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Preparation of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ Amorphous Spheres by Containerless Solidification Process and Their Dielectric Properties

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Abstract: A series of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders with the composition of x= 0~1.0 have been firstly prepared by a sol-gel method. Then as-prepared powders were pressed into 10 mm diameter discs of 1~2 mm thickness, part of one disc was rapidly solidified to form homogeneous amorphous sphere by aerodynamic levitator method, which involved a containerless solidification process. The prepared $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous samples are spherical and exhibit transparent property with wide-banded transmittance from 1000 nm to 3000 nm. The apparent transmittance has a maximum of about 81.7% for x=0. The dielectric constant is higher than 19 and dielectric loss is lower than 0.006 for all the fabricated samples from 10 kHz to 1 MHz. The nature of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous spheres are identified by XRD and Raman spectrum.

Key words: amorphous materials; La-Al-O; Ga^{3+}dopant; containerless solidification process

So far, much effort has been devoted to forming bulk glass without adding any network former oxides such as SiO_2, because this kind of glass has outstanding optical properties and electrical properties. In 2006, Yue et al. prepared $BaTi_2O_5$ glass involving a containerless solidification process and obtained a giant dielectric through crystallized the glass[1]. In 2015, Mao et al. prepared $20La_2O_3$-(80–x)TiO_2- $x$$Nb_2O_5$ (x=0~65) glasses with a high refractive index involving a containerless solidification[2], in 2012, Zhang et al. prepared a TiO_2-La_2O_3-Ta_2O_5 glass co-doped with Er^{3+}/Yb^{3+} using containerless processing and obtained perfect visible upconversion luminescence [3].

The fabrication of oxide glass without adding any network former requires a higher cooling rate, so the fabrication of bulk inorganic oxide glass is difficult to realize and the studies on oxide glasses confined to a few systems, for example, La -Al-O system. It just simply discussed the glass forming ability in 2012 [4], but still lacked systematic study.

Containerless solidification process can suppress inhomogeneous nucleation from the container wall minimum heterogeneous nucleation, so deep undercooling for glass forming in molten materials can be gained. It is useful for vitrifying oxides by containerless processing without adding any network former [5].

In this paper, a series of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous spheres doped with Ga^{3+} have been prepared by containerless solidification process in an aerodynamic levitation furnace (ALF). The detailed description of aerodynamic levitation furnace has been already reported[6].

1 Experiment

In this paper, a series of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders with the composition of x=0~1.0 have been prepared by the sol-gel method. The analytically pure reagents lanthanum nitrate $La(NO_3)_3\ 6H_2O$, aluminum nitrate $Al(NO_3)_3\ 9H_2O$, gallium nitrate $Ga(NO_3)_3\ 6H_2O$ and bismuth nitrate $Bi(NO_3)_3\ 5H_2O$ were chosen as starting materials. The molar proportions of metal nitrates were La:Bi:Al:Ga in the ratio of 0.85:0.15:1–x:x (x=0, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0). Firstly Bismuth nitrate was completely dissolved into concentrated nitric acid and then with the right amount of lanthanum nitrate, aluminum nitrate, gallium nitrate and citric acid dissolved in an amount of deionized water to form clear solution. The solution was heated at 80 ℃ for 6.5 h in a water bath and aged for

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12 h in the desiccator, dried at 120 ℃ for 1 h, and then turned into xerogel. The xerogel was ground into powders and calcined at 750 ℃ for 2 h, in order to remove the nitrate ions and organic groups. 5 wt% polyvinyl alcohol (PVA) was added into the powders as a binder; after granulation the powders were compressed into discs with a uniaxial pressure of 2 MPa. The discs were heated at 500 ℃ for 2 h to burn the glue. Then one disc was cut into four parts, each part can be levitated by ALF and be melted with CO_2 laser and quenched quickly into a solid spherical amorphous sphere with a diameter of ~2.5 mm. The amorphous spheres were carefully polished into discs, and silver ink electrodes were applied to both faces of the amorphous samples.

