Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Effects of Sr substitution for Ba on dielectric and energy-storage properties of SrO-BaO-K_2O-Nb_2O_5-SiO_2 glass-ceramics

Haitao Wang [a,b], Jinhua Liu [a,c], Jiwei Zhai [a,*], Zhongbin Pan [a], Bo Shen [a]

[a] Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, Functional Materials Research Laboratory, School of Materials Science & Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China
[b] College of Materials and Chemical Engineering, Key laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, China
[c] School of Physics and Electronic Science, Guizhou Normal University, Guiyang 550001, China

ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form 19 April 2017
Accepted 20 April 2017
Available online xxx

Keywords:
Glass-ceramic
Breakdown strength
Energy-storage density
Discharge efficiency
Power density

ABSTRACT

In this work, [xSrO, $(1-x)$BaO]-K_2O-Nb_2O_5-SiO_2 (SBKNS, x = 0.2, 0.4, 0.6, 0.8) glass-ceramics were synthesized through the controlled crystallization method. The phase structure, dielectric and energy-storage properties were systematically studied through the Sr substitution for Ba. It was found that the dielectric properties were improved due to the formation of solid liquid phase $Sr_{0.5}Ba_{0.5}Nb_2O_6$. Breakdown strength firstly increases and then decreases, which strongly depends on the variation in interfacial polarization. The highest value of breakdown strength reaches 1828 ± 88 kV/cm for x = 0.4, which is attributed to more uniform and dense microstructure and lower interfacial polarization. Correspondingly, the optimized theoretical energy-storage density reaches up to 17.45 ± 0.74 J/cm^3. The maximum of discharged energy-storage density of 1.45 J/cm^3 from P-E loop was acquired under electric field of 500 kV/cm. Moreover, discharged power density of the capacitor was evaluated and reached a high value of 1.76 MV/cm^3 in pulsed charged-discharged circuit.

1. Introduction

Capacitors as the basic components have been widely applied in fields of electrical and electronic systems, such as medical defibrillators, portable electronics, power grids, and hybrid electric vehicles [1–3]. Dielectric capacitors have the intrinsic fast charged-discharged performance and high power density [4,5], which is crucial for various power systems. However, dielectric materials for preparing capacitors have low energy-storage density, compared to batteries [6] and electrochemical supercapacitors [7,8]. Thus, improving energy-storage density of dielectric material is still a great challenge to meet needs in the development of power systems. In order to achieve this goal, an amount of researches have been performed on dielectric materials, such as ferroelectric ceramics [9], anti-ferroelectric ceramics [10,11], polymer-based dielectrics [12,13], and glass-ceramics [14]. The glass-ceramics are regarded as one of the most promising candidates for high energy density capacitors due to the composites of ferroelectric phase with high dielectric constant and the glass matrix with high breakdown strength (BDS), as well as the merit of high thermal stability.

In glass-ceramic heat-treating process including the conventional heat treatment and microwave heat treatment [14–16], the controlled crystallization technology can effectively tailor dielectric constant and BDS, which can further improve the energy-storage density, charged-discharged efficiency, and discharged power density. As is known, energy-storage density of a linear dielectric material is linearly proportional to the dielectric constant and the square of BDS. This means that energy-storage density can be improved by enhancing dielectric constant and especially BDS. BDS is mainly affected by interfacial polarization [17,18], grain size [19], and porosity [20]. In order to improve BDS of glass-ceramics, researchers employed different approaches, such as microwave crystallization [16], two-step crystallization [21,22], and rare-earth doping methods [23–27]. In fact, these approaches effectively improved the microstructures of glass-ceramics. In order to obtain high dielectric constant, (Ba, Sr)TiO_3 based glass-ceramics were investigated by varying Ba/Sr [28] and Ba/Ti [29] ratios. Gorzkowski et al. showed high dielectric constant of ~1000, but relatively low BDS of 800 kV/cm [28]. In addition, the niobate-based glass-ceramics with high dielectric constant have been widely investigated, such as (BaO, Na_2O)-Nb_2O_5-SiO_2 ($\varepsilon_r \sim 155$) [30],

* Corresponding author.
E-mail addresses: htwangjh@cqu.edu.cn (H. Wang), apzhai@tongji.edu.cn (J. Zhai).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.049
0955-2219/

