

Electrical and Thermal Properties of Glass Matrix-Al₂TiO₅ Composites Prepared at Low Temperature

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Summary: In this research, the electrical and thermal properties of glass matrix composites filled with different amounts of aluminium titanate (Al₂TiO₅) powder varying from 5 to 15 wt. % have been investigated. In order to optimize the processing route, some sintering strategies were tested. The densest specimens were obtained by less pressure of the sintering. The composites were characterized by means of SEM micrography, X-ray diffraction (XRD), differential thermal analysis (DTA), dilatometry and impedance spectrometry. XRD results showed that the main crystallization phases were Wollastonite, Aluminium titanate, Rutile, and Alumina in all sintered glass matrix composites. It was also revealed that addition of 15 wt.% aluminium titanate has increased the relative density and decreased thermal expansion coefficient (TEC) ($6.9 \times 10^{-6}/^{\circ}\text{C}$) and electrical conductivity (3.1×10^{-4} Ohm.cm) in comparison with other composites. The results would be explained considering nature and concentration of the formed crystalline phases and their micro-structures.

Keywords: Composite; Wollastonite; Aluminium titanate; Micro-structure; Thermal expansion of coefficient; Electrical conductivity.

Introduction

Silicate glasses were proved to be promising matrix materials for the development of glass matrix composites (GMCs). Some advantages of silicate matrixes are availability in a wide range of compositions; in which thermal expansion may be matched with different types of reinforcements, easy fabrication, better control over crystallization and formability. Easy densification of these composites could be achieved from the viscous flow of glass matrixes at relatively low temperature and under further densification; they offer superior thermal and mechanical properties.[1] Such composite can be fabricated by incorporating a second constituent in the glass matrix at the form of long or chopped fibers, whiskers, platelets or particles.[2-5] A great variety of composite systems have been developed by the use of numerous matrix compositions and many types of ceramic and metallic fiber reinforcements. Aluminium titanate (AT) particles can improve properties of these materials as a reinforcing phase in the glass matrix composites among different kinds of ceramics and metallic particles.[6] This paper describes the effect of AT on the thermal properties in glass ceramics. The research focuses on decreasing of thermal coefficient expansion which is needed to reach optimum resistance in glass ceramic materials.

Aluminum titanate, is a typical synthetic material with pseudo-brookite structure and unusual

macroscopic properties such as very low thermal conductivity ($0.9-1.5 \text{ Wm}^{-1}\text{K}^{-1}$), low thermal expansion coefficient (0.2×10^{-6} to $1.0 \times 10^{-6} / ^{\circ}\text{C}$), high thermal shock resistance and melting point $>1860^{\circ}\text{C}$, low Young's modulus, and low strength of 10-40 MPa. Properties concerning high residual porosity and micro-cracks were resulted from highly anisotropic thermal expansion in the individual AT crystals. These crystals show different coefficients of thermal expansion along their three primary axes. As a result, tensions would be developed on the microscopic scale during formation, especially in cooling step, and consequently micro-cracks in the microstructure would be formed. Because of the macroscopic expansion and the anisotropic thermal expansion of the individual crystals, the material would have very low thermal expansion along with the micro-cracks; thus, the cracks would be closed.[7-13] The use of this material as a reinforcement in mullite-At and in alumina-AT composites has been reported to improve thermal shock resistance and mechanical properties.[11]

At the present work, sintering behavior, thermal, and electrical properties of SiO₂-CaO-Na₂O-Fe₂O₃-WO₃ system of glass are discussed *via* cold pressing of glass powders, then by viscous flow sintering. Crystal type, microstructure, density, electrical conductivity, and thermal expansion behaviors are controlled by the sintering conditions

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including heating rate, sintering temperature, and soaking time. Improving thermal and electrical properties, sintering behavior, thermal properties, and electrical features of the glass-ceramic was investigated as obtained by incorporating AT micro-powders. The optimum composition and sintering conditions were determined and were compared with the glass-ceramic base.

