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Preparations and Properties of Amorphous $LaAl_{1-x}Ga_xO_3$

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Abstract: $LaAl_{1-x}Ga_xO_3$ powder and its amorphous sphere have been prepared by a sol-gel method and containerless solidification technology, respectively. Ga^{3+} was used to substitute Al^{3+} in *B*-site with the composition of *x* from 0 to 1.0. The X-ray diffraction results show that powders with no impurity phase are obtained when calcined at 850 ℃ which are all perovskite structure. The transparent spheres are proved to be amorphous by XRD analysis. With the increase of Ga^{3+} content, the dielectric constant ranges from 15 to 19 at 100 kHz and its corresponding dielectric loss is smaller than 0.007. The amorphous material has a low leakage current of 10^{-11} A/cm^2, and shows a high refractive index, which is more than 1.8 in 633 nm.

Key words: amorphous; La-Al-O; Ga^{3+} doping; containerless solidification technology

In recent years, there has been an increasing interest in amorphous materials, while the glass was first invented, and the most typical amorphous solid. In 1959, in the study of whether the two elements which are totally different crystal structure and valence can be dissolved, the California Institute of Technology Duwez discovered Au-Si amorphous alloy[1]. Different from traditional materials, amorphous alloys have many unique properties. For example, amorphous alloy metallic material is one of the strongest ever found and most soft (Co amorphous alloy with the strongest strength reaching a record 6 GPa, Sr based amorphous alloy with the most soft strength low to 300 MPa); metal materials of amorphous alloy was found so far the corrosion resistance of metal materials[2,3]. A series of preparation methods have been explored to prepare new amorphous materials. Therefore a large number of excellent properties of amorphous materials were found, and widely used in various fields[4, 5]. However, there are few researches focused on amorphous oxides especially dielectric properties, and the Ga doped $LaAlO_3$ system are still few reported.

According to the theory of irregular network, R_2O_3-Al_2O_3 system (*R*, rare earth elements), without the addition of network forming agents such as V_2O_5 and SiO_2[6], the system could not use the traditional method for the preparation of glass, which limits the development and application of amorphous oxide. With the development and maturity of the containerless solidification technology, the R_2O_3-Al_2O_3 bulk amorphous without network forming agent has been successfully prepared. This is due to the contactless environment and the greater degree of cooling provided by the containerless solidification technology[7]. The amorphous material has a regular spherical shape, with excellent optical properties and thermal stability, and the application prospect of the optical lens is wide.

In this paper, the $LaAl_{1-x}Ga_xO_3$ series powder was prepared by a sol-gel method, and the amorphous ball was obtained by the containerless solidification technology. Changing the doping amount of Ga^{3+} at *B*-site is used to study the influences on the phase structure, optical properties and dielectric properties. It is expected to develop materials with good optical and electrical properties, and practical use in our life.

1 Experiment

$LaAl_{1-x}Ga_xO_3$ powders were prepared by the sol-gel method. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Ga(NO_3)_3 \cdot 6H_2O$ and citric acid were dissolved in deionized water to form clear solution. Then we put the beaker on water bath pot, at the temperature of 80 ℃ for 6.5 h. After ageing for 12 h, we put it in a tray and then put them in a drying chamber at 120 ℃ for 2 h, and finally the yellow sticky wet gel was turned into white dry gel. We put the crucible with powder in the muffle furnace, followed by calcining at 850 ℃ for 3 h. The powder was pressed into

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9 mm diameter and l mm thick disks with the polyvinyl alcohol binder. An amorphous ball can be made by the containerless equipment. For electrical measurements, silver electrodes were fired on both surfaces at 600 ℃ for 30 min.

The prepared samples were characterized by various techniques. The crystal structure of materials were analyzed by X-ray diffraction (DX-2500, Dandongfangyuan, China) using Cu Kα radiation in a 2θ range of 20 °~80 °. The refractive index characteristics of the samples were also evaluated using an ellipsometer (SE 850 DUV type, SENTECH, Germany). The dielectric properties were measured using an impedance analyzer (E4991A, Agilent, USA) in the frequency range from 10^4 Hz to 10^6 Hz at room temperature. The leakage current was tested by electrometer (6517B, KEITHLEY, USA).

