Effect of Fe$_2$O$_3$ addition on microstructure and dielectric properties of PbO-SrO-Na$_2$O-Nb$_2$O$_5$-SiO$_2$ glass ceramic

F H Tan$^1$, Q M Zhang$^2$, H B Zhao$^1$, F Wei$^1$, P Zhou$^2$, J Y Chen$^2$ and J Du$^{1,3}$

$^1$ State Key Laboratory of Advanced Materials for Smart Sensing, General Research Institute for Nonferrous Metals, Beijing 100088, China.
$^2$ Advanced Electronic Materials Institute, General Research Institute for Nonferrous Metals, Beijing 100088, China.
$^3$ e-mail: dujun@grinm.com.

Abstract. Glass ceramic with the addition of 0-2.0 mol% Fe$_2$O$_3$ were synthesized by cast quenching followed by controlled crystallization, and the effect of Fe$_2$O$_3$ addition on the microstructure and dielectric properties of PbO-SrO-Na$_2$O-Nb$_2$O$_5$-SiO$_2$ (PSNNS) glass ceramic were investigated. DTA measurements revealed that the crystallization temperature of (Pb,Sr)Nb$_2$O$_6$ can be decreased by adding Fe$_2$O$_3$, meanwhile, the grain sizes of PSNNS glass ceramic increase with the increasing amount of additives. Dielectric properties of PSNNS glass ceramic were obviously affected by Fe$_2$O$_3$ addition. With 1.5 mol% Fe$_2$O$_3$ addition, the dielectric constant increased from 720 to 917, the dielectric loss increased from 0.012 to 0.0124. The PSNNS glass ceramic with 1.5% Fe$_2$O$_3$ addition show great promise for high voltage capacitors applications.

1. Introduction

Niobate glass ceramic used as dielectric material for high voltage capacitors and high energy storage capacitor has attracted increasing attention in recent decades [1-6]. The excellent dielectric properties for glass ceramic are mainly due to their unique microstructure. Glass ceramic, which are composites of nanocrystallites embedded in the glass matrix obtained by reheating glasses at high temperatures. Ceramic phase have large permittivity, glass matrix enjoys high electric breakdown field strength [7]. Meanwhile, the dielectric properties of niobate glass ceramic were greatly affected by crystal phase as well as glass phase. Since the glass ceramic have high breakdown strength(>90 kV/mm) [8], the key to improving the dielectric performance of glass ceramics is to increase the dielectric constant, numerous methods was investigated, such as change the ratio of Pb and Sr [9], rare earth elements addition [10] and titanate glass ceramics [11].

Fe$_2$O$_3$ is probably one of the most frequency used acceptors in ferroelectrics, the effects of Fe$_2$O$_3$ on titanate ceramics and lead zirconate titanate ceramics have been studied [12-15]. The found that dielectric properties could be enhanced by substituting the ions at the A or B site of the ABO$_3$ perovskite structure [16]. However, information regarding the effect of Fe$_2$O$_3$ addition on the glass ceramic composites materials was scarcely reported. The purpose of this study was to investigate the effect of Fe$_2$O$_3$ modification on the microstructure and dielectric properties of PbO-SrO-Na$_2$O-Nb$_2$O$_5$-SiO$_2$ (PSNNS) glass ceramic. Based on the previous research, P$_{0.6}$S$_{0.4}$NNS was chosen as the base material system [9], and then Fe$_2$O$_3$ was added according to different ion ratios.

2. Experimental

Reagent grade PbO, SrO, Na$_2$O, Nb$_2$O$_5$, SiO$_2$, Fe$_2$O$_3$ were used as starting materials. The basic composition of P$_{0.6}$S$_{0.4}$NNS powder was first prepared and then added with x mol% Fe$_2$O$_3$ (where x =0,
0.1, 0.5, 1, 1.5, 2). The samples with increasing Fe$_2$O$_3$ concentration were denoted as PSNNS-0, PSNNS-0.1, PSNNS-0.5, PSNNS-1, PSNNS-1.5 and PSNNS-2. Mixtures of the desired composition were ball-milled with zirconia balls as grinding media and deionized water as a lubricant for 12 h. After mixing and milling, the powders were dried for 12 h. Then, well-mixed oxide powders containing appropriate amounts of the above compositions were melted in a platinum crucible for 2-3 h at 1420 °C. The initial glasses were formed by rapid melt-quenching. The temperature of controlled crystallization of glass sheets was determined by Differential Thermal Analysis (DTA; Model WCT-2C, BoFei, Beijing) analysis method. After the crystallization temperature was determined, the initial glass bulks gone through the controlled crystallization process. Then the glass ceramics were cut and polished into sheets of 4 mm in thickness. Gold electrodes were sputter deposited on both sides of the glass ceramic sheets.

