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Glass-ceramic nanocomposites in the $[(1-x)PbO–xBaO]–Na_2O–Nb_2O_5–SiO_2$ system: Crystallization and dielectric performance

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ABSTRACT

The crystallization process, microstructure and dielectric properties of $[(1-x)PbO–xBaO]–Na_2O–Nb_2O_5–SiO_2$ (PBNNS) ($0 \le x \le 1$) glass-ceramics prepared by controlled crystallization were investigated. The crystallization strategies for acquiring nano-crystallized PBNNS glass-ceramics were monitored by differential thermal analysis (DTA). X-ray diffraction (XRD) analysis revealed a major crystal phase transition in PBNNS glass matrix as the crystallization temperature increased. At low temperatures (700–750 °C), the major crystal phases precipitating in the glass matrix are identified as $Pb_2Nb_2O_7$ for $x = 0$, $Ba_2NaNb_5O_{15}$ for $x = 1$ and their solid solution for $0.2 \le x \le 0.8$; while at higher temperatures (≥850 °C), heat treatment produces different crystalline phases, $PbNb_2O_6$ and $NaNbO_3$ for $x = 0$, $Ba_2NaNb_5O_{15}$ and $NaNbO_3$ for $x = 1$, and the solid solution of these three phases for $0.2 \le x \le 0.8$. Corresponding to the result of phase transition, microstructural observation proves increasing crystallite sizes with increasing temperature of heat treatment. At different crystallization temperatures, the dielectric properties of the $[(1-x)PbO–xBaO]–Na_2O–Nb_2O_5–SiO_2$ glass-ceramics show a strong dependence on the chemical composition x. At low temperatures (700–750 °C), a maximum of the dielectric constant of the PBNNS glass-ceramic is found for the composition $x = 0.6$; while at higher crystallization temperatures (≥850 °C), the dielectric constants of all samples ($0 \le x \le 1$) exhibit decreasing values with increasing x.

1. Introduction

Glass-ceramic dielectrics can be prepared through controlled crystallization method [1,2], by heat-treatments of as-quenched melt-casting glasses. High dielectric constant crystal phases are precipitated from the glass matrix during isothermal treatments [3]. Owing to the excellent dielectric properties of the ceramic precipitation and the porosity-free matrix microstructure [4,5], the glass-ceramics can serve as strong candidates for applications in high energy capacitors over solid-state sintered ceramics [2].

In the field of dielectric glass-ceramic materials, a large number of studies focused on niobate glass-ceramic systems. Recently, some authors have investigated correlations between dielectric properties and crystal phases of niobate-based glass-ceramics with multiple phase precipitation such as the lead sodium niobate system ($Pb_2Nb_2O_7$, $NaNbO_3$ and $PbNb_2O_6$ phases) [3,6], the barium sodium niobate system ($Ba_2NaNb_5O_{15}$ and $NaNbO_3$ phases) [4,7], the strontium potassium niobate system ($Sr_2KNb_5O_{15}$ and $KNbO_3$ phases) [7] and the lead strontium sodium niobate system ($Pb_2Nb_2O_7$, $NaNbO_3$, $PbNb_2O_6$ and $Sr_2Nb_2O_7$ phases) [8]. They have found most of these glass-ceramics to perform with high dielectric constant, dielectric breakdown strength and hence high energy density. Typical dielectric phases precipitated in niobate-based glass-ceramics are tungsten-bronze (*TB*) phases $[(A_1)_2(A_2)Nb_5O_{15}$ (A_1 = Ba or Sr, A_2 = Na or K) or ANb_2O_6 (A = Pb)] and perovskite (*P*) phases [$MNbO_3$ (M = Na or K)]. Excellent dielectric properties from *TB* or *P* phases result in high dielectric constant of the glass-ceramics, while the high breakdown strength of these materials is based on the defect-free inherence of the glass matrix.