(BaO, K_2O) $-Nb_2O_5$-SiO_2 ($\varepsilon_r \sim 70$) [18], PbO-BaO-Na_2O-Nb_2O_5-SiO_2 ($\varepsilon_r \sim 650$) [31], PbO-SrO-$Na_2O-Nb_2O_5$-SiO_2 ($\varepsilon_r \sim 600$) [32], and BaO-SrO-Na_2O-Nb_2O_5-SiO_2 ($\varepsilon_r \sim 240$) [33]. Compared with single bivalent element at A-site, the bivalent element substitution (Ba^{2+}, Sr^{2+}, or Pb^{2+}) at A-site of tungsten-bronze phases can significantly improve dielectric constant [32,33], which is attributed to the solid solution phases, such as ANb_2O_6 [A = (xSr, $(1-x)$Ba), (xSr, $(1-x)$Pb), and (xBa, $(1-x)$Pb)], $A_1A_2Nb_5O_{15}$ [A_1 = (xSr,$(1-x)$Ba), A_2 = Na or K].

In this work, a new glass-ceramic system (xSrO, $(1-x)$BaO)-K_2O-Nb_2O_5-SiO_2 (SBKNS) was designed to obtain high dielectric constant of the glass-ceramics with relatively high BDS. And we studied effects of the Sr substitution for Ba on dielectric properties, microstructures, dielectric breakdown strength, and energy-storage performance of SBKNS glass-ceramics in details. In addition, discharged energy density and power density were obtained to estimate the charged-discharged properties in RLC pulse circuit.

2. Experimental procedure

In order to investigate an effect of element substitution on dielectric properties and energy-storage performance in SBKNS glass-ceramics, the analytical reagent $SrCO_3$, $BaCO_3$, K_2CO_3, Nb_2O_5, and SiO_2 powders as the raw materials were used to prepare the glass-ceramics. The compositions of SBKNS glass-ceramics were designed to follow 25.6 (x SrO, $(1-x)$ BaO)-6.4 K_2O-32 Nb_2O_5-36 SiO_2 (mol%). The weighted powders were well mixed by ball milling in the ehtylalcohol with zirconia for 20 h and were dried at 100 °C. The dried powers were melted at 1520 °C in an alumina crucible for 2 h. Then the glass lava was quickly poured into the preheated copper mold to form transparent glass at 650 °C for 6 h. The transparent glass was cut into the piece-shaped sheets with about 1.2 mm thickness. Thereafter, all glass samples were crystallized at 900 °C for 3 h in air with the heating rate of 2 °C/min.

The crystallization behavior of the glass powder was analyzed by using differential scanning calorimetry (DSC, model STA449C, Netzsch). The phase structure of the glass-ceramics was detected by X-ray diffraction (XRD, D/max 2550 V B3+/PC, Rigaku, Japan) with Cu Kα radiation in the 2θ range from 20 °C to 80 °C. A LCR meter (Agilent E4980A, Palo Alto CA USA) was used to measure dielectric constant and dielectric loss of the glass-ceramics. And dielectric constant as a function of electric field was tested by use of a Keithley 2410 (Cleveland, OH, USA) high-voltage source and a TH2816A LCR (Tonghui Electronics, Changzhou, China) analyzer. The microstructure was observed by a field scanning electron microcopy (SEM) (HITACHI S-4700, Japan). A LCR meter (E4980A, Agilent, USA) was used to measure the frequency dependence of imaginary part of impedance (Z") over frequency from 150 Hz to 2 MHz with an AC electric field of 4 V/mm. A voltage-withstand testing device (ET2671B, Entai, Nanjing, China) was used to measure DC breakdown strength of the glass-ceramics at room temperature. A DC voltage ramp of about 0.2 kV/s was applied to the specimens until the BDS occurred. The glass-ceramic samples were ground into about 0.05–0.08 mm thickness and immersed in silicone oil to prevent surface flashover. A ferroelectric test system (Precision Premier II; Radiant Technologies, Albuquerque, NM, USA) was used to measure polarization-electric field (P-E) hysteresis loops at the frequency of 1 kHz and at room temperature.

