Crystallization and Dielectric Properties of BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ Glass-Ceramic Composites with La$_2$O$_3$ Addition

Qingmeng Zhang$^{1,*}$, Junyou Chen$^1$, Min Zhou$^1$, and Yanyun Zhao$^1$

$^1$GRIMAT Engineering Institute Co., Ltd, Advanced Electronic Materials Institute, 101407 Beijing, China

* Corresponding author: zhangqm@grinm.com

Abstract. Glass-ceramic composite samples with different La$_2$O$_3$ content were prepared via melt-quenching followed by controlled crystallization. X-ray diffraction (XRD) analysis reveals that when the addition amount of La$_2$O$_3$ in the glass sample is less than 1mol%, two phases of perovskite structure and tungsten-bronze structure are formed after annealing at 1000°C for 3h. When the addition amount of La$_2$O$_3$ in the glass sample is increased to 2mol%, a new phase of pyrochlore structure is formed. Moreover, the addition of La$_2$O$_3$ causes the change in the lattice parameters of the glass-ceramic crystal phase. The microstructure observed that the ceramic phase grain size is in the nanometer level. The shape of some grains becomes an elongated structure when the La$_2$O$_3$ content in the sample increases to 2 mol%, and the grain size is increased significantly. The dielectric constant of the BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ glass-ceramic system is decreased with the increase of La$_2$O$_3$ addition, and the dielectric loss of the sample is decreased to the range of 0.003-0.008. The electric field stability of the dielectric constant was significantly improved with the addition of La$_2$O$_3$, indicating that adding a certain proportion of La$_2$O$_3$ to the BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ glass-ceramic system can effectively improve the dielectric properties, and it has a promising application as a dielectric material.

1 Introduction

The energy density of the capacitor is greatly affected by the dielectric constant and breakdown strength[1]. It is difficult for sintered dielectric ceramics to have both high dielectric constant and high breakdown strength, which limits the increase in energy storage density[2-4]. Glass-ceramic is a fully dense nano-composite material which has a high dielectric constant ceramic phase and a high breakdown strength of glass phase, so the material can obtain both the high dielectric constant and a high breakdown strength, ultimately achieving a higher energy storage density[5-7]. Dielectric materials of titanate system and niobate system are widely reported. Edward P. et al.[8] added a certain proportion of Al$_2$O$_3$ to the (Ba, Sr)TiO$_3$ system to inhibit the formation of low dielectric constant ceramic phases in glass-ceramics. The research results prevented that the addition of Al$_2$O$_3$ effectively inhibits the formation of silicate phase and increases the precipitation of (Ba, Sr)TiO$_3$ high dielectric constant ceramic phase. With the addition of a small amount of Al$_2$O$_3$, the dielectric constant of the glass-ceramic reaches 1000, and the dielectric loss are 0.02. In the glass-ceramic system of NaNbO$_3$-PbNbO$_3$-SiO$_2$, Du et al.[9] studied the dielectric properties, structure and crystallization behavior of this system. The experimental results showed that with the change of crystallization temperature, the types of ceramic phases precipitated in the glass matrix are change. With the change...
in crystallization temperature, Pb_{2}Nb_{2}O_{7}, NaNbO_{3} and PbNb_{2}O_{6} phase gradually precipitates. Optimal dielectric properties appeared at the crystallization temperature of 850°C, at this time the dielectric constant reaches to 700, the dielectric loss are 0.03. Zheng et al. [10] studied the effect of adding La_{2}O_{3} on the dielectric properties of SrO-BaO-Nb_{2}O_{5}-B_{2}O_{3}-ZnO glass-ceramic system, and found that the introduction of La^{3+} ions inhibited the formation of the high dielectric constant Sr_{0.5}Ba_{0.5}Nb_{2}O_{6} crystal phase, and the dielectric constant of the SrO-BaO-Nb_{2}O_{5}-B_{2}O_{3}-ZnO system decreased. Zhou et al.[11] added different contents of Gd_{2}O_{3} to the BaO-Na_{2}O-Nb_{2}O_{5}-SiO_{2} system glass-ceramics, and studied the influence of Gd_{2}O_{3} on the dielectric properties of the system. The results showed that when 1 mol% Gd_{2}O_{3} is added, the best dielectric properties of the BaO-Na_{2}O-Nb_{2}O_{5}-SiO_{2} system is obtained. Titanate and niobate dielectric glass-ceramic systems have been extensively studied. However, there are few reports on the effect of adding La_{2}O_{3} on the dielectric properties of glass-ceramic systems containing both niobate and titanate ceramic phases. In this paper, the BaO-SrO-PbO-TiO_{2}-Nb_{2}O_{5}-SiO_{2} system of glass-ceramics is selected, and the influence of La_{2}O_{3} on the dielectric properties of glass-ceramics is studied.

