Journal of Non-Crystalline Solids 427 (2015) 191–198

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Correlation between structure, crystallization and thermally stimulated luminescence response of some borate glass and glass-ceramics

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ARTICLE INFO

Article history:
Received 28 May 2015
Received in revised form 24 July 2015
Accepted 27 July 2015
Available online 11 August 2015

Keywords:
Borates;
Thermally stimulated luminescence;
Glass ceramics

ABSTRACT

Borate glasses with the composition $MO \cdot 2B_2O_3$ (M: Pb, Sr and Ba) and $N_2O \cdot 2B_2O_3$ (N: Li and Na) were prepared. Glass-ceramics of the same composition were obtained by heat treating glass powder. The structure of the glasses, was studied by FTIR and ^{11}B NMR resulted in a similar structure (having BO_3 and BO_4 species). The $PbO \cdot 2B_2O_3$ sample shows the lowest fraction of four coordinated boron, N_4, of the set. Glass crystallization was analyzed by thermal analysis, using the Kissinger method. The evaluated activation energy shows that the $BaO \cdot 2B_2O_3$ sample presents the highest value; meanwhile $Li_2O \cdot 2B_2O_3$ shows the lowest one. Thermally stimulated luminescence was measured in glasses and glass-ceramics using a ^{90}Sr radiation source. In most cases, glass-ceramics present a higher sensitivity than glasses. Defects present in glasses are increased by the crystallization to improve the TL response of these materials. When we compare the response, as the area under the curve, (which is related to the absorbed dose) barium borate glass-ceramics present the best response compared to the other studied borates.

1. Introduction

Borate glasses have been studied for many years due to their interesting properties, tunable with the concentration of alkaline and alkaline earth modifiers. Much effort has been made in understanding the structure of these glasses and their relation with properties. In recent years these glasses have attracted the attention of many researchers, due to their optical properties, especially those related to the emission of light during sample heat treatment (thermally stimulated luminescence or thermoluminescence, TL).

It is well known that different preparation methods for these materials result in rather different TL characteristics, including TL glow curve, sensitivity, dose linearity, etc. Glasses and crystals were studied as dosimetric materials indistinctly without any reason to prefer one or the other. In the particular case of borates, polycrystalline barium borates (Cerium doped and undoped) show good TL response, and doped samples present higher TL efficiency. Interactions between intrinsic defects and Ce-ions seem to be responsible for their improvements, meanwhile intrinsic defects are responsible for the poor response of undoped samples in the low dose range [1]. Also, polycrystalline doped strontium borate has been studied as a TL material [2]. It was found that the metaborate crystalline phase presents better results compared to the tetraborate phase, independently of the use of dopants. This was explained in the base of the presence of more defects in the metaborate phase compared to the tetraborate which is more compact [2]. On the other hand, borate glasses present also good TL characteristics. For example, Magnesium doped lithium borate glass presents a good performance as dosimetric material. In this glass, Magnesium acts as a color center and in the absence of this ion the TL was explained by the recombination of electrons from the electron center and oxygen hole center [3]. In all these works the improvement in the TL response was achieved by using dopants. However, other strategies were used to improve material performance, for example by the development of a crystalline phase in a glass matrix which yields a rich material microstructure. For instance, the TL response was improved in boro-silicate glasses by the crystallization of the CaF_2 phase [4]. Some attempts have been made to find the reasons for the observed differences in the TL response of glasses and crystals with the same composition [5,6]. Recently, a comparison of the response of glasses, polycrystalline and single crystals of lithium tetraborate exposed to X rays was published, and the differences in the TL glow curves were explained by the difference in the efficiency of the recombination process involved in the TL phenomena [7].

In our previous work, we have demonstrated that another way to improve the TL response could be achieved with congruent crystallization

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http://dx.doi.org/10.1016/j.jnoncrysol.2015.07.045
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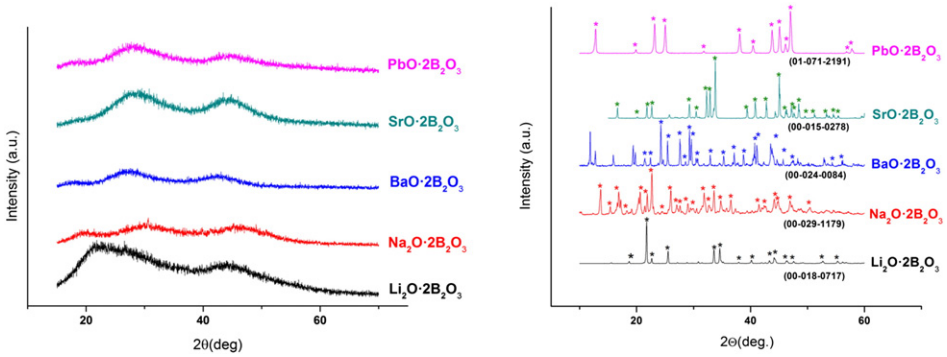

Fig. 1. X ray diffraction pattern of glass samples (a). X ray diffraction pattern of glass-ceramics samples (b). In the case of $BaO \cdot 2B_2O_3$ samples, unassigned peaks are due to the presence of secondary phases BaB_2O_4 (01-085-0914).

for the case of a lead borate glass. Structural defects generated during the crystallization are considered responsible for this kind of improvements [8]. Here, we present an extended work with other borates in which a detailed study of the structure, crystallization and TL response was carried out. In order to address the idea that crystallization process induces a better TL response, we study a set of glasses with similar characteristics, and their isochemical glass-ceramics obtained through the same process. Additionally, we try to respond to the question "Is there a correlation between material and TL response?"