For this kind of *TB* + P + SiO_2 glass-ceramic systems, original work has focused on *A*-site of *TB* phases occupied by single bivalent elements such as $PbNb_2O_6$ [3], $Ba_2NaNb_5O_{15}$ [4,7] and $Sr_2KNb_5O_{15}$ [7]. J. Du *et al.* [3] found that the dielectric constant of lead sodium niobate glass-ceramic could achieve ~600. F. Peng *et al.* discovered that barium sodium niobate glass-ceramic (ε_r = ~250 – 350) exhibit other excellent dielectric performances [7]: stable dielectric constant with temperature and low dielectric loss values (0.015). Furthermore, it is well known that *A*-site bivalent element substitution can achieve more outstanding electric properties comparing to single bivalent element at *A*-site in the conventional solid-state sintering *TB*-type ceramics [9–11]. For example, K. Kakimoto *et al.* [11] have studied the *TB*-type of ANb_2O_6 with Ba^{2+}

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substitution for Sr^{2+}, and concluded that the $Sr_xBa_{1-x}Nb_2O_6$ could achieve a higher dielectric constant and a larger polarization than that of single $SrNb_2O_6$ or $BaNb_2O_6$ phase. Therefore, in this paper, the crystallization, microstructure and dielectric performances of a *TB* + P + SiO_2 glass-ceramic system with Ba^{2+} substitution for Pb^{2+} at *A*-site are systemically investigated. Also, we present a detailed study of the relationship between the dielectric properties and the phase evolution of this glass-ceramic system in the couple of heat-treatments at temperatures from 700 °C to 1000 °C.

2. Experimental procedures

The nanocomposites with nominal composition of $10[(1-x)PbO-xBaO]-20Na_2O-_{40}Nb_2O_5-_{30}SiO_2$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) in cation mole percentage were prepared using reagents of barium carbonate ($BaCO_3$, Analytical Reagent viz. A.R.), sodium carbonate (Na_2CO_3, Analytical Reagent viz. A.R.), lead(II) oxide (PbO, A.R.), niobium pentoxide (Nb_2O_5, A.R.) and silicon dioxide (SiO_2, A.R.). The starting reagents in the desired composition were mixed as a dispersion in ethanol using agate balls. The slurry was then dried at 120 °C for 8 h and the powders were melted in a platinum crucible for 3 h at 1400 °C to form a transparent glass, which was cast into a preheated stainless steel mold and was immediately placed in an annealing oven at 500 °C and held for 2 h to reduce the residual stress.

Approximately 0.5 g of ground PBNNS glass with x = 0, 0.2, 0.4, 0.6, 0.8 and 1 was used for differential thermal analysis (Model SDT 2960, TA Instruments, New Castle, DE) up to 1050 °C using a rate of 10 °C/min. Based on the crystallization temperature determined by DTA, the controlled crystallization was carried out at temperatures of 700 °C, 750 °C, 850 °C and 1000 °C to precipitate nanometer-sized dielectric ceramic phases from the glass matrix. Then, pieces of glass-ceramics were cut and polished to sheets of 0.2–0.25 mm in thickness. Au metal films as electrodes of the parallel plate dielectric capacitor were coated on the surfaces of the glass-ceramic sheets by dc magnetron sputtering deposition (Model JK-200B, Instrument Company Ltd., Beijing, China).

Phase identification was performed by X-ray diffraction (XRD; Model MSAL-XD2, Micro-Structure Analysis Laboratory, Beijing) using Cu–K_α radiation. Complementary to XRD to provide more detailed information, transmission electron microscopy (TEM; JEOL 2010F, 200 kV) was used to study the microstructure of the glass-ceramics. The dielectric constant and the dielectric loss were measured by using a multifrequency meter (LCR; Model HP-4284A, Agilent Technologies, Inc., USA). Capacitance-voltage (*C*–*V*) measurements were performed at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technology, Albuquerque, NM). Each sample was clamped between a pair of hemispherically ended brass electrodes. The entire system was run in silicon oil to avoid flashover behavior.