Experimental

The chemical composition of the base glass was 59.68 SiO₂, 27.25 CaCO₃, 5.08 Na₂CO₃, 6.00 Fe₂O₃ and 2.00 WO₃ (Wt. %). All of the powdered raw materials used for the preparation of glasses were reagent grade. After thorough mixing, the batch (250 g) was melted in a platinum crucible in an electric furnace at 1410 °C for 30 min (heating rate 5 °C/min). The melt was quenched in water to obtain frits and dried in a dry box. The frits were ground in an electric agate mortar for 1 h and then fast-milled for 2 h in aqueous media until average particle size of 9 μm was reached. The particle size distribution of the powdered glass was carried out by using a laser particle size analyzer (Fritsch, Analysette 22). Then, the glass powder was mixed with 5, 10 and 15 wt. % AT particles (Aldrich: mean particle size 4.81 μm) and fast-milled for 15 min, in water media.

The crystallization temperature of the selected specimens was determined using a simultaneous thermal analysis, STA (Polymer Laboratories, model 1640) in a platinum crucible in an air atmosphere with a heating rate of 5 °C/min. The granulated powders were mixed with 7 wt. % PVA (Poly vinyl alcohol, 3 wt.%) and pressed into discs (13 mm in diameter and 4 mm thickness) using uniaxial pressure of 60 MPa. These specimens were first heated at 450 °C for 60 min to remove organic binders of the green compacts. Then, the glass-ceramic and composite specimens were sintered at 710 °C for 180 min with the rate of 5 °C/min. In order to study the effects of glass compositions on the sintering characteristics, bulk density was measured by use of liquid displacement method, in water media according to the ASTM C373-88 standard test method. The linear shrinkage during sintering was also calculated from the dimensions of the green and the sintered specimens. Determination of relative density was measured by a gas pycnometer (model AccuPyc 1330).

The crystal phase identification and quantification of the sintered specimens were

investigated by an X-ray diffractometer (XRD, Siemens model D500) using CuK_α radiation. The applied voltage and current were 40 kV and 30 mA, respectively, for a 2θ range from 10°-80°. The microstructure of the sintered specimens was evaluated by means of scanning electron microscope, (SEM, Philips XL30) equipped with an energy dispersive X-ray spectrometer, EDS, (Oxford, UK). Electron microscopy was used to observe both fractured and polished surfaces. The specimens were polished, etched with diluted acidic solution (5% NH₄/HF) and Au-coated for SEM observations. Measurement of the linear thermal expansion coefficients of the glass-ceramic and composites were carried out using a Netzsch, E402 dilatometer. Specimen rods of about 5 cm length were prepared and heated at the rate of 10 °C/min, then subjected to thermal treatment and their expansions were again measured from room temperature up to the maximum heat-treatment temperature. The electrical conductivity of the specimens was performed in a wide frequency range from 10⁻¹-10⁶ Hz and at 25 – 500 °C by using an impedance spectrometer. The thermal condition was controlled with a programmable oven.

Results and Discussion

The particle size distribution of the glass sample and AT particles was studied. Fig. 1(a) and 1(b) define the relative amount by passing based on the type and size of the particles. The results were obtained from differential thermal analysis (DTA) of the base glass and glass/AT composite precursors. The glass exhibited a distinct and strong exothermic crystallization peak, (T_c) around 875 °C with an onset crystallization temperature, (T_o), around 842 °C (Fig. 2a). This exothermic peak is attributed to the crystallization temperature, (T_c). The estimated (T_o) and (T_c) matched well with the corresponding values reported for similar composition and heat treatment.[14]

An exothermic peak at 870 °C showed formation of AT in the composite precursors. According to the DTA analysis, it may be concluded that increasing of AT content had no influence on rising formation temperature of AT in the composites. Moreover, by adding AT, enhancing intensity of crystallization peak was observed with respect to the base glass, which was due to the precipitation of AT, alumina, and rutile phases resulting from addition of AT (Al₂TiO₅).