The measurements of dielectric constant and dielectric loss for PSNNS glass ceramics were performed using 4284A precision LCR meter. And the crystal structure of the samples was analyzed using X-ray diffractometry (XRD; Model MSAL-XD2, Micro Structure Analysis Laboratory, Beijing) with a 2θ range from 10°-90°. Microstructure evolution was observed using scanning electron microscopy (SEM; Model Hitachi S4800) equipped with a field emission gun. Dielectric properties including leakage current and polarization-electric field (P-E) were measured by ferroelectric tester (RT6000HVA, Radiant Technology, Albuquerque, NM).

3. Results and discussion

Figure 1 demonstrates the DTA curves of PSNNS-0, PSNNS-0.1, PSNNS-0.5, PSNNS-1, PSNNS-1.5 and PSNNS-2. The inflection around 630~670 °C on the DTA curves was considered as the glass transition effect. Three main exothermal crystallization peaks were observed on the curve of each sample. It’s obvious that the crystallization temperature of PSNNS glass could be decreased by adding Fe$_2$O$_3$. It’s well known that Fe$_2$O$_3$ could acted as a nucleating agent during the crystallization process, thus, ferroelectric phases were more easily crystallized from the glass matrix, PSNNS crystallization process was promoted. On the previous research, the crystallization process of the PSNNS glass was studied in detail, on this basis the crystallization temperature was chosen at 1000 °C for 3 h in this study, and the XRD patterns of the samples were shown in Fig. 2 to see if there was phases change when Fe$_2$O$_3$ was added to the precursor.

![Figure 1. DTA curve of Fe$_2$O$_3$ doped PSNNS glass ceramic.](image1)

![Figure 2. XRD patterns of PSNNS glass ceramic with different Fe$_2$O$_3$ addition.](image2)

The XRD patterns of PSNNS glass ceramic with the addition of 0-2 mol% Fe$_2$O$_3$ are shown in Fig. 2; all of the samples were crystallized at 1000 °C for 3 h. As is shown, the main crystal phases of PSNNS glass ceramic is (Pb,Sr)Nb$_2$O$_6$ with tungsten bronze structure and NaNbO$_3$ with perovskite structure. The dielectric constant of (Pb,Sr)Nb$_2$O$_6$ and NaNbO$_3$ is about 200 and 600 [17,18], respectively, They are responsible for raising the overall dielectric constant of PSNNS glass ceramic. Compared with the results of DTA and XRD, it can be concluded that there was no phase changed with Fe$_2$O$_3$ addition. Moreover, with the addition of Fe$_2$O$_3$, it exhibits a more sharp diffraction peak and the diffraction
intensity was enhanced, indicted that PSNNS glass ceramic with higher degree of crystallization was obtained though Fe$_2$O$_3$ addition.

Figure 3 shows the SEM photographs of the PSNNS glass ceramic with different Fe$_2$O$_3$ addition crystallized at 1000 °C. Seen from the image of the microstructure, the PSNNS glass ceramic was dense, smooth and without holes and cracks. The crystal grains are uniformly dispersed, suggesting that the rate of nucleation is relatively high, and the transformation of glass phase to crystalline phase is therefore completed with a minimum of time. Furthermore, Fe$^{3+}$ in glass matrix acted as a nucleating agent during crystallization process, therefore, there are more ceramic phase precipitated from the glass matrix. It is seen from the photograph that the grain sizes remarkably increase with the increasing of Fe$_2$O$_3$ addition. In general, the increase in grain size results in an increase of dielectric constant [19], furthermore, the addition of Fe$_2$O$_3$ can reduce the crystallization activation energy and promote the crystallization of ceramic phase, and ultimately improve the overall dielectric constant.

Figure 4. Polarization-electric field loops of the PSNNS specimens with different Fe$_2$O$_3$ addition.

Figure 5. Dielectric constant and loss tangent of PSNNS glass ceramic with different Fe$_2$O$_3$ addition.

