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Crystallization and sinterability of glass-ceramics in the system La_2O_3–SrO–B_2O_3

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Abstract

Glasses with a constant B_2O_3 and an increasing La_2O_3 content in the system La_2O_3–SrO–B_2O_3 were obtained by the usual melt quenching procedure. The crystallization and sinterability of the glasses were investigated by hot stage microscopy (HSM), differential thermal analysis (DTA), X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD analysis of the bulk samples evidenced the formation of the crystalline phases: $La_2SrB_{10}O_{19}$, SrB_6O_{10} and $SrLaBO_4$. XRD and TEM/SAED analyses showed a polymorphic crystallization of the glass sample containing 14.3 mol% La_2O_3 with precipitation of the $La_2SrB_{10}O_{19}$ phase. SEM analysis confirmed the surface crystallization mechanism of this sample. The kinetics of crystallization of the same sample was examined by DTA and the activation energy of crystal growth was calculated by the Kissinger model to be $E_a = 458 \pm 63$ kJ mol^{-1}.

Keywords: A. Sintering; B. Electron microscopy; D. Glass; Glass-ceramics

1. Introduction

Glass-ceramics materials show good properties, such as: low thermal expansion, low dielectric constant, high abrasion resistance and chemical resistance [1]. The specific properties of these ceramics materials recommend glass-ceramics for numerous applications [1,2]. Glass-ceramics can be formed from the bulk glass through the processes of controlled nucleation and crystallization by adequate heat treatment. Regarding the preparation of glass-ceramics with desired microstructure and properties using this method, the determination of the parameters for these two processes is crucial. The crystalline phase formed by the process of crystallization in the glass determines specific properties of glass-ceramics. Lanthanide borate glasses and glass-ceramics are recognized as materials for the application as laser hosts, nonlinear optical materials, and in the optoelecrtonics. Lanthanide materials showed improved NLO properties which are explained by the f–f electron transition. [3–6]. Addition of lanthanum oxide in the alkaline earth borate glasses improves optical properties and chemical durability [7].

The glass-ceramics can be also obtained through the sintering and crystallization of glass powder [8–10]. It is preferable that densification is performed prior to the crystallization; hence these processes are independent. The quality of the obtained glass-ceramics material is determined by the densification of the glass powder compact [11–13]. Lanthanide alkaline borate glasses showed improved durability and high glass-transition temperatures, due to that these glasses can be applied as specialized hermetic candidates [14]. These glasses are also potential candidates for the application in various electronic industries such as display panels, low-temperature co-fired ceramics and packaging where there is requirement for the low-temperature sinterable glasses [15,16].

The crystallization behavior of glasses from the ternary system La_2O_3–CaO–B_2O_3 was previously the subject of investigation and the crystalline phase $La_2CaB_{10}O_{19}$ with the desired properties was identified after heat treatment of these glasses [4–6].

The sintering and crystallization behavior of the glasses from the La_2O_3–SrO–B_2O_3 system, to the best of our

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Table 1
Compositions of the glass samples.

Glass sample	La_2O_3	x_i (mol%) SrO	B_2O_3
GLa5.7	5.7	22.9	71.4
GLa9.5	9.5	19.1	71.4
GLa14.3	14.3	14.3	71.4
GLa19.1	19.1	9.5	71.4

knowledge, have not been studied in detail. The aim of this study was to investigate the processes of sintering and crystallization of the glass system La_2O_3–SrO–B_2O_3 under isothermal and non-isothermal conditions.

2. Experimental

Glasses with different compositions (Table 1) were obtained by the usual melt quenching procedure. Reagent-grade H_3BO_3, $SrCO_3$ and $La_2(CO_3)_3$ were mixed and homogenized. The mixture was placed in a platinum crucible in an electric furnace and melted at 1200 °C for 30 min. The platinum crucible was covered, melting was in short time at relatively low melting temperatures to minimize boron evaporation. The melt was cast and cooled on a stainless steel plate in air at room temperature. Measurements of the weight loss due to melting indicate that the glasses are within 1–2 wt% of desired compositions. The obtained glass samples were transparent, without visible bubbles. X-Ray powder diffraction (XRD) measurements confirmed that the samples were amorphous. Differential thermal analysis (DTA) and hot stage microscopy (HSM), and a combination of these two techniques, were used for the investigation of crystallization and sintering behavior of the glass powder samples. Glass powder samples were prepared by crushing and grinding the bulk glass in an agate mortar and sieving it to grain size < 0.048 mm. DTA curves were recorded on a Netzsch STA 409 EP instrument at different heating rates 5, 10, 12 and 20 °C min^{-1}, using Al_2O_3 powder as the reference material and 100 mg of glass powder. From the DTA curves, the glass transition, T_g, crystallization onset, T_x, and crystallization peak, T_p, temperatures were determined. The DTA method was employed for the determination of the kinetic parameters of glass crystallization including the activation energy of crystal growth E_a.