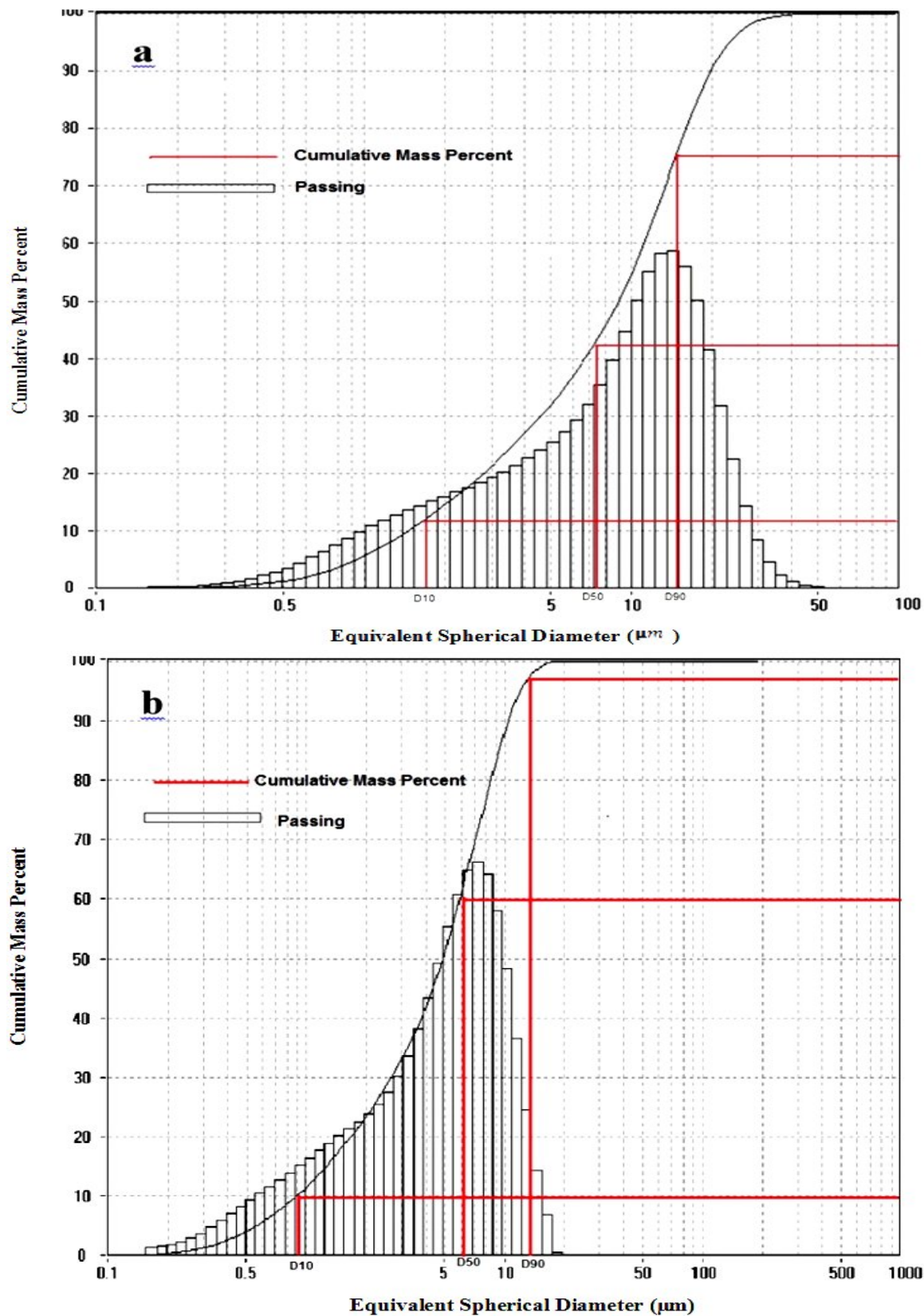


Fig. 1: Particle size distribution of (a) glass powder and (b) aluminium titanate particles.