2 Results and Discussion

2.1 XRD of the $LaAl_{1-x}Ga_xO_3$

Fig.1 shows XRD patterns of the $LaGaO_3$ samples at different calcining temperatures by the sol-gel method. All the peaks can be indexed, which correspond to standard PDF card number 89~4796. When the calcination temperature is 750 ℃, the perovskite structure has been formed in the powder. When the temperature is increased to 850 ℃, the powder with single phase and high crystallinity is obtained.

Fig.2 is the XRD patterns of x=0~1.0 series of powder after calcination at 850 ℃ for 2 h. With the increasing doping of Ga, the crystallographic phase changes from triclinic to rhombohedral phase, and the position of the strongest peak also gradually moves to the left, as shown in Fig.3, which is ascribed to that the much larger ionic radii of Ga^{3+} (0.062 nm) than that of Al^{3+}(0.0535 nm).

Fig.4 shows XRD patterns of amorphous ball after grinding and polishing. With the limit of the containerless solidification technology, the amorphous ball of x=0.4, 0.5 was failed to made. From the figure, steamed buns peak can be observed in all components. According to this characteristic, all transparent samples are amorphous phase, which proves that the amorphous ball can be prepared successfully by the containerless solidification technology.

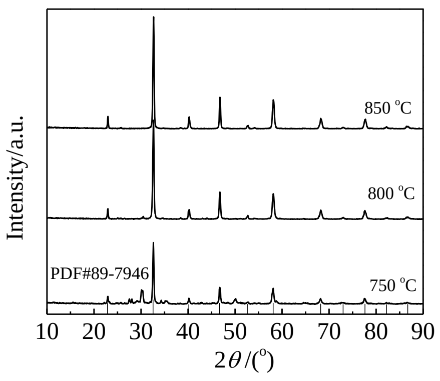

Fig.1 XRD patterns of $LaGaO_3$ calcined at different temperatures

2.2 Refractive index

Fig.5 shows the refractive index of amorphous $LaAl_{1-x}Ga_xO_3$ at the wavelength of 300~900 nm. When the doping amount of Ga is 0 and 1.0, with the increase of the wavelength, the refractive index of the sample firstly increases, then declines, and finally tends to be relatively stable. When the Ga doping amount ranges from 0.1 to 0.9 except for 0 and 1.0, the refractive index of the sample decreases with the increase of the wavelength, and is gradually stabilized in a certain range.

Fig.6 shows the refractive index with the increase of Ga doping amount when the wavelength is 632.8 nm, the refractive

