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Effect of Y_2O_3 and La_2O_3 on structure and dielectric properties of aluminoborosilicate glasses

Jiling Zhao[a], Yadong Lu[a], Junfeng Kang[a], Ya Qu[a], G.A. Khater[b], Sheng Li[a], Yanling Wang[a], Yunlong Yue[a,c,*]

[a] *School of Materials Science and Engineering, University of Jinan, Jinan 250022, China*
[b] *Glass Department, National Research Centre, Cairo, Egypt*
[c] *Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan, China*

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ABSTRACT

The aluminoborosilicate glass samples with substituting La_2O_3 for Y_2O_3 were prepared in order to obtain excellent dielectric properties. The samples were prepared by the conventional melting method. The structure, thermal properties and dielectric properties of the samples were investigated by FTIR, DSC and impedance instrument. It can be seen from IR curves that with the increasing of La_2O_3 (from 0.5 mol% to 3.0 mol%) the average number of bridging oxygen per tetrahedron first increased and then decreased. The DSC curves revealed that $\triangle T$ ($\triangle T = T_c - T_g$, T_c and T_g represent the glass crystallization temperature and the glass transition temperature, respectively) first increased and then decreased. It is found that, the glass network structure reached the maximum degree of polymerization when the sample contain 1.5 mol% La_2O_3. Then continue to increase the content of La_2O_3 reduced the degree of polymerization. Dielectric constant (ε_r) and dielectric loss ($\tan\alpha$) decreased with the increasing of polymerization of the network structure. As a result, aluminoborosilicate glass with 1.5 mol% La_2O_3 and 1.5 mol% Y_2O_3 achieved the best structure and dielectric properties ($\varepsilon_r = 4.67$, $\tan\alpha = 7.9 \times 10^{-4}$).

1. Introduction

The printed circuit board (PCB) made of copper clad plate (CCL) is widely used in mobile phones, home appliances, aerospace, military and other fields. The application of CCL is due to its good dielectric properties, which increases the signal propagation speed and reduces the energy loss in the circuit. The basic components of CCL include glass fiber and resin, their low dielectric constant and dielectric loss make CCL has better dielectric properties [1].

Aluminoborosilicate glass is the first to be used in the electronics industry as a reinforcement for CCL due to its good electrical insulation and glass melting properties [2–6]. Studies indicated that the relative proportions of network modifiers with varying cation field strengths affect the structure and dielectric properties of aluminoborosilicate glasses [7]. L. Zhang et al. [8] found the optimum composition of the glass samples with excellent dielectric properties by the orthogonal experiment. In addition, X. Zhang et al. [9] found that as MgO/CaO in aluminoborosilicate increased the dielectric constant and loss decreased, which attribute to the increased in the rigidity of the glass network.

Rare earth ions with high ion field strength are filled into the glass network as the network modifiers to increase the free oxygen ions in the glass and make up for the lack of network outside body in the glass system state. When rare earth ions are incorporated in small amounts, the glass forming ability, the structure and dielectric properties of the glass can be improved. According to H. Liu et al. [10], better dielectric properties occurred when the CaO/La_2O_3 ratio reached 44.83 and 1.86. Besides, Y. Lu et al. [11] found out that the dielectric properties achieved the best when the sample contains 0.5 mol% La_2O_3 or 1 mol% CeO_2. Recent studies showed that when two kinds of rare earth oxides were co-doped into glass samples, the effects on the structure and properties were better than doped singly. M. Wang et al. [12,13] investigated the effect of co-doping Gd_2O_3 and Y_2O_3 on the soda lime silicate glass structure and free volume. The results showed that the depolymerization effect of co-doped with Gd_2O_3 and Y_2O_3 on silicate glass structure is less than that of doping singly with Gd_2O_3 or Y_2O_3. The effect of rare earth single doping on the structure and dielectric properties of aluminoborosilicate glass was investigated in our lab previous studies. When La_2O_3 or Y_2O_3 is doped alone, the dielectric properties of the glass can be improved. However, few studies have

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[*] Corresponding author at: School of Materials Science and Engineering, University of Jinan, Jinan 250022, China.
E-mail address: YueylQuy@outlook.com (Y. Yue).

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Table 1
Glass compositions (mol%) of the investigated glasses.

Glass no.	Al_2O_3	B_2O_3	SiO_2	Na_2O	CaO	Y_2O_3	La_2O_3
LY-1	8	20	57	1	11	3.0	0.0
LY-2	8	20	57	1	11	2.5	0.5
LY-3	8	20	57	1	11	2.0	1.0
LY-4	8	20	57	1	11	1.5	1.5
LY-5	8	20	57	1	11	1.0	2.0
LY-6	8	20	57	1	11	0.5	2.5
LY-7	8	20	57	1	11	0.0	3.0

been conducted on whether the co-doped of two rare earth oxides has a greater effect on the dielectric properties. Therefore, the aim of this paper is to focus on the effects of co-doped with La_2O_3 and Y_2O_3 on structure and dielectric properties of aluminoborosilicate glasses by substituting La_2O_3 for Y_2O_3.

2. Experimental procedures

2.1. Glass preparation

High purity powders of Al_2O_3, B_2O_3, SiO_2, Na_2CO_3, $CaCO_3$, Y_2O_3 and La_2O_3 were used to produce the glass samples. The detail composition ratio is shown in Table 1. Homogeneous mixtures were placed in alumina crucibles then melted in a high temperature resistance furnace at 1550 °C for 3 h. The materials were poured on graphite plates to solidify and then annealed at 650 °C for 100 min. The structure and dielectric properties of the obtained glass samples were tested then the optimal composition was obtained by analysis.