The crystal structure of amorphous samples were determined by XRD (DX-2500, Dandongfangyuan, China) using Cu Kα radiation operated at 30 kV and 25 mA in a 2θ range of 20°~80°. The EDX analyses of amorphous samples were investigated by oxford energy dispersive X-ray spectrometer (SUPRA-55, Zeiss, Germany). The densities of the amorphous samples were measured by electronic balance and its density component (AL104, Mettler Toledo, China). The transmittance spectra of the amorphous samples were carried out on a UV-vis spectrometer (Cary 5000, Varian, USA). The dielectric properties were measured using an impedance analyzer (E4980A, Agilent, USA) in the frequency range from 20 Hz to 2 MHz at room temperature. The leakage current analyses were carried out on Ferroelectric analyzer (Multiferroic, Radiant, USA) in the using voltage range −10~10 kV.

2 Results and Discussion

2.1 Structure

Fig.1 shows XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders with the composition of x from 0 to 1 calcined at 750 ℃ for 2 h. The patterns exhibit a perovskite structure with space group R3m, which is consist with the standard $LaAlO_3$ peaks. The standard diffraction peaks are cited from $LaAlO_3$ (PDF# 31-0022).

Fig.2 shows XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders with the composition of x from 0 to 1 calcined at 750 ℃ for 2 h between 2θ range of 32°~35°. The figure shows that with the increasing of Ga^{3+} doping amount, the XRD peaks between 2θ range of 32°~35° gradually shift to the lower angles, which is ascribed to that the radius of Ga^{3+} (0.062 nm) is bigger than that of Al^{3+} (0.0535 nm), and Ga^{3+} substituting Al^{3+} in B-site causes expansion in the crystal lattice.

Fig.3 shows XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials with the composition of x=0~1.0. The XRD patterns in the 2θ range of 20° to 40° are steamed buns peaks, which can explain that main components existing in these samples are amorphous in nature.

Fig.4 shows Raman spectra of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials with the composition of x =0~1.0. There are four obvious Raman-active modes lying in 309.836, 660.688, 1283.89, 1605.3 cm^{-1}. Four obvious Raman-active modes give a standard for comparison of this kind of amorphous materials.

EDX analysis of $La_{0.85}Bi_{0.15}Al_{0.6}Ga_{0.4}O_3$ amorphous materials indicates that molar proportions of Bi^{3+} and O^{2-} are much lower than the designed. The designed molar proportion of Bi^{3+} is 3.0%, but it is only 0.18 mol% in the amorphous materials. The molar proportions of other elements are the same to the designed.

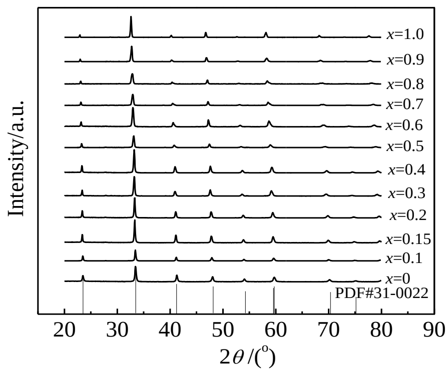

Fig.1 XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders calcined at 750 ℃ for 2 h

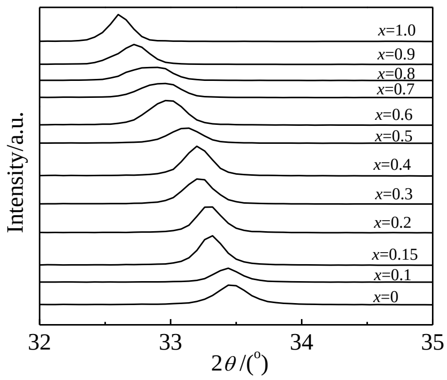

Fig.2 XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders calcined at 750 ℃ for 2 h between the 2θ range of 32°~35°

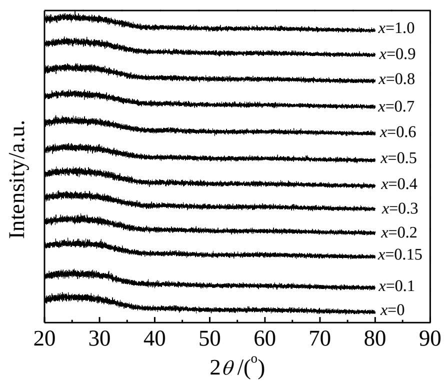

Fig.3 XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials

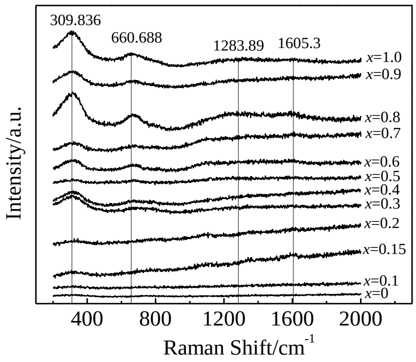

Fig.4 Raman spectra of fabricated amorphous materials

2.2 Density

Fig.5 shows the densities of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials with the composition of x=0~1.0. Archimedes drainage method was adopted. Densities increase with the increasing of Ga^{3+} doping amount.

2.3 Transmittance

Fig.6 shows the transmittance spectra of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ (x=0, 0.4, 0.6, 0.8, 1.0) amorphous samples, with wide-banded transmittance from 1000 nm to 3000 nm. In the UV-vis region the transmittance increases along with the increasing wavelength; in the infrared region, transmittance firstly declines, then increases, and finally tend to be stable with the increasing wavelength. The apparent transmittance has a maximum of about 81.7% for x=0.

2.4 Dielectric properties

Fig.7 shows dielectric constants of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials with the composition of x= 0~1.0. At 10 kHz~1 MHz dielectric constants of Ga^{3+} doped samples are higher than that of undoped ones. The dielectric constants of x=0 is approximately 19~19.5, while the highest dielectric constant for x=0.8 is 26~26.5. Fig.8 shows that the dielectric loss of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ (x = 0, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0) amorphous materials is smaller than that of 0.006.

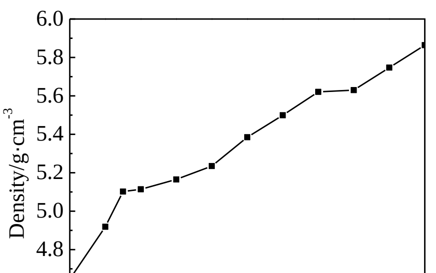

Fig.5 Densities of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials

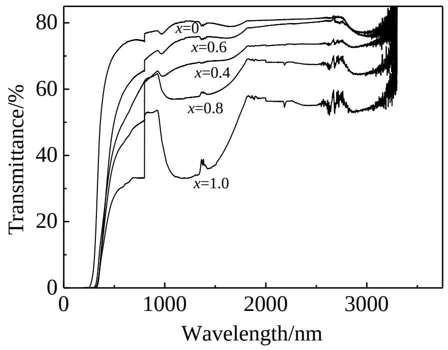

Fig.6 Transmittance spectra of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous samples

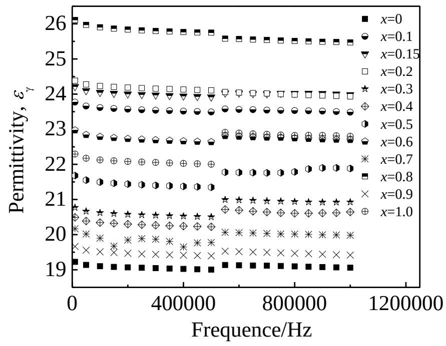

Fig.7 Dielectric constant of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials at 10 kHz~1 MHz