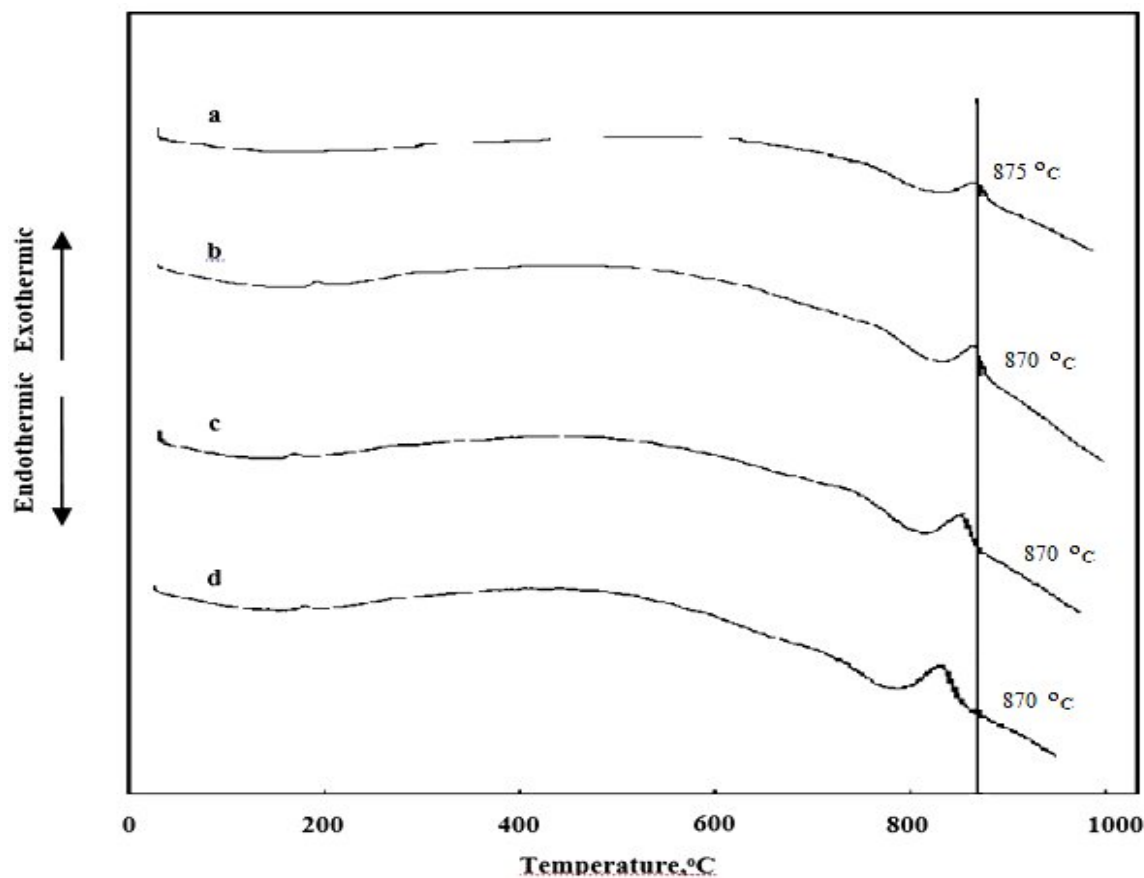


Fig. 2: DTA analysis of glass powder (a), DTA analysis of G-5% AT (b), DTA analysis of G-10% AT (c), and DTA analysis of G-15% AT (d).

As depicted in Fig. 3, well-sintered dense glass-ceramic and composites A, B and C were obtained after heat treatment at 750 and 810 °C, respectively. In terms of the comparison between the sintering results and crystallization peak of specimens, it can be concluded that the maximum temperature that leads to full density was lower than the crystallization peak of the base components.[15] There was no evidence for detrimental effects, such as deformation or formation of open porosity in the temperature interval 750-800 °C. It seems that addition of aluminium titanate particles leads to a decrease in maximum linear shrinkage of the composites. Among the specimens, addition of AT (Al_2TiO_5) up to 15 wt% in the glass matrix improved the sintering ability of the compositions, which reduced the porosity of the resultant glass matrix composites and improved their relative densities.

XRD patterns of the sintered glass-ceramics and the composites are shown in Fig. 4. Besides the mentioned phases, AT and minor amounts of

aluminum oxides and rutile phases were detected in the composites. Accordingly, the intensity of wollastonite peak was increased by the addition of weight percent of the second constituent in composite C. It was due to the distribution of AT particles and reduction of the residual glassy phase during sintering. The presence of aluminium oxide and rutile in a minor amount represented decomposition of AT in the specimens.

Morphologies that the glass-ceramic and composite specimens filled in different amounts of AT powder from 5 to 15 wt% are shown in SEM micrographs in Fig. 5. It appears that the wollastonite was observed in glass-ceramic (Fig. 5a). Moreover, at the lower filler concentration (5 and 10 wt. %), AT particles were discretely distributed with a relatively large inter-particle distances. In the higher filler concentration (15 wt%), the SEM micrographs revealed large agglomerates of AT particles that were dispersed within the glass matrix.

