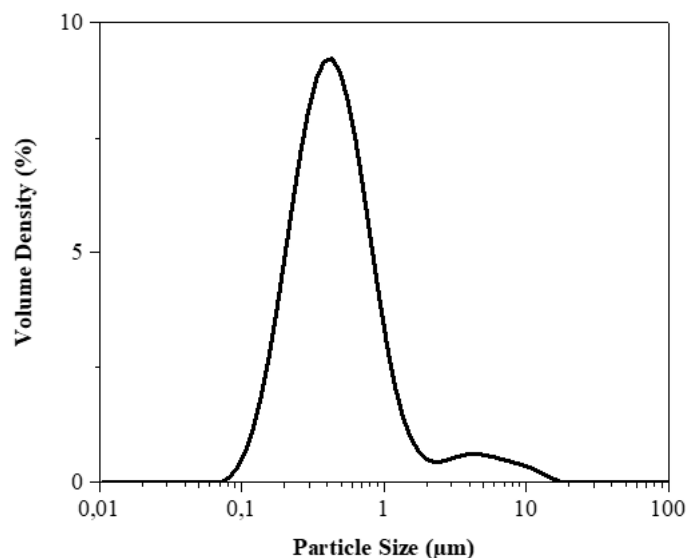


**Figure 3.4** Particle size distribution of  $\text{Al}_2\text{O}_3$  powder after ball milling for 24 hours.

### 3.2 Phase formation and densification

The densification behavior of the  $\text{Al}_2\text{O}_3$ /glass composites is compared in Figure 3.5. The grid lines are drawn to guide eye. Densification behavior of the composites differed from each other in that full densification was attained at lower temperatures with increasing glass content. Correspondingly, the apparent porosities were decreased with increasing densification. The G-50, G-55 and G-60 composites were sintered well below  $1000^\circ\text{C}$ , and densification was completed above  $1000^\circ\text{C}$  for the G-20 and G-40 composites. These results clearly indicate that the glass content and temperature have remarkable effect on densification of the composites produced.

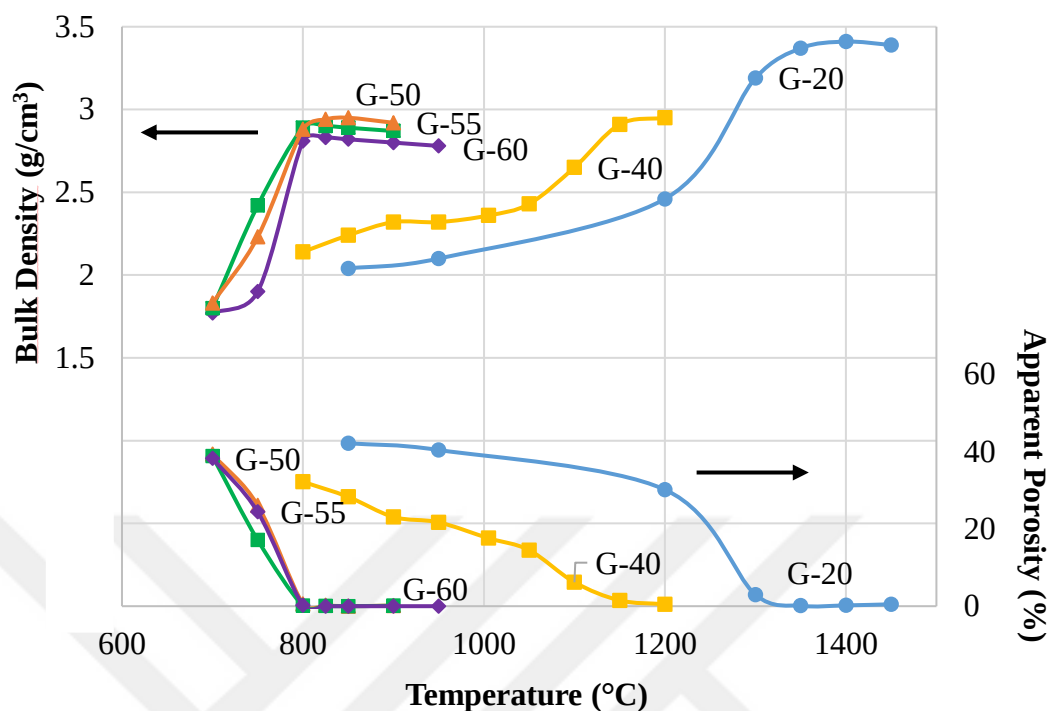


**Figure 3.5** Densification of the  $\text{Al}_2\text{O}_3$ /glass composites as a function of glass content and temperature.

The densification temperatures derived from Figure 3.5 is compared in Figure 3.6.  $\text{Al}_2\text{O}_3$  (0 wt% glass) and glass (100 wt% glass) are the end members and given for better evaluation of the composite behavior. The densification temperatures of the composites were determined according to 0% apparent porosity as calculated from the Archimedes' method. Note that 0% apparent porosity does not necessarily mean fully densified composites because Archimedes' method inherently has some uncertainty in measurements. Therefore, composites can definitely have some closed porosities at the 0% apparent porosity.  $\text{Al}_2\text{O}_3$  was sintered at  $1540^\circ\text{C}$  as given in Table 2.1 and bulk density was  $3.93 \pm 0.02 \text{ g/cm}^3$ . Moreover, the sintering temperature of glass powder was determined to be  $726^\circ\text{C}$  by a heating microscope as given in Figure 3.2. The bulk density of glass sintered at near sintering and softening temperatures (e.g.,  $750^\circ\text{C}$  and  $825^\circ\text{C}$ ) was  $2.43 \pm 0.01 \text{ g/cm}^3$  for 0 % apparent porosity. The optimum sintering temperature of the composites followed a continuous decrease up to 40 wt% glass content (G-40). Then, a sharp decrease was observed in the optimum sintering temperature. Hence, the optimum sintering temperatures were determined, within the

applied temperature range, to be 1350°C for the G-20, 1200°C for the G-40 and 850°C for the G-50, G-55 and G-60 composites. Water absorption of the composites was very low; such that, 0.02% for G-20, 0.1% for G-40 and 0% for 50, 55, 60 at their optimum sintering temperatures, proving that the composites almost had no open pores.

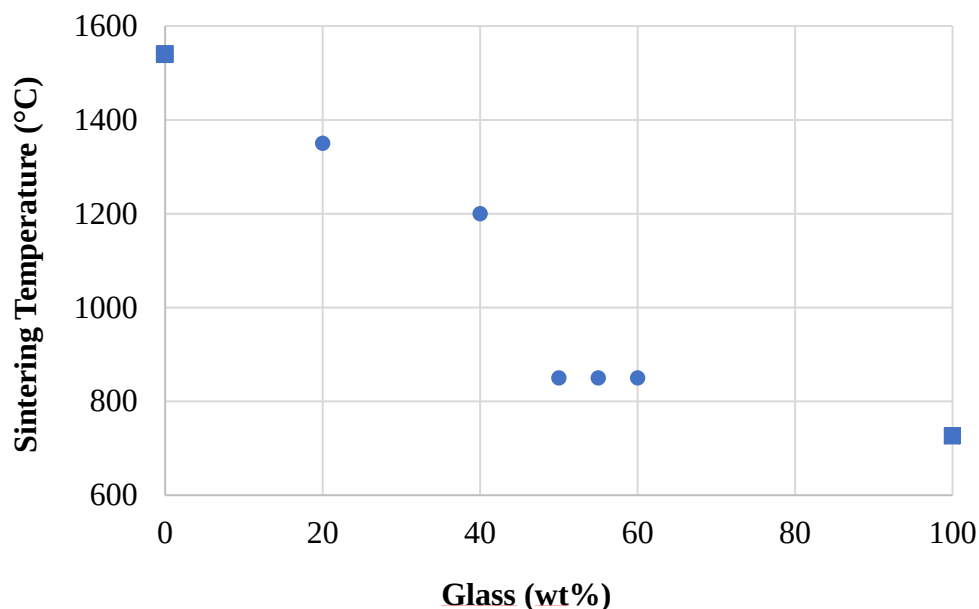


**Figure 3.6** Optimum sintering temperatures of the  $\text{Al}_2\text{O}_3$ /glass composites.

The bulk densities derived from Figure 3.5 at the optimum sintering temperatures is compared in Figure 3.7. In order to evaluate the variation of bulk densities, parallel, series, and logarithmic mixing models were considered as given in Equations 2.9 to 2.11. The values calculated from the parallel, series and logarithmic models are shown with dashed lines. Two phases were evaluated in the system;  $\text{Al}_2\text{O}_3$  ( $\rho=3.93 \text{ g/cm}^3$ ) and glass ( $\rho=2.43 \text{ g/cm}^3$ ). Hence, it is seen that increasing amount of glass content resulted in decrement of the bulk densities. Experimentally determined bulk densities were in good agreement with both the parallel and series models but much closer to the logarithmic one.

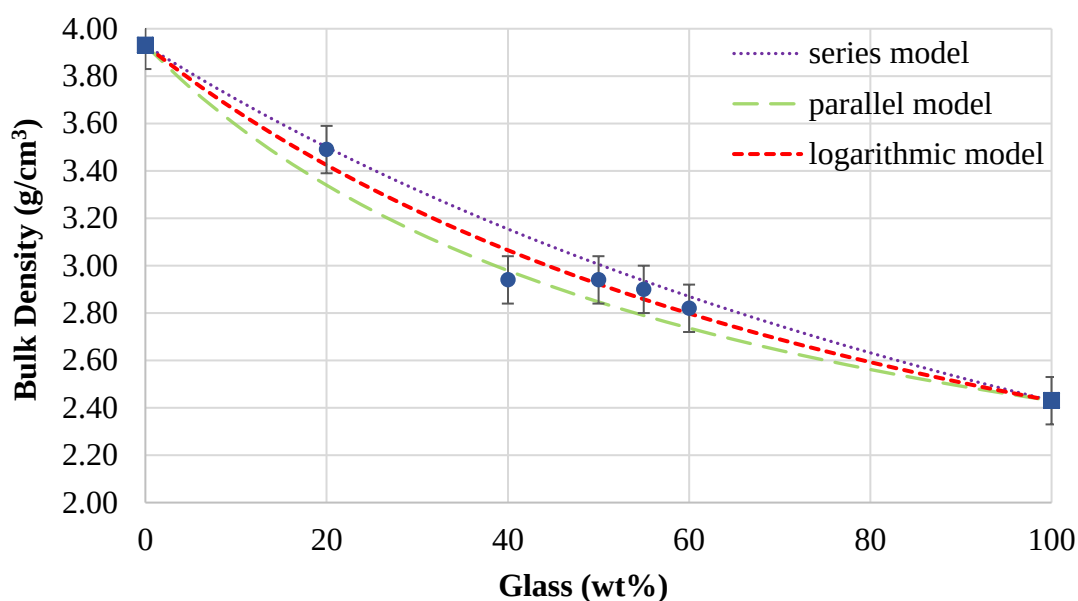


**Figure 3.7** Bulk densities of the  $\text{Al}_2\text{O}_3$ /glass composites.

The glass content in the G-20, G-40, G-50, G-55, and G-60 corresponds to 28.6, 51.7, 61.6, 66.7, and 70.7 vol%, respectively. Softening and melting temperatures of the glass itself are 852°C and 1180°C, respectively, as determined from Figure 3.2, which indicates that the liquid amount in the G-20 and G-40 strongly affected full densification temperature; the higher the liquid content, the lower the densification temperature. In other words, bulk density started to increase at the softening point and the optimum sintering temperature was obtained at 1200°C for the G-40 due to higher liquid content. However, bulk density sharply increased at the melting point and the optimum sintering temperature was obtained at 1350°C for the G-20 due to lower liquid content (or more rigid  $\text{Al}_2\text{O}_3$  network). The G-50 to G-60 composites were fully densified at the glass softening temperature due to high glass volume with respect to the  $\text{Al}_2\text{O}_3$  phase.

Figure 3.8 shows backscattered SEM images of polished composite surfaces sintered at optimum sintering temperature for each composition. Lighter regions are  $\text{Al}_2\text{O}_3$  and darker regions are glass phase, as determined by EDS. Note that the brighter parts in Figure 3.8 (a, b) are due to electron charging on the samples. The composites had distinct characteristics based on  $\text{Al}_2\text{O}_3$  grain size in that the G-20 (Figure 3.8 (a, b)) and G-40 (Figure 3.8 (c, d)) had larger grain size, and the G-50 to G-60 (Figure 3.8 (e,

f, g, h, i, j)) had smaller and similar grain size. The G-50 to G-60 composites were sintered at the same temperature and SEM pictures (Figure 3.8 (e, f, g, h, i, j)) show that glass phase homogeneously embraced  $\text{Al}_2\text{O}_3$  grains.

Both the G-20 and G-40 composites had larger grains, but the grains were more faceted in the former and more rounded in the latter. Therefore, densification mechanism was attributed to liquid phase sintering in the G-20 and G-40 by means of solution-precipitation process. Seabaugh et al. [55] studied anisotropic grain growth (or texture) of  $\text{Al}_2\text{O}_3$  in the presence of CaO and  $\text{SiO}_2$  (1:1 ratio) added as a liquid phase former. Crystallization of anorthite and gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) took place on slow cooling from eutectic temperature of  $1380^\circ\text{C}$ . They varied liquid content from 2.7 to 40.5 vol% and further stated that matrix grain coarsening increased as the liquid content decreased. They also observed faceted grains due to grain growth by means of solution-precipitation mechanism during liquid phase sintering, particularly similar to the G-20 (Figure 3.8 (a, b)).

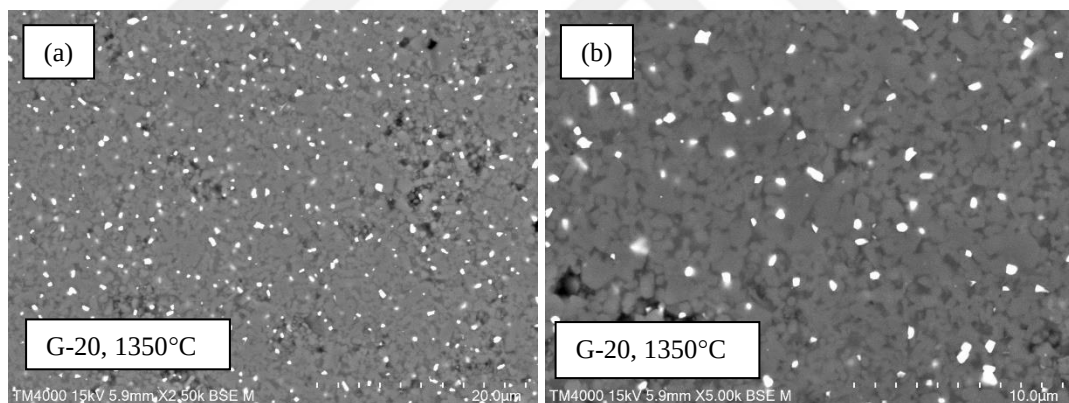


**Figure 3.8** Backscattered SEM images of the composites.

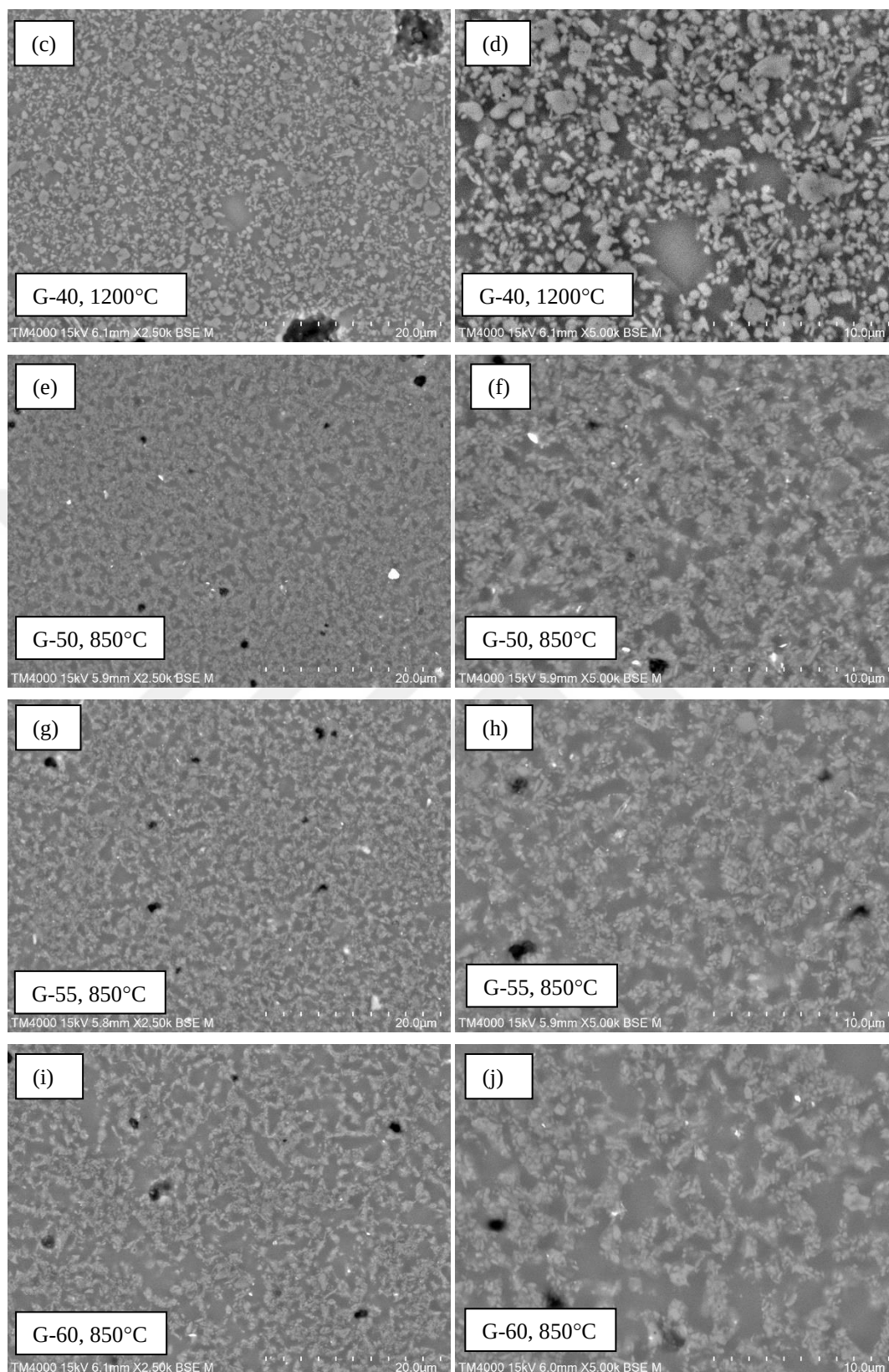


**Figure 3.8 (continued)** Backscattered SEM images of the composites.

Varying the liquid content changes the diffusion distance between the  $\text{Al}_2\text{O}_3$  grains and it is equivalent to the thickness of the grain boundary layer (or grain-to-grain distance) which is proportional to:

$$2/3 \cdot (V_{\text{Liq}}/V_{\text{Sol}}) \quad (3.1)$$

where  $V_{\text{Liq}}$  is the liquid content and  $V_{\text{Sol}}$  is the solid content in the composites [56].