2.2. Sample characterization

The infrared spectra (IR) of the glass samples were measured at room temperature using the Nicolet-380 infrared spectrometer and KBr disc technique to characterize the internal structure of the samples. The spectra were measured in 400–2000 cm^{-1} region.

Differential scanning calorimetry (DSC) analysis of the glasses was done using Mottler Toledo TGA thermal analyzer. The samples were heated up from 50 °C to 1250 °C at a rate of 10 °C/min. Physical and chemical changes can be obtained during the heating process to find the glass transition temperature (T_g) and glass crystallization peak temperature (T_c), so as to characterize the thermal performance of glasses.

The density (ρ) was measured at 25 °C by the Archimedes' principle using distilled water to immerse the glass samples. Theoretical density (ρ_{cal}) was calculated by formula.

$$\rho_{cal} = \sum \rho_i x_i$$

where ρ_i and x_i is the density and molar fraction of each component i. The packing density (V_t) was calculated by formula.

$$V_t = (1/V_m) \sum V_i x_i$$

$$V_i = 6.023 \times 10^{23} (4\pi/3) (XR_M{}^3 + YR_O{}^3)$$

where V_i is peaking factor of an oxide M_XO_Y and V_m is the molar volume, R_M and R_O are the respective ionic radius of M and O [14]. The dissociation energy (G_i) was calculated by formula.

$$G_i = (\rho_i/M_i) [X \Delta H_f (M, gas) + Y \Delta H_f (O, gas) - \Delta H_f (M_X O_Y, crystal) - (X + Y) RT]$$

where M_i is the molecular weight of the oxide and ΔH_f is the molar heats [15]. The parameter G_i that we used to calculate elastic modulus was derived from the Makishima–Mackenzie theory [16]. Table 2 shows calculated dissociation energy (G_i) of various oxides. Elastic modulus (E) of the glasses by Makishima and Mackenzie theory was calculated according to the following expression [17,18].

Table 2
Dissociation energy (G_i) of various oxides.

Oxide	Al_2O_3	B_2O_3	SiO_2	Na_2O	CaO	Y_2O_3	La_2O_3
G_i (kJ/cm^3)	134.0	77.9	64.5	37.3	64.9	74.1	67.8

$$E = 2V_t \sum G_i x_i$$

Dielectric properties of the glass samples were measured using the Agilent 4292A impedance analyzer at 1 MHz with air atmosphere and room temperature. The glass samples were placed on CNC dicing saw to cut the cube into 10 × 10 × 3 mm. The dielectric loss (tanα) of the samples can be read out directly, dielectric constant was calculated as follows.

$$\varepsilon = \frac{Cl}{A\varepsilon_0}$$

where C is the measured capacitance (F), l is the thickness of glass sample (m), A is area of glass sample (m^2), ε_0 is dielectric constant in vacuum (8.854×10^{-12} Fm^{-1}) [19,20].

3. Results and discussion

3.1. IR

The infrared spectra of the samples in the wavenumber range of 400–2000 cm^{-1} are shown in Fig. 1. The absorption band in 837–940 cm^{-1} can be assigned to the Si—O—B bending vibration. The intense absorption band in 940–1200 cm^{-1} indicates the asymmetric stretching vibration of Si—O—Si in [SiO_4] tetrahedral. Its width is affected by the Q^n unit in the glass structure, where Q refers to a silicon tetrahedron containing n bridging oxygen (BO, n = 0,1,2,3,4), which moves toward higher wavenumbers as n increases from 0 to 4 [21,22]. The absorption peak at 460 cm^{-1} is due to the bending vibration of Si—O—Si [23,24]. The absorption peak at 690 cm^{-1} is due to the symmetric stretching vibration of Si—O—Al band formed by [SiO_4] and [AlO_4] and the bending vibration of the B—O—B bonds in the borate network [25–27]. The absorption peak near 1405 cm^{-1} is due to the asymmetric stretching vibration of B—O—B in [BO_3] [28–30].

It can be seen from Fig. 1 that the increase of La_2O_3 has slight effect on the infrared spectra, however, it can be observed that the increase of

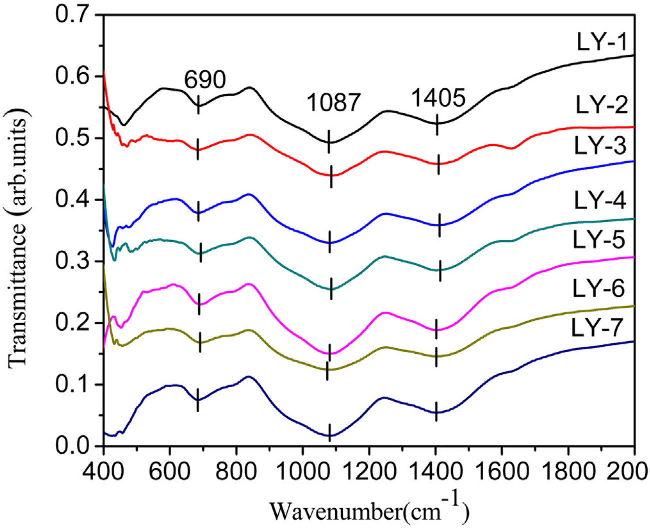

Fig. 1. IR spectra of aluminoborosilicate glasses with substituting La_2O_3 for Y_2O_3 from 0 to 3.0 mol%.