



The effect of strontium oxide replacing calcium oxide on the crystallization and thermal expansion properties of $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$ glasses

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Abstract

The crystallization process and thermal expansion characteristics of glass compositions based on $17.80\text{Li}_2\text{O}-(32.20-x)\text{CaO}(x\text{SrO})-50\text{SiO}_2$ system (where $x=3, 6, 9$ and 12 mol%) were investigated. The crystallization characteristics of the glasses, the type of crystalline phases formed as well as the resulting microstructure were traced by means of differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The addition of SrO at the expense of CaO has led to a slight decrease in both the transition (T_g) and softening (T_s) temperatures of the glasses. The main crystalline phases, formed after controlling heat-treatment are lithium metasilicate- Li_2SiO_3 , wollastonite- CaSiO_3 together with pseudowollastonite-like phase. The incorporation of Sr into CaSiO_3 structure has partially promoted the phase transition from wollastonite to pseudowollastonite-like phase. A slight increase of thermal expansion coefficients (α -values) of the glasses and their corresponding glass-ceramics has been detected. The α -values of the obtained glasses are 114 to $130 \times 10^{-7} \text{K}^{-1}$ in the $25-300$ °C temperature range while those of the crystalline materials are 90 to $121 \times 10^{-7} \text{K}^{-1}$ in the $25-700$ °C temperature range. The present results provide valuable information about the role of Sr^{2+} in determining the type of crystalline phases formed in the glasses and the thermal expansion data of the material were obtained.

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1. Introduction

The glass-ceramic technology is based on controlled nucleation and crystal growth in certain glasses and has several advantages such as very low or null porosity, uniformity, and reproducibility of microstructure. The crystalline phases precipitated in some glass matrices typically enhance and sometimes lead to an entirely new combination of properties; some of the technologically most important glass-ceramics have, for instance, low thermal expansion coefficients, high thermal and chemical stability, high mechanical strength, and optical transparency [1]. The properties of glass-ceramics are determined by crystalline phases precipitated from the glasses and their microstructures based on the composition of the parent glass as well as the thermal treatment and the presence of

nucleating agent. The crystallization process greatly altered the thermal expansion of the glasses. Therefore, the glass-ceramic materials may have high or low coefficients of expansion depending on the expansion coefficients and elastic properties of the crystal phases formed as well as the residual glassy phase [2].

The structure and crystallization process of a glass based on $\text{Li}_2\text{O}-\text{CaO}-\text{SiO}_2$ system was studied by Tarlavov et al., [3]. They found that the glasses had high crystallization consolidation and on increasing Li_2O and CaO , the temperature interval of crystallization was increased. For the majority of the glasses, the decrease of silica and the increase of Li_2O had increased the crystal dimension and repaired the crystal structure.

The wollastonite (calcium metasilicate- CaSiO_3) is an important substance in ceramic and cement industries. It is a host of favorable properties such as low shrinkage, good strength, lack of volatile constituents, body permeability, fluxing characteristics, whiteness,

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and a circular shape that renders wollastonite useful in several ceramic and other applications. The growing demands for wollastonite in recent years are attested by the steady increase in production worldwide [4]. Wollastonite is a white glassy silicate mineral that occur as masses or tabular crystals of meta-morphosed limestone [5]. Generally, there are three normal modifications of calcium metasilicate; pseudowollastonite (β -CaSiO₃), the high temperature form, that is triclinic (pseudo-orthorhombic), parawollastonite, and wollastonite. The two latter are referred to as the low temperature modification (α -CaSiO₃) [6]. Pseudowollastonite commonly occurs in slag, cement, and ceramic materials [7].

