Effect of crystallization in Sm^{3+} doped B_2O_3-Li_2O-Nb_2O_5 glass system

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Sm^{3+} doped B_2O_3-Li_2O-Nb_2O_5 glass was prepared by the conventional melting method in air atmosphere. The glassy nature of as-prepared glass was established by differential thermal analysis. X-ray powder diffraction confirmed crystallization behavior and process in heat-treated glass ceramic samples. Ferroelectric hoops were detected in glass ceramic samples which were heat treated at 500℃ and 550℃. Compared to as-prepared glass, luminescence behavior was improved in transparent glass ceramic samples that were heat treated at 500℃. Crystallization of ferroelectric phase optimized ferroelectric and luminescence properties at the same time. Therefore this glass ceramic system can be a potential new material for combining ferroelectric and optical properties.

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1. Introduction

Crystallization of glass is a popular method to fabricate glass ceramics. Ferroelectric crystals in glass ceramics are relative to many special functions that include nonlinear optical, high energy density capacitance, electrooptic (EO) switching and wavelength conversion [1]. Therefore, ferroelectric glass ceramics have been an important material.

At the same time, there has been a considerable amount of interest in studying physical properties of rare earth doped glass. Because rare earth doped laser glasses have many advantages. For example rare earth doped laser glasses are simple to prepare and form large size Moreover rare earth laser glasses can gain optimal properties easily by adjusting composition of glass. These glasses have widely been applied in modern industry, medicine, scientific and military affairs [2-3]. In rare earth laser glasses, low phonon energy is the key to obtain great luminescence performance [4-12]. Compared to glass matrixes, nanocrystals of glass ceramics have lower phonon energy. Therefore crystallization may be helpful to improve luminescence behavior. Rare earth doped ferroelectric glass ceramics may be a significative way to prepare multifunctional materials which integrate luminescence and ferroelectric properties.

In this study, Sm3+ doped B_2O_3-Li_2O-Nb_2O_5 glass was prepared at high temperature in air atmosphere. The as-prepare glass was heated in different temperature. The phase and process of crystallization was investigated by using X-ray diffraction. Luminescence properties of the sample and ferroelectric properties have been studied. Ferroelectric crystals in glass ceramics improved luminescence behavior and ferroelectric properties at the same time.

2. Experimental

Sm^{3+} doped B_2O_3-Li_2O-Nb_2O_5 glass with composition of $65B_2O_3+30Li_2O+5Nb_2O5+1Sm_2O_3$ was prepared by conventional melting method. The starting materials of H_3BO_3, Li_2CO_3, Nb_2O_5, and Sm_2O_3 were mixed and melted in a corundum crucible at 1050℃ for 30min. The glass melt was poured into a brass plate. Then the sample was cooled to room temperature automatically. The glass transition temperature (Tg) and crystallization temperature (Tcr) were determined by using differential thermal analyses (DTA). In order to obtain glass-ceramics, as-prepared samples were heat-treated at 500℃ and 550℃ with a heating rate of 250℃/h. These temperatures were chosen according to differential thermal analysis of as-prepared glass.

The as-prepared glass and heat-treated glass ceramics were examined by X-ray diffraction (XRD) analysis at room temperature by using X'Pert PRO. The ferroelectric hysteresis loops were examined by the ferroelectric tester. A FP-6500 spectrometers (Jasco) was used to measure the emission spectrum of glasses and glass ceramics.

3. Results and discussion

Fig. 1 shows the DTA curve that was obtained from as-prepared glass. The glass transition temperature (Tg) and the exothermic peak (Tcr) were approximately 470℃ and 570℃ respectively. The heat treatments were made in agreement with this result. Obvious exothermic peak observed at 570℃ was crystallization onset temperatures. And the result was good agreement with literatures about the ferroelectric transparent glass ceramics in B_2O_3-Li_2O-Nb_2O_5 system [13, 14].

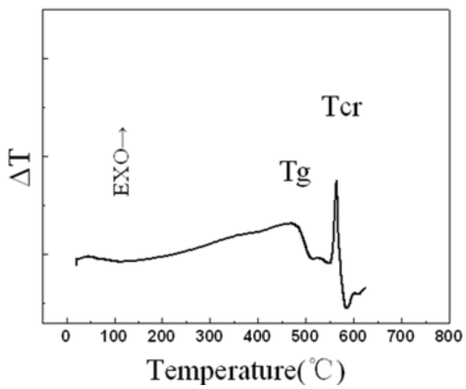

Fig. 1. Differential thermograms for the as-prepared glass sample.