3. Results and discussion

3.1. DSC and XRD analysis

The DSC curves of as-quenched SBKNS glass at the heating rate of 20 °C/min are illustrated in Fig. 1. From DSC results, the glass transition-temperature (Tg ~ 700 °C) almost does not change. In addition, all DSC curves show two exothermic peaks, one T_{p1} in the range of 833 °C–839 °C and the other T_{p2} in the range of 891 °C–902 °C. According to the DSC, the glass-ceramics were crystallized at the high temperature 900 °C to obtain crystallized phases with relatively high dielectric constant.

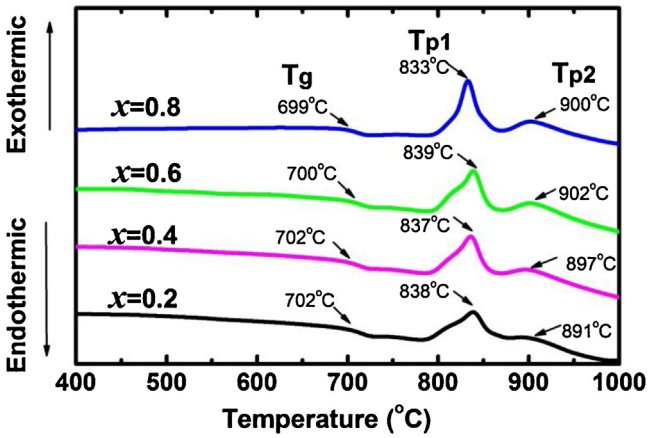

Fig. 1. Differential scanning calorimeter (DSC) curves of as-quenched SBKNS glass at heating ratio of 20 °C/min.

Phase evolution of SBKNS glass-ceramics was studied by XRD analysis with the increase of SrO content, as shown in Fig. 2(a). To further obtain the content of the crystal phases, XRD Rietveld refinements were performed by using pseudo-Voigt functions. Fig. 2(b) shows the refinement result of glass-ceramic sample for x = 0.4, which well fits the observed data. The refinement results including the weight percentage of crystalline phases (wt%) and refined residual error (Rp) for all compositions are listed in Table 1. As shown in Table 1, the glass-ceramics for x = 0.2 and 0.4 have main phases $BaNb_2O_6$ and $Sr_{0.5}Ba_{0.5}Nb_2O_6$ with a tungsten-bronze (T. B.) structure, while the glass-ceramics for x = 0.6 and 0.8 have main phases $Sr_{0.5}Ba_{0.5}Nb_2O_6$, $KSrBaNb_2O_{15}$, $BaNb_2O_6$ with T. B. structure. Partial substitution of Sr for Ba at the A-site of T. B. phase ($Sr_{0.5}Ba_{0.5}Nb_2O_6$) helps to improve dielectric properties of the glass-ceramics. In addition, refinement results show that solid liquid phase $Sr_{0.5}Ba_{0.5}Nb_2O_6$ increase firstly and then decreases with the substitution fraction x, which affects the dielectric properties of glass-ceramics.

3.2. Dielectric properties

To understand effect of the Sr substitution for Ba on dielectric properties of SBKNS glass-ceramics, dielectric constant and loss were measured at frequency of 10 kHz and temperature range from −100 °C to 120 °C for different substitution fraction x in Fig. 3(a). With the x increasing from 0.2 to 0.8, Curie temperature firstly shifts to low temperature from −31 °C for x = 0.2 to −43 °C for x = 0.4, and then shifts to high temperature of −33 °C, and −23 °C for 0.6 and 0.8, respectively, which is attributed to the different A-site occupation in the tungsten-bronze phase [34]. Fig. 3(b) shows dielectric constant and loss versus x at room temperature for the SBKNS glass-ceramics. It is shown that dielectric constant exhibits a trend of increase before decrease when increasing the substitution fraction x. Its maximal value of ~118 is located near x = 0.4, which is attributed to element substitution (Sr substitution for Ba) at A-site in the tungsten-bronze phases. The similar phenomenon was also found in previous studies [31,35]. However, dielectric loss presents a change trend opposite to dielectric constant. Its minimal value of ~ 0.006 is also located near x = 0.4 at the frequency of 10 kHz and at room temperature. This indicates that the element substitution

Please cite this article in press as: H. Wang, et al., Effects of Sr substitution for Ba on dielectric and energy-storage properties of SrO-BaO-K_2O-Nb_2O_5-SiO_2 glass-ceramics, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.049