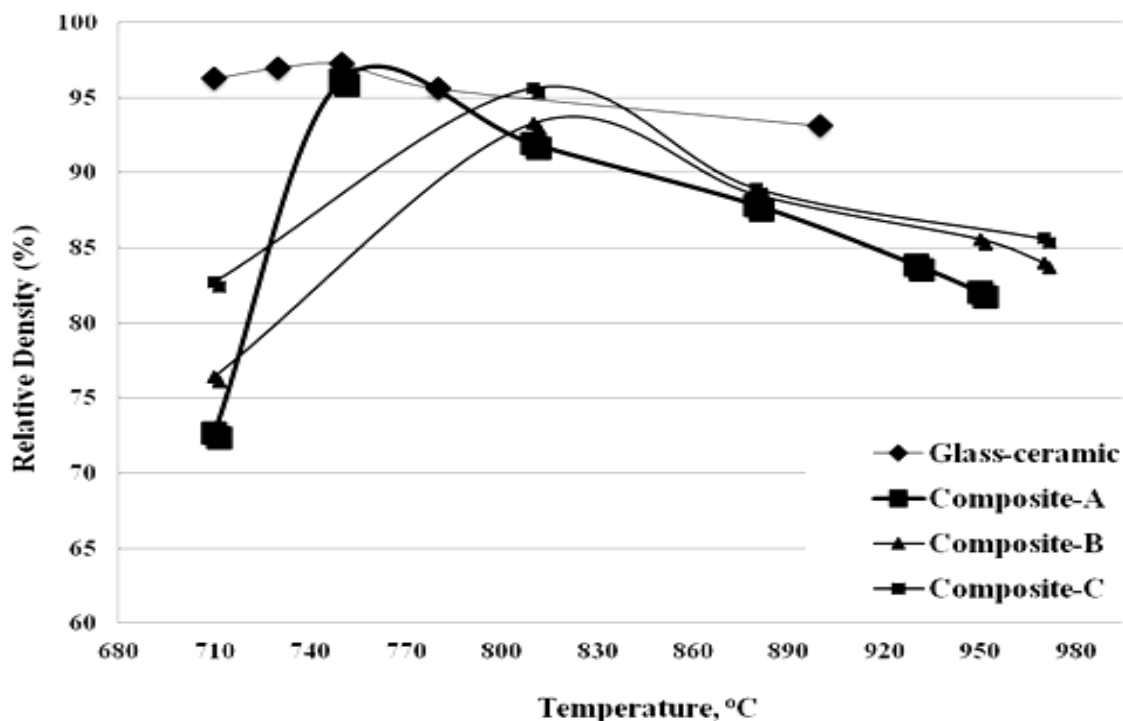


Fig. 3: Relative densities of the specimens vs sintering temperature.