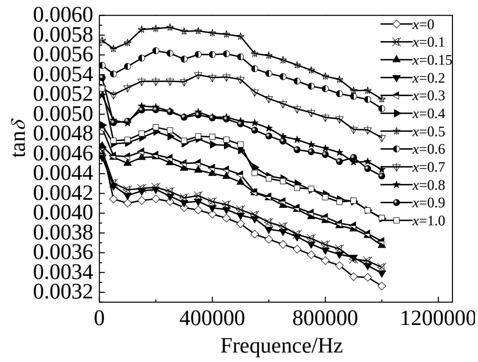

Fig.8 Dielectric loss of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials at 10 kHz~1 MHz

2.5 Leakage current analysis

Fig.9 and Fig.10 show the leakage current of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ (x=0, 0.1, 0.2, 0.4, 0.5, 0.7, 1.0) amorphous materials. The applied voltage is from −20 V to 20 V, and the leakage current changes with the electric field changing. The leakage current of x=0, 0.5, 1.0 is about 10^{-8}A/cm^2 and when x=0.4 it is about 10^{-7}A/cm^2, when x=0.2 it is about 10^{-9}A/cm^2. Leakage current is small indicating that amorphous materials have good insulation.

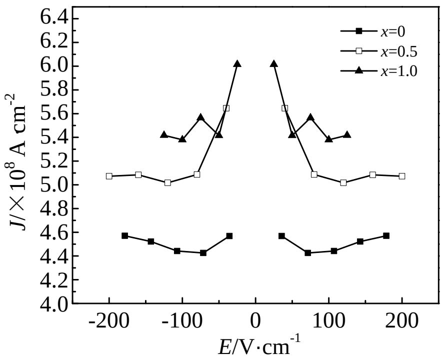

Fig.9 Leakage current of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ (x=0, 0.5, 1.0) amorphous materials

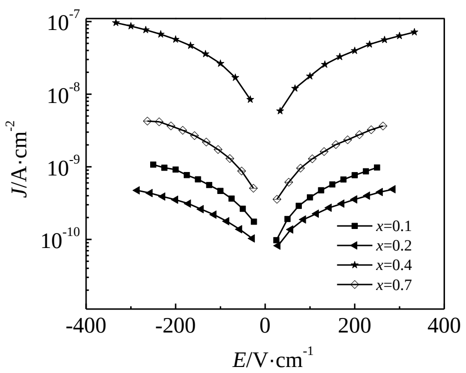

Fig.10 Leakage current of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ (x=0.1, 0.2, 0.4, 0.7) amorphous materials

3 Conclusions

1) XRD patterns of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ powders with the composition of x=0~1.0 calcined at 750 ℃ for 2 h exhibit a perovskite structure with the increasing of Ga^{3+} doping amount. The XRD peaks between the 2θ range of 32 °~35 ° gradually shift to the lower angles.

2) The nature of $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials are identified by XRD and Raman spectrum.

3) Densities increase with the increasing of Ga^{3+} doping amount.

4) $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ amorphous materials have wide-banded transmittance from 1000 nm to 3000 nm. The apparent transmittance has a maximum of about 81.7% for x=0.

5) The dielectric constant is higher than 19 and dielectric loss is lower than 0.006 for all the fabricated glass samples from 10 kHz to 1 MHz.

6) The leakage current of all amorphous samples are 10^{-7}~10^{-10} A/cm^2. Leakage current is small, indicating that amorphous materials have good insulation.

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$La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ 非晶的无容器方法制备及介电性能研究

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摘　要：采用溶胶凝胶法制备了 $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$（$x$=0~1）系列粉体。粉体被压成直径 10 mm 厚度 1~2 mm 的圆片，取一个圆片的一部分利用无容器凝固，在空气悬浮炉中快速的冷却成均相的非晶球。制备的非晶样品是球形透明的，透过率从 1000 nm 到 3000 nm，表观最大透过率达到 81.7%是在 x=0 时获得的。在 10 kHz~1 MHz 测得的介电常数高于 19，介电损耗低于 0.006，通过 XRD 图谱和拉曼光谱分析证明利用无容器过程所制备的 $La_{0.85}Bi_{0.15}Al_{1-x}Ga_xO_3$ 样品是非晶态。

关键词：非晶材料；La-Al-O；Ga^{3+}掺杂；无容器凝固过程

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