3. Results and discussion

3.1. Crystallization

Heat treatment protocols for the as-quenched glass were guided by DTA analysis. DTA traces for the PBNNS glasses are shown in Fig. 1. It is apparent that all systems show endothermic peaks at lower temperatures, which signify their glass transition temperatures, before showing exothermic peaks at higher temperatures. The transition temperature continuously increases from 616 °C to 686 °C with increasing x. The exothermic peaks at higher temperatures are associated with the generation of crystalline phases within the various glass matrices. As the barium to lead ratio increases, the first exothermic peak starts shifting from 672 °C to 769 °C, while the second peak changes from 892 °C to 989 °C. Additionally, DTA traces of the PBNNS glasses with x = 0 and 0.2 show peaks at 997 °C and 1007 °C, which disappear for $x \geq 0.4$. In order to study the crystallization behavior of all glasses and to optimize their properties, they were crystallized at four different temperatures around those peaks.

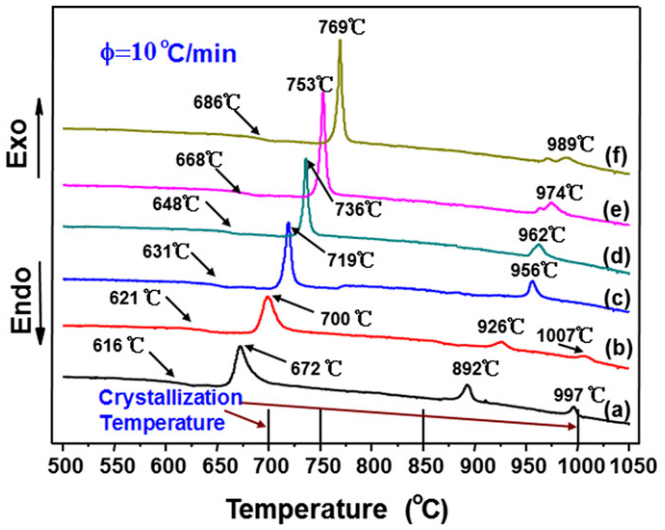

Fig. 1. DTA profiles of as-quenched PBNNS glass with (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8 and (f) x = 1 showing glass transition temperatures and crystallization peaks.

Fig. 2 illustrates XRD data of the PBNNS samples with variation in x crystallized at different temperatures for 3 h. Phase evolution during crystallization of glasses can be divided into the following four stages of the heat treatment:

(1) At 700 °C, for the glass-ceramic with x = 1 no Bragg peaks of crystalline phases are detected by XRD. The diffractogram shows a broad peak around 30° (2θ) indicating the amorphous character of the sample. For x = 0.8, $Ba_2NaNb_5O_{15}$, as the primary phase with a *TB* structure [12], crystallizes in the glass matrix. As x decreases from 0.8 to 0, the decrease of the $Ba_2NaNb_5O_{15}$ fraction is accompanied by an increase of $Pb_2Nb_2O_7$ phase with a rhombohedral pyrochlore (*Py*) structure [13,14]. Evidently, the major crystalline phases change into $Pb_2Nb_2O_7$ for the lead-rich samples.
(2) At 750 °C (Fig. 2(II)), for $0 \leq x \leq 0.8$, $Pb_2Nb_2O_7$ and $Ba_2NaNb_5O_{15}$ are still the only crystalline phases, which grow in this temperature range, while the *TB* phase, $Ba_2NaNb_5O_{15}$, begins to precipitate in the glass matrix with x = 1.
(3) XRD patterns for the PBNNS samples heat-treated at 850 °C (Fig. 2(III)) show the presence of two phases, $PbNb_2O_6$ with *TB* structure and $NaNbO_3$ with *P* structure. The $Pb_2Nb_2O_7$ phase completely disappears at this temperature. For barium-rich samples, the intensities of XRD reflections of the $Ba_2NaNb_5O_{15}$ phase are still relatively high. As x decreases, the phases gradually change from $Ba_2NaNb_5O_{15}$ + $NaNbO_3$ to $PbNb_2O_6$ + $NaNbO_3$.
(4) As the crystallization temperature is raised to 1000 °C, $PbNb_2O_6$, $Ba_2NaNb_5O_{10}$ and $NaNbO_3$ are still the only crystalline phases grown in this temperature range.

The summary of crystallization sequence from glass matrices and phases in final PBNNS glass-ceramic samples annealed at different temperatures is given in Table 1. It is worth noting that the glass-ceramics treated at low temperatures (700 °C–750 °C)