Preparation and dielectric properties of Nb$_2$O$_5$-BaO-Na$_2$O-SiO$_2$ glass-ceramic for energy storage capacitors

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Abstract. Full density Nb$_2$O$_5$-BaO-Na$_2$O-SiO$_2$ Glass-ceramics, which could be used as the dielectric energy-storage materials to fabricate high energy density devices, were prepared by means of rapid quenching and succeeding annealing under different temperature. DTA and X-ray diffraction analysis showed that Na$_3$Ba$_2$Nb$_5$O$_{15}$ with tungsten bronze structure and NaNbO$_3$ with perovskite structure were formed as the dielectric phases from the glass matrix at above 750°C. Dielectric constant of the crystallized glass-ceramics were measured at the frequency from 100 Hz to 100 kHz under the testing temperature from -40 to 150°C. The results indicated that theoretical energy storage density of the material crystallized at 800°C could reach up to 1.87x10$^6$J/m$^3$, which would be suitable to be used as the innoxious dielectric media for high-energy storage capacitors.

1. Introduction

Controlled crystallization full density glass-ceramic composites, which have high dielectric constant and breakdown strength simultaneously, are recently attracting more attention as the dielectric materials in fabricating high energy density devices$^{[1][2][3]}$. Until now glass-ceramics with Pb content, such as PbO-Na$_2$O-Nb$_2$O$_5$-SiO$_2$, are still the most common-used materials due to their high Curie point and dielectric constant$^{[2]}$. However, because of the high temperature during the melting of glass-ceramic mixture, mostly above 1400°C, the volatilization of Pb would be harmful to human health. So how to replace Pb with some other elements is the main challenge to solve the above problems. Moreover, the instability of the temperature dependence of dielectric constant is another disadvantage for the further application of this glass-ceramic material system$^{[3]}$. In this study, Ba was used to replace Pb in a niobate based glass-ceramic material based on the high dielectric constant and easy-controlled crystallization of barium niobate phase. Full density Nb$_2$O$_5$-BaO-Na$_2$O-SiO$_2$ glass-ceramics were prepared by means of rapid quenching and succeeding annealing under different temperature. Then the influence of crystallization temperature, testing temperature and frequency on dielectric properties were mainly investigated. Since energy storage density of the materials is proportional to dielectric constant ($\varepsilon$) and square of breakdown strength ($E_b$), another purpose of this study is to balance $\varepsilon$ and $E_b$ through controlled crystallization of the glass-ceramic, which would be suitable for the preparation of high energy storage density capacitors.
2. Experimental

35.8Nb_2O_5-16.2Na_2CO_3-10.4BaO-37.6SiO_2 in weight percentage was selected as the nominal composition in this study. Well-mixed powder mixtures were melted in a platinum crucible for 2 h at 1450°C. Then the melting was poured to a rapid melt-quenching device containing two cold rotating stainless rollers to form 0.5~1 mm thick glass sheets. The glass sheets were immediately annealed at 400°C for 2 h to eliminate internal stress before furnace-cooling to room temperature.

About 0.5g as-quenched glass sheet was used for differential thermal analysis (DTA, WCT-2C), which was heated from room temperature to 1000°C at a heating rate of 5°C/sec. According to the crystallization temperature determined by DTA, controlled crystallization was carried out in air at 600°C, 700°C, 750°C, 800°C and 900°C for 2h, respectively. Phase structure of the samples was identified by powder X-ray diffraction (XRD, MSAL XD2 Diffract Meter) patterns with Cu Kα radiation over the range of 2θ from 20°~80°.

Dielectric properties of the glass-ceramics were tested by 4284A precision LCR meter (Agilent) in the temperature range of –40~150°C and frequency range of 10K~100KHz. Gold electrodes were sputter-deposited on both sides of the glass-ceramic sheets.

Breakdown strength testing was performed by a self-assembly clamp which was fully immersed in glycol to avoid electric breakdown of the air under high voltage, which was provided by TREK 30 high voltage amplifier with 0.1 sec triangle wave pulses.

