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Original Article

Ferroelectric phase transition and electrical properties of high-T_C PMN-PH-PT ceramics prepared by partial oxalate route

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ABSTRACT

The high-Curie temperature (T_C) $0.15Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.38PbHfO_3$-$0.47PbTiO_3$ (PMN-PH-PT) piezoelectric ceramics were prepared by the partial oxalate route via the B-site oxide mixing method. The obtained uniform nm-sized PMN-PH-PT precursor powders provide high calcining and sintering activity for synthesizing ceramics, based on which the synthesis conditions were tailored as calcining at 775 °C and sintering at 1245 °C. The partial oxalate route synthesized PMN-PH-PT ceramics are far superior to the counterparts synthesized by the columbite precursor method and exhibit excellent thermal stability of the piezoelectric properties under T_C (~292 °C), ensuring the potential application in transducers under elevated environmental temperatures. The temperature dependent Raman spectroscopy not only proves the occurrence of the ferroelectric to paraelectric phase transition around T_C, but also confirms the successive phase symmetry transitions, which correlate with the polar nanoregions (PNRs) and/or the coexistence of multiple ferroelectric phases, revealing the origin of the enhanced electrical properties in the PMN-PH-PT ceramics.

1. Introduction

Searching for high-Curie temperature (T_C) high performance ferroelectrics has been a continuous task due to the urgent demands for the high-temperature and high-power-density piezoelectric applications in the fields of geothermal exploration, automotive, aerospace fields and so on [1–8]. The traditional $Pb(Zr_{1-x}Ti_x)O_3$ (PZT)-based piezoelectric materials with widespread commercial applications in transducers and actuators can not meet such severe requirements due to their relatively low T_C, e.g., only 193 °C for the commercial PZT5H piezoceramics (piezoelectric constant d_{33} = 593 pC/N) [9,10].

Although many piezoelectric materials with higher T_C temperature than that of PZT were discovered, their low piezoelectricity and difficult preparation process seriously hindered their applications in the electronic industries [3–8]. Among which, $LiNbO_3$ is a typical example, whose T_C is higher than 1000 °C, whereas the d_{33} value is only 6 pC/N even in single-crystal-form [3,4]. $BiMO_3$-$PbTiO_3$ (where M is cation in the octahedral coordination) are relatively novel perovskite ferroelectric systems, which are difficult to prepare whether in single-crystals or ceramics form due to the large lattice parameter ratio c/a and to pole under large direct current electric field because of the large leakage current caused by the evaporation of some metal elements sintered under high sintering temperatures, such as Bi^{3+} [5–8].

Recently, a pseudo-ternary system $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbHfO_3$-$PbTiO_3$ ceramics with excellent piezoelectric property (d_{33} = 680 pC/N) and relatively high T_C (~276 °C) were synthesized [9,11–13]. Such ferroelectrics were composed of binary solid solution $Pb(Hf_{1-x}Ti_x)O_3$ (PH-PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). In the past few decades, the PZT isostructural material PH-PT has attracted great concerning, however, its piezoelectric property was worse (d_{33} = 140 pC/N) than that of PZT and the corresponding applications were few [14–16]. As comparison, the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbHfO_3$-$PbTiO_3$ ceramics with the optimum composition exhibit similar piezoelectric property to that of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbZrO_3$-$PbTiO_3$ (PMN-PZT) (d_{33} = 698 pC/N, T_C 200 °C) but with higher T_C [17–21], indicating important promising applications in high-temperature and high-power-density piezoelectric

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fields.

In order to enhance ceramics performance further, trying novel ceramic synthesis method and tailoring processing conditions are really wonderful alternatives, which exert huge impacts on phase structure, microstructure morphology and homogeneity, density, crystal chemistry defects and so on [22–29]. As compared with the conventional oxide mixing method and the columbite precursor method, the partial oxalate route is an efficient technique to synthesize the lead-based ferroelectric ceramics, which has been used successfully in preