



# Correlation between dielectric properties and crystallization treatment in potassium sodium niobate glass-ceramics for energy storage application



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## ABSTRACT

$K_2O-Na_2O-Nb_2O_5-SiO_2-B_2O_3$  glass-ceramics was prepared via melt-quenching and controlled crystallization route. To investigate the effect of crystallization treatment schedule on the dielectric properties of potassium sodium niobate (KNN) glass-ceramics, this report measured six glass samples with different crystallization treatment by XRD, SEM and LCR measurements. By means of changing heat-treatment schedule, it could be inferred that crystallization process and optimal treatment condition for KNN glass-ceramic with pore-free and high energy density. When the original glass samples crystallized at 707 °C for 2 h and 900 °C for 3 h, this crystallization treatment was beneficial to obtaining the glass-ceramic samples with purer perovskite structure  $K_{0.1}Na_{0.9}NbO_3$  crystal phase and finer grains which possessed relative higher energy storage density ( $1.899 \text{ J/cm}^3$ ). The crystallization behavior and dielectric properties have exhibited a regular change at different crystallization temperature. Comprehensive results and analysis demonstrated that crystallization treatment played a role in dielectric properties of KNN glass-ceramics. In order to optimize energy storage, this experiment controlled transition from matrix glass phase of high breakdown strength (BDS) to ferroelectric crystal phase of high dielectric constant.

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## 1. Introduction

Presently, as the evolution of pulsed power technology has largely relied on the energy storage capability, capacitors with high storage play an increasingly significant role [1]. Ferroelectric ceramics capacitors possess higher dielectric constants without lower loss owing to inherent pores, which leads that energy storage density of ceramics materials is unfavorable and not beneficial to be candidates for electric power systems. Numerous studies of borosilicate glasses are important in various fields such as optoelectronics, solar energy technology, astronomical reflecting telescope and in microelectromechanical systems [2]. The high density and high refractive index of these glasses make them suitable for shielding materials and laboratory glassware [3]. Thus, compared with conventional ceramics, glass materials without pores and defects show higher breakdown strength (BDS). The energy storage density (J) of dielectrics is given [4,5] as:

$$J = \int E dp = \int E d(\epsilon E) \quad (1)$$

where  $\epsilon$  is dielectric constant, and E is breakdown strength. According to Eq. (1), dielectric constant and dielectric breakdown strengths (BDS) are two important parameters relation to the energy storage, in other words, energy storage capability strongly depends on BDS particularly. In consideration of requirement of higher dielectric constants and higher BDS, the ferroelectric glass-ceramics are considered the most available candidates due to the synergistic effect of high dielectric constant (from the precipitated crystalline phases) and high BDS (due to the pore-free nature of the residual glass) [6]. It is well acquired that the dispersed ferroelectric ceramic phase is typically structurally incompatible with the host glass. In addition, the dielectric constant of ferroelectric ceramic and glass phase are vastly different, under the influence of electric field, due to the interfacial polarization [7,8].

In recent years, researchers frequently exploit the environment friendly lead-free systems due to restriction of the lead-based ferroelectric materials [9]. Niobate based ferroelectric glass-

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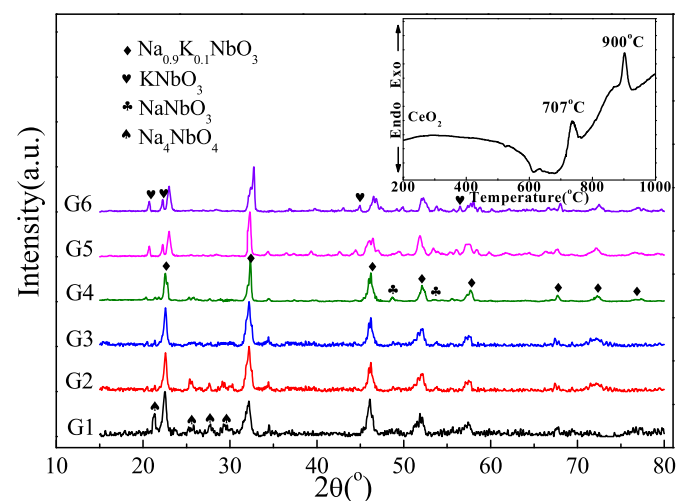
ceramic has attracted much attention for many decades, because of the crystallization of (K,Na)NbO<sub>3</sub>(KNN) crystals on account of the typical perovskite crystal structure with pronounced electrooptical properties leading to good nonlinear photonic properties [10]. While (K,Na)NbO<sub>3</sub> glass-ceramics can be a strong candidate for application field of energy storage capacitor due to its good ferroelectric properties [11]. What's more, KNN performs energy storage properties with the relevant to antiferroelectric NaNbO<sub>3</sub> crystal phase. Antiferroelectrics which usually contain environmentally harmful element Pb such as PbZrO<sub>3</sub> are more likely to be used for high-energy storage because of their larger Ps, smaller Pr and moderate BDS [12]. Generally speaking, it is very meaningful to prepare and research at a higher level the KNN glass-ceramics for development of applications in high-voltage capacitors and pulsed power systems.