2 Experimental procedure

2.1 Materials preparation

The starting materials include BaCO_{3}, SrCO_{3}, PbO, TiO_{2}, SiO_{2}, Nb_{2}O_{5}, and La_{2}O_{3}, all of which are analytical reagent grade powders. The component ratios are listed in Table 1. The oxides were mixed uniformly and melted in a platinum crucible at 1450°C for 3 hours, and then the uniform melt were rapidly cooled to form the glass blocks, and the internal stress of the glass block was reduced in a crystallization oven at 600°C. The glass bulks were annealed at 1000°C to form glass-ceramics, and the dielectric properties of glass-ceramics were studied.

| Designation | L0 | L0.5 | L1 | L2 |
|-------------|----|------|----|----|
| BaO         | 3.2| 3.2  | 3.2| 3.2|
| SrO         | 24 | 24   | 24 | 24 |
| PbO         | 11 | 11   | 11 | 11 |
| Nb_{2}O_{5} | 26 | 26   | 26 | 26 |
| TiO_{2}     | 10 | 10   | 10 | 10 |
| SiO_{2}     | 25.8| 25.8 | 25.8| 25.8|
| La_{2}O_{3} | 0  | 0.5  | 1  | 2  |

2.2 Material characterization

Phase identification was performed by X-ray diffraction (XRD; model MSAL-XD2, Micro-Structure Analysis Laboratory, Beijing) using Cu-Kα radiation at room temperature and over the 2 theta range from 20° to 70°. Observed the microstructure of the annealed sample using a scanning electron microscope (FE-SEM: Hitachi S4800). The dielectric constant and dielectric loss were measured by a precision LCR meter (HP-4284A, Agilent Technologies, Inc., USA). The P-E hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technology, Albuquerque, NM, USA). All the glass-ceramic samples were immersed in silicon oil to avoid flashover.
3 Results and discussion

3.1 Crystallization
The XRD method was used to study the crystallization behavior and phase evolution of BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ system glass-ceramic composites with different La$_2$O$_3$ content. The XRD patterns of glasses with different La$_2$O$_3$ content after crystallization treatment at 1000°C for 3h are shown in Figure 1(a). It can be seen that all the crystalline phases of the glass ceramic without addition of La$_2$O$_3$ and the glass ceramic with 0.5 mol% and 1 mol% La$_2$O$_3$ content can be indexed perovskite structure and tungsten-bronze structure. After annealing the basic component glass without La$_2$O$_3$, the tungsten-bronze structure phase was corresponded to (Ba, Sr, Pb)Nb$_2$O$_6$ and the perovskite structured phase to (Sr, Pb)TiO$_3$. When the amount of La$_2$O$_3$ addition increases to 2 mol%, a new peak appears in the XRD pattern, which is found to be a pyrochlore structure phase. Fig. 1. (b) and Fig. 1. (c) shows enlarged peaks of tungsten-bronze and perovskite structure. It shows that with the increases of La$_2$O$_3$ content, the 2θ angles of the two crystal phases peaks move towards the higher values. It shows that the crystal lattice parameters of the glass-ceramic crystal phase have changed, the radius of La$^{3+}$ ion is smaller than both Sr$^{2+}$, Pb$^{2+}$ and Ba$^{2+}$[12], so that La$^{3+}$ can occupy the position of Sr$^{2+}$, Pb$^{2+}$ and Ba$^{2+}$, which leads to the change of the lattice parameters of the ceramic phase[13].

![XRD patterns](image1)

Fig. 1. (a) XRD patterns of La$_2$O$_3$-added glasses annealed at 1000 °C for 3 h; (b) the enlarged pattern at 2θ of 42.3°; (c) the enlarged pattern at 2θ of 39°.

3.2 Microstructure analysis
The microstructure of glass samples with different La$_2$O$_3$ content after crystallization treatment is shown in Figure 2. It obviously displays that the grain size of the glass-ceramic samples with La$_2$O$_3$ content under 1mol% is less than 500nm after annealing at 1000°C. However, the grain size increased significantly when the La$_2$O$_3$ content in the sample increases to 2 mol%, at the same time, part of the grain shape became an elongated structure.
3.3 Dielectric behavior

The dielectric constant and dielectric loss tested at room temperature and 1kHz for samples of different compositions after annealing at 1000°C are shown in Figure 3. As seen, the dielectric constant decreased with the increase of La$_2$O$_3$ content. The dielectric constant decreases significantly when the La$_2$O$_3$ content increases to 2mol%, which may be related to the existence of the low dielectric constant pyrochlore structure ceramic phase. The dielectric loss of the glass composition with different La$_2$O$_3$ addition amount are in the lower range of 0.003-0.008 after annealing at 1000°C, and adding La$_2$O$_3$ significantly reduces the glass-ceramic dielectric loss.