A hot stage microscope (HSM), E. Leitz Wetzlar, supplied with a Cannon camera, was used for determining the sintering behavior of the glass powder samples [17–24]. The glass powder samples were pressed into cylinders. The specimens were placed on a platinum plate and then on an alumina support. The temperature was measured with a (Pt/Rh/Pt) thermocouple. The heating rate was 10 °C min^{-1}. The sample images were analyzed using computer software for image analyzing and the changes in the area at different heating temperatures were calculated.

The crystallization of bulk glass samples was performed by heating the samples in a Carbolite CWF 13/13 electric furnace with automatic regulation and a temperature accuracy of ± 1 °C, up to the crystallization temperatures determined by DTA, at a heating rate 10 °C min^{-1}, and maintained at these temperatures for different times. After the heat treatment, the samples were removed from the furnace and crushed.

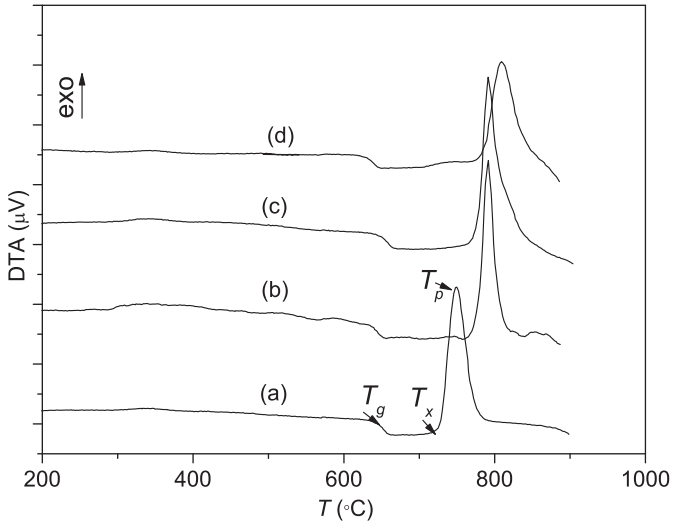

Fig. 1. DTA curves of the glass powder samples (a) GLa14.3, (b) GLa9.5, (c) GLa19.1, and (d) GLa5.7.

The XRD technique was used for identification of the crystalline phases in the powdered samples. The XRD patterns were obtained using a Philips PW-1710 automated diffractometer with a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and an Xe-filled proportional counter. The diffraction data were collected in the 2θ Bragg angles from 5 to 70°, counting for 1 s, except for the sample containing 14.3 mol% La_2O_3 (see Table 3).

A Jeol JSM-6610LV scanning electron microscope and a TOPCON transmission electron microscope (TEM) using the selected area electron diffraction (SAED) method were employed to observe the microstructure of the samples. Gold sputtered bulk samples were used for the SEM analyses. For the TEM observation, the powdered samples, obtained from heat treated bulk samples, were suspended in ethanol and mixed by ultrasound for 10 min and then applied to a copper grid coated with carbon.

3. Results and discussion

The compositions of the prepared glasses are given in Table 1. The samples were labeled depending on the amount of lanthanum oxide in the glass.

3.1. Differential thermal analyses

The DTA curves of the glasses are shown in Fig. 1. The small endothermic shoulders on the DTA curves represent the glass transition temperatures, T_g. The temperatures, T_x, crystallization onset, were determined by extrapolation. The exothermal temperature peaks T_p at the DTA curves correspond to the crystallization of glass. These characteristic temperatures are shown in Table 2.

It may be seen from Table 2 that the crystallization onset temperature, T_x, generally increased with increasing content of