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Effect of doping La_2O_3 on the structure and properties of the titanium barium silicate glass

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ABSTRACT

Glasses with the composition $50SiO_2$-$20TiO_2$-15BaO-7.5SrO-7.5CaO doped varied content of La_2O_3 have been prepared by the conventional melt quench technique. The effect of La_2O_3 on structure of the glasses was investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectra and Raman spectra. The density, thermal stability and dielectric properties of glass were measured and compared by the Archimedes method, differential thermal scanning analysis (DSC) and impedance spectroscopy, respectively. The results showed that the coordination of the titanium remained invariable with the addition of La_2O_3, while the number of Si-O-Ti bonds increased and the distribution of Q^n changed. And the depolymerization of the glass network was observed. The thermal stability and resistance to crystallization increased significantly for glass containing 4 mol% of La_2O_3 resulting from the strong strength of La—O bond and the La^{3+} clustering. However, the resistance to crystallization for glasses was decreased with further increasing La_2O_3. The dielectric constant of glass decreased first and then increased with the increase of La_2O_3 content, while the dielectric loss was almost constant.

1. Introduction

Decreasing the size of electronic devices have aroused considerable interest in fields such as electronic communication, satellite communication and mobile communication with the development of information technology [1]. And almost all electronic devices contain printed circuit boards so that it's urgently necessary to manufacture the copper clad laminate with high dielectric constant [2]. As the main reinforced material of copper clad laminate, the glass fiber has a great impact on the dielectric properties of copper clad laminate. Generally, copper clad laminates mainly adopts E glass fiber as a reinforcing material. However, the permittivity of E glass fiber is low, about 7, some are even < 5 [3], which is unable to meet the requirement. Although the lead silicate glasses have showed a dielectric constant of 13.0 sufficient to fabricate copper clad laminates of desired dielectric characteristics. Lead content of such glass composition is higher than 70%, which is harmful to health and the environment. In addition, the glass fiber is easy to be broken because of the volatilization of lead during the production process. Consequently, another glass system, titanium barium silicate glass, begins to be studied due to its high dielectric constant and chemical stability. But the titanium barium silicate glass has been found not to be applicable to continuous drawing due to the higher devitrification temperature [4].

One way to solve the problem is to change the composition of glass. For example, Kiyotaka Komori et al. [4] added an appropriate proportion of Nb_2O_5 into the titanium barium silicate glass. It's established that Nb_2O_5 could ensure the high dielectric constant and improve the chemical stability of glass. Naka et al. [5] further optimized such composition and found that the glasses with the composition $50SiO_2$-30RO-14MO_2-6$NbO_{2.5}$ and $50SiO_2$-30RO-12MO_2-8$NbO_{2.5}$ (R: Ba, Sr, Ca; M: Zr, Ti) showed a good thermal stability, which was expected to be used for preparation of glass fiber with high dielectric constant. And more recently, Tong chao et al. [6] reported that doping proper Nb_2O_5 can effectively reduce devitrification temperature of titanium barium silicate glass. Unfortunately, most investigation was focused on adding Nb_2O_5 into the glass, little attention has been paid to selecting rare earth elements to improve the properties of the glass.

Compared with alkali metal and alkaline earth metal ions, rare earth ions with higher cationic field strengths [7] can effectively depress the crystallization of glass. Furthermore, glasses containing rare earth also tend to have higher hardness, elastic modulus, glass transition temperature (T_g) and chemical stability [8]. Consequently, rare earth is widely introduced to improve the properties of glass, among which La_2O_3 is the most common one. However, few researchers have

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Table 1
The composition of glasses[a] (mol %).

Experiment	SiO_2	TiO_2	BaO	SrO	CaO	La_2O_3
x = 0 mol%	50.0 (50.2)	20.0 (20.3)	15.0 (14.7)	7.5 (7.4)	7.5 (7.3)	0
x = 2 mol%	50.0 (50.3)	20.0 (20.1)	15.0 (14.8)	7.5 (7.4)	7.5 (7.4)	2.0 (2.0)
x = 4 mol%	50.0 (50.1)	20.0 (20.2)	15.0 (14.8)	7.5 (7.5)	7.5 (7.4)	4.0 (4.1)
x = 6 mol%	50.0 (50.4)	20.0 (20.4)	15.0 (14.6)	7.5 (7.3)	7.5 (7.3)	6.0 (5.9)
x = 8 mol%	50.0 (50.4)	20.0 (20.5)	15.0 (14.5)	7.5 (7.4)	7.5 (7.2)	8.0 (7.8)

[a] The composition of glasses were analyzed by an x-ray fluorescence spectrometer and the results are given in parentheses.

reported the structure and properties of titanium barium silicate glasses containing La_2O_3. In this study, the effect of doping La_2O_3 on the structure and properties of titanium barium silicate glass and the relationship between dopant induced structural change and the properties are investigated.

2. Experimental

Reagent grades $BaCO_3$, $CaCO_3$, $SrCO_3$, TiO_2, SiO_2, and La_2O_3 were used as raw materials for preparing glasses with the composition $50SiO_2$-$20TiO_2$-15BaO-7.5SrO-7.5CaO-xLa_2O_3 mol %, ($0 \le x \le 8$) where x varies from 0 to 8 in steps of 2. The compositions of as-prepared glasses were confirmed by an x-ray fluorescence spectrometer (XRF-1800). And the nominal and analyzed molar compositions of the as-prepared glasses were shown in Table 1. Initially homogeneous mixtures (100 g) in a platinum crucible obtained by full grinding was melted in laboratory electric furnace at 1450 °C for 2 h in air atmosphere. The melts were poured into the preheated graphite model to form bulk glass. Bulk glass was transferred into the muffle furnace and annealed at 550 °C for 2 h, then slowly cooled to room temperature.