Table 3.3 shows the calculated grain boundary layer and Al/Si ratios in the glass phase as determined by EDS. The lower the initial glass content (or, alternatively, the higher the initial  $\text{Al}_2\text{O}_3$  content), the higher the Al/Si ratio in the glass composition, indicating more dissolution of  $\text{Al}_2\text{O}_3$  in the glass phase. Therefore, only the G-20 sample (Figure 3.8 (a, b)) exhibited grain coarsening (i.e., dissolution of smaller grains and precipitation on the bigger grains) as well as faceting due to both shorter grain boundary layer and anisotropic grain growth of the  $\text{Al}_2\text{O}_3$  grains during liquid phase sintering [55]. Figure 3.8 (c, d) show that grain growth also happened in the G-40 but they were rounded rather than faceted due to less amount of  $\text{Al}_2\text{O}_3$  (and correspondingly much longer grain-to-grain distance).

It has been theoretically reported that if a liquid content is more than 36 vol%, densification takes place by rearrangement of liquid alone without requiring other mechanisms such as solution-reprecipitation [11]. Therefore, from the observed densification behavior and microstructures, sintering mechanism was solid-state sintering for the  $\text{Al}_2\text{O}_3$  due to absence of a liquid, liquid phase sintering for the G-20 and G-40 due to grain coarsening and faceting, and viscous sintering for the G-50, G-55, and G-60 composites due to the high enough volume fraction of liquid where densification was achieved without any  $\text{Al}_2\text{O}_3$  grain shape change during sintering [9]. As for the G-20 and G-40, both rearrangement and solution-precipitation stages were effective during liquid phase sintering, but rearrangement step was more dominant in the G-40 due to higher liquid content and lower densification temperature. Grain growth kinetics depending on glass content must be studied separately to investigate diffusion coefficients pertaining to grain boundary diffusion and viscous diffusion.

**Table 3.3** Calculated grain boundary thickness and Al/Si ratios in the glass phase.

|                            | G-20 | G-40 | G-50 | G-55 | G-60 |
|----------------------------|------|------|------|------|------|
| Grain-to-grain distance    | 0.27 | 0.71 | 1.07 | 1.31 | 1.60 |
| Al/Si ratio in glass phase | 2.45 | 1.68 | 1.22 | 0.98 | 0.72 |

Shrinkage of the  $\text{Al}_2\text{O}_3$ /glass composites in diameter and thickness as a function of glass content and temperature are given in Figure 3.9. The grid lines are drawn to guide eye. Shrinkage increased with increasing temperature as did densification, and the maximum shrinkage values were attained at their optimum sintering temperatures. Shrinkage of the G-50, G-55, and G-60 at 850°C was 16.4 %, 15.9 % and 15.9 % in diameter and 17.5, 18.4, 16.5 % in thickness, respectively. Shrinkage of the G-40 at 1200°C and G-20 at 1350°C in diameter and thickness was the same as 12.6 % and 15.2 %, respectively. The lowest shrinkage was obtained in the G-40 composition due possibly to enhanced crystallization of anorthite crystals.

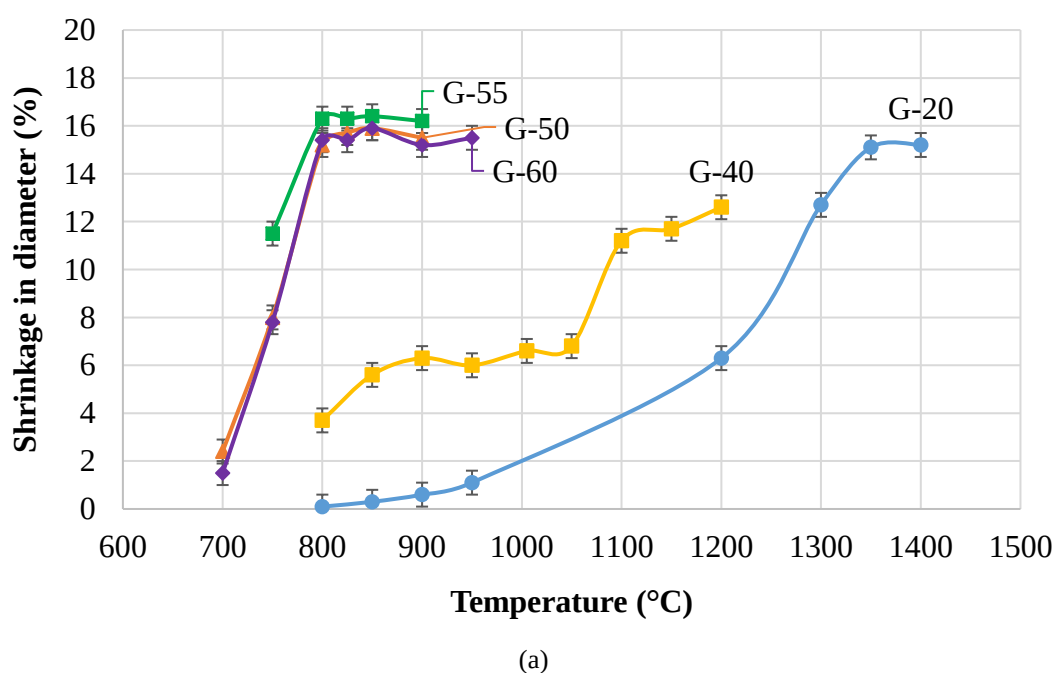
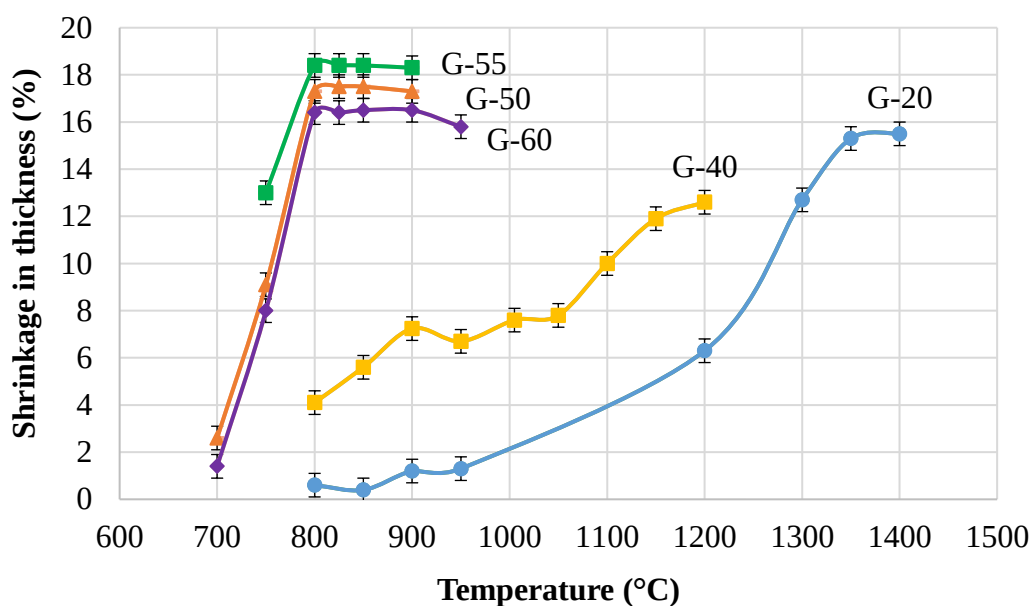


**Figure 3.9** Shrinkage of the  $\text{Al}_2\text{O}_3$ /glass composites as a function of glass content and temperature; (a) in diameter; (b) in thickness.



(b)

**Figure 3.9 (continued)** Shrinkage of the  $\text{Al}_2\text{O}_3$ /glass composites as a function of glass content and temperature; (a) in diameter; (b) in thickness.

Normalized XRD patterns of the glass and heat-treated powders at  $825^\circ\text{C}$  are given in Figure 3.10. The glass powder did not show any crystallization with increasing temperature except for a small quartz peak at  $2\theta=26.77^\circ$  (Card number: 00-009-0466) present in both powders. The presence of quartz may be due to incomplete vitrification during glass production. Heat treatment considerably decreased the background, showing tendency for crystallization.

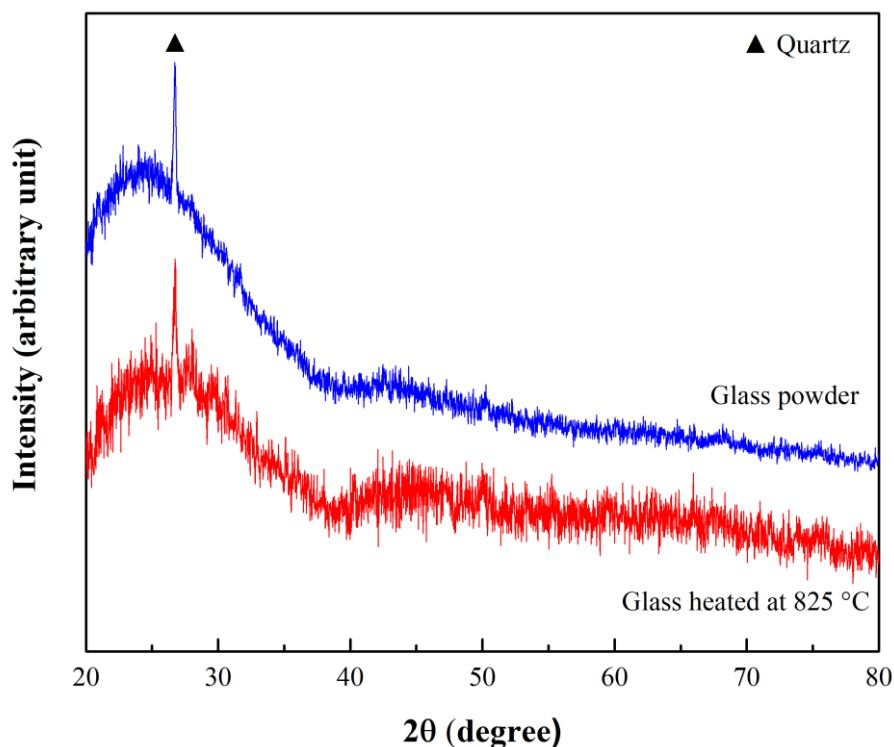


**Figure 3.10** XRD patterns of the glass and heat-treated powders at 825°C.

XRD patterns of the composites sintered at temperatures between 800°C and 1450°C are examined as a function of glass content in Figure 3.11 and Figure 3.13 to 3.16. In general,  $\text{Al}_2\text{O}_3$  (Corundum, Card number: 00-010-0173) was the main crystalline phase for each composition at all sintering temperatures. Anorthite phase with a chemical formula of  $(\text{Ca},\text{Na})(\text{Si},\text{Al})_4\text{O}_8$  (Card number: 00-041-1481) matched well with the remaining crystal peaks. Note that anorthite and albite ( $\text{NaAlSi}_3\text{O}_8$ ) had similar peaks at  $2\theta$  values of 21.97-22.04° and 27.96-28.09° but according to the EDS results (see Table 3.1), anorthite phase was favored due to a higher amount of CaO present in the glass composition.

Figure 3.11 shows XRD patterns of the G-20 samples normalized according to  $\text{Al}_2\text{O}_3$  peak at  $2\theta=43.36^\circ$ . Anorthite phase first appeared at 850°C with a very low intensity. The intensity of the main peaks at  $2\theta=22.03^\circ$  and  $28.09^\circ$  slightly enhanced up to 1350°C. After 1350°C, no anorthite peaks were observed within the detection limit of XRD, which may be attributed to  $\text{Al}_2\text{O}_3$  grain coarsening dominating the microstructure (see Figure 3.8 (a, b)) or evaporation of alkaline materials at very high

temperatures. The weight loss of the G-20 powder containing 2 wt% of polymer was measured by thermogravimetric analysis in order to understand the evaporation of the alkaline cations (Figure 3.12). The polymer in the powder was removed up to 750°C and weight loss was 2.84 wt% (e.g., polymer and moisture). After 750°C, a slope change was observed, and weight loss was accelerated after 1180°C. The total weight loss was 6.69 wt% up to 1450°C, which yielded 3.85 wt% loss from the composition. This powder was then analyzed by EDS and compared with the initial ratios given in Table 3.1. It was found that 47 wt% of the initial Na<sub>2</sub>O (1.27 wt% loss from the composition) and 94 wt% of the initial K<sub>2</sub>O (2.58 wt% loss from the composition) were evaporated during heating. Note that these evaporation ratios were calculated with respect to the SiO<sub>2</sub> amounts detected in EDS analysis for both powders separately. SiO<sub>2</sub>/CaO ratios were checked before and after each heat treatment to make sure, and it was figured out that both ratios did not change due to their higher melting temperatures. In addition, more volatilization indicated that crystalline phase was Na-rich anorthite (Ca,Na)(Si,Al)<sub>4</sub>O<sub>8</sub>. It has been reported K<sub>2</sub>O and Na<sub>2</sub>O volatilization from silica melts containing SiO<sub>2</sub>, CaO, Na<sub>2</sub>O and K<sub>2</sub>O between 1240°C and 1670°C as well [57].

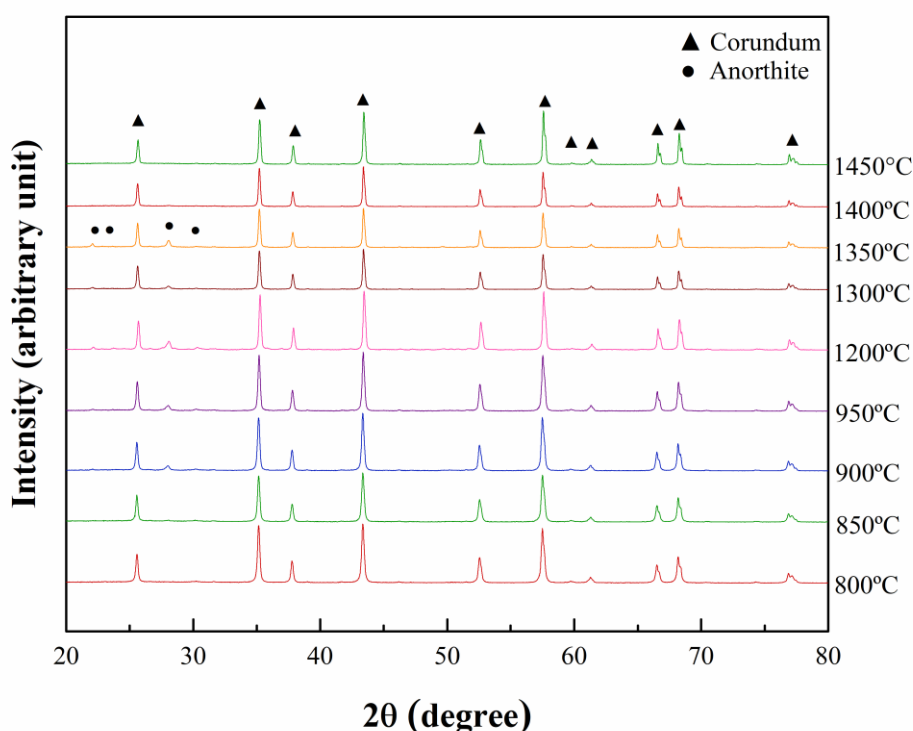


**Figure 3.11** XRD patterns of the G-20 sintered at different temperatures.

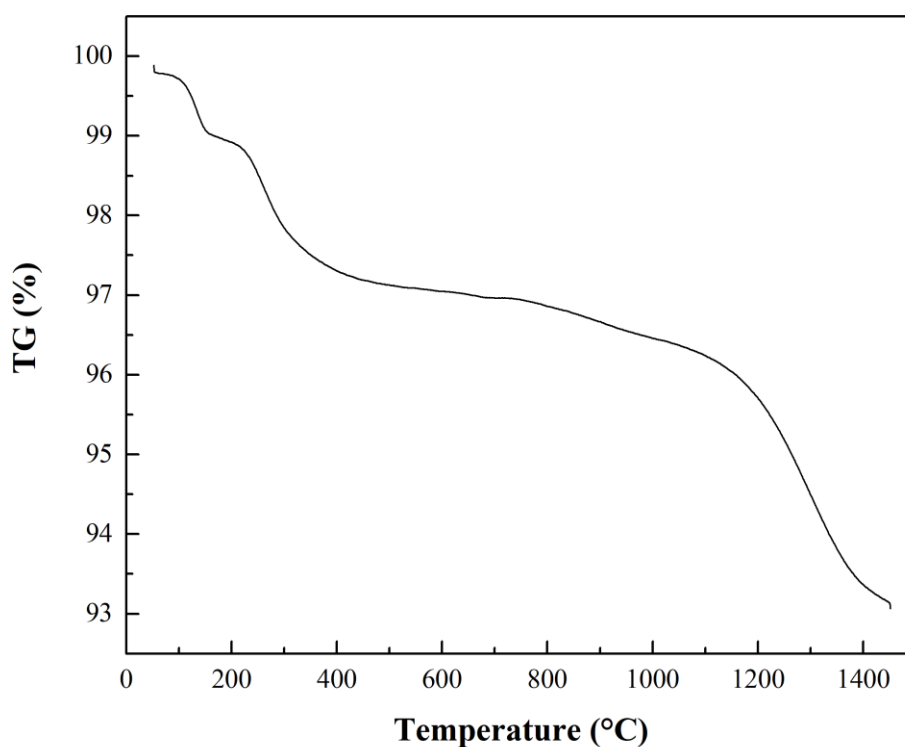


**Figure 3.12** Thermogravimetric result of the G-20 with 2 wt% of polymer.

Figure 3.13 to 3.16 show XRD patterns of the G-40, G-50, G-55 and G-60 composites normalized according to  $\text{Al}_2\text{O}_3$  peak at  $2\theta=43.36^\circ$  as a function of temperature. The crystallization of the anorthite phase in the G-40 sample first appeared at  $850^\circ\text{C}$  and enhanced significantly with increasing temperature. Similarly, crystallization of the anorthite started at  $825^\circ\text{C}$  in the G-50, G-55 and G-60 with the main peak at  $2\theta=28.02^\circ$ ,  $28.09^\circ$ ,  $28.03^\circ$ , respectively. Also, background of the XRD patterns  $20^\circ\sim 30^\circ$  decreased upon increasing temperature due to the crystallization of the anorthite phase.

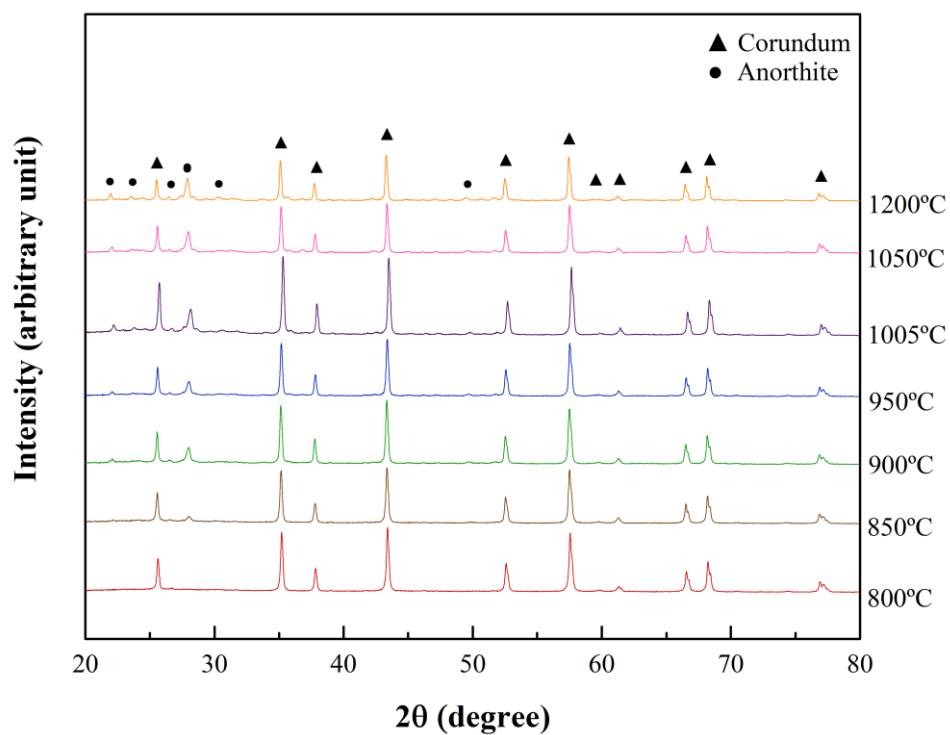


Figure 3.13 XRD patterns of the G-40 sintered at different temperatures.