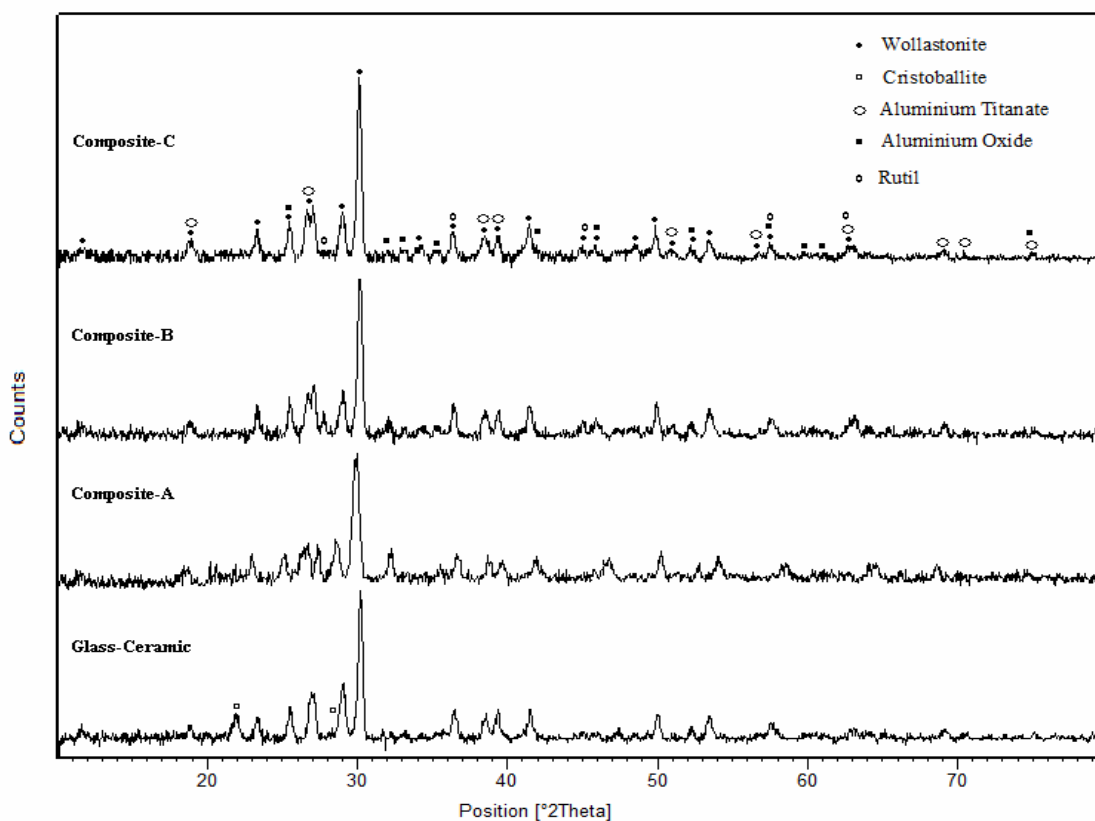


Fig. 4: XRD patterns of composite specimens after heat treatment at final sintering temperature for 3h.