XRD was realized to check amorphous nature of the samples in the 2θ range from 10° to 90°. XPS was carried out with in a KESCALAB250XI spectroscopy (Thermo Scientific company, USA) using monochromatic Al Kα radiation (hυ = 1486.6 eV). FTIR spectra of the glasses from 400 to 4000 cm^{-1} were performed at room temperature by a Nicolet iS10 Fourier transform infrared spectrometer using the standard KBr pellet method with a resolution of 4 cm^{-1}. The Raman spectra of the glasses were measured with Labram aramis in 100–1200 cm^{-1} spectrum range and the resolution of the system was < 1 cm^{-1}. Density was measured using the Archimedes method with deionized water as the immersion medium. And the various physical quantities [9] were calculated from the density. At least three samples were examined for each composition and mean value was provided.

Molar volume of the glasses, V_m, was calculated as a function of the molar fraction of each component, using the relation:

$$V_m = \frac{M}{\rho} = \frac{\Sigma x_i \cdot M_i}{\rho} \quad (1)$$

where x_i is the molar fraction of each component i, M_i is the molecular weight and ρ is the density of the glass sample.

Oxygen molar volume of the glasses, V_o, was calculated using the following formula:

$$V_o = \left(\frac{\Sigma x_i \cdot M_i}{\rho}\right) \cdot \left(\frac{1}{\Sigma x_i \cdot n_i}\right) \quad (2)$$

where n_i is the number of oxygen atoms in each constituent oxide.

Oxygen packing density of the glasses, OPD, was calculated using the density and composition values by applying the following formula:

$$OPD = 1000N \cdot \frac{\rho}{M} \quad (3)$$

Where N is the number of oxygen atoms per each composition, M is the molecular weight of the glass sample.

Glass transition onset (T_g), crystallization onset (T_c) and crystallization peak (T_p) temperatures of the glasses were conformed using differential scanning calorimetry (DSC) analysis (Netzsch STA449F3 thermal analyzer) in the temperature range from 30 to 1200 °C with the heating rate of 10 °C/min in N_2 atmosphere. At least two samples were examined for each composition and the uncertainty of characteristic temperatures was ± 2 °C. The three glass samples for each composition were polished and reduced to the final diameter of 2.0 cm and thickness of 2.0 mm. A silver coating was given to glasses on both sides so as to act as electrodes for dielectric measurements. The measurement of the dielectric properties was reproducible within 5%.

3. Results and discussion

3.1. XRD patterns

The amorphous nature of these samples were tested by XRD and the results were depicted in Fig. 1. Glasses were found that there is no diffraction peaks or diffraction rays of any crystal. It can be confirmed that all samples were amorphous and indicated that the doping of La_2O_3 do not affect the glass forming in this system. In addition, a broadened dissemination peak for each pattern at 20–35° region which indicated that the glass built its structure by highly distorted SiO_4 tetrahedral to be random 3D network that presented short-range order but long-range disorder.

3.2. XPS spectra

Fig. 2 showed the XPS spectra near the Ti 2p core level region for the glasses. It's clearly observed that the position of the Ti 2p doublet (458.0 eV for Ti $2p_{3/2}$ and 463.8 eV for Ti $2p_{1/2}$).The peak of Ti $2p_{3/2}$ binding energies are close to each other at range of 457.9–458.0 eV and are similar to the value of Ba_2TiO_4 crystal (457.9 eV). It's suggested that the chemical environment of Ti is similar to that of Ba_2TiO_4 crystal and mainly entered the glass as network former in [TiO_4] tetrahedron units, which is in a good agreement with the results of Tong Chao et al. [6] The chemical shift of the binding energy depends on the charge density

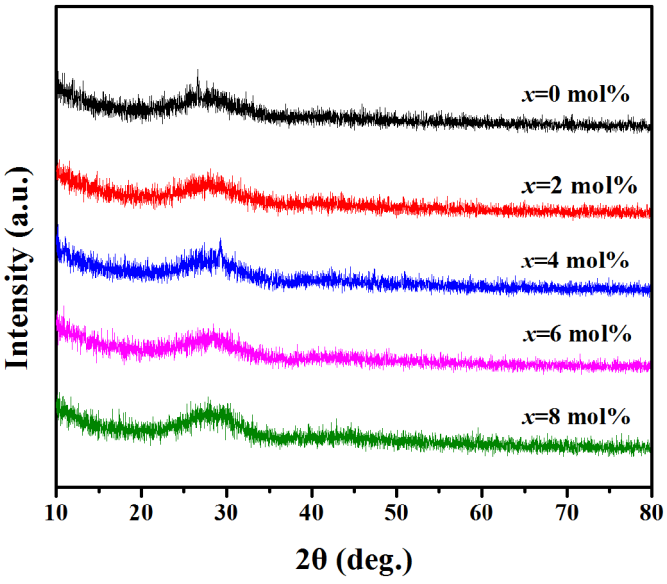

Fig. 1. XRD patterns of pristine and doped glasses with various content of La_2O_3.