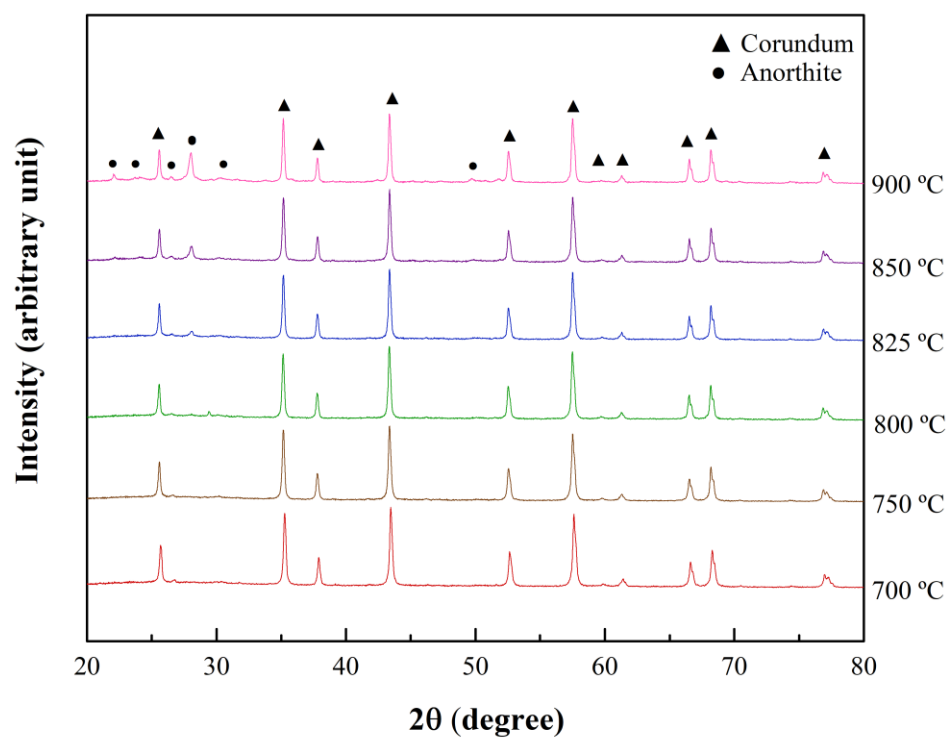


Figure 3.14 XRD patterns of the G-50 sintered at different temperatures.

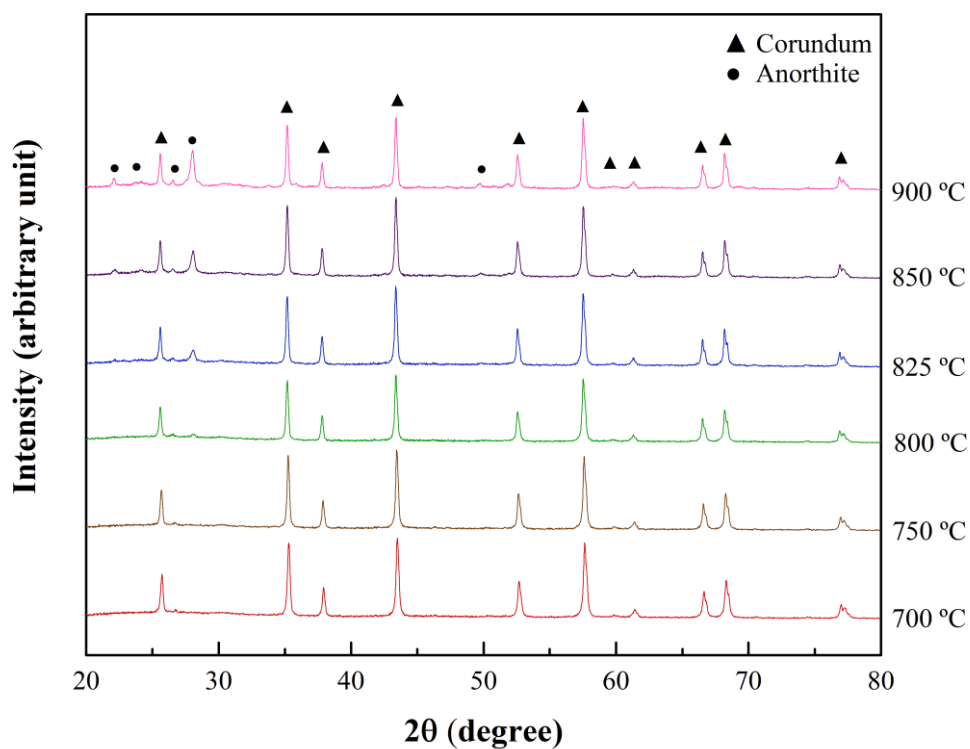


Figure 3.15 XRD patterns of the G-55 sintered at different temperatures.

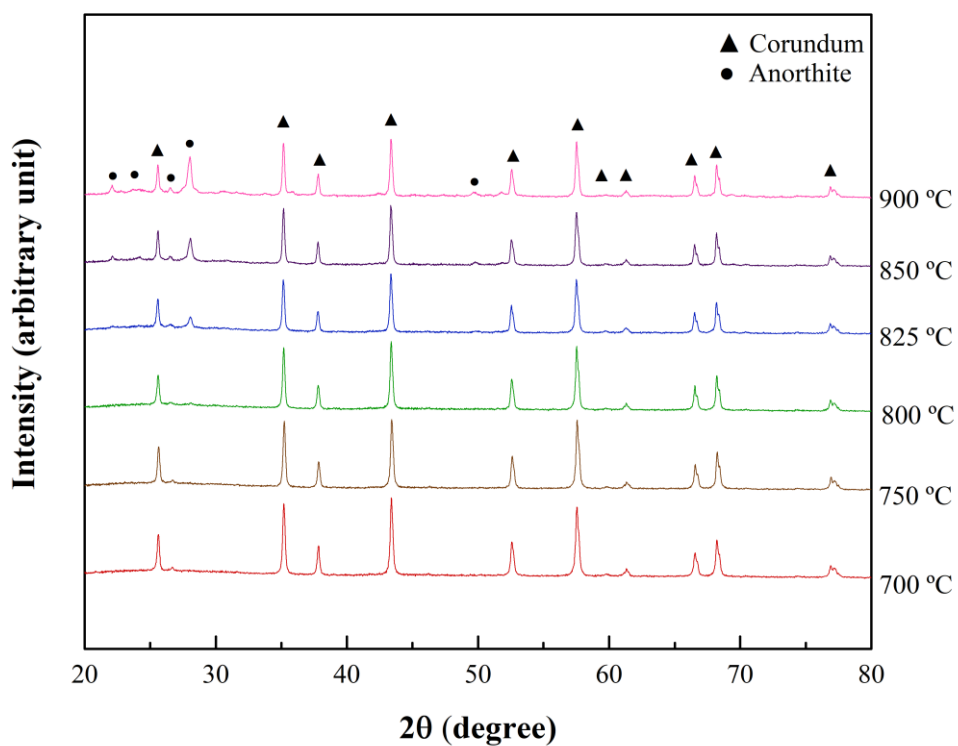


Figure 3.16 XRD patterns of the G-60 sintered at different temperatures.

Figure 3.17 compares normalized XRD patterns of the glass and the  $\text{Al}_2\text{O}_3/\text{glass}$  composites sintered at optimum sintering temperature for each composition (see Figure 3.6). When the G-50, G-55, and G-60 composites sintered at  $850^\circ\text{C}$  were compared, the main peak intensity of anorthite at  $2\theta=28.08$  increased from the G-50 to G-60, which showed that higher glass content resulted in more crystallization of the anorthite phase. However, crystallization of the anorthite phase was more pronounced in the G-40 sintered at  $1200^\circ\text{C}$  even though the glass amount was lower than that of the G-60. These results indicate that enhanced crystallization is dependent on both glass content and temperature such that higher temperature induces more crystallization. In other words, melting temperature of the glass is  $1180^\circ\text{C}$ , which decreases glass phase viscosity and increases crystallinity at the densification temperature of the G-40. The G-20 showed little crystallinity due to the least amount of the glass content.

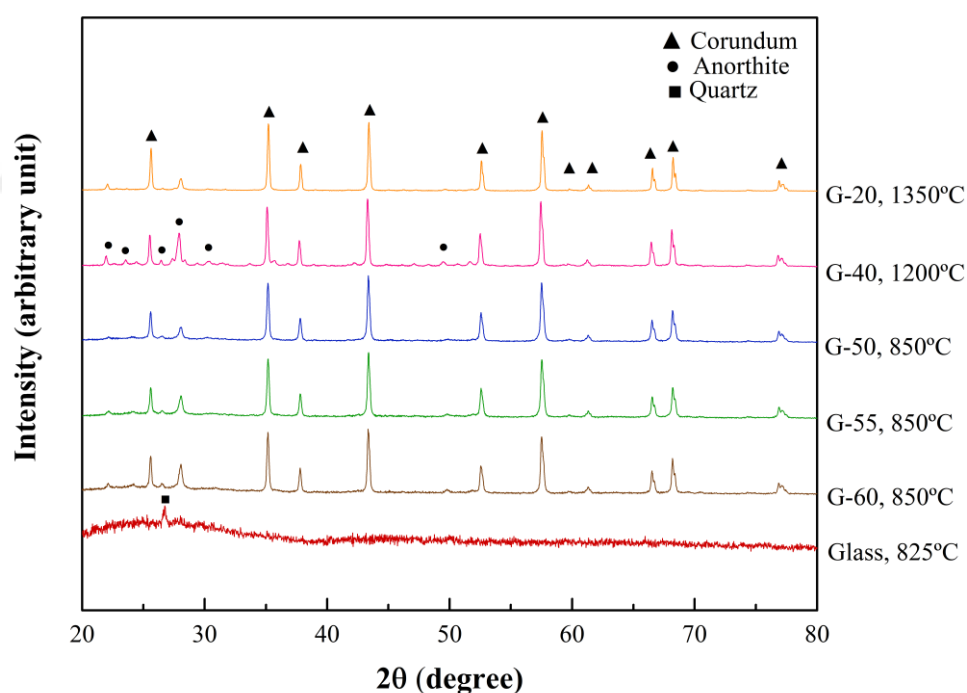


**Figure 3.17** XRD patterns of the  $\text{Al}_2\text{O}_3/\text{glass}$  composites sintered at optimum sintering temperature for each composition.

Figure 3.17 also shows a background between nearly  $2\theta=20-35^\circ$  for each composition. The backgrounds indicate that there remains an amorphous phase, irrespective of sintering temperatures, due to the presence of the glass phase in the composites. The amount of the amorphous phase was qualitatively determined from the area underneath each XRD background between  $2\theta=20-35^\circ$  and corrected for the initial glass wt%. The amount of the amorphous phase was between 49-56 wt% in the G-50 to G-60, nearly 20 wt% in the G-40 and 19 wt% in the G-20. The amorphous region is less in the G-40 when compared to the others, which is due to extensive crystallization of the anorthite phase as a result of both high amount of glass and sintering temperature.

### 3.3 Mechanical Properties

Young's modulus of the  $\text{Al}_2\text{O}_3$ /glass composites were calculated using Equations 2.1 and 2.2. Figure 3.18 compares the Young's modulus of the composites sintered at optimum sintering temperature for each composition.  $\text{Al}_2\text{O}_3$  (0 wt% glass) is the end member and given for better evaluation of the composite behavior. The dashed line represents the best fit to the data. The Young's modulus of  $\text{Al}_2\text{O}_3$  and soda lime glass is 390 GPa [18] and 70 GPa [3], respectively. The Young's modulus showed a significant decline from 231 GPa for the G-20 to 121 GPa for the G-40 and remained almost constant after 40 wt% of glass. This significant decrement is ascribed to the different sintering mechanism, namely, liquid phase sintering of  $\text{Al}_2\text{O}_3$  in the G-20 and G-40, and viscous sintering due to higher amount of glass phase present in the G-50 to G-60 composites. In other words, in the G-50 to G-60 composites, glass phase uniformly embraced all  $\text{Al}_2\text{O}_3$  grains without any grain growth (see Figure 3.8) and hence the low-modulus glass phase dominated the microstructure and property with increasing glass content.

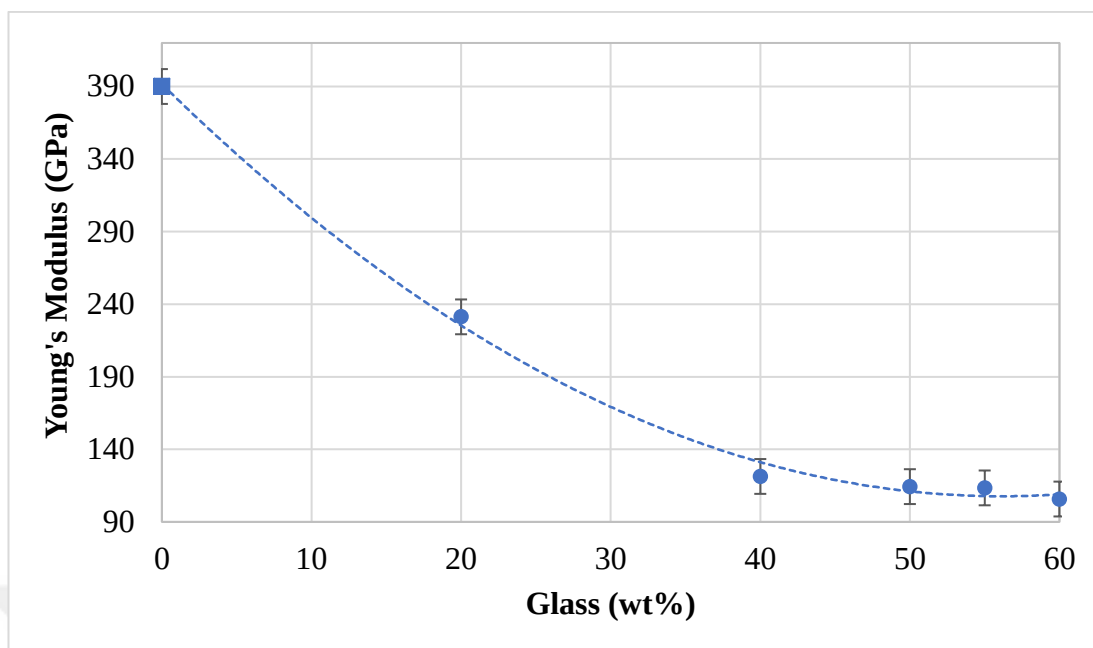


**Figure 3.18** Young's modulus of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition.

Flexural strength of the  $\text{Al}_2\text{O}_3$ /glass composites were calculated using Equation 2.3 and are compared in Figure 3.19. The flexural strength of  $\text{Al}_2\text{O}_3$  was 411 MPa and consistent with the literature values between 330 and 460 MPa [18]. The flexural strength decreased to  $387 \pm 67$  MPa in the G-20 and then sharply to  $164 \pm 11$  MPa in the G-40, and then followed a slightly increasing trend to  $213 \pm 23$  MPa in the G-60. General macroscopic views of the fractured composites are compared in Table 3.4. In the G-20, the flexural strength was the highest within the composites because larger  $\text{Al}_2\text{O}_3$  grains still supported the skeleton of the composite structure in spite of the glass phase interpenetrating between the  $\text{Al}_2\text{O}_3$  grains during liquid phase sintering (see Figure 3.8). The higher amount of glass in the G-40, although its larger  $\text{Al}_2\text{O}_3$  grains due to liquid phase sintering, decreased the strength sharply. Viscous-sintered G-50 to G-60 composites exhibited different fracture patterns as represented in Table 3.4 in that, although uniform embracement of the  $\text{Al}_2\text{O}_3$  grains by the glass matrix, fracture type changed considerably with increasing glass content. For example, much straighter single fracture in the G-40, more crooked single fracture in the G-50 and G-55, and multiple fractures in the G-60 samples. Fractures with low level of energy generally result in fractures only two pieces (i.e., single fracture without chip off). However,

ceramics break into more pieces in high level fractures (i.e., multiple fractures with/out chip off and/or crack branches) according to ASTM standard C1161-18. In general, fracture behaviors of the composites exhibited both single and multiple mode fractures particularly for the G-50 and G-55 but multiple mode fracture was the only one observed in the G-60. Therefore, flexural strength increased towards the G-60 as fracture types switched towards high level fracture in the viscous-sintered G-50 to G-60 composites.

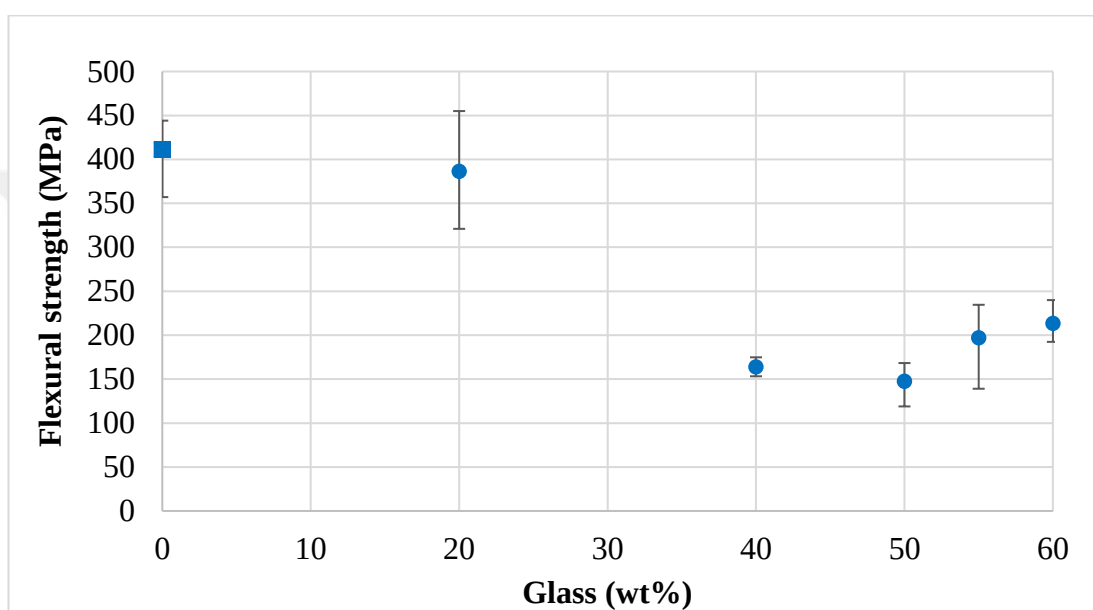
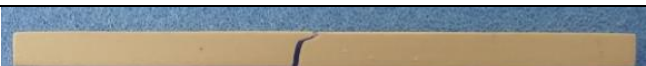


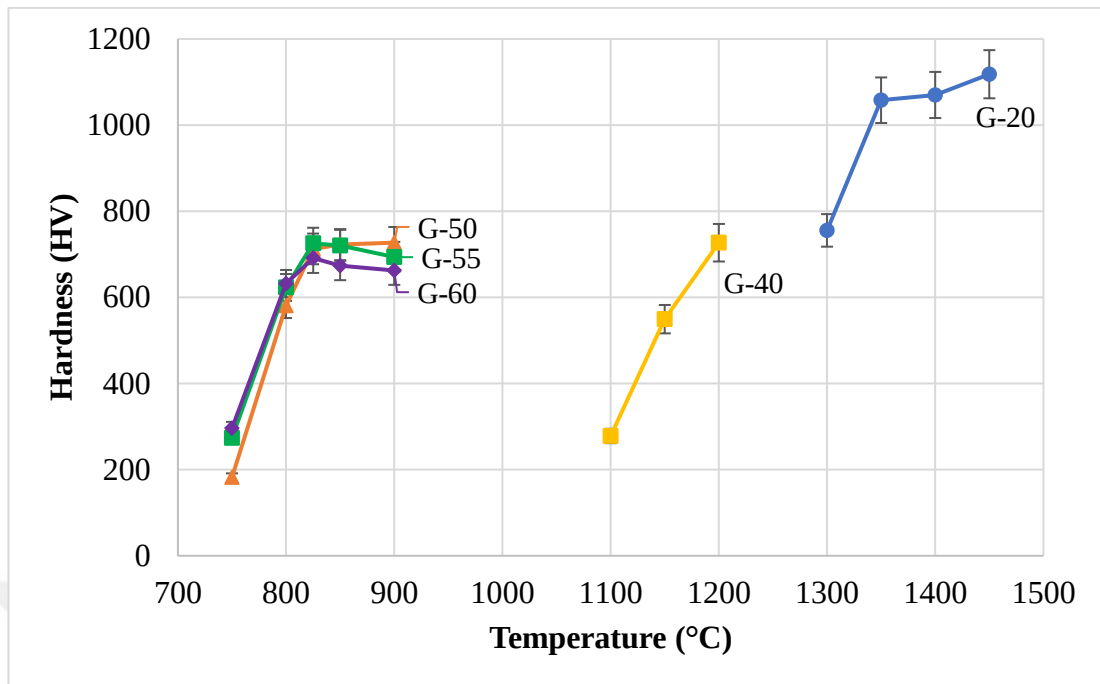
**Figure 3.19** Flexural strength of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition.