Wren et al., [8] stated that strontium is known to behave in a similar fashion to calcium, where it is re-circulated through the blood stream and re-used for bone growth or excreted from the body. Sr²⁺ and Ca²⁺ are interchangeable in the crystal lattice of hydroxyapatite, due to their ions having similar ionic size and polarity. Hill et al., [9] studied the influence of substituting strontium for calcium on the nucleation and crystallization behavior in a glass composition: 4.5SiO₂–3Al₂O₃–1.5P₂O₅–3CaO–2CaF₂. Strontium–calcium hydroxyapatite (Sr,Ca)₁₀(PO₄)₆(OH)₂ solid solution and pure strontium apatite phases were developed. The change in mechanism for the nucleation may be possibly associated with the increased size of the strontium cation compared to calcium. Therefore, strontium may be substituted in these glass compositions for calcium and may also be substituted in crystalline structures. Liebau's [10] suggested also that SrGeO₃ and SrSiO₃, as well as the low-temperature phase of BaSiO₃ were structural analogs of pseudowollastonite.

The aim of the present study is to investigate the effect of adding SrO at the expense of CaO, on the crystallization process of the glasses based on Li₂O–CaO–SiO₂ system. The thermal expansion property of the glasses and corresponding glass–ceramics are also determined.

2. Experimental

2.1. Batch composition and glass preparation

The present glass compositions, in mole %, are based on 17.80 Li₂O–(32.20–*x*) CaO (*x*SrO)–50SiO₂ system (where *x*=3, 6, 9 and 12 mol%). The glass oxide constituents are given in Table 1. The glass batches prepared from reagent grade powders of Li₂CO₃, CaCO₃, SiO₂ (quartz), and SrCO₃ were melted in Pt-2% Rh crucible, covered with Pt foil to minimize the evaporation, in an electric furnace with SiC

Table 1
Chemical compositions of the studied glasses.

Glass no	Oxide constitutions (mol%)			
	Li ₂ O	CaO	SrO	SiO ₂
17.80	32.20	–	–	50
17.80	29.20	3	–	50
17.80	26.20	6	–	50
17.80	23.20	9	–	50
17.80	20.20	12	–	50

heating elements at 1300°–1400 °C for 3 h. Melting continued until clear homogeneous melt was obtained; this was achieved by swirling the melt several times at about 40 min intervals. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at 500–550 °C to minimize the strain.

2.2. Differential thermal analysis (DTA)

The thermal behavior of the finely powdered glass samples was examined using a SETARAM LabsysTMTG-DSC16. The powdered samples were heated in Pt-holder against another Pt-holder containing Al₂O₃ powder as a standard material. A uniform heating rate of 10 °C/min was adopted up to the appropriate temperature of the glasses. The results obtained were used as a guide for determining the heat-treatment temperatures applied to induce crystallization.

2.3. Crystallization and glass–ceramic formation

Double stage heat-treatment regimes were used, in the crystallization of the glass, for each class to obtain a glass–ceramic material of holocrystalline mass with minimum residual glassy phase without deformation. For crystallization, a suitable controlled heat-treatment schedule was applied to prepare the glass–ceramic materials. Thermal treatment of the glasses was carried out at temperature in the region of the main DTA exothermic peak determined for each glass. Therefore, at endothermic temperature (*T_g*) of each glass composition, the glass sample was soaked for 5 h and then the temperature was raised up to the exothermic temperature, specific for each glass for 10 h, which was found to be suitable duration for nucleation and complete crystallization of the glasses. A heating rate of 10 °C/min was used during the double stage heat-treatment regimes. After crystallization, the muffle furnace was switched off and the samples were allowed to cool down to room temperature.

2.4. Material investigation

Identification of the precipitating crystal phases formed was conducted by the X-ray diffraction (XRD) analysis using XSPeX, X-ray diffraction with search / match option, version 5.45, Dianocorporation, Woburn Massachusetts 01801, USA. The crystallization characteristics and internal microstructures of fractured surface of the crystalline samples, coated with gold spray, were examined using scanning electron microscopy (SEM). Representative electron micrographs were obtained by using Jeol, JXA-840 on Electron Probe Microanalyzer.

2.5. Thermal expansion measurements

The thermal expansion coefficients (α -values) of the investigated samples were measured using 1.5 cm long rods using Linseis L76/1250 automatic recording multiplier dilatometer with a heating rate of 5 °C/min. The linear thermal expansion

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