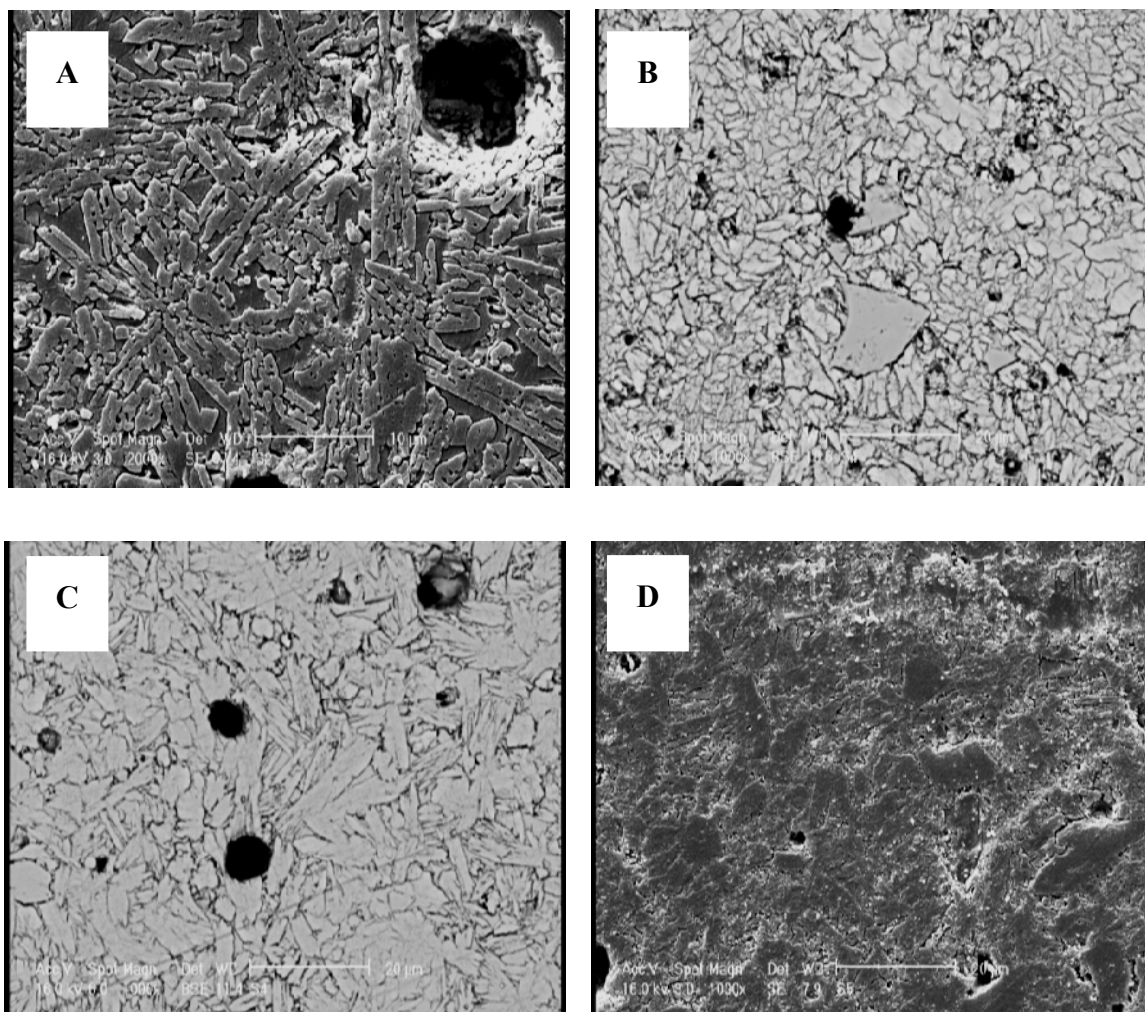


Fig. 5: SEM micrographs of the sintered specimens: (a) glass-ceramic, (b) composite A, (c) composite B and (d) composite C.

Table-1: Properties of the prepared composites and the glass ceramic.

Samples	Relative Density (%)	Thermal expansion coefficient ($\times 10^{-6} \text{K}^{-1}$)				Electrical conductivity (Ohm.cm)
		36-200 °C	36-300 °C	36-400 °C	36-600 °C	
Glass-ceramic	97.2	6.2	6.7	7.0	7.6	2.2×10^{-3}
Composite-A	91.9	7.6	8.0	8.3	8.8	2.3×10^{-3}
Composite-B	93.3	7.3	7.5	7.8	8.3	(nd) ^a
Composite-C	95.6	6.3	6.7	6.9	7.3	3.1×10^{-4}

Not determined.

Thermal and electrical characteristics of the glass-ceramic and composites as well as their relative densities at sintering temperatures, are listed in Table-1. The value of thermal expansion coefficient (TEC) was gradually decreased from $8.3 \times 10^{-6} / ^\circ\text{C}$ to $6.9 \times 10^{-6} / ^\circ\text{C}$ with increasing AT content in the glass matrix as shown in Fig. 6 (a-b). Since, AT has low thermal expansion coefficient (0.2×10^{-6} to $1.0 \times 10^{-6} / ^\circ\text{C}$), the decrease in thermal expansion coefficient

(TEC) was attributed to increasing wollastonite phase during enhancing AT in the glass matrix. From this observation, it could be concluded that wollastonite glass-ceramics has a wide range of moderate thermal expansion coefficients (TEC) and could be produced by changing AT content.[5] The relative values of densities, thermal expansion coefficients, and electrical conductivities are shown in Table-1.