**Table 3.4** Fractured composites.

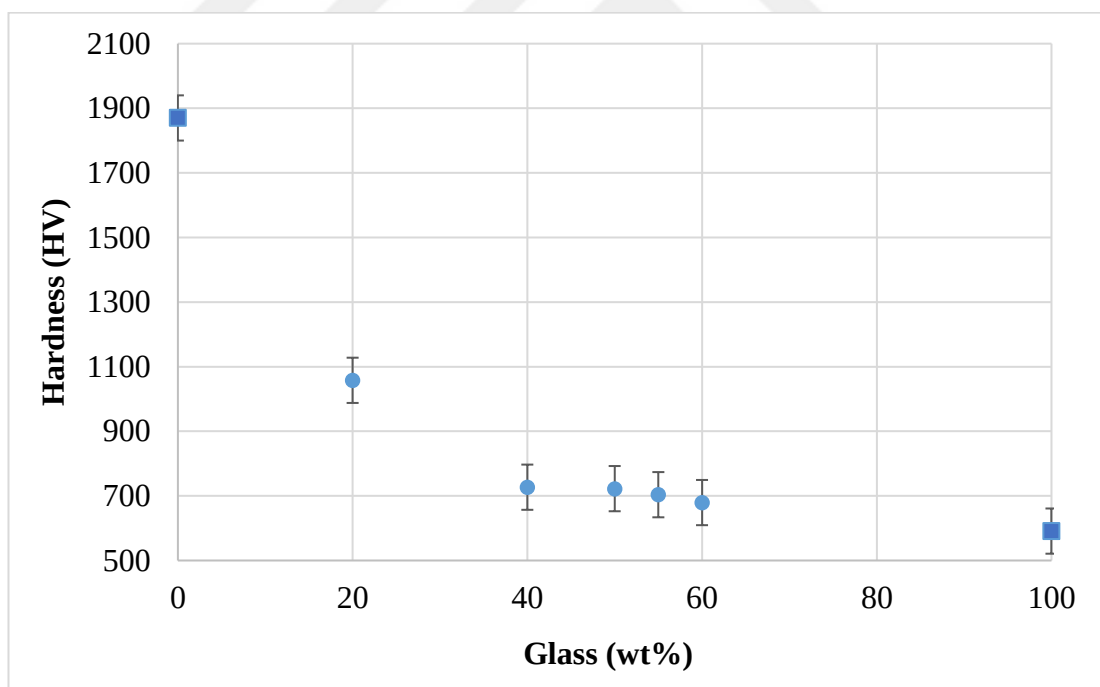
|      | Fractured Composites                                                                 |
|------|--------------------------------------------------------------------------------------|
| G-20 |  |
| G-40 |  |
| G-50 |  |
| G-55 |  |
| G-60 |  |

Hardness of the  $\text{Al}_2\text{O}_3$ /glass composites were calculated using Equation 2.4 and are compared in Figure 3.20.  $\text{Al}_2\text{O}_3$  (0 wt% glass) and glass (100 wt% glass) are the end members and given for better evaluation of the composite behavior. Figure 3.20 (a) shows the hardness of the  $\text{Al}_2\text{O}_3$ /glass composites with increasing sintering temperature. The grid lines are drawn to guide eye. Increasing temperature improved densification and decreased porosity in the composites, which resulted in higher hardness. Maximum hardness for the G-50 to G-60 composites (e.g., HV 725 for the G-50, HV 712 for the G-55, and HV 691 for the G-60) was achieved at 825°C. A slight decrease in hardness was noticed at 850°C due to more anorthite crystallization. The G-20 and G-40 composites had higher hardness upon increasing temperature due to removal of porosity, 727 HV at 1200°C for the G-40 and HV 1060 at 1350°C for the G-20.

Figure 3.20 (b) compares the hardness values at optimum sintering temperature for each composition. The hardness of  $\text{Al}_2\text{O}_3$  was HV 1870 which is reported between HV 1500 and 2000 [58]. A significant decrease in hardness was observed with increasing glass content. As of the 40 wt% of glass content, the hardness gradually decreased due to the fact that the glass became the dominant phase in the microstructure. The glass sample had the lowest hardness values of HV 591, which indicated that dispersed  $\text{Al}_2\text{O}_3$  particles strongly improved the hardness. Micrograph of indented surfaces are represented in Figure 3.21 for comparison. It is clearly seen that indentation area is increased with decreasing hardness. For the glass itself, 10 N and 20 N loading did not change the hardness values, but 10 N gave a better micrograph.



(a)



(b)

**Figure 3.20** Hardness of the  $\text{Al}_2\text{O}_3$ /glass composites (a) Sintered at different temperatures; (b) Sintered at optimum sintering temperature for each composition.

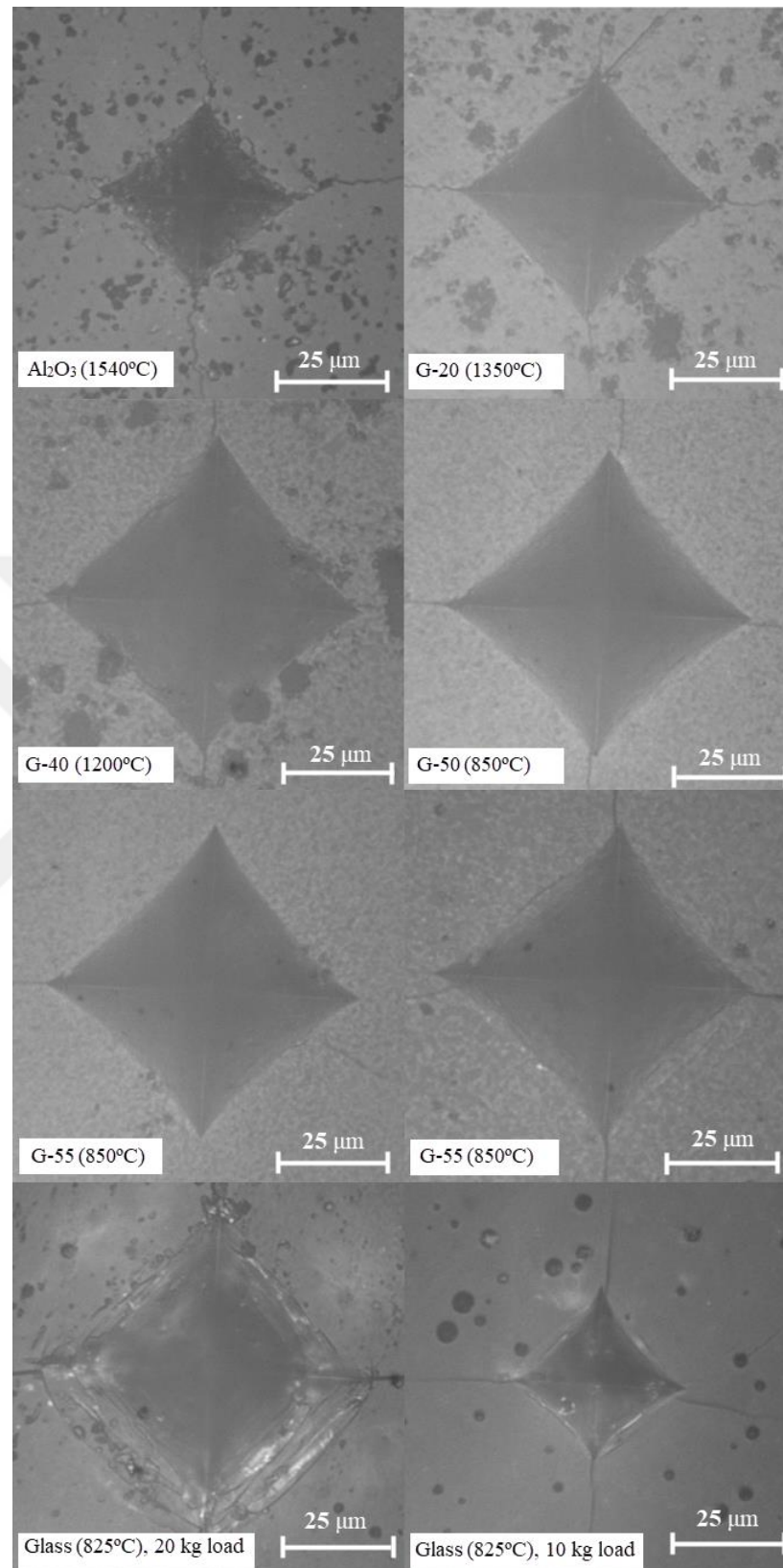


**Figure 3.21** Micrograph of the indented surfaces of the  $\text{Al}_2\text{O}_3$ , glass and composites sintered at optimum sintering temperature for each composition.

Fracture toughness of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition is given in Figure 3.22.  $\text{Al}_2\text{O}_3$  (0 wt% glass) and glass (100 wt% glass) are the end members and given for better evaluation of the composite behavior. In the calculations of the fracture toughness values, the Young's moduli for each set measured (see Figure 3.18) was used in Equation 2.5. The Young's modulus of  $\text{Al}_2\text{O}_3$  was taken as 390 GPa [18]. For silicate glasses, a typical value of the Young's modulus is 70 GPa [3] and taken for the fracture toughness calculations of the glass itself. The fracture toughness of polycrystalline  $\text{Al}_2\text{O}_3$  is between 3.5-4  $\text{MPa}/\sqrt{\text{m}}$  and for silicate glasses it is between 0.7-0.9  $\text{MPa}/\sqrt{\text{m}}$  [3]. Similar to the literature values, the fracture toughness of  $\text{Al}_2\text{O}_3$  and glass was measured as 4.0  $\text{MPa}/\sqrt{\text{m}}$  and 1.0  $\text{MPa}/\sqrt{\text{m}}$ , respectively.

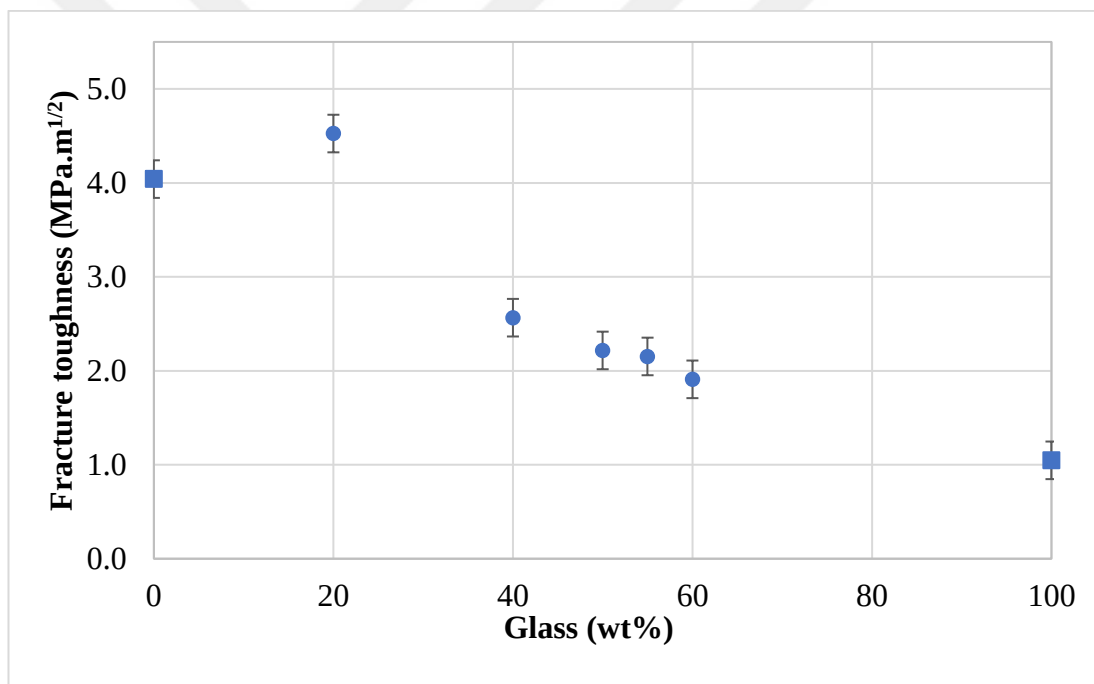


**Figure 3.22** Fracture toughness of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition.

The fracture toughness showed an increment from 4.0  $\text{MPa}/\sqrt{\text{m}}$  for  $\text{Al}_2\text{O}_3$  to 4.5  $\text{MPa}/\sqrt{\text{m}}$  for the G-20. After 20 wt% of glass, fracture toughness of the composites sharply decreased to 2.6  $\text{MPa}/\sqrt{\text{m}}$  for the G-40 and to 1.9  $\text{MPa}/\sqrt{\text{m}}$  for the G-60. Unlike the G-20 and G-40, the G-50, G-55 and G-60 composites sintered by viscous

sintering and did not does not possess distinct grain boundaries. Consequently, the fracture toughness of the composites declined with increasing amount of glass phase, particularly after 20 wt% of glass.

Backscattered SEM images of the cracks in the G-20, G-40, G-60, and glass are compared in Figure 3.23. The G-20 sintered at 1450°C had coarsened as well as faceted/elongated  $\text{Al}_2\text{O}_3$  grains within the glass matrix and the crack pathway was like a crooked line, which was an indication of more energy absorption and preferential pathway thru intergranular glassy phase by means of crack bridging and deflection by the  $\text{Al}_2\text{O}_3$  grains (Figure 3.23 (a)). Crack propagation pathways became much straighter towards increasing glass content in the composites. The G-40 had both straight and crooked crack pathways in that the crack propagation was through the intergranular glass phase similar to the G-20 but very straight in glass dominant regions as compared with arrows in Figure 3.23 (b). Crack pathway became almost straight in the G-60 with nearly no crack bridging and deflection due to dominant glass phase (Figure 3.23 (c)). Correspondingly, very flat crack pathways were obtained in the glass sample (Figure 3.23 (d)). In glasses, the crack pathway is very flat because glasses have easy cleavage planes and low fracture toughness due to lack of grain boundaries [3]. Therefore, fracture toughness was only improved in the G-20 due to an optimal glass addition in such a way to induce densification at a lower temperature than  $\text{Al}_2\text{O}_3$  as well as providing a very near grain-to-grain distance to bridge or deflect crack efficiently.

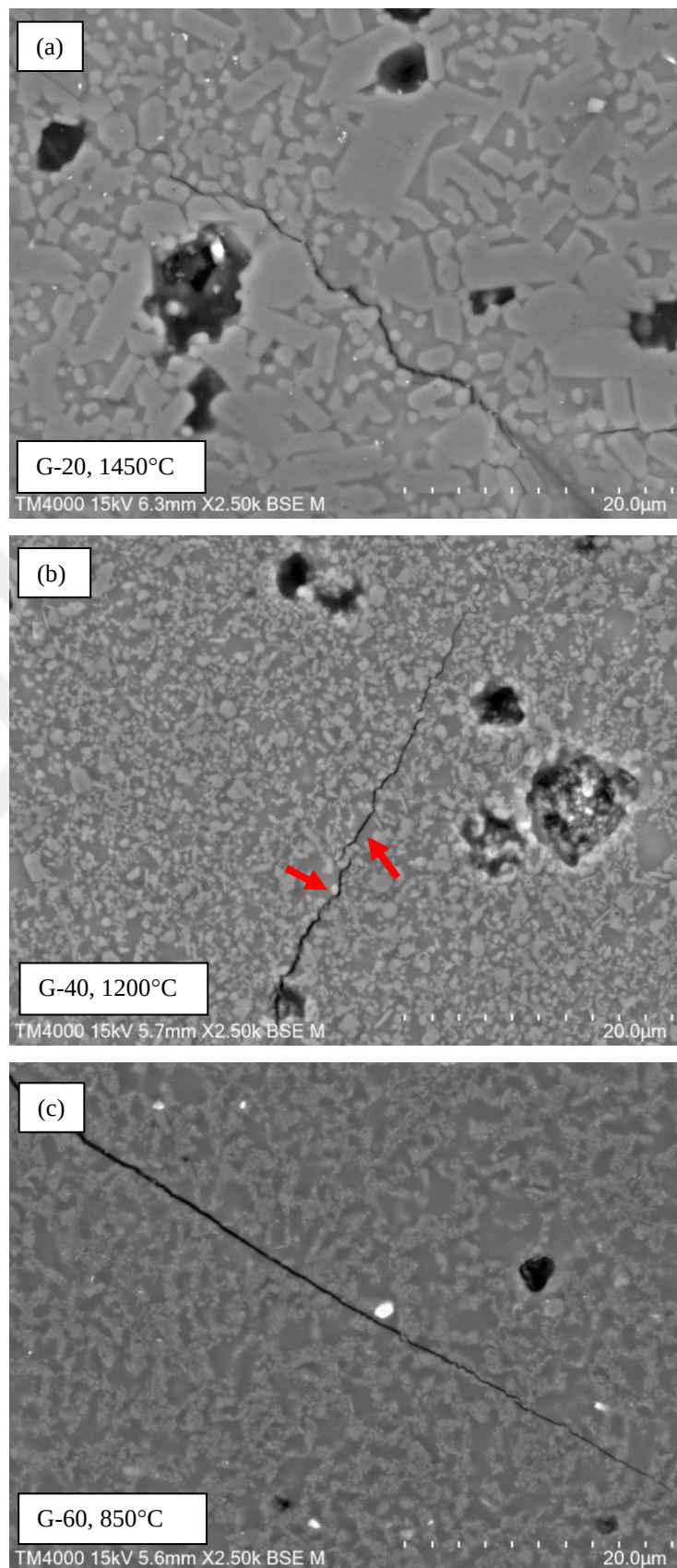


**Figure 3.23** Backscattered SEM images of the cracks formed by indentation.

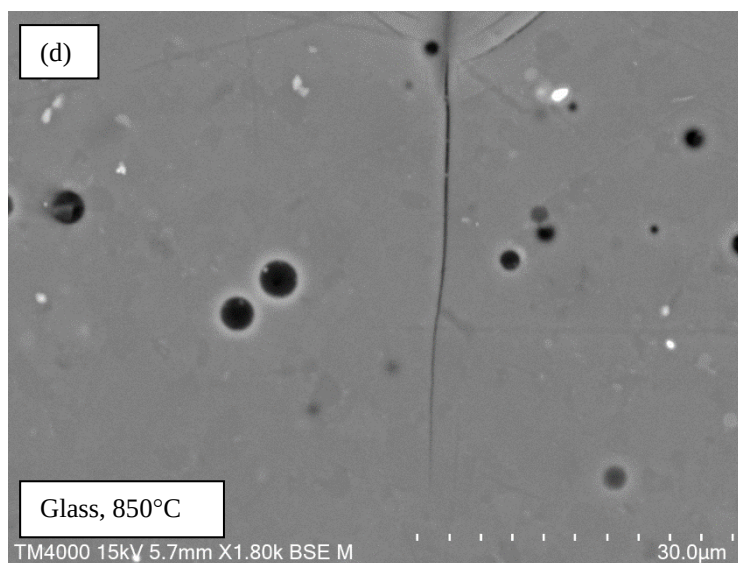


**Figure 3.23 (continued)** Backscattered SEM images of the cracks formed by indentation.

### 3.4 Dielectric Properties

Figure 3.24 shows dielectric constant of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition. The capacitance was measured at 5 MHz and dielectric constant was then calculated from Equation 2.6.  $\text{Al}_2\text{O}_3$  (0 wt% glass) and glass (100 wt% glass) are the end members and given for better evaluation of the composite behavior. The dielectric constants of the end members  $\text{Al}_2\text{O}_3$  and glass measured at 5 MHz were calculated as 10.19 and 6.37, respectively. The values calculated using parallel, series and logarithmic models using Equations 2.12 to 2.14, as applied to the data measured at 5 MHz, are shown with dashed lines in Figure 3.24. Increasing amount of glass content resulted in lowering dielectric constant due to lower dielectric constant of the glass phase. Experimentally determined dielectric constants were in good agreement with both parallel and series models and very close to the logarithmic model. The dielectric loss values were 0.0018, 0.0022, 0.0034, 0.0043, 0.0030, 0.0081, and 0.0016 for  $\text{Al}_2\text{O}_3$ , G-20, G-40, G-50, G-55, G-60, and glass, respectively.

The dielectric constant of the G-40 was further measured at 1 GHz and 10 GHz using a network analyzer to determine intrinsic electromagnetic properties of the dielectric materials by measuring the material's response to radio frequency or microwave

energy. These results indicate that dielectric constant decreased at higher frequencies in that 7.99 at 5 MHz to 6.9 at 1 GHz and to 6.7 at 10 GHz, which is due to the lack of polarizations mainly from space charge and dipolar contributions (see Figure 1.20).

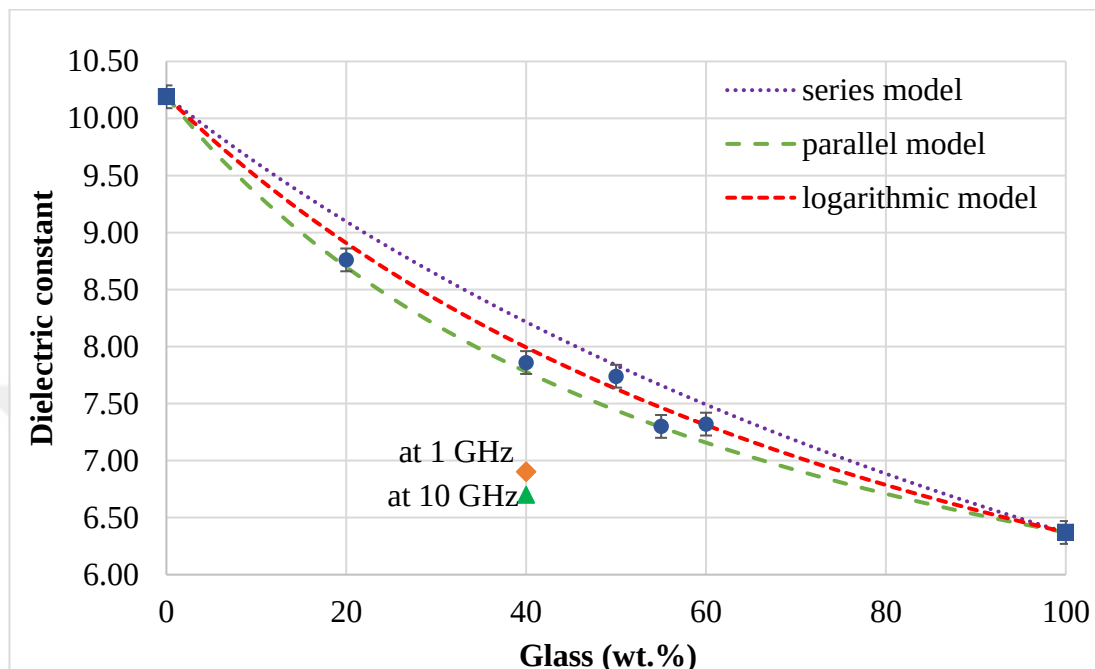


**Figure 3.24** Dielectric constant of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition.

### 3.5 Thermal Properties

Thermal conductivity of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition is calculated from Equation 2.7 and compared in Figure 3.25. The grid lines are drawn to guide eye. The thermal conductivity of all composites exhibited similar behavior in that thermal conductivity increased with increasing temperature from 0.98-1.31 W/m.K at 75 °C to 1.67-2.33 W/m.K at 600 °C. The G-40 reached the highest one due to both the presence of the most  $\text{Al}_2\text{O}_3$  content and larger  $\text{Al}_2\text{O}_3$  grain size, and vice versa for the G-60. Larger grain size decreases the phonon scattering in crystalline ceramics due to less grain boundary area and hence increases the thermal conductivity in the composites [59].

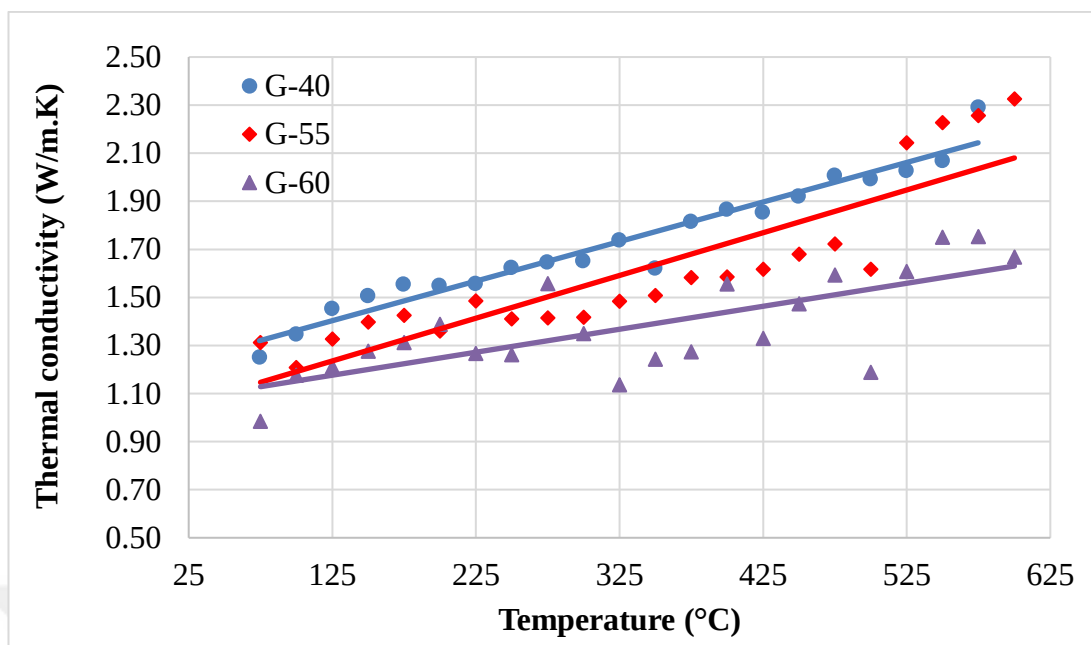


**Figure 3.25** Thermal conductivity of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition.

The thermal conductivity of crystalline and amorphous ceramics is compared in Table 3.5. Crystalline and amorphous materials show opposite thermal conductivity with temperature in that thermal conductivity decreases in the former. The thermal conductivity of single crystal  $\text{Al}_2\text{O}_3$  is 36 W/m.K at 25°C and continuously decreases to 6.3 W/m.K at 900°C [18]. However, the thermal conductivity of vitreous silica (100 wt%  $\text{SiO}_2$ ) is 0.85 W/m.K at -150°C and increases to 1.50 W/m.K at 100°C. Similarly, thermal conductivity of soda lime glass (72 wt.%  $\text{SiO}_2$  and other oxides of  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ) is 0.80 W/m.K at -100°C and 1.15 W/m.K at 100°C [60]. Thermal conductivity is determined by mean free path of phonons in crystalline ceramics. An increase in temperature decreases the mean free path of phonons and suppresses phonon contribution, and, as a result, decreases the thermal conductivity. As the crystal or structure becomes less perfect due to chemical impurities, dislocations and secondary phases, thermal conductivity also decreases due to phonon scattering (e.g., soda lime glass has lower conductivity with respect to vitreous silica given in Table 3.5). Thermal conductivity of amorphous materials is lower than that of crystalline materials because the thermal conduction in glasses is provided by atomic or molecular migration and shows an increase with increasing temperature [17].

**Table 3.5** Thermal conductivity of crystalline and amorphous ceramics.

| Al <sub>2</sub> O <sub>3</sub> [18] |              | Vitreous silica [60] |              | Soda lime glass [60] |              |
|-------------------------------------|--------------|----------------------|--------------|----------------------|--------------|
| T<br>(°C)                           | k<br>(W/m.K) | T<br>(°C)            | k<br>(W/m.K) | T<br>(°C)            | k<br>(W/m.K) |
| 25                                  | 36           | -150                 | 0.85         |                      |              |
| 100                                 | 29           | -100                 | 1.05         | -100                 | 0.8          |
| 300                                 | 16           | -50                  | 1.2          |                      |              |
| 500                                 | 10           | 0                    | 1.3          | 0                    | 1            |
| 700                                 | 7.5          | 50                   | 1.4          |                      |              |
| 900                                 | 6.3          | 100                  | 1.5          | 100                  | 1.15         |

Addition of glass into Al<sub>2</sub>O<sub>3</sub> decreased the thermal conductivity of the composites dramatically. The composites sintered at optimum sintering temperatures have significant amount of amorphous phase, which dominates the microstructure (see Figure 3.8). Even though there are crystalline phases such as Al<sub>2</sub>O<sub>3</sub> and crystallized anorthite, they are embraced by an amorphous phase, which lowers the overall thermal conductivity of the composites [17]. Trend in thermal conductivity given in Figure 3.25 is compatible with the literature in that the thermal conductivity of composites increases with increasing temperature similar to the glass compositions given in Table 3.5.

The relative thermal expansion of the composites as a function of temperature is compared in Figure 3.26. Maximum temperatures for the CTE measurements were chosen to be lower than the optimum sintering temperatures (800°C for the G-20 and G-40 and 600°C for the G-50, G-55 and G-60) in order not to cause sticking of the samples to dilatometer probes. To determine the CTE values, linear fittings to the relative expansion lines ( $\Delta L/L$ ) were applied between 35°C-600°C and 600°C-800°C. R<sup>2</sup> values were greater than 0.99 for each fit. The CTE values between 35°C and 600°C decreased with increasing glass content, that is, 7.72 ppm/°C for the G-20, 7.06 ppm/°C for the G-40 and 6.66 ppm/°C for the G-50 to G-60 composites. In addition, a glass transition temperature (T<sub>g</sub>) was not observed in any of these composites in this temperature range. However, a change in the slopes (and the CTE values) was observed in the G-20 and G-40 composites with increasing temperatures above 600°C,

that is, 10.59 ppm/°C for the G-20 and 15.59 ppm/°C for the G-40. The CTE was more pronounced in the G-40 due to higher amount of the glass present. Change in the CTE values with increasing temperature reveals a glass transition temperature in the G-20 and G-40 composites. A DSC analysis to the G-40 composite was applied and compared with the dilatometer result in Figure 3.27. A transition in thermal curve at the glass transition region was observed in the DSC result. According to ASTM standard E1356-08, tangent lines drawn on transition curve and extrapolated to figure out onset temperature ( $T_f$ ) by intersecting the tangent lines, and midpoint temperature ( $T_m$ ) corresponding to the half point between the extrapolated onset and end points, were determined to be 634°C and 664°C, respectively. In the dilatometer result, the slope change was evaluated from intersection of the linear fits of the relative expansion lines with  $R^2$  values greater than 0.998. The dilatometric glass transition temperature was estimated as 638°C which is compatible with the DSC result. Similarly, the dilatometric glass transition temperature of the G-20 was estimated as 649°C from the slope change of the relative expansion lines.

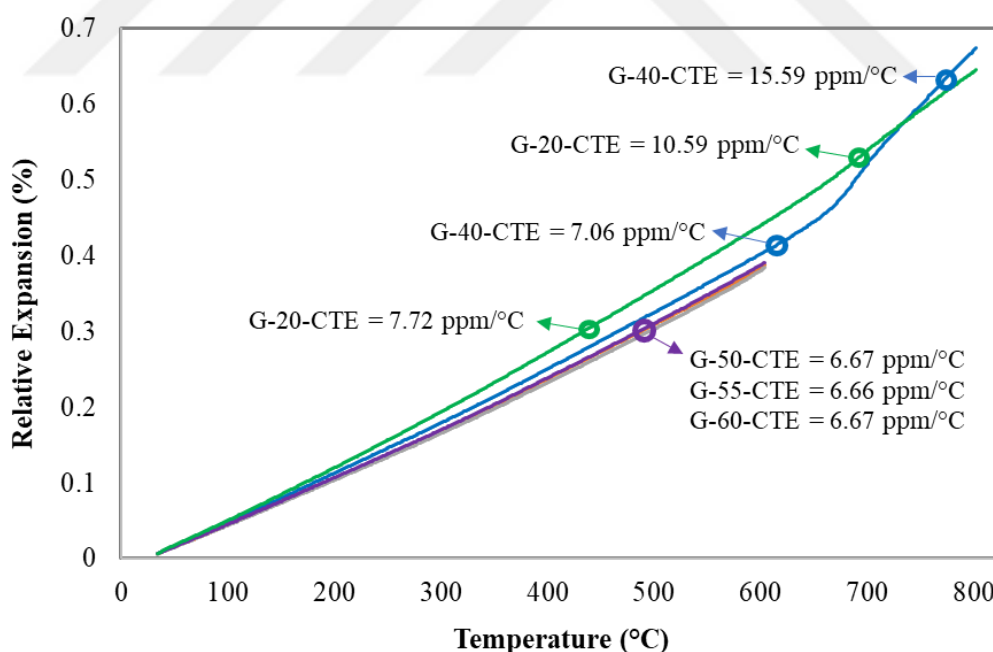


**Figure 3.26** The relative expansion of the composites as a function of temperature.

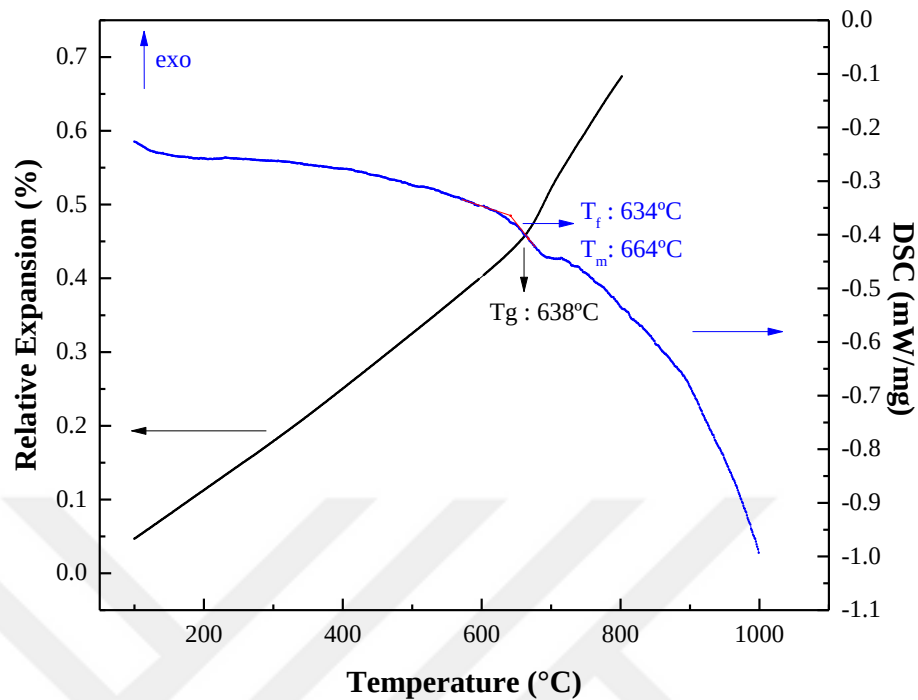


**Figure 3.27** DSC and dilatometer results of the G-40.

Figure 3.28 shows the CTE of the composites between 35°C and 600°C. The dashed line represents the best fit to the data.  $\text{Al}_2\text{O}_3$  (0 wt% glass) is the end member and given for better evaluation of the composite behavior. The CTE value of  $\text{Al}_2\text{O}_3$  between 0°C-1000°C is 8.8 ppm/°C [2]. Increasing amount of the glass phase significantly suppressed the CTE values up to 40 wt% glass and remained almost constant after 50 wt% of glass content, which can be attributed to the lower CTE of the glass phase, particularly due to the presence of  $\text{SiO}_2$ . The CTE of vitreous silica between 0°C-1000°C is 0.55 ppm/°C [2]. Aside from the crystallization of anorthite phase, a distinct amount of glass phase remained in composite at their optimum sintering temperatures. In other words, when the stoichiometric ratio of glass and anorthite was considered, after crystallization of the anorthite, a significant amount of  $\text{SiO}_2$  remained in the amorphous phase. Furthermore, the CTE of anorthite is 4.5 ppm/°C [61], which also contributes to lower the CTE of the composites.