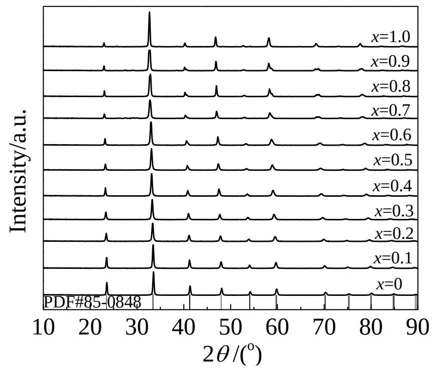

Fig.2 XRD patterns of the $LaAl_{1-x}Ga_xO_3$

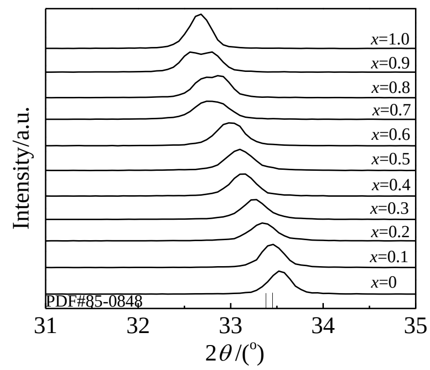

Fig.3 XRD patterns of the $LaAl_{1-x}Ga_xO_3$ at 31 °~35 °

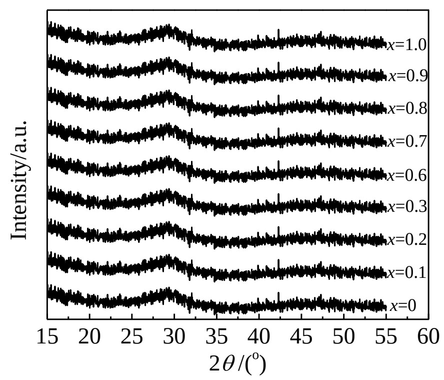

Fig.4 XRD patterns of fabricated amorphous $LaAl_{1-x}Ga_xO_3$

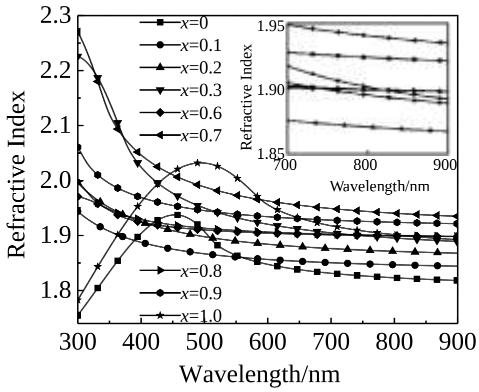

Fig. 5 Refractive index of amorphous $LaAl_{1-x}Ga_xO_3$ at the wavelength of 300~900 nm

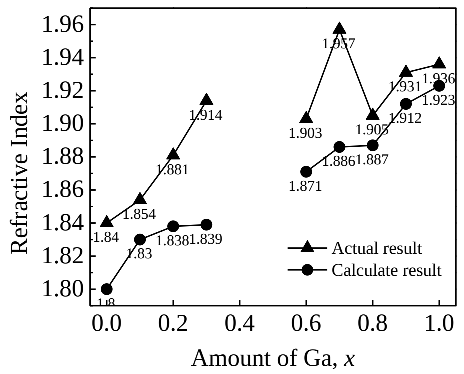

Fig. 6 Refractive index of the amorphous $LaAl_{1-x}Ga_xO_3$

index is bigger than that of 1.8. At the same time, the refractive index is calculated by the Gladstone-Dale empirical equation. With the increase amount of Ga from 0 to 1, the refractive index of the sample increases, and the change trend is consistent with the calculation results. But when the Ga content is 0.3 and 0.7, the refractive index of the sample is about 4% larger than that of calculation. Due to the lack of refractive index data of 0.5 and 0.4 groups, the variation of refractive index can not be obtained accurately.

2.3 Dielectric properties

Fig.7 shows the dielectric constant of the amorphous $LaAl_{1-x}Ga_xO_3$ at 10^4~10^6 Hz. With the increase of the frequency, the dielectric constant of the sample is stable. With the increase of *x*, the dielectric constant tends to increase firstly and then decrease. For 100 kHz, *x*=0, ε_r is 15; *x*=0.7, ε_r is 19.

Fig. 8 is the variation of dielectric loss at 10^4~10^6 Hz of amorphous $LaAl_{1-x}Ga_xO_3$. With the increase of frequency, the dielectric loss gradually decreases. The dielectric loss of all the amorphous is smaller than that of 0.007.

2.4 Leakage current

Fig. 9 and Fig.10 is the leakage current of the amorphous $LaAl_{1-x}Ga_xO_3$ for *x*=0~0.3, 6 and *x*=0.7~1.0 respectively. It can be seen that the measured leakage current is similar to the