At present, reports of (BaO, SrO)-TiO<sub>2</sub> [1,8,13], (BaO, SrO)-Nb<sub>2</sub>O<sub>5</sub> [14] and (BaO, Na<sub>2</sub>O)-Nb<sub>2</sub>O<sub>5</sub> [8,15,16] glass-ceramics become more and more systematic with the development of deep research, while study of (Na,K)NbO<sub>3</sub> glass-ceramics still remains explored a little [11]. Effect of different nucleating agents for Na<sub>0.9</sub>K<sub>0.1</sub>NbO<sub>3</sub> energy storage glass-ceramic was researched in previous paper by our group. It is said that CeO<sub>2</sub> in BaO–SrO–Nb<sub>2</sub>O<sub>5</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> reduces the activation energy of crystallization, whereas La<sub>2</sub>O<sub>3</sub> increases the activation energy [16]. Therefore, we try to choose the (Na,K)NbO<sub>3</sub> glass-ceramics with agent CeO<sub>2</sub> as our destination to get comprehensive properties of higher dielectric constant and higher BDS by controlling crystallization treatment in this report.

## 2. Experimental

### 2.1. Preparation process

Glass-ceramics with nominal composition of 15Na<sub>2</sub>O–15K<sub>2</sub>O–30Nb<sub>2</sub>O<sub>5</sub>–27SiO<sub>2</sub>–10B<sub>2</sub>O<sub>3</sub>–3CeO<sub>2</sub> (in cation molecular percent) were prepared by using reagents of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, Analytical Reagent viz. A.R.), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, A.R.), niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>, A.R.), silicon dioxide (SiO<sub>2</sub>, A.R.), boric acid (H<sub>3</sub>BO<sub>3</sub>, A.R.), and cerium dioxide (CeO<sub>2</sub>, A.R.). The well-mixed reagent powders were put into an alumina crucible at 1100 °C and melted for 2 h at 1400 °C to form molten glass, which was cast into a preheated copper mold to form transparent glass by cooling rapidly. Then the glass samples were placed into an annealing oven by preserving for 10 h at 650 °C to



**Fig. 1.** The XRD patterns of samples with different crystallization treatments and DSC curve of initial glass sample (insert).

reduce residual stress. Owe to  $T_{p1}$  and  $T_{p2}$  in DSC curve (insert of Fig. 1) of as-quenched glass sample, the glass was crystallized according to different crystallization treatment in Table 1 to precipitate dielectric ceramic phases from glass matrix. The glass-ceramics were cut and polished into sheets of 0.35–0.55 mm in thickness and were coated with silver paste electrode on both sides.

### 2.2. Characterization

The glass crystallization temperatures were determined by using DSC (Model STA 409Pc, Netzsch, Germany, with a rate of 10 °C min<sup>-1</sup>). Glass-ceramics were examined by an X-ray diffractometer (D-MAX 2200pc, Rigaku Co, Tokyo, Japan) at room temperature to investigate the phase evolution. The microstructure observation of those crystallized samples was carried out using a scanning electron microscope (SEM; Model: JSM-5610LV, JEOL). For electrical measurements, these samples were polished to achieve parallel, smooth faces, and silver electrodes were coated on both faces. Then painting samples with silver pasted on both sides were treated at 600 °C for 10 min to prepare electrodes for dielectric measurements. The measurements of dielectric constant for glass-ceramics were performed by using a precision multifunction LCR meter (E4980A, Agilent Tech, CA, U.S.) with the measuring frequency of 100 Hz to 1 MHz. The specimens were used to measure the dielectric breakdown strength with a high-voltage source (Model 610E) using a voltage ramping rate of about 1 kV/s at room temperature until dielectric breakdown, and at least 10 specimens were used for each composition during BDS testing. The polarization–electric field (P-E) ferroelectric hysteresis loops were measured using a ferroelectric tester (TF Analyzer 2000, aixACCT, Aachen, Germany) at room temperature. The energy storage density of the glass-ceramics could be calculated from P-E ferroelectric hysteresis loop.

## 3. Results and discussion

The inset of Fig. 1 shows DSC curve of initial glass sample at heating rate of 15 °C min<sup>-1</sup>. As the inset shown, the glass sample with CeO<sub>2</sub> as nucleating agent has both two crystallization peak temperature at 707 °C ( $T_{p1}$ ) and 900 °C ( $T_{p2}$ ) respectively, and the crystallization treatments schedules of the samples are shown in Table 1.

Phase development on the surface region of K<sub>2</sub>O–Na<sub>2</sub>O–Nb<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> glass-ceramics during heat treatment was monitored by XRD. Fig. 1 shows the X-ray diffraction patterns of the six specimens after heat-treatment with different crystallization treatments schedule. The structural evolution as a function of the crystallization treatment schedule is clearly illustrated. It was clear that any slight changes with various crystallization treatment schedule might lead to dramatic effect on the chronology and morphology of the phases. Broad dispersion peak and rough as noise level, are seen for the sample G1 crystallized at  $T_{p1}$  for 5 h, indicating the growth of small and not well-shaped

**Table 1**  
Samples with different crystallization treatment (temperature and time parameters).

Sample	Heat-treated parameters (°C, h)
G1	5 h at 707 °C
G2	4 h at 707 °C + 1 h at 900 °C
G3	3 h at 707 °C + 2 h at 900 °C
G4	2 h at 707 °C + 3 h at 900 °C
G5	1 h at 707 °C + 4 h at 900 °C
G6	5 h at 900 °C

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