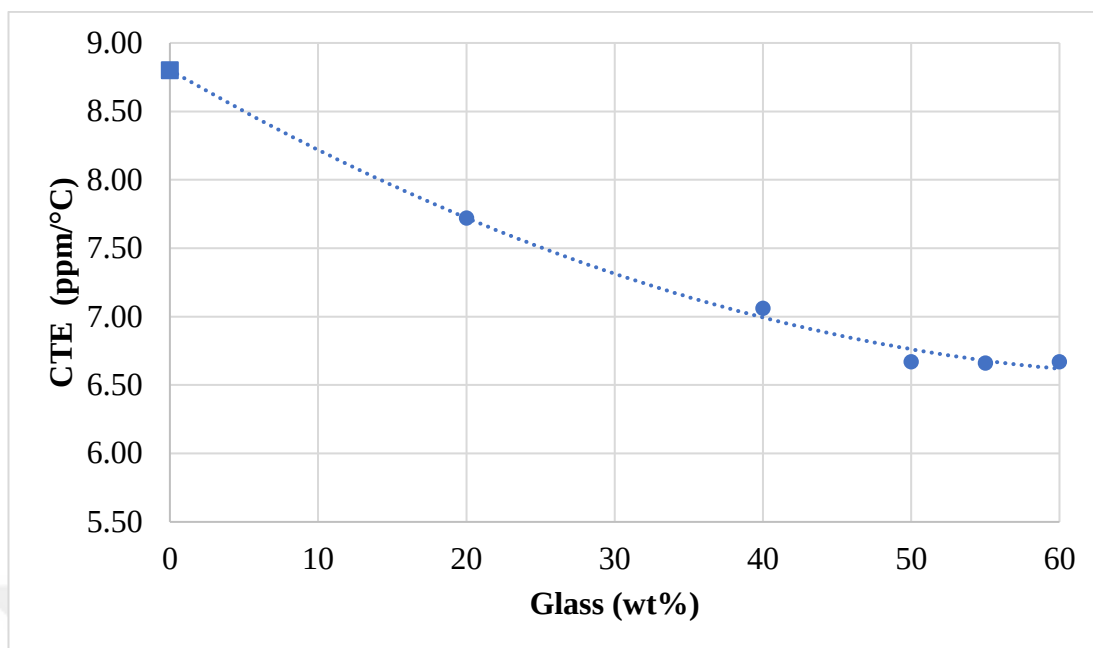


**Figure 3.28** Thermal expansion coefficient of the composites between 35°C and 600°C.

### 3.6 Applications

The overall properties of the  $\text{Al}_2\text{O}_3$ /glass composites sintered at optimum sintering temperature for each composition are summarized in Table 3.6. Note that  $\text{Al}_2\text{O}_3$  and glass are the end members, not composites. They are given to compare the properties with the composites.

For substrate applications, dielectric constant is the key parameter. All composites are suitable for substrate applications because glass addition lower the dielectric constant with respect to  $\text{Al}_2\text{O}_3$ . In addition, dielectric loss did not almost change. Reduced sintering temperature was another asset to decrease production costs as well.

As for LTCC applications, due to the requirement of sintering temperature to be lower than 950°C, the G-50 to G-60 composites can be proposed because they are sintered at 850°C enabling cofiring with metals. Their dielectric constant ranges between 7.74 and 7.32 while keeping low dielectric loss in the range of 0.0030-0.0081 at 5 MHz. For the commercial LTCCs (see Table 1.4), dielectric constant varies between 5.75 and 9.35.

**Table 3.6** The overall properties of the composites.

| Composition                    | Sintering Temperature (°C) | Dielectric Properties        |                                |                            | Thermal Properties      |                              | Mechanical Properties   |                       |               |                                            |
|--------------------------------|----------------------------|------------------------------|--------------------------------|----------------------------|-------------------------|------------------------------|-------------------------|-----------------------|---------------|--------------------------------------------|
|                                |                            | Density (g/cm <sup>3</sup> ) | Dielectric constant (at 5 MHz) | Dielectric loss (at 5 MHz) | CTE (ppm/°C) (25-600°C) | Thermal Conductivity (W/m.K) | Flexural Strength (MPa) | Young's Modulus (GPa) | Hardness (HV) | Fracture Toughness (Mpa.m <sup>1/2</sup> ) |
| Al <sub>2</sub> O <sub>3</sub> | 1540                       | 3.93±0.02                    | 10.19±0.02                     | 0.0018                     | 8.8 [2]                 | 36 [18]                      | 411±47                  | 390 [18]              | 1870±60       | 4.0±0.3                                    |
| G-20                           | 1350                       | 3.5±0.04                     | 8.76±0.03                      | 0.0022                     | 7.72                    | -                            | 379±66                  | 231±17                | 1040±77       | 4.5±0.8                                    |
| G-40                           | 1200                       | 2.94±0.05                    | 7.86±0.04                      | 0.0034                     | 7.06                    | 1.25                         | 154±11                  | 121±9                 | 727±103       | 2.6±0.3                                    |
| G-50                           | 850                        | 2.94±0.02                    | 7.74±0.08                      | 0.0043                     | 6.67                    | 1.04                         | 151±25                  | 114±6                 | 717±50        | 2.2±0.2                                    |
| G-55                           | 850                        | 2.9±0.02                     | 7.3±0.10                       | 0.0030                     | 6.66                    | -                            | 192±48                  | 113±6                 | 704±33        | 2.2±0.2                                    |
| G-60                           | 850                        | 2.82±0.02                    | 7.32±0.05                      | 0.0081                     | 6.67                    | 0.98                         | 207±24                  | 106±4                 | 680±55        | 1.9±0.2                                    |
| Glass                          | 825                        | 2.43±0.01                    | 6.37±0.02                      | 0.0016                     | 4.5 [61]                | 0.85 [60]                    | 55-138[2]               | 72-89 [2]             | 591±33        | 1.0±0.1                                    |

The coefficient of thermal expansion is another important parameter in LTCC due to integration of ceramics with other materials in circuit. CTE value of silicon is 3.5 ppm/°C which indicates that the composites can be used in microelectronic applications because the CTE values of the glass-ceramic systems generally vary between 3.5 and 9.7 ppm/°C [47]. Thermal conductivity is also important for removal of heat from circuit. Low thermal conductivity is one main disadvantage of LTCC systems due to poor thermal conductivity of glass phase. Due to high amount of glass in the composites, thermal conductivity values are relatively low. For the commercial LTCCs, thermal conductivity vary between 1.8 and 6.4 W/m.K. Mechanical properties are good compared with the commercial ones, as tabulated in Table 1.4.

### 3.6.1 Substrate and Low Temperature Co-Fired Ceramic (LTCC)

To demonstrate the fabrication of substrate and LTCC products, the G-55 and Al<sub>2</sub>O<sub>3</sub> were chosen. Al<sub>2</sub>O<sub>3</sub> was used because it was one of the most widely used substrate materials [22]. Therefore, the G-55 composite and Al<sub>2</sub>O<sub>3</sub> were successfully tape casted to obtain thin layers. Figure 3.29 shows the G-55 green tape, green tapes cut and laminated, single green tapes on which Ag paste was screen printed. Blade gap was 250 µm during casting and dried thickness of the tapes was 80 µm. For substrate applications, green tapes were laminated and sintered at 825°C and 850°C for the G-55 and 1540°C for the Al<sub>2</sub>O<sub>3</sub>. An intermediate burn out step was added to ensure the complete binder burn out of polymers at a slower heating rate of 2°C/min before sintering in order to avoid cracking since tape casting slurries had higher amount of organics than dry press powders. Densities of the G-55 composites were 2.93 ± 0.02 g/cm<sup>3</sup> and 2.92 ± 0.02 g/cm<sup>3</sup> at 825°C and 850°C with 0% apparent porosity, respectively. Compared with the dry pressed composites, the bulk density increased from 2.90 g/cm<sup>3</sup> to 2.93 g/cm<sup>3</sup> at 825°C and from 2.89 g/cm<sup>3</sup> to 2.92 at 850°C (see Figure 3.5), which proves that colloidal techniques such as tape casting produces more homogeneous packing of particles in the green bodies. Besides, shrinkage in x and y directions was 15.2 % in tape casted composites while 16.2 % in dry pressed ones. Shrinkage in z dimension was 16.6 % which is similar with dry press results.

The tapes were successfully sintered without delamination, cracking or warping. Green and sintered  $\text{Al}_2\text{O}_3$  substrates are shown in Figure 3.30 and 3.31. After sintering, screen printing of Ag paste was applied on the sintered ceramic surfaces with different Ag patterns and baked at  $600^\circ\text{C}$  for 15 min. to obtain substrates as shown in Figure 3.32 and 3.33. Compatibility of Ag with the G-55 and  $\text{Al}_2\text{O}_3$  ceramics were very good with smooth Ag film coatings on the surfaces without any peeling off. The XRD pattern taken from the Ag coated surface (Figure 3.34) showed that Ag did not react to form other phases and only  $\text{Al}_2\text{O}_3$ , anorthite and Ag (Card number: 01-087-0720) peaks were observed.