3. Results and discussion

3.1. Crystallization

Controlled crystallization of dielectric phases under different heat-treatment temperature is an important prerequisite in the preparation of glass-ceramics for high energy storage density capacitors. Since controlled crystallization temperature could be guided by DTA test, figure 1 shows the DTA curve of 35.8Nb_2O_5-16.2Na_2CO_3-10.4BaO-37.6SiO_2 glass-ceramic in the range from room temperature to 1000°C at a heating rate of 5°C/sec. As temperature is increased to about 720°C, an endothermic dip appears in the DTA curve, which is attributed to the softening of the glass. With the increase of temperature, two exothermic peaks, which is related to the crystallization of dielectric phases, are observed with maximum intensities located at 790 and 970°C, respectively. Therefore, five temperatures, which are 600°C, 700°C, 750, 800°C and 900°C, are chosen as the isothermal treatment temperatures to investigate the crystallization behavior of the glass-ceramic materials.

![Figure 1. DTA profile of as-quenched Nb_2O_5- Na_2CO_3-BaO-SiO_2 glass](image-url)
XRD patterns for Nb$_2$O$_5$-Na$_2$CO$_3$-BaO-SiO$_2$ glass-ceramic materials crystallized at 600, 700, 750, 800 and 900°C are shown in figure 2. Typical amorphous feature with a broad peak at about 30° appears in the samples crystallized under 700°C. As the temperature is increased to 750°C, a little trace of NaBa$_2$Nb$_5$O$_{15}$ with tungsten bronze structure is observed. When the temperature is further increased to above 800°C, large amount of NaNbO$_3$ with perovskite structure and NaBa$_2$Nb$_5$O$_{15}$ precipitate from the glass matrix. It seems that NaNbO$_3$ and NaBa$_2$Nb$_5$O$_{15}$ phases almost appear simultaneously with the increase of crystallization temperature. For the crystallization process of the glass-ceramic is so complex that the exact composition of the dielectric phases would be very difficult to be evaluated. Figure 3 shows the phase diagram of NaNbO$_3$ and NaBa$_2$Nb$_5$O$_{15}$ [5]. As the amorphous structure of the as-quenched glass could also be likely regarded as the liquid phase, figure 3 was used to analyze the crystallization process and composition of the precipitated dielectric phases. Since a little NaBa$_2$Nb$_5$O$_{15}$ precipitates firstly and then followed by the co-precipitate of NaNbO$_3$ and NaBa$_2$Nb$_5$O$_{15}$ during crystallization as indicated in figure 2, the final ratio of the two dielectric phases would locate at the position which is a little higher than the eutectoid point (~78mol% NaNbO$_3$) shown in figure 3. However, further research is still necessary to confirm this analysis.

**Figure 2.** XRD patterns of Nb$_2$O$_5$-Na$_2$CO$_3$-BaO-SiO$_2$ glass-ceramic

**Figure 3.** Phase diagram of NaNb$_2$O$_3$ and BaNb$_2$O$_6$
3.2. Dielectric properties

Figure 4(a) shows the dielectric constant of the annealed glass-ceramic samples tested at room temperature from 100Hz~100KHz. The initial dielectric constant of the as-quenched glass is about 30, which is relatively higher compared with ordinary glass probably due to the high content of polarizable ions\(^4\). With the increase of crystallization temperature, the dielectric constant increases with the formation of dielectric phases. Firstly, the dielectric constant is improved significantly from 600\(^\circ\)C to 750\(^\circ\)C. This is mainly due to the formation of high-\(\varepsilon_r\) NaBa\(_2\)Nb\(_5\)O\(_{15}\) phase (\(\varepsilon_r\approx 240\)) at this temperature range\(^5\). Upon the crystallization temperature is further increased to 800\(^\circ\)C and 900\(^\circ\)C respectively, the gradual increase of dielectric constant comes from two facts: One is the result of the co-crystallization of NaBa\(_2\)Nb\(_5\)O\(_{15}\) and NaNbO\(_3\) (\(\varepsilon_r\approx 500~600\)), and the second is the increase of the content of dielectric phases. Moreover, from figure 4(a), it is also indicated that the dielectric constant of each crystallization sample keeps steady from 100Hz to 100KHz. The difference of the dielectric constant value is less than 10\% at this frequency range.

