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Improved discharged property for (BaO, Na_2O)–Nb_2O_5–SiO_2 glass-ceramics by La_2O_3 addition

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Abstract

The (BaO, Na_2O)–Nb_2O_5–SiO_2 glass-ceramics with various amounts of La_2O_3 addition, were fabricated through melt casting followed by controlled crystallization. The effect of La_2O_3 addition on the phase transition, microstructure, and dielectric properties for (BaO, Na_2O)–Nb_2O_5–SiO_2 glass-ceramics was investigated. With the addition of La_2O_3, the dielectric constant and the breakdown strength for the glass-ceramics were drastically improved, which resulted in the improvement of the discharged property. The maximum energy-storage density of 8.4 J/cm^3 was achieved in the niobate glass-ceramics with 0.5% La_2O_3 addition, indicating that the glass-ceramic with this composition is a promising dielectric material for high energy storage density capacitors.

Keywords: C. Dielectric properties; Glass-ceramics; Breakdown strength; Energy density

1. Introduction

The dielectric materials with high discharged energy density are urgently required by high-voltage capacitors and pulsed power systems because they can effectively minimize the volume of the capacitors. The traditional ferroelectric ceramic has been widely used for capacitors due to its high dielectric constant, but the low breakdown strength (BDS) limits its further application in high-voltage capacitors and pulsed power systems [1–4]. Glass-ceramic dielectrics, which are prepared by first obtaining a glass matrix by melt casting and then precipitating a crystal phase in the glass matrix during subsequent heat treatment, have been considered as a more attractive candidate in the fields of high-voltage and high energy density applications. In contrast to conventional ceramics, glass-ceramic dielectrics have high dielectric constant (from the precipitated ceramic phases) and high breakdown strength E_b (from the near pore-free inherence of the residual glass) [5–8]. Generally, the energy storage density for dielectric capacitors is proportional to the dielectric constant ε_r and the square power of the applied electric field E^2 ($E < E_b$, E_b is the breakdown strength), so the glass-ceramic dielectrics possess the potential to achieve a much higher energy storage density.

In the field of ferroelectric glass-ceramic materials, a large number of studies are focused on the niobate glass-ceramic system, different types of ferroelectric glass-ceramic systems such as (PbO, Na_2O)–Nb_2O_5 [9], (SrO, BaO)–Nb_2O_5 [10,11], (PbO, SrO, BaO)–Nb_2O_5 [12] glass-ceramics, have been investigated widely. However, most of these materials containing lead, are harmful to the environment, which limits their wide application. Lead-free (BaO, Na_2O)–Nb_2O_5–SiO_2 system (BNNS) is a promising candidate in which $Ba_2NaNb_5O_{15}$ and $NaNbO_3$ as the main crystalline phase have high dielectric constant and high Curie temperature (about 600 °C).

In our previous research work [13], the ratio of Ba/Na was systematically studied for the optimized purpose of energy storage density in (BaO, Na_2O)–Nb_2O_5–SiO_2 system. The x ($4BaO$–Na_2O–$5Nb_2O_5$)–(100–x)SiO_2 is a promising system in which $Ba_2NaNb_5O_{15}$ as the main crystalline phase has high

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dielectric constants and high Curie temperature (about 600 °C). However, the dielectric breakdown strength was still not high enough. It is well known that the additives play an important role in improving the dielectric properties of niobate glass-ceramics. In the (BaO, Na_2O)–Nb_2O_5–SiO_2 glass-ceramic (BNNS) system, B. Rangarajan and M. Lanagan reported that 1.5% MnO_2 additives can refine the microstructure and enhance the dielectric constant of the glass-ceramics [14]. It was reported that BaF_2 additives can effectively improve dielectric properties in B_2O_3–Nb_2O_5–SrO–BaO system, which resulted in the improvement of the energy storage density [15]. As we know, rare earth ions can change the electronic structure of materials, and accordingly, influence the dielectric properties of glass-ceramics. In recent years, a huge body of literature has reported the effect of rare earth addition on the crystallization behavior and dielectric properties in niobate-based glass-ceramics. Recently, Zhou et al. found that the 1 mol% Gd_2O_3 addition to (BaO, Na_2O)–Nb_2O_5–SiO_2 glass-ceramic system changed the dielectric constant and breakdown strength remarkably [16]. However, the few studies deal with the effect of La_2O_3 addition on the discharged property in BNNS glass-ceramic system. For this study, BNNS glass-ceramic system doped with La_2O_3 was prepared through crystallization route, and the phase transition, the microstructure and the dielectric properties were investigated.

