Preparation and microstructure of Pb$_{0.99}$Nb$_{0.02}$((Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$)$_{0.98}$O$_3$ ceramics

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Abstract: The Pb$_{0.99}$Nb$_{0.02}$((Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$)$_{0.98}$O$_3$ antiferroelectric ceramics were synthesized by two different preparing routes (molten salt method and conventional solid state method). It was found that the sample synthesizes by a solid state method which owns smaller grain size leading to a higher energy storage density of 1.3 J/cm$^3$. From the S-E loops, it was found that the sample prepared by a molten salt method owns less micro-cracks and larger grain size which induced a higher switchable polarization and strain. From the results of situ TEM, the existence of 90° domain indicates the existence of antiferroelectric phase.

1. Introduction

In the past few years, the antiferroelectric(AFE) ceramics have been extensively studied due to the unique electrical properties, like energy storage performance and strain etc.\cite{1-4}. Comparing with other types of materials, PbZrTiO$_3$ (PZT)-based ceramics own the relatively high energy storage density and have widely application in many regions like hybrid electric vehicles, capacitors and mobile electronic devices \cite{5-8}. Chen et.al \cite{9} synthesized the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.60}$Sn$_{0.40}$)$_{0.95}$ Ti$_{0.05}$]$_{0.98}$O$_3$ (PNZST) AFE ceramics whose energy storage density of the ceramic is 0.67 J/cm$^3$ at 38 kV; Wang et. al \cite{10} prepared the Ba, Sr co-doped PLZST ((Pb$_{0.85}$Ba$_{0.08}$Sr$_{0.03}$La$_{0.03}$)(Zr$_{0.74}$Sn$_{0.22}$Ti$_{0.04}$)) antiferroelectric ceramics by a conventional solid state method which had the energy storage performance with 1.2 J/cm$^3$ at 100 kV. Meanwhile, the strain performance of AFE materials is also very important and it is induced by the antiferroelectric-to-ferroelectric phase transition, accounts for the large displacement, which will benefit large transducer or actuator applications \cite{11}.

It is well known that the final electrical properties of ceramics are mainly affected by their morphology, such as density, grain size and uniformity and so forth \cite{12}. As a result, different procedures would influence the final performance of materials. Solid state reaction route is widely used for bulk lead-containing ceramics \cite{13-14}. Meanwhile, molten salt method is another efficient way to prepare AFE ceramics, because molten salt method is a simple way to obtain complex compounds and it is also quiet environmentally friendly and cost relatively lower than solid state method \cite{15-17}. And PLZST AFE materials synthesis by a molten salt method was reported that obtaining a high relative density in 2006 \cite{18}.

In this study, the Pb$_{0.99}$Nb$_{0.02}$[(Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$]$_{0.98}$O$_3$ antiferroelectric ceramics were prepared by two different routes (molten salt method and solid state method). The results reveal that the grain size of sample which is prepared by a molten salt method is relatively large and the relative density is higher than those by a solid state method. Moreover, the microstructure was studied by the situ TEM, and the relationship between morphology, microstructure and electrical properties was also...
investigated.

2. Experimental

The \( \text{Pb}_{0.99}\text{Nb}_{0.02}\left(\text{Zr}_{0.52}\text{Sn}_{0.48}\right)_{0.955}\text{Ti}_{0.045}\) \( 0.98\text{O}_3 \) ceramics was prepared using \( \text{PbO} \) (99%), \( \text{Nb}_2\text{O}_5 \) (99.5%), \( \text{ZrO}_2 \) (99%), \( \text{SnO}_2 \) (99.5%), \( \text{TiO}_2 \) (98%) as starting materials and using \( \text{KCl} \) as a flux. The starting materials and molten salt (KCl) were ball-milled for 12 h, the dried slurries were calcined at 1123 K for 2 h, after cooling to room temperature naturally, the as-prepared powder were washed thoroughly with deionized water to get rid of chloride ions. And then the obtained powder were dried at 80 °C for 24 h. The dried powders were pressed into disks at the pressure of 40 MPa. The disks using the powders by a molten salt method were heated at 1473 K for 2 h and named S1. As a contrast, the starting materials without molten salt were experienced the same profile of ball-milling, calcined method and named S2.

The phase identification of ceramics S1 and S2 was performed by X-ray diffractometer (Smart-Lab 3 kW, Rigaku Ltd, Japan) using Cu K\( \alpha_1 \) radiation. The microstructure of the ceramics was examined using a scanning electron microscope (JSM-6510, JEOL Ltd, Japan). P-E loop and S-E loop measurements were made using a ferroelectric test system (Precision Premier II, America)

3. Results and discussion

Fig. 1 shows the XRD patterns of the ceramics S1 and S2. The XRD patterns revealed a pure perovskite structure for ceramics S1 and S2. No significant change or extra phase in the crystallographic structure was identified. It indicated that both the ceramic S1 and S2 possessed good crystallinity.