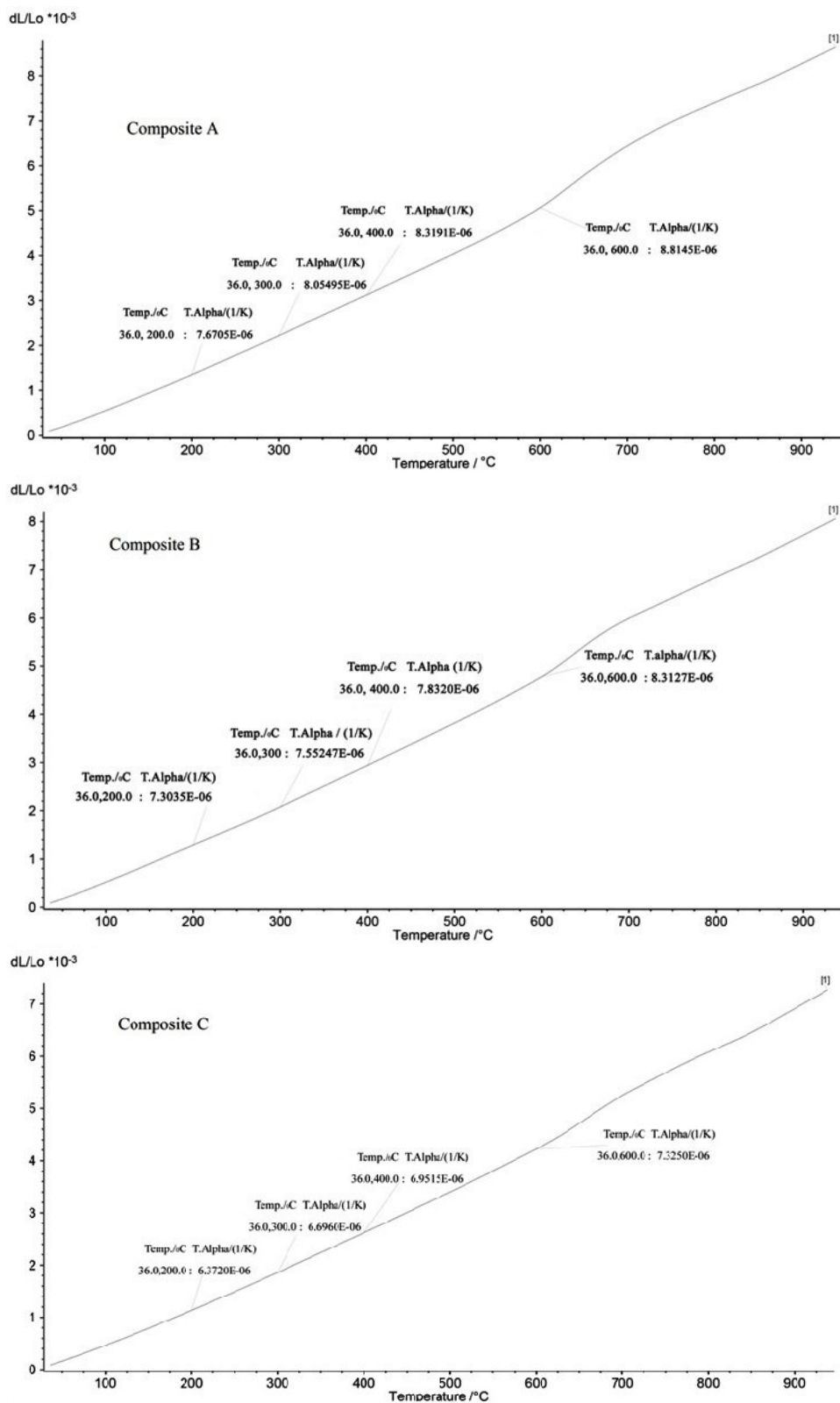


Fig. 6: Thermal expansion coefficients of the composites A, B and C at the sintering temperature with soaking time of 3h.

The electrical conductivity of glass-ceramic specimen was relatively lower than in composites filled with different (5 to 15 wt.%) content of AT powder (Table-1). Clearly, the electrical conduction in specimens was mainly attributed to the migration of mobile ions under the influence of an applied field or thermal energy. Type of the crystals and proportion of crystals to matrix glass are responsible for many physical and chemical properties, such as thermal and electrical characteristics. Addition of Al_2TiO_5 particles to glass matrix led to ohm conductivity increase, due to the existence of large cations which are responsible for blockage of mobile ions.[16-18]

A comparison between relative densities of composites revealed that the relative density of composites A and B were much lower than composite C (Fig. 6). However, composite C had better thermal expansion coefficient and electrical conductivity compared to composites A and B. As it is mentioned, at the sintering temperature, AT with lower density (3.15 g/cm^3) was decomposed to phases such as aluminium oxide and rutile with higher density (4 and 4.23 g/cm^3). This reaction in composites A and B would be the reason for increasing porosity, thermal expansion coefficient, and electrical conductivity compared to composite C.

Conclusion

From the experimental results, we found that glass matrix composites filled in different contents of aluminium titanate powder (5 to 15 wt. %) would be prepared by pressure-less sintering. The sintering behavior of the prepared glass-ceramic and composites was also investigated around 710°C and soaking time of 3 h. Moreover, XRD results revealed that the main crystallization phases in all sintered glass matrix composites were wollastonite, aluminium titanate, rutile, and alumina. It was revealed that increasing aluminium titanate content to the glassy powder, improved the electrical and thermal properties of the glass matrix composites. Composites with 15 wt% aluminium titanate showed maximum relative density, minimum coefficient thermal expansion ($6.9 \times 10^{-6}/^\circ\text{C}$) and electrical conductivity ($3.1 \times 10^{-4} \text{ Ohm.cm}$) compared to other composites. Finally, SEM micrographs of glass matrix composite, containing different contents of aluminum titanate powder, indicated large agglomerates of aluminum titanate particles dispersed within the glass matrix at higher aluminum titanate concentration (15 wt%).

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