2. Experimental procedure

BNNS glass samples used in this study were prepared from well-mixed powders of 25.6$BaCO_3$, 6.4Na_2CO_3, 32Nb_2O_5 and 36SiO_2 (mol%), which doped with x mol% La_2O_3 (x=0, 0.5, 1.0, 2.0, 3.0). Analytical reagent grade powders of Na_2CO_3, $BaCO_3$, Nb_2O_5, SiO_2 and La_2O_3 were ball mixed for 24 h in a high density polyethylene bottle with ethanol as milling media for homogenous mixing. The as-dried powders were melted in an alumina crucible and heated to 1500 °C in an elevator furnace for 3 h and then quenched by pouring into a copper mold that placed in an annealing oven at 500 °C. The casting glass was annealed for 6 h to remove internal thermal stress. The as-annealed glass was cut into sheet-shaped samples. The controlled crystallization of glass sheets was carried out at the temperature of 1000 °C for 2 h. Differential scanning calorimeter (DSC) was used to predict the crystallization temperature.

X-ray diffraction (D8 Advance, Bruker AXS, Germany) were used to investigate the phase evolution. Field-emission scanning electron microscopy (FE-SEM) (S-4700, HITACHI, Japan) was used to investigate the microstructure of the polished and etched surfaces for the glass-ceramics. For electrical measurements, the samples were polished to achieve smooth, parallel faces, and coated with silver electrodes. The temperature dependence of dielectric constant was measured using a LCR meter (AgilentE4980A) at the frequency of 1 MHz and in the temperature range from −100 °C to 150 °C. The DC dielectric breakdown strength (BDS) measurement was performed using a Voltage-withstand testing device (ET2671B, Entai, Nanjing, China) at room temperature. A DC voltage ramp of about 1 kV/s was applied to the specimens until the dielectric breakdown occurred. At least 8 specimens were used for each composition during BDS testing. All samples were ground into about 0.15 mm thickness and immersed in silicone oil to prevent surface flashover. Complex impedance spectrum were carried out by a LCR meter (E4980A, Agilent, USA) over frequencies from 0.15 kHz to 2000 kHz in the temperature range of 420–480 °C with the AC electric field of 4 V/mm.

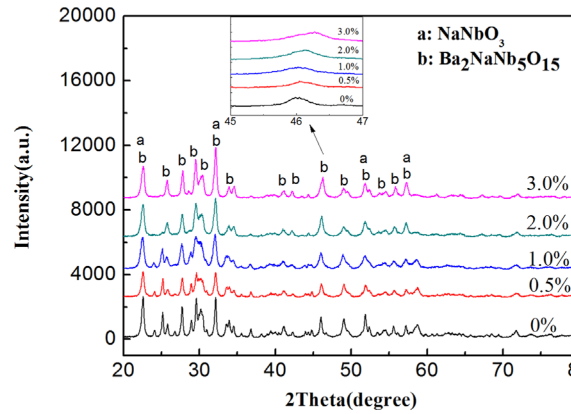

Fig. 1. XRD profiles of the glass-ceramics with different content of La_2O_3 additives. a: $NaNbO_3$(ICDD:01-074-2441), b: $Ba_2NaNb_5O_{15}$ (ICDD:01-086-0739).

3. Results and discussion

The phase transition of La_2O_3-adoped BNNS glass-ceramics was studied by XRD. Fig. 1(a) shows XRD patterns of the as-devitrified BNNS glass-ceramics with La_2O_3 addition from 0 to 3 mol%. All the tested glass-ceramic samples were annealed at 1000 °C for 2 h. By comparing the XRD patterns with international center for diffraction data (ICDD), two phases of tetragonal tungsten bronze (T.T.B.) and cubic perovskite (C.P.) were indexed, the crystalline phase with T.T.B structure is related to $Ba_2NaNb_5O_{15}$ and the C.P. structure is related to $NaNbO_3$. It is supposed that the chemical reaction during heat treatment process will follow the formula:

$$xNa_2O+2BaO+(2+x)\ Nb_2O_5\text{—}Ba_2NaNb_5O_{15}+(2x-1)\ NaNbO_3 \quad (1)$$

On the basis of the formula, the structure of all as-devitrified samples can be reasonable analyzed. As the ratio of $BaCO_3$, Na_2CO_3 and Nb_2O_5 in raw materials was 4:1:5, the formula will be:

$$BaO+\ Na_2O+\ 5Nb_2O_5\text{—}2Ba_2NaNb_5O_{15} \quad (2)$$

As shown in Fig. 1, a main $Ba_2NaNb_5O_{15}$ phase and a minor $NaNbO_3$ phase were identified in all four samples, which can be explained by formula (1).

Although no new crystal phases were observed in the La_2O_3-added BNNS glass-ceramics, the peaks position shift slightly to higher angle with increasing La_2O_3 addition (inset), which indicated that the La_2O_3 additives acted as dopant into the crystalline phases. In addition, the peaks position to higher angle means that the lattice parameters of $Ba_2NaNb_5O_{15}$ phase decrease with the addition of La_2O_3. As the ionic radius of La^{3+}, Ba^{2+}, Na^{+} are 0.106, 0.134, 0.097 nm, respectively.