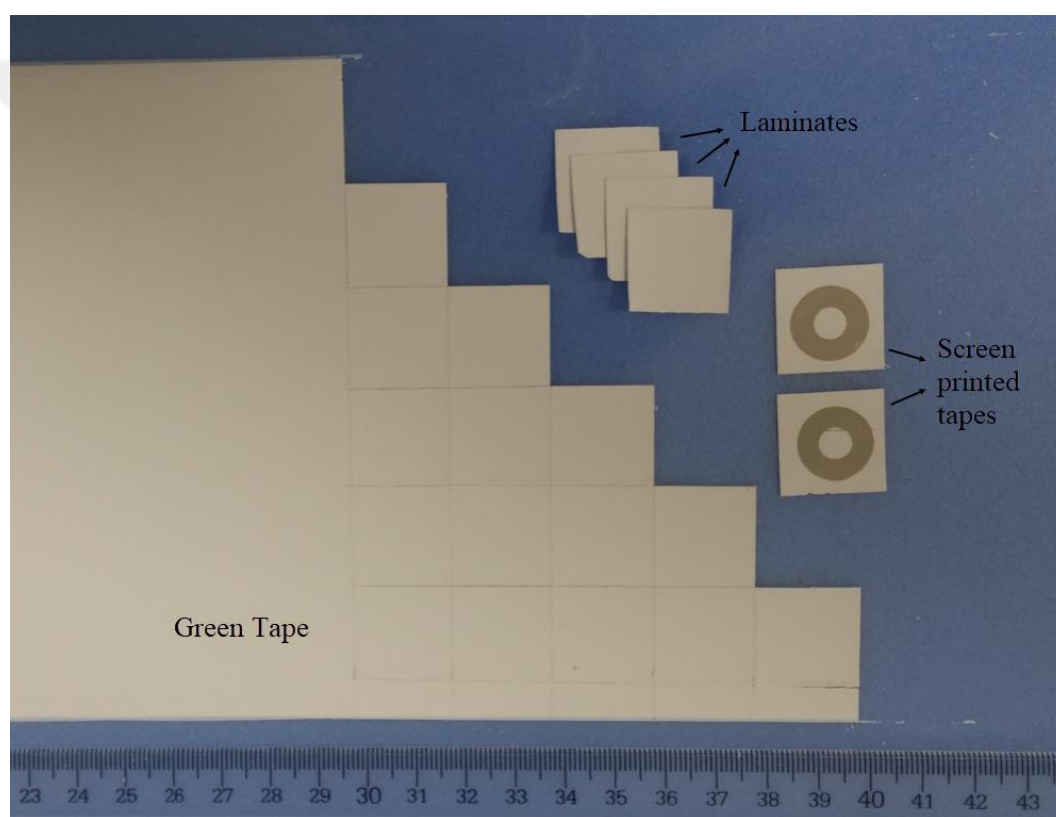


**Figure 3.29** The G-55 green tapes and Ag screen printed tapes.

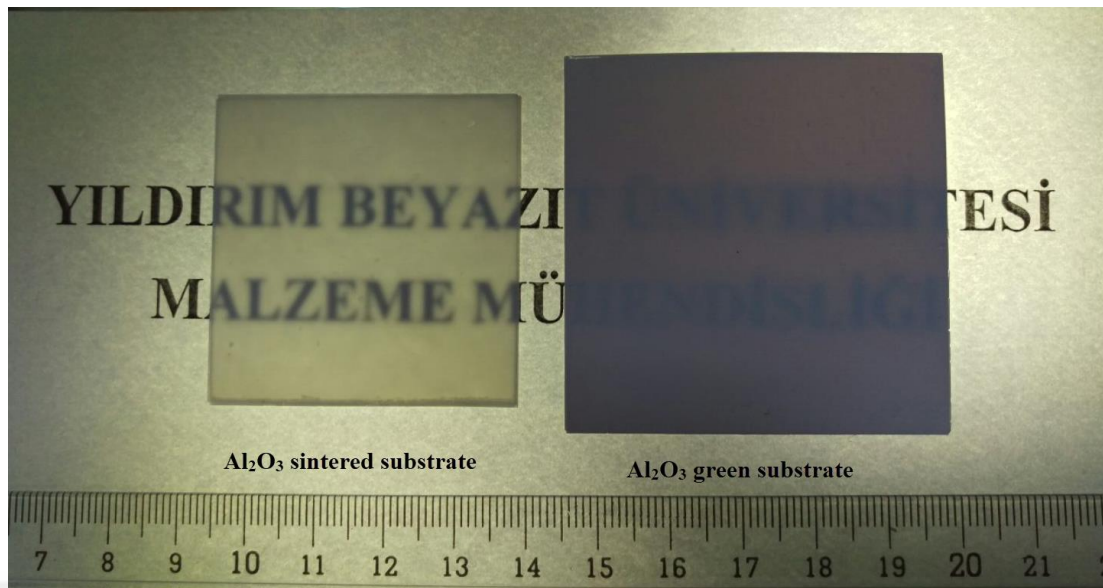


**Figure 3.30** Green and sintered Al<sub>2</sub>O<sub>3</sub> substrate.

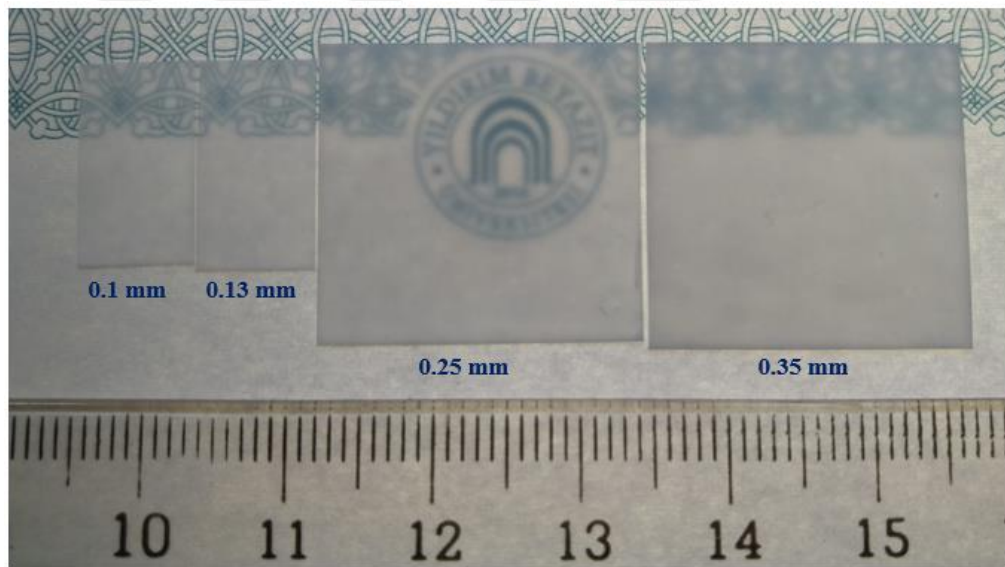


**Figure 3.31** Sintered Al<sub>2</sub>O<sub>3</sub> substrates at various dimensions.

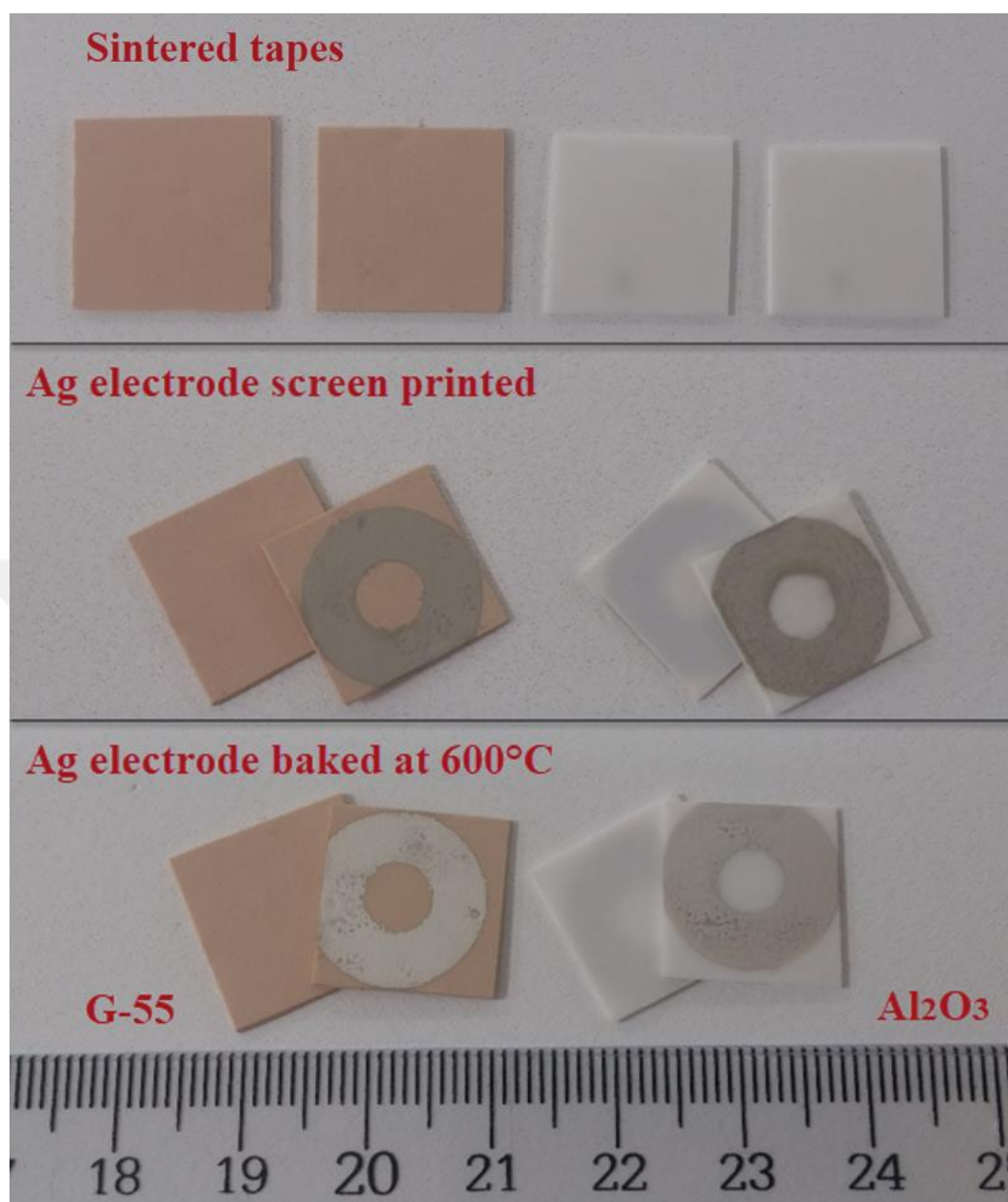


**Figure 3.32** Sintered and Ag paste screen printed G-55 and Al<sub>2</sub>O<sub>3</sub> substrates.

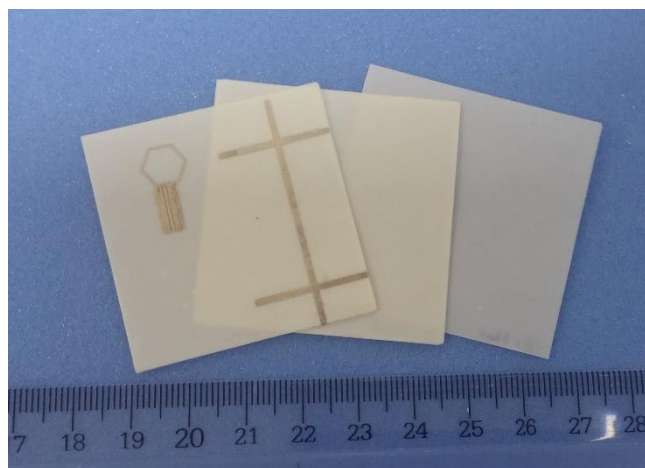


**Figure 3.33** Sintered and Ag paste screen printed  $\text{Al}_2\text{O}_3$  substrates.

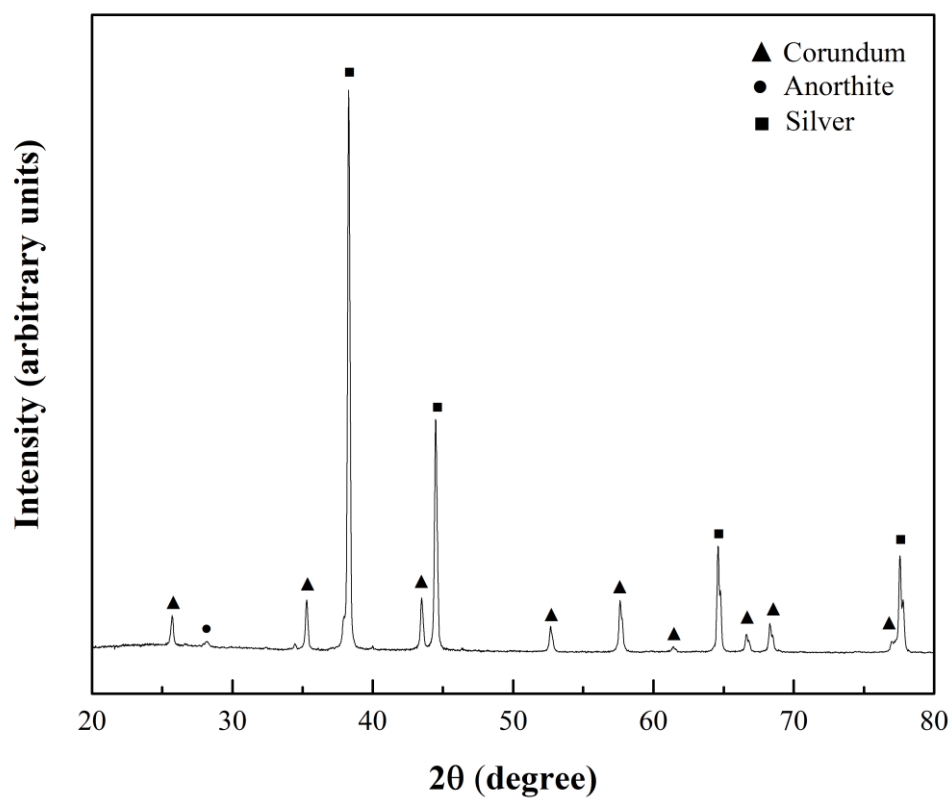


**Figure 3.34** XRD pattern of the G-55 baked with silver on the surface.

Different from the sintered tapes used for substrate applications, green tapes were laminated with an electrode pattern only at the top surface and co-fired at  $850^\circ\text{C}$  with Ag paste. The tape sintered with electrode warped due to differential shrinkage of the

composite and Ag paste as shown in Figure 3.35. This ceramic was not sintered between setter plates due to possible reaction between Ag paste and setter, which also facilitated warping. However, when the sintered tapes were screen printed and baked, no warping was observed as represented in Figure 3.32. It is main reason why substrate materials are first sintered.

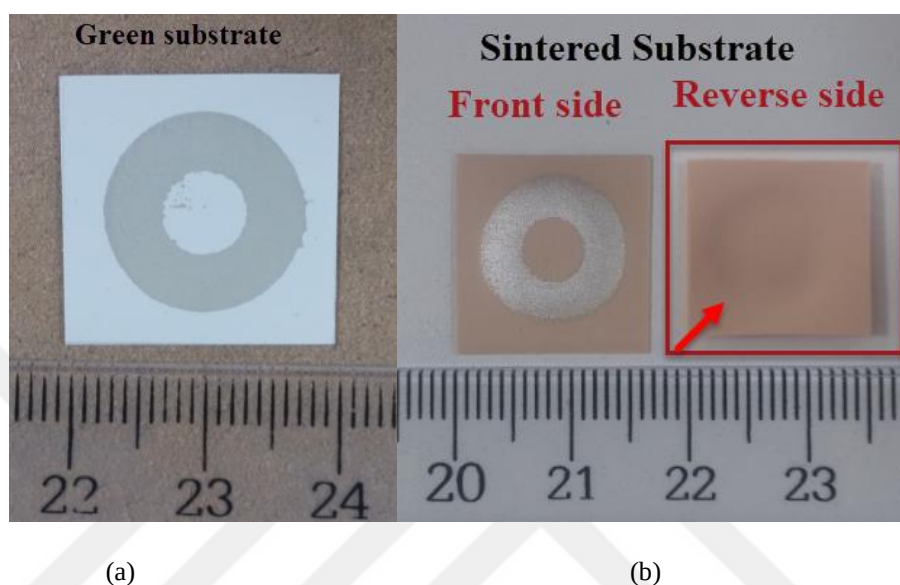


**Figure 3.35** The G-55 co-fired substrate; (a) green; (b) sintered.

For LTCC applications, the G-55 tapes with internal screen-printed Ag electrodes at alternating interlayers of 1, 2 and 6 were laminated. Green samples are shown in Figure 3.36. The cross section of the laminated stacks observed by an optical microscopy are given in Figure 3.37. The LTCC samples were successfully fabricated without delamination or warping at different dimensions as shown in Figure 3.38. The composite has also satisfied the shrinkage requirement with Ag electrode. Micrograph of the cross section after sintering at 850°C is given in Figure 3.39. The silver electrode lines were evenly spaced between the composite sections. Some discontinuities in the Ag lines were due to peel-off caused by the polishing (Figure 3.39 (a)). Figure 3.39 (b) proves that the G-55 composite were successfully co-fired with Ag electrodes without microcracking or delamination.

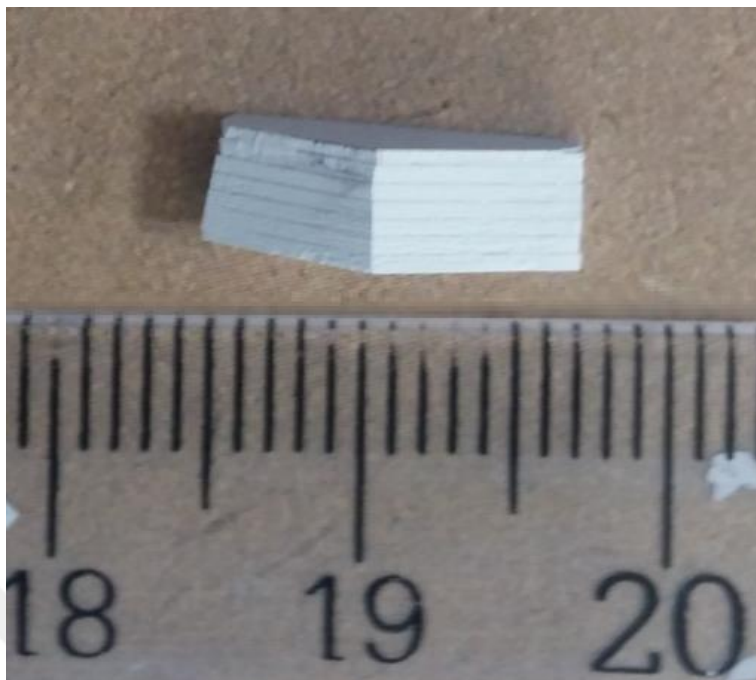
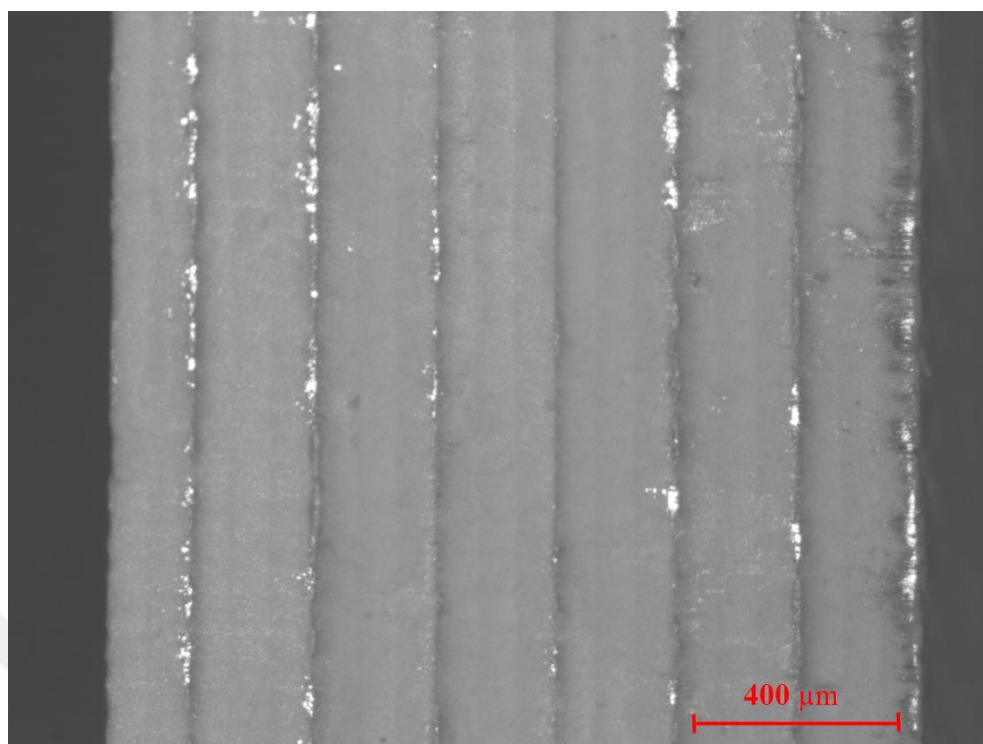
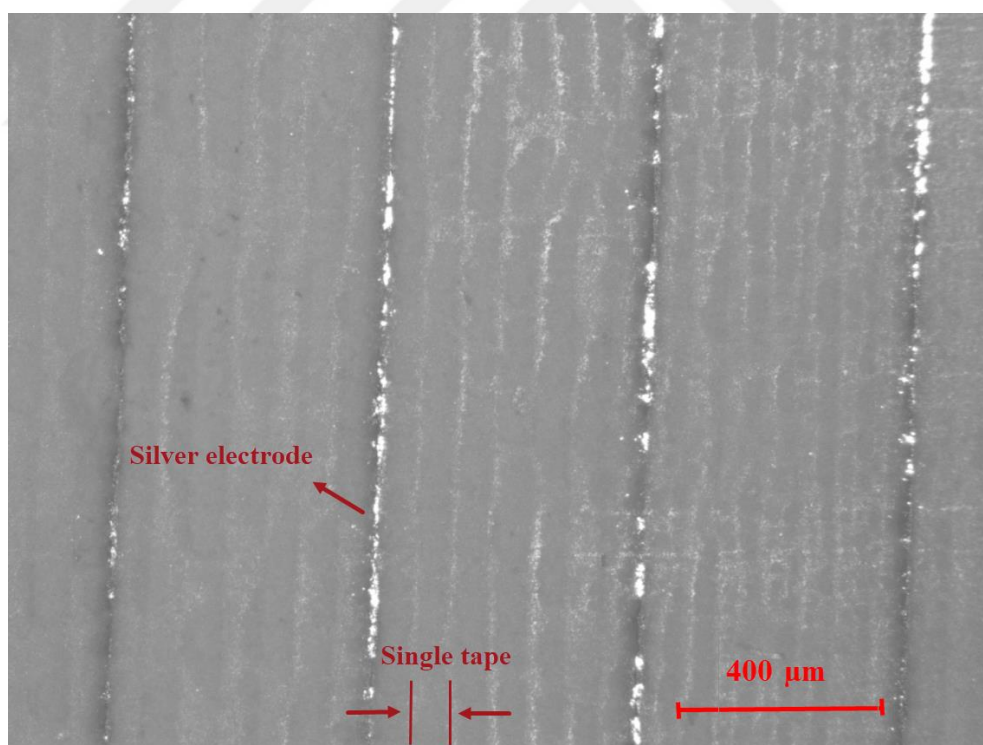


**Figure 3.36** Green LTCC sample, 6 blank interlayers between each electroded layer.



(a)



(b)

**Figure 3.37** Micrograph of the green samples; (a) 2 blank interlayers between each electrode; (b) 6 blank interlayers between each electrode layer.

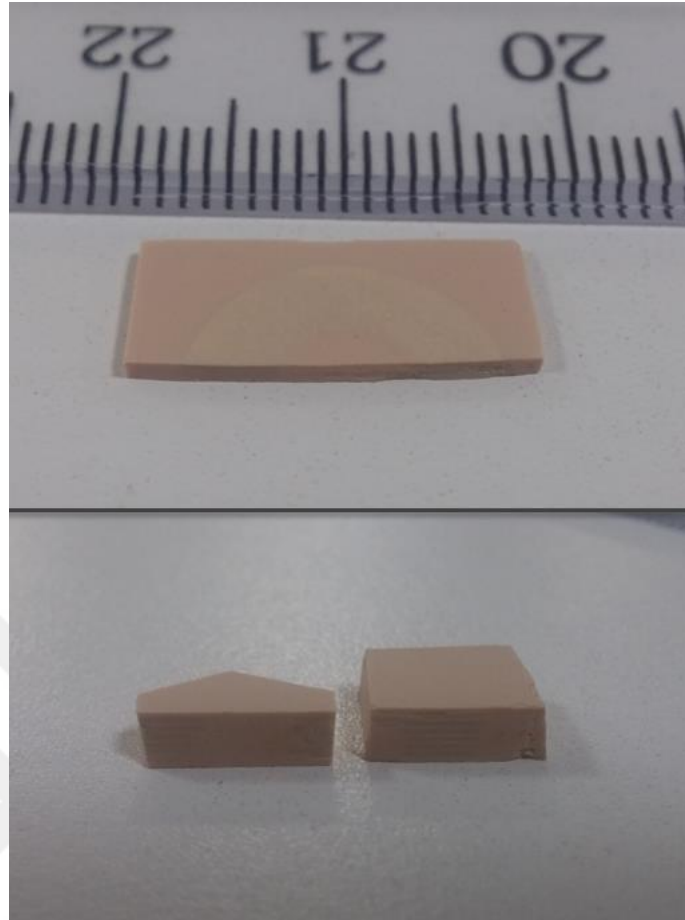
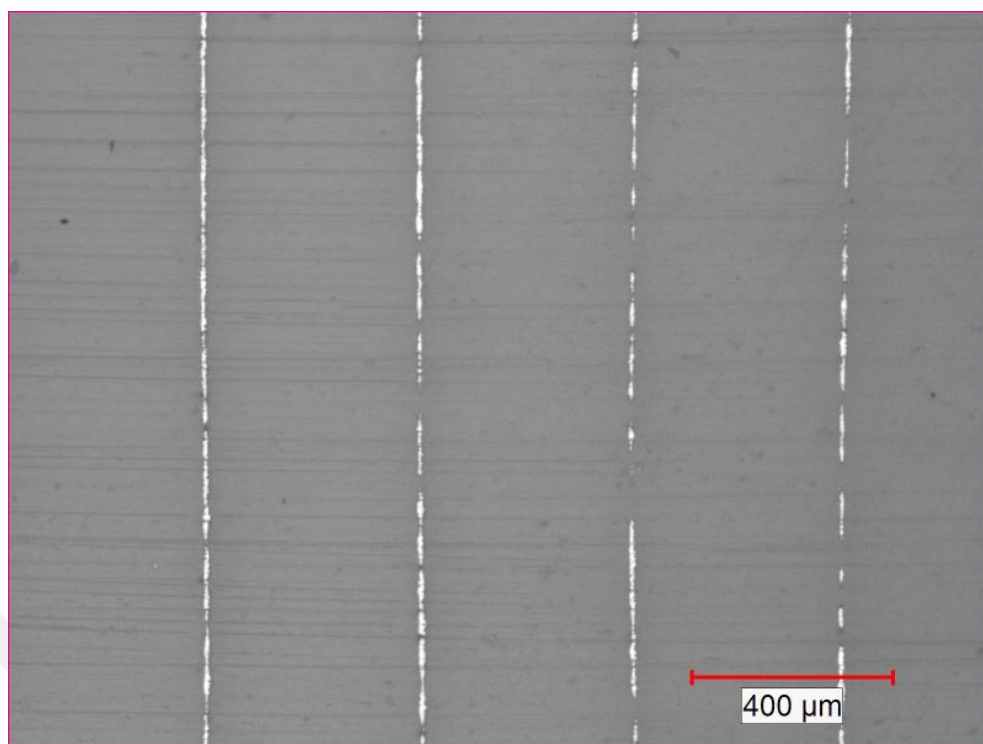
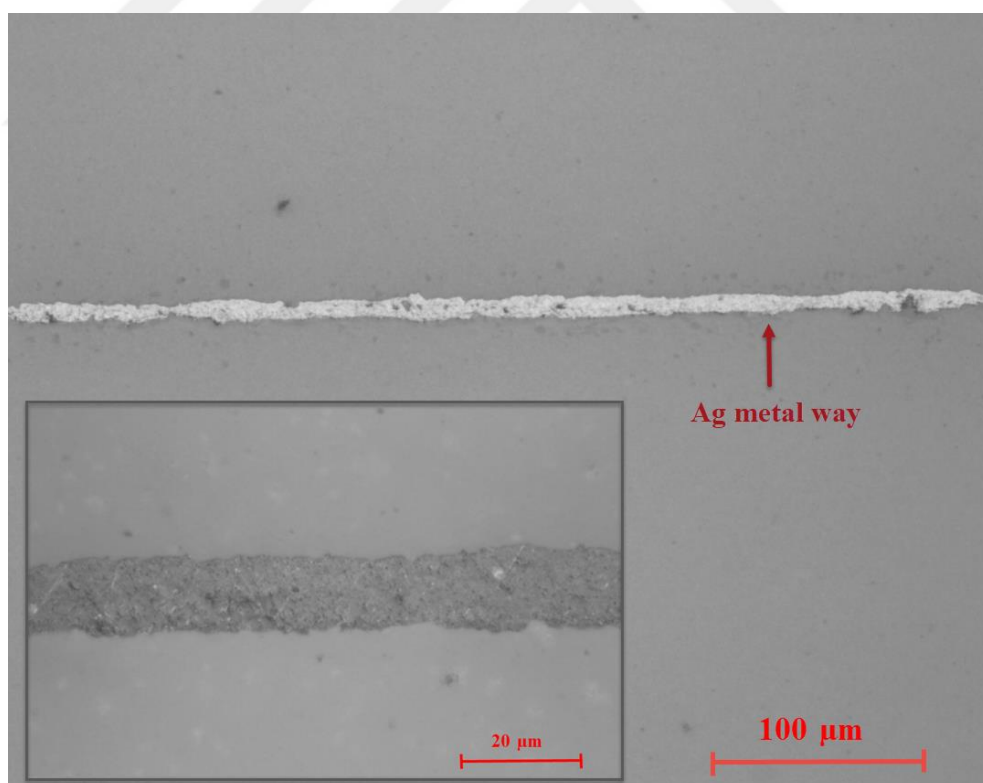


**Figure 3.38** Sintered LTCC samples.



(a)



(b)

**Figure 3.39** Microstructure of the G-55 co-fired with Ag electrode; (a) 6 interlayers between each electrode; (b) sintered Ag electrode.