The polarization-electric field ferroelectric hysteresis loops were carried out at room temperature for the glass ceramic samples in order to verify the effect of Fe$_2$O$_3$ addition on the polarization characteristics in Fig. 4. The plots of hysteresis loops driven at the same electric of 5 kV/mm for all samples. Obviously, with the increment of the concentration of Fe$_2$O$_3$, the P-E hysteresis loops of the
glass-ceramic samples grow thicker, and the coercive field ($E_c$), the maximum polarization ($P_{max}$), and remnant polarization ($P_r$) gradually increase with the increasing concentration of Fe$_2$O$_3$ additive. All the hysteresis loops are of the nature of non-saturation, which is due to the small grain size of the crystal particles precipitated within the glass matrix and the stresses applied by the surrounding glass matrix [20].

All of the dielectric property was measured at room temperature by using an Agilent 4284A precision LCR meter. Fig. 5 shows the plots of the dielectric constant and dielectric loss of the PSNNS glass ceramic with $x$ mol% Fe$_2$O$_3$ addition ($0 \leq x \leq 2$). The measurement result demonstrates that the dielectric constant increases with the increasing amount of Fe$_2$O$_3$ addition in the range of $0 \leq x \leq 1.5$, whereas it decreases slightly in the range of $1.5 \leq x \leq 2$. A maximum dielectric constant of 917 was obtained at compositions with 1.5 mol% Fe$_2$O$_3$ additions. Furthermore, it can be seen that the dielectric loss increased slightly when the Fe$_2$O$_3$ content is increased from 0-1 mol%, the increase in dielectric loss is mainly due to the accumulation of space charge at grain boundary phases. Then the dielectric loss increased significantly when the addition of Fe$_2$O$_3$ exceeds 1 mol%, probably due to the existence of metastable Fe$^{3+}$ ions. Acceptor dopants Fe$^{3+}$ create oxygen vacancies for ionic charge compensation and tend to pin the domain wall, which is evident by an increase in the internal bias field. Oxygen vacancies acted as carriers produce electrical losses. Moreover, Fe$^{3+}$ ions may trapped by defects or the interfaces in the dielectric materials, interfacial polarization occurs at the interface between the glass phase and the ceramic phase, polarization relaxation of the interfacial polarization is detrimental to the dielectric loss.

![Figure 6. Leakage current density of PSNNS glass ceramic with different Fe$_2$O$_3$ addition. (Inset is the resistivity of PSNNS specimens)](image)

The relationship of leakage current density and applied electric field for the PSNNS glass ceramic is given in Fig. 6. As usual, the leakage current increase with the applied field. It is seen that at the electric field of 10 kV/mm, the sample with 0.1 mol% Fe$_2$O$_3$ additions shows the minimal leakage current density of $9 \times 10^{-7}$ A/cm$^2$, while the maximum leakage current density of $1.3 \times 10^{-6}$ A/cm$^2$ was obtained with the composition of 2 mol% Fe$_2$O$_3$ additions. For dielectric materials, the low dielectric loss is often indicative of high resistivity, which can be confirmed by the resistivity measurements results of Fe$_2$O$_3$ doped PSNNS glass ceramic, and the results is given in the inset in Fig.6. When 0.1 mol% Fe$_2$O$_3$ was added to the glass, PSNNS-0.1 had the highest resistivity, when the mount of exceeded 0.1 mol%, the resistivity decreased, which matched the dielectric loss and leakage current well. And it confirmed that the Fe$^{3+}$ occupy the substitution in the lattice when $x$ is less than 1 mol%, while larger $x$ would make the Fe$^{3+}$ occupy the interstitial sites, thus the dielectric loss has an increment and resistivity decreases.

4. Conclusions

The effect of Fe$_2$O$_3$ doping on the microstructure and dielectric performance of PSNNS glass ceramic was investigated. DTA measurements revealed that the addition of Fe$_2$O$_3$ can decrease the
crystallization temperature of (Pb,Sr)Nb₂O₆, SEM and XRD results suggest that the addition of Fe₂O₃ could refine the grains and enhance the degree of crystallization. With 1.5 mol% Fe₂O₃ addition, the dielectric constant increased from 720 to 917, the dielectric loss increased from 0.012 to 0.0124. However, excessive Fe₂O₃ is detrimental to the dielectric loss and leakage current. These excellent dielectric properties of PSNNS+1.5% glass ceramic indicate its promising application in electronic devices.

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