2. Experimental section

2.1. Glass sample preparation

Borate glasses with the composition $MO \cdot 2B_2O_3$ (M: Pb, Sr, Ba) and $N_2O \cdot 2B_2O_3$ (N: Li and Na) were prepared using the melt quenching method. An appropriate weight of analytical grade H_3BO_3 99.5% (Aldrich) was fused at 500 °C to eliminate the major fraction of water content in a platinum crucible. After that, we added PbO 99.9% (Aldrich), $SrCO_3$ 99.9% (Aldrich), or $BaCO_3$ 99.9% (Aldrich) to obtain the $MO \cdot 2B_2O_3$ glasses, and Li_2CO_3 99.9% (Aldrich), or Na_2CO_3 99.9% (Aldrich) in order to obtain $N_2O \cdot 2B_2O_3$ glasses. The complete fusion was achieved in the 950–1100 °C range, depending on the glass composition, and was maintained for 1 h. Once the compound was homogeneously melted, we poured the fused glass into a steel mold at room temperature. Glass samples were re-melted to ensure homogeneity. The as-prepared samples were stored in a desiccator to avoid moisture absorption and therefore the possibility of undesired crystallization during further thermal treatment.

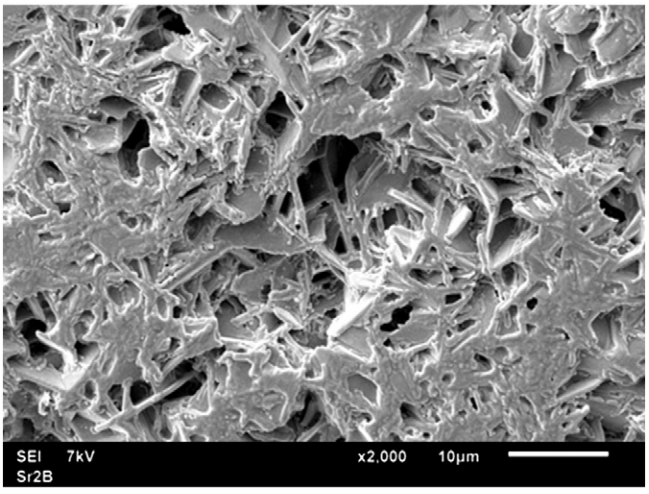

Fig. 2. Scanning electron microscopy of a representative glass-ceramic sample ($SrO \cdot 2B_2O_3$) heat treated for 60 min.

2.2. Glass-ceramics preparation

Glass samples were crushed and sieved by different particle sizes. Granular glass particles in the range 25–90 μm were pressed (10 ton) in a stainless steel die into a disc 13 mm in diameter. Samples of 1500 mg of powdered glass were used. Samples were heat treated at the temperature corresponding to the maximum of the DTA crystallization peak for 60 min in order to obtain glass-ceramic samples.

2.3. Sample characterization

In order to confirm the amorphous state of the glass, X-ray diffraction was performed using a θ–2θ PANalytical EMPYREAN, with an X-ray source of Cu(Kα) radiation (λ = 1.5418 Å). The identity of the crystalline phase in the glass-ceramic samples obtained after heat treatment was investigated by X-ray powder diffraction at room temperature, using a θ–2θ Rigaku Ultima IV diffractometer and Cu(Kα) radiation (λ = 1.5418 Å).

Structural characterization was performed using a Fourier transform infrared spectrometer (FTIR) Shimadzu Prestige-21, with a Pike (EasiDiff) reflectance diffuse accessory. Transmittance signals in the range 1600 to 400 cm^{-1} were normalized, and after deconvolution of the signal, the corresponding transformation to absorbance was applied. The deconvoluted signal was then used to interpret the spectra. High-resolution ^{11}B nuclear magnetic resonance spectroscopy (^{11}B NMR) was used in order to obtain information of boron speciation, i.e. the fraction of three- and four-fold coordinated species. Experiments were carried out in a Varian Unity INOVA spectrometer operating at a field of 9.4 T. Samples were packed in 4 mm silicon nitride rotors and spun at 10 kHz. Spectra were obtained from single pulse experiments using radiofrequency pulses with nutation frequencies of 120 kHz and duration of 0.5 μs, recycle delays of 3 s and 1200 scans. A solution of 0.1 M of boric acid was used as reference for ^{11}B chemical sifts (0 ppm).

Thermal analysis was carried out using a Shimadzu Differential Thermal Analysis (DTA), DTA-50, under air atmosphere; 16.0 (±0.2) mg of representative glass samples were used in all the experiments. This amount was chosen to ensure good thermal contact between sample and crucible, in order to avoid temperature gradients in the sample [9]. α-Al2O3 was employed as reference in DTA. It is well known that the particle size affects the value of thermal parameters [10], therefore glass sample analysis was performed on fractions with particles 23–65 μm in size. The Kissinger method was used to analyze glass crystallization [11]. In this method glasses were heated at different rates and from the DTA curves the temperature at which the maximum of the peak (T_p) occurs was determined (±2 °C). The variation of T_p as a function of the heating rate (β) is plotted in order to obtain the activation