Co-fired G-55 sample was prepared to check electrical leakage between the electrode layers A and B, as shown in Figure 3.40. Electrical leakage or short-cut was not observed between the electrodes, stating that the G-55 composites had enough electrical resistance.

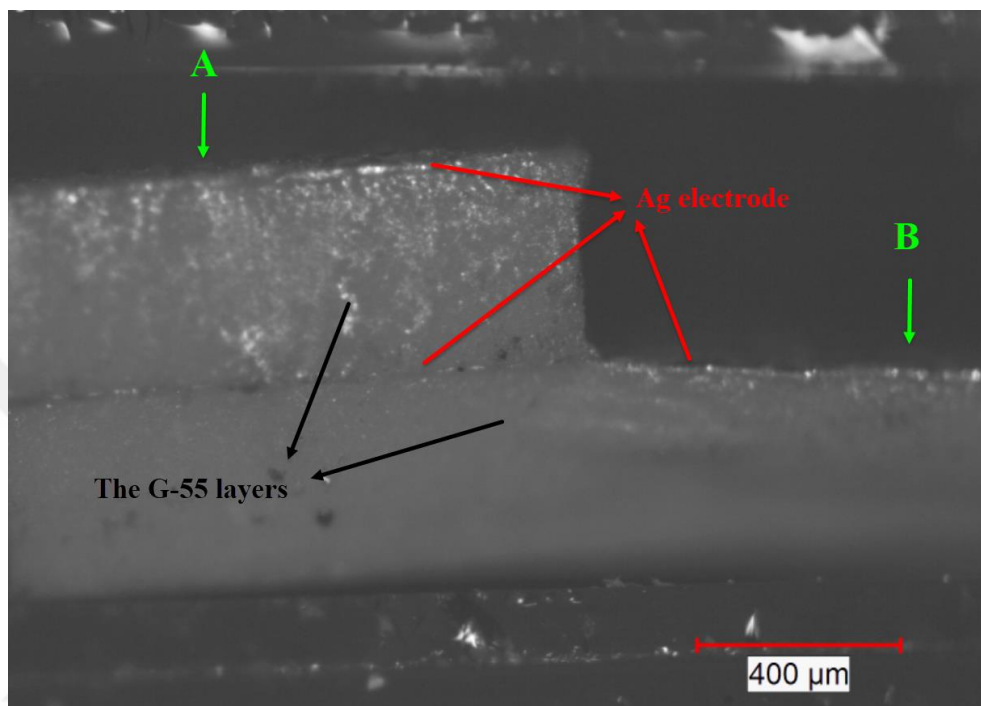


**Figure 3.40** Sintered G-55 LTCC with 2 interlayers between electrodes.

### 3.6.2 Radome

For radome applications, the G-20 and G-40 composites can be proposed since they have sintering temperature higher than 1000°C, which can be used for relatively high temperature applications (see Table 3.6). Density and dielectric constant of the composites are lowered compared with Al<sub>2</sub>O<sub>3</sub>. Mechanical properties are lower due to glass addition, but they can be used for particular applications. Also, lower Young's modulus and CTE will give higher thermal shock resistance. Thermal shock resistance of the composites is calculated from Equation 1.2 by using measured values (see Table 3.6).  $R_f$  value of Al<sub>2</sub>O<sub>3</sub> is 101 K [15] while 161 K and 141 K for the G-20 and G-40, respectively.  $R_f$  values of composites increased by increasing glass amount which shows critical temperature for crack propagation is increased.

Some properties of the commercial glass-ceramic MACOR are listed in Table 3.7. When the properties of the G-20 and G-40 compared with MACOR, the G-20 and G-40 have better flexural strength and Young's modulus as well as a lower CTE (see Table 3.6). Thermal conductivity of the G-40 is close to that of MACOR. The dielectric constant of the G-20 and G-40 at 5 MHz are 8.76 and 7.86, respectively. However, at microwave range, dielectric constant of the G-40 is decreased to 6.7 at 10 GHz.

**Table 3.7** Properties of commercial glass-ceramic MACOR [51].

| Density<br>(g/cm <sup>3</sup> ) | Dielectric<br>constant<br>(at 1 kHz) | Dielectric<br>loss<br>(at 1 kHz) | CTE<br>(ppm/°C)<br>(25-600°C) | Thermal<br>conductivity<br>(W/m.K) |
|---------------------------------|--------------------------------------|----------------------------------|-------------------------------|------------------------------------|
| 2.52                            | 6.01                                 | 0.0040                           | 11.2                          | 1.46                               |

| Flexural<br>strength<br>(MPa) | Young's<br>modulus<br>(GPa) | Continuous<br>operating<br>temperature | Maximum<br>no load<br>temperature |
|-------------------------------|-----------------------------|----------------------------------------|-----------------------------------|
| 94                            | 66.9                        | 800°C                                  | 1000°C                            |

Glass transition temperature was observed in the G-20 and G-40 composites at 649°C and 638°C, respectively, which may degrade the mechanical properties at high temperatures. However, MACOR has a glass transition temperature at about 475°C

which offers operating temperature up to 800°C. The temperature dependence of mechanical properties of MACOR are given in Figure 3.41. Compared with these results, the G-20 and G-40 composites can be recommended as promising ceramics but temperature-dependent mechanical properties must be completed.

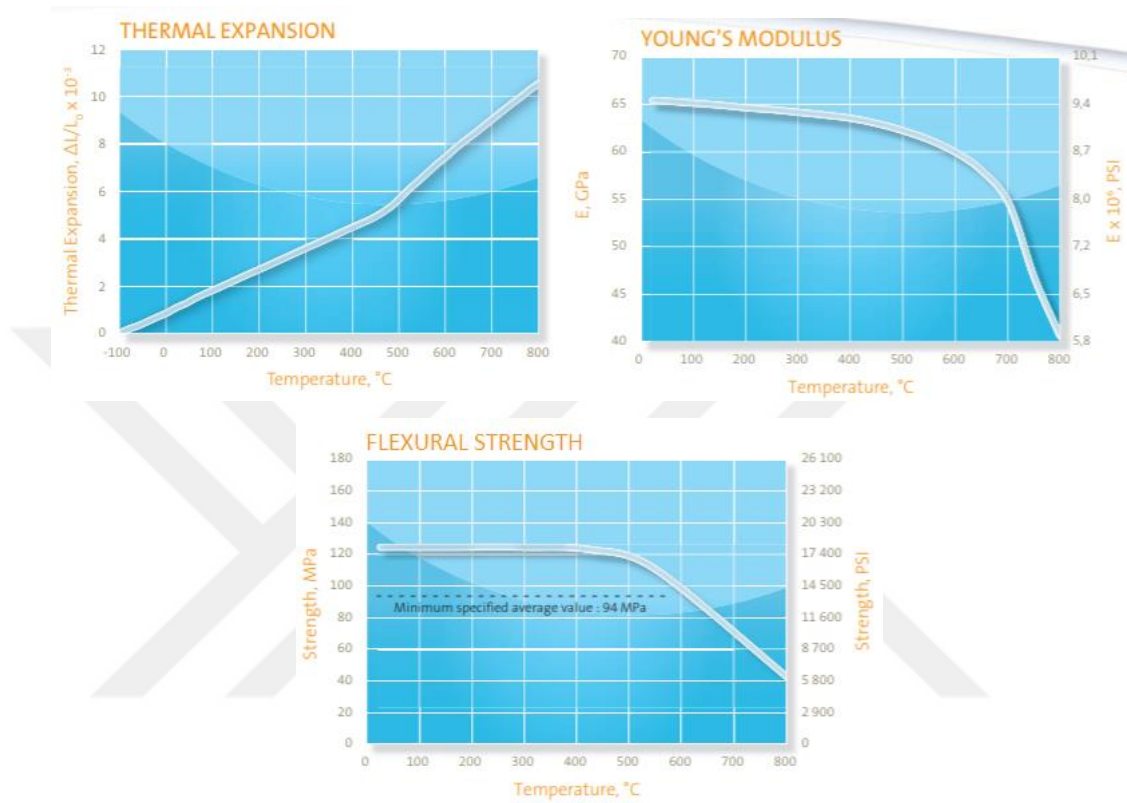


**Figure 3.41** Thermal expansion, Young's modulus and flexural strength of MACOR [51].

# CHAPTER 4

## CONCLUSION

Ceramic materials offer desirable mechanical and electrical properties for electronic applications. Alumina is the most widely used ceramic which offers high strength, good thermal conductivity and relatively good electrical properties. However, basically the requirement of lower dielectric constant and lower sintering temperature involves the development of new ceramic phases. Alumina/glass composites have received much attention because they can meet requirements of electrical, mechanical and thermal properties. For the development of complex miniaturized circuits, LTCC applications require sintering temperature lower than 950°C to enable co-firing with highly conductive metals (e.g. silver, gold and copper). The major requirements are low sintering temperature (lower than 950°C), low dielectric constant (lower than that of alumina  $\text{Al}_2\text{O}_3$  or as low as possible) to diminish the propagation delay, low loss to improve efficiency, high thermal conductivity to dissipate the heat and low thermal expansion coefficient to match with other components. For radome applications, low dielectric constant and low loss to transmit the electromagnetic signal, low density, high mechanical properties, high thermal shock resistance and high erosion resistance are desired properties.

In this thesis,  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -CaO based glass was added to  $\text{Al}_2\text{O}_3$  in order to investigate specific compositions for specific industrial applications such as substrate, LTCC and radome. Densification, phase formation and characterization of dielectric (dielectric constant and loss), mechanical (hardness, fracture toughness, Young's modulus and flexural strength) and thermal properties (thermal conductivity and thermal expansion coefficient) of the  $\text{Al}_2\text{O}_3$ /glass composites were studied in detail.  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -CaO based commercial glass ( $\text{SiO}_2=67.7$  wt%,  $\text{Al}_2\text{O}_3=15.6$  wt%,  $\text{CaO}=10.7$  wt%,  $\text{Na}_2\text{O}=4.8$  wt%,  $\text{K}_2\text{O}=3.2$  wt%) was added to  $\text{Al}_2\text{O}_3$  at 20, 40, 50, 55, and 60 wt% ratios (G-20, G-40, G-50, G-55, and G-60, respectively). First, the particle size of glass frits was decreased to  $d_{50}=2.13$   $\mu\text{m}$  and  $d_{90}=3.91$   $\mu\text{m}$  by ball milling. Then, sintering, softening and melting temperatures were determined to be 726°C, 852°C and 1180°C,

respectively. The sintering temperatures (or optimum densification temperatures within the applied temperature schedules) were determined as 1350°C for the G-20, 1200°C for the G-40, and 850°C for the G-50, G-55 and G-60 composites according to 0% apparent porosity. The bulk densities at densification temperatures were 3.49 g/cm<sup>3</sup> for G-20, 2.94 g/cm<sup>3</sup> for G-40, 2.94 g/cm<sup>3</sup> for G-50, 2.90 g/cm<sup>3</sup> for G-55, and 2.82 g/cm<sup>3</sup> for G-60. The sintering mechanisms were attributed to a liquid phase sintering in the G-20 and G-40 due to grain coarsening and faceting of Al<sub>2</sub>O<sub>3</sub> grains, and a viscous sintering in the G-50, G-55 and G-60 due to lack of Al<sub>2</sub>O<sub>3</sub> grain growth. The glass heat treated at 825°C did not show crystallization. For the composites, main crystalline phase was corundum (Al<sub>2</sub>O<sub>3</sub>) as well as anorthite ((Ca,Na)(Si,Al)<sub>4</sub>O<sub>8</sub>) crystallized after 825°C and enhanced with increasing sintering temperature and initial glass content. However, crystallization of the anorthite was more pronounced in the G-40 sintered at 1200°C indicating that enhanced crystallization was dependent on both high glass content and high temperature. Shrinkage in diameter was 12.6 % for G-20, 15.2 % for G-40, 16.4 % for G-50, 15.9 % for G-55, and 15.9 % for G-60 and shrinkage in thickness was 12.6 % for G-20, 15.2 % for G-40, 17.5 % for G-50, 18.4 % for G-55, and 16.5 % for G-60.

The Young's modulus values of the composites sintered at optimum sintering temperature for each composition were 231 GPa for the G-20, 121 GPa for the G-40, 114 GPa for the G-50, 113 GPa for the G-55, 105 GPa for the G-60. The significant decrement from G-20 to G-40 was ascribed to either higher amount of glass phase in the G-40 or higher amount of Al<sub>2</sub>O<sub>3</sub> forming a stronger skeleton in the G-20. The flexural strength values were 387 MPa for the G-20, 164 MPa for the G-40, 147 MPa for the G-50, 197 MPa for the G-55, 213 MPa for the G-60. The increment in the flexural strength in viscous-sintered G-50 to G-60 was due to the different fracture mechanisms such as single fracture in the G-50 and multiple fractures in the G-60. The hardness values sintered at optimum sintering temperature for each composition were 1058 for the G-20, 727 for the G-40, 722 for the G-50, 724 for the G-55, 679 for the G-60. Hardness decreased with increasing amount of glass. Fracture toughness of the composites sintered at optimum sintering temperature for each composition were 4.5 MPa/√m for the G-20, 2.6 MPa/√m for the G-40, 2.2 MPa/√m for the G-50, 2.2

MPa/ $\sqrt{\text{m}}$  for the G-55, and 1.9 MPa/ $\sqrt{\text{m}}$  for the G-60. High fracture toughness of the G-20 composite was due to intergranular crack propagation with crooked line as crack deflection. Crack propagation pathways became much straighter with increasing glass content (i.e., almost no crack deflection or bridging), which resulted in lower fracture toughness.

Dielectric constant of the composites sintered at optimum sintering temperature for each composition at 5 MHz were 8.76 for the G-20, 7.86 for the G-40, 7.74 for the G-50, 7.30 for the G-55, and 7.32 for the G-60. Increasing amount of glass content resulted in lowering dielectric constant. The dielectric loss values were 0.0022 for the G-20, 0.0034 for the G-40, 0.0043 for the G-50, 0.0030 for the G-55, and 0.0081 for the G-60 at 5 MHz. The dielectric constant of the G-40 measured at 1 GHz and 10 GHz was 6.9 and 6.7, indicating that dielectric constant decreased at higher frequencies due to a less contribution of polarization mechanisms.

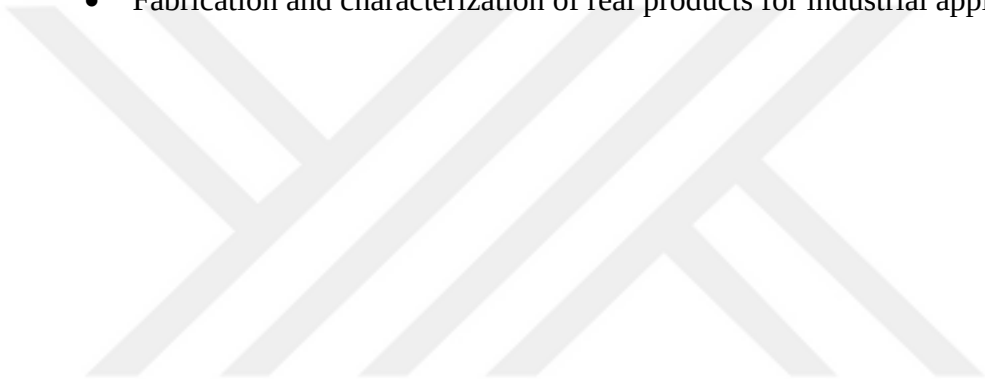
Thermal conductivity of the composites sintered at optimum sintering temperature for each composition at 75°C was 1.25 W/m.K for G-40, 1.31 W/m.K for G-55, and 0.98 W/m.K for the G-60. Thermal conductivity increased with increasing temperature due to the presence of a glass phase in each composite. Thermal expansion coefficients (CTE) of the composites sintered at optimum sintering temperature for each composition and between 35°C-600°C were 7.72 ppm/°C for the G-20, 7.06 ppm/°C for the G-40 and 6.66 ppm/°C for the G-50 to G-60. The CTE values decreased with increasing glass amount due to lower CTEs of anorthite (4.5 ppm/°C) and glass (0.55 ppm/°C) with respect to Al<sub>2</sub>O<sub>3</sub> (8.8 ppm/°C). Also, glass transition temperature ( $T_g$ ) was observed in the G-20 and G-40 at 649°C and 638°C, respectively. The CTE values after  $T_g$ , between 600°C-800°C, was 10.59 ppm/°C for the G-20 and 15.59 ppm/°C for the G-40, indicating that CTE increased more when a higher amount of glass was present.

Mechanical, thermal and dielectric properties must be considered together for possible industrial applications. For substrate applications, all composites are proposed to be suitable because dielectric constant is the key parameter for substrate applications and glass addition lowered the dielectric constant with respect to Al<sub>2</sub>O<sub>3</sub>. However, thermal

conductivity must be increased in general because commercially available glass ceramic composites also have lower conductivity values. For LTCC applications, due to a requirement of low sintering temperature ( $<950^{\circ}\text{C}$ ) to enable cofiring with metals, the G-50 to G-60 composites are proposed due to their sintering temperature of  $850^{\circ}\text{C}$ . They have low dielectric constant, low dielectric loss, CTE values close to silicon and good mechanical properties. Furthermore,  $\text{Al}_2\text{O}_3$  and the G-55 composite were successfully fabricated by tape casting for substrate and LTTC applications. Silver electrode was screen printed on sintered ceramics for substrate and on green tapes for LTTC ceramics. There happened no delamination, warping and undesired chemical reaction after sintering. For radome applications, the G-20 and G-40 composites are proposed because they have sintering temperature higher than  $1000^{\circ}\text{C}$  and can be used for relatively high temperature applications. Density and dielectric constant of the composites are lowered compared with  $\text{Al}_2\text{O}_3$ . Also, lower Young's modulus and CTE will give higher thermal shock resistance.

In summary,  $\text{Al}_2\text{O}_3$ /glass composites at various glass contents were successfully fabricated and characterized for specific applications such as substrate, LTCC and radome. Glass phase changed the densification behavior from liquid phase sintering to viscous sintering with increasing its amount. In order to decide suitability of the composites for the targeted applications, a comprehensive characterization including phase formation and densification, dielectric, mechanical, and thermal were completed and evaluated in detail. At the end, all composites were proposed for substrate applications, the G-50, G-55 and G-60 composites were proposed for LTTC applications, and the G-20 and G-40 were proposed for high temperature radome applications. The G-55 composites were successfully fabricated for substrate and LTTC applications without any delamination, warping and undesired chemical reaction after sintering.

## FUTURE STUDIES

- Detailed investigation of the microstructures by SEM and EDS
  - Grain growth mechanism as a function of glass content
  - Detailed investigation of thermal conductivity
  - Effect of  $\text{Al}_2\text{O}_3$  grain size in thermal conductivity of composites
  - Determination of thermal shock resistance by indentation method
  - Frequency and temperature dependence of dielectric constant and loss
  - Temperature dependence of the mechanical properties
  - Fabrication and characterization of real products for industrial applications
- 

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- Development of Ceramic and Ceramic/Metal Components Used in the Electronic Industry, Project Researcher (2016), TÜBİTAK (2241-A)

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- Processing of ceramics
- Tape casting
- Gel casting
- Dry pressing
- LTCC
- Substrate