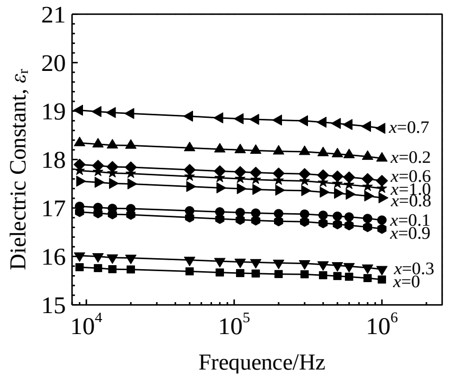

Fig. 7 Dielectric constant of the amorphous

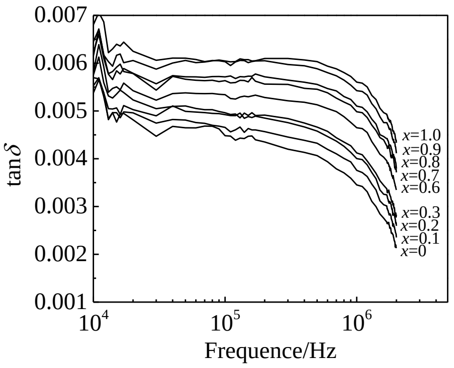

Fig. 8 Dielectric loss of amorphous $LaAl_{1-x}Ga_xO_3$

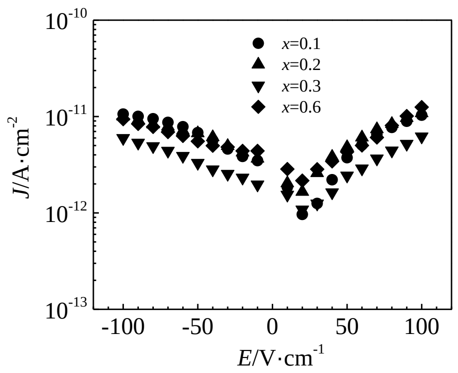

Fig.9 Leakage current of the amorphous $LaAl_{1-x}Ga_xO_3$ (*x*=0~0.3, 6)

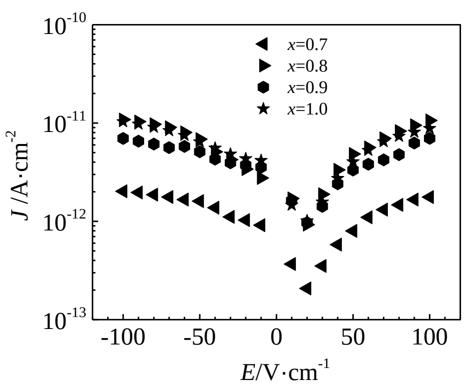

Fig.10 Leakage current of the amorphous $LaAl_{1-x}Ga_xO_3$ (*x*=0.7~1.0)

"Butterfly Effect" feature, the curve is V type with symmetry, but the symmetry axis moves from 0 V to the right to the position of 4 V. Moreover, the leakage current of all the amorphous is very small, only about 10^{-11} A/cm^2.

3 Conclusions

1) The $LaAl_{1-x}Ga_xO_3$ powder with no impurity phase is obtained when calcined at 850 ℃, which are all perovskite structure.

2) The amorphous ball is prepared by the containerless solidification technology, and the amorphous structure has been proved.

3) With the increase of Ga^{3+} doping, the refractive index has a trend of increase. In 632.8 nm, the refractive index is bigger than that of 1.8.

4) With the increase of Ga^{3+}, the dielectric constant at 10^5 Hz ranges from 15 to 19. For dielectric loss, the dielectric loss of all amorphous ball is smaller than that of 0.007.

5) The leakage current of the amorphous is very small, only about 10^{-11} A/cm^2.

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$LaAl_{1-x}Ga_xO_3$ 非晶制备及性能研究

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摘 要：采用溶胶-凝胶法和无容器凝固技术制备了 $LaAl_{1-x}Ga_xO_3$ 粉末和非晶。在 *B* 位，Ga^{3+}取代 Al^{3+}的掺杂量从 x=0 增加到 x=1.0。XRD 结果表明，煅烧温度为 850 ℃时，所有组分得到的粉体均为无杂相的钙钛矿相。XRD 的数据也证明了实验制备的非晶球为非晶。随着 Ga^{3+}含量的增加，100 kHz 的介电常数在 15~19 之间，对应的介电损耗小于 0.007。所制备的非晶材料具有低至 10^{-11} A/cm^2 的漏电流，同时呈现较高的折射率，在 633 nm 均大于 1.8。

关键词：非晶；La-Al-O；Ga^{3+}掺杂；无容器凝固技术

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