The SEM image and EDS of pre-synthetic powders was displayed in the Fig. 2. It can be seen in the Fig. 2(a), the morphology of Powders is various, including several octahedron-like, rod-like and irregular particles with size of 500-800 nm. And the result of EDS shows there is not exist any solid-solution of \( \text{K}^+ \) in the pre-synthetic products. The SEM images of ceramics S1 and S2 are shown in the Fig. 3. Comparing with the ceramics S2, the average grain size of S1 is relatively larger than that of S2. Meanwhile, the porosity of S1 is quiet lower than S2 which is indicating a higher relative density of ceramics S1.
Fig. 2 (a) the SEM image and (b) EDS of pre-synthetic powders of S1

Fig. 3 SEM images of ceramics (a) S1 and (b) S2

The room temperature P-E loops and S-E loops of S1 and S2 are shown in the Fig. 4. As can be seen in the Fig. 4(a), the P-E loops of both S1 and S2 display the double loops and indicate the AFE nature. Obviously, the switchable polarization of S1 is much lower than that of S2, this may due to the micro-cracks (porosity also can be one kind of micro-cracks) of S1 is much more than S2, the quantity of micro-cracks can affect the intensity of switchable polarization and actually the micro-cracks pin the domain wall motion, resulting in the lower switchable polarization [19]. The energy storage density \( W \) is calculated by using the formula \( W = \int P \, dE \). And the \( P_r \), \( P_{\text{max}} \) and \( E_c \) contribute significant to \( W \). The \( P_r \), \( P_{\text{max}} \) and \( E_c \) of S1 is 0.58 \( \mu \text{C/cm}^2 \), 30.81 \( \mu \text{C/cm}^2 \) and 1.09 kV/cm² respectively, and the \( W \) is 0.9 J/cm². Comparing with S1, however, the \( W \) of S2 is relatively higher than S1, which is 1.30 J/cm². This phenomenon of different electrical properties of S1 and S2 is due to the different grain size and microstructure by different preparing routes. And as can be seen in the Fig. 3, the grain size of S1 is relatively smaller than that of S2, and this leads to the higher energy storage performance [20-21].

Fig. 4(b) shows the S-E loops of ceramics S1 and S2. Comparing with ceramics S1 (0.19%), the monopolar strain of S2 is relatively high which reaches 0.21%. It is clearly that the molten salt method can make some contribution for the enhanced strain due to moderation of micro-structure. And though using molten salt method (as shown in the Fig. 3), the porosity of ceramics is lower than that of using conventional solid state method, and this leads to the higher switchable polarization and the higher strain. And a large strain is achieved when the maximum polarization remains large throughout the application regime [22unchino 1997chabudao]
The [001] zone-axis SEAD patterns of Pb$_{0.99}$Nb$_{0.02}$((Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$)$_{0.98}$O$_3$ under different heating temperature was shown in the Fig. 5(a)-(c). When the temperature is 298 K, it can be seen that the satellite spots surround the fundamental spots. Combining with the relating HRTEM image (Fig. 5(d)), it is found the existence of 90° AFE domains and indicating the origin of P-E loops. When the temperature rises to 400K, as can be seen in the Fig. 5(b), the satellite spots still exist but not very obviously, and the 90° domain in the HRTEM (Fig. 5(e)) are also not very clearly. And when the heating temperature gets to 423 K, the satellite spots are disappeared (Fig. 5(c)), revealing the 90° domain can stably exist under 423 K, indicating a sound thermal stability below 423K.

Fig. 4 (a) P-E loops and (b) monopolar S-E loops of ceramics S1 and S2
Fig. 5 [001] SAED patterns of Pb$_{0.99}$Nb$_{0.02}$((Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$)$_{0.98}$O$_3$ on heating: (a) 298K, (b) 400K, (c) 423K, (d) HRTEM image of the phase showing the incommensurate modulation across the 90°domainwall, and (e) the incommensurate modulation in one domain

4. Conclusion

In conclusion, the Pb$_{0.99}$Nb$_{0.02}$((Zr$_{0.52}$Sn$_{0.48}$)$_{0.955}$Ti$_{0.045}$)$_{0.98}$O$_3$ antiferroelectric ceramics were synthesized by two different preparing routes (molten salt method and conventional solid state method). The results of SEM images reveal that comparing with the sample using the conventional solid state method, the grain size is larger and the porosity is lower by using molten salt method. And the smaller grain size of sample leads to a higher energy storage density which is 1.30 J/cm$^2$. And the P-E loops of the two samples also indicate the higher switchable polarization of the sample which use the molten salt method. The S-E loops displayed that there is a higher strain of sample by a molten salt method due to the lower porosity and the higher switchable polarization. The results of situ TEM studies indicating that the 90 ° AFE domains can exist stably below 423 K.

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