Fig. 2 is XRD patterns of as-prepared glass and glass ceramics. No obvious diffraction peaks were found in XRD patterns of the as prepared glass. Therefore the as-prepared glass should be completely amorphous. Intense diffraction peaks, which could be ascribe to $LiNbO_3$ and Li_2B4O_7 crystal, could be observed in glass ceramic samples. When temperature of heat treating was increased from 500℃ to 550℃, the diffraction peaks became more obvious and sharper. It indicated gradual formation of $LiNbO_3$ and Li_2B4O_7 in the glass ceramic which was heat-treated at 550℃. In addition, the samples treated at 550℃ are opaque. The main reason might be too large size of crystal. Compared to B_2O_3 glass, $LiNbO_3$ phase that was the main crystal in the glass ceramics has higher refractive index. And the difference between refractive indices resulted in decrease of transparency.

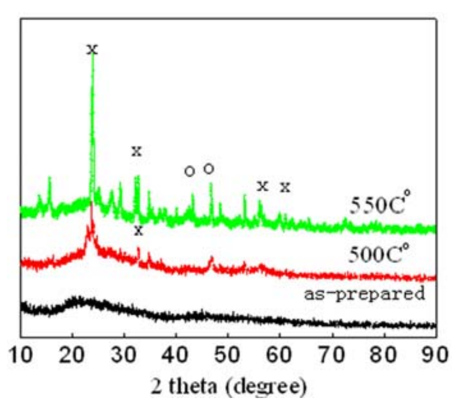

Fig. 2. XRD patterns of the as-prepared sample and the samples heat-treated at 500℃/2h and 550℃/2h (peaks marked: X $LiNbO_3$; O: $Li_2B_4O_7$).

Fig. 3 shows the ferroelectric hysteresis loop of Sm^{3+} doped B_2O_3-Li_2O-Nb_2O_5 glass-ceramics. Regarding the sample heat treated at 500℃, the value of Pr and Ec is 0.820uC/cm^2 and 15.467KV/cm respectively. To the sample heat treated at 550℃, the value of Pr and Ec is 3.368uC/cm^2 and 23.481KV/cm. The ferroelectric hysteresis loop of glass ceramics could prove that crystallization of ferroelectric phase $LiNbO_3$ in glass ceramics improve ferroelectric performance. More crystals that were originated from higher temperature enhanced ferroelectric property.

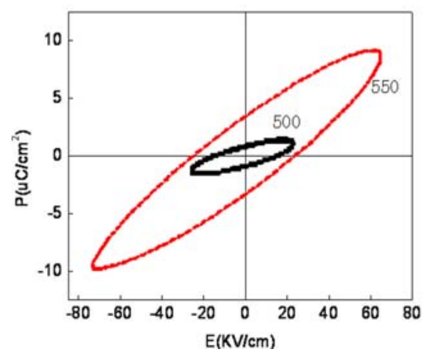

Fig. 3. Ferroelectric hysteresis loop for the glass ceramic samples heat-treated at 500℃/2h and 550℃/2h.

Fig. 4 shows the emission spectra of glass without Sm^{3+}, Sm^{3+} doped glass and glass ceramic. The emission spectra of Sm^{3+} doped glass and glass ceramics showed fluorescence lines at 567nm, 604nm and 649nm, which were due to $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$ transitions [15]. The glass ceramic that was heat treated at 500℃ had more intensive emission. The emission of the rare earth ion was influenced by the concentration of rare earth ion. Crystallization of ferroelectric phase $LiNbO_3$ was helpful to concentrate Sm^{3+} ions. Sm^{3+} doped glass materials were sensitive to the multiphonon relaxation (MPR) rate of rare earth , which strongly depended on the phonon energy of materials [15]. Phonon energy of $LiNbO_3$ nanocrystals (~800cm^{-1}) is less than borate glass (1400cm^{-1}). These $LiNbO_3$ crystals in glass ceramics were helpful to improve luminescence intensity of glass ceramics.

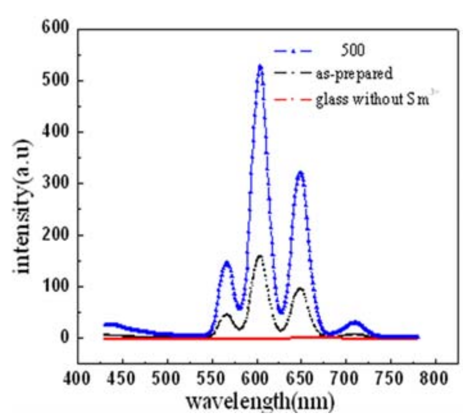

Fig. 4. Excitation spectrum (λem=405nm) of glasses and glass ceramic heat treated at 500℃/2h.

4. Conclusions

The Sm^{3+} doped glasses and glass ceramics containing $LiNbO_3$ nanacrystals have been prepared. Crystallization process and phase were observed by XRD analysis. Obvious ferroelectric hysteresis loops were found in glass ceramics heat treated at 500℃ and 550℃. The emission intensity of the Sm^{3+} B_2O_3-Li_2O-Nb_2O_5 glass ceramic significantly was improved by heat treatment at 500℃. Transparent glass ceramic heat treated at 500℃ exhibited an integrated ferroelectric and luminescence performance.

Acknowledgments

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