![Figure 3](image-url)  
**Fig. 3.** The dielectric properties of the glass-ceramic samples with different La$_2$O$_3$ content.

The polarization curves of glass-ceramics with different compositions are shown in Figure 4. It is evident that the samples with different La$_2$O$_3$ content have less remanent polarization and little energy loss during charging and discharging process, and high efficiency energy released. Meanwhile, the maximum polarization of the sample decrease with the increases of La$_2$O$_3$ content, which is consistent with the change of dielectric constant.
The electric field dependence of the dielectric constant of different compositions of glass-ceramics is shown in Figure 5. It can be seen that the dielectric constant of the glass-ceramic sample without La$_2$O$_3$ has a strong dependence on the electric field strength, and the typical shape of the $\varepsilon_r - E$ Gaussian curve can be observed. When the La$_2$O$_3$ content of the glass-ceramic sample increases to 0.5mol% and 1mol%, the electric field stability of the dielectric constant increases significantly. It is worth noting that the best electric field stability of the dielectric constant is obtained when the La$_2$O$_3$ content of the glass-ceramic sample is 2mol%.

4 Conclusion
In this paper, the effect of La$_2$O$_3$ addition on the crystallization and dielectric properties of BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ system glass-ceramics have been studied. Crystallization and dielectric properties of BaO-SrO-PbO-TiO$_2$-Nb$_2$O$_5$-SiO$_2$ glass-ceramic composites with La$_2$O$_3$ additive have been studied in this paper. When the addition amount of La$_2$O$_3$ in the glass sample is less than 1mol%, two phases of perovskite structure and tungsten-bronze structure are formed after annealing at 1000°C for 3h. When the addition amount of La$_2$O$_3$ in the glass sample is increased to 2mol%, a new phase of pyrochlore structure is formed after annealing at 1000°C for 3h. The addition of La$_2$O$_3$ causes the change in the lattice parameters of the glass-ceramic crystal phase. The dielectric constant of the BaO-
SrO-PbO-TiO2-Nb2O5-SiO2 glass-ceramic system decreases with the increases of La2O3 addition, and the dielectric loss of the sample decrease to the range of 0.003-0.008. At the same time, the electric field stability of the dielectric constant is obviously improved with the increases of La2O3 addition. The results indicated that adding a certain proportion of La2O3 to the BaO-SrO-PbO-TiO2-Nb2O5-SiO2 glass-ceramic system can effectively improve the dielectric properties, and it has a promising application as a dielectric material.

References

[1] C. Li, Q. M. Zhang, Q. Tang, H. Zhou, F. H. Tan, J. Du, Electron. Mater, 45, 6 (2016)
[2] R. Gerson, T. Marshall, Appl. Phys, 30, 11 (1959)
[3] J. A. Young, G. Hilmas, S. C. Zhang, R. W. Schwartz, J. Am. Ceram. Soc, 90, 5 (2007)
[4] J. C. Chen, Y. Zhang, C. S. Deng, X. M. Dai, J. Am. Ceram. Soc, 92, 8 (2009)
[5] B. Rangarajan, B. Jones, T. Shrout, M. Lanagan, J. Am. Ceram. Soc, 90 (2007)
[6] A. Herezog, IEEE Transactions on Parts, Hybrids, and Packaging PHP, 9 (1973)
[7] G. H. Beall, J. Mater. Educ, 14 (1992)
[8] E. P. Gorzkowski, M. J. Pan, B. Bender, J. Electroceram, 18, 3-4 (2007)
[9] J. Du, B. Jones, M. Lanagan, Mater. Lett, 59 (2005)
[10] J. Zheng, G. H. Chen, C. L. Yuan, C. R. Zhou, X. Chen, Q. Feng, M. Li, Ceram. Int. 42 (2016)
[11] Y. Zhou, Q. M. Zhang, J. Luo, Scripta. Materialia 65, 4 (2011)
[12] R. D. Shannon, Acta Crystallogr. Sect, 32(1976)
[13] R. Guo, H. T. Evans, A. S. Bhatta, Ferroelectrics, 206, 1 (1998)