![Figure 4(a)](image)

**Figure 4.** (a) Frequency and annealing temperature dependence of dielectric constant. (b) Dielectric constant as a function of testing temperature for the samples at different crystallization temperature (\(f = 50kHz\) )

Figure 4(b) shows the dielectric constant as a function of testing temperature for the samples at different crystallization temperature. The dielectric constant of the initial glass (600\(^\circ\)C) almost keeps constantly at this testing temperature range because there is not any dielectric phase occurred in the material. With the crystallization temperature is increased to 750\(^\circ\)C and 800\(^\circ\)C respectively, dielectric constant of the glass-ceramic reduces slightly with the increase of testing temperature. This trend may come from the large ratio of NaBa\(_2\)Nb\(_5\)O\(_{15}\) phase at the beginning of crystallization process with Curie temperature of \(~560\)\(^\circ\)C\(^5\), which is too much higher than the testing temperature to affect the temperature dependence of the dielectric constant. However, as the crystallization temperature reaches to 900\(^\circ\)C, dielectric constant increases with testing temperature, which may due to the increasing content of NaNbO\(_3\) phase with a lower Curie temperature of 365\(^\circ\)C\(^6\)\(^7\).

3.3. Breakdown strength and energy storage density

Five Nb\(_2\)O\(_5\)-Na\(_2\)CO\(_3\)-BaO-SiO\(_2\) glass-ceramic samples crystallized at 800\(^\circ\)C were chosen to be finely polished to flakes with thickness of about 0.3~0.4mm. Then, the flakes were immersed in glycol to test the breakdown strength. Table 1 shows the result of the tests. The difference of individual value of the breakdown strength appears to be about 30\%. This result suggests that the breakdown strength of the glass-ceramic is a structure-sensitive parameter ascribed to the distribution of dielectric phases and
glass matrix. Moreover, it seems that the breakdown strength is reduced with the increase of sample thickness.

Table 1. Breakdown strength of Nb$_2$O$_5$-Na$_2$CO$_3$-BaO-SiO$_2$ glass-ceramic material (800°C)

| Sample thickness(mm) | 0.310 | 0.325 | 0.335 | 0.355 | 0.370 |
|----------------------|-------|-------|-------|-------|-------|
| Breakdown strength(KV/mm) | 63.9  | 59.7  | 54.3  | 57.6  | 47.2  |

From Table 1 the average breakdown strength of 56.5 kV/mm could be obtained. In this study, the following formula was used to evaluate the theoretical energy storage density of glass-ceramic.

\[ W = \varepsilon_0 \varepsilon_r \varepsilon_r^2 / 2 \]

where \( W \) is energy storage density (J/m$^3$), \( \varepsilon_0 \) is the vacuum permittivity (8.85×10$^{-12}$ F/m), \( \varepsilon_r \) is the relative permittivity. Then the energy storage density of the sample crystallized at 800°C could reach to 1.87×10$^6$ J/m$^3$, which is suitable to be used as the innoxious dielectric media for high-energy storage capacitors.

4. Conclusion

In this study, fully densified Nb$_2$O$_5$-BaO-Na$_2$O-SiO$_2$ glass-ceramics were prepared by rapid quenching and controlled crystallization process. The influence of crystallization temperature, testing temperature and frequency on dielectric properties were investigated. Theoretical energy storage density was evaluated. The results show that:

1. NaNbO$_3$ with perovskite structure and NaBa$_2$Nb$_5$O$_{15}$ with tungsten bronze structure precipitate from the glass matrix during controlled crystallization process.

2. Dielectric constant increases with crystallization temperature, and the difference of the dielectric constant is less than 10% at the frequency range from 100 Hz to 100 kHz.

3. Dielectric constant of the materials crystallized at 750°C and 800°C has negative linear relationship at the temperature range from -40°C to 150°C, which is contrary to the material crystallized at 900°C.

4. Theoretical energy storage density of the material crystallized at 800°C could reach to 1.87×10$^6$J/m$^3$, which is suitable to be used as the innoxious dielectric media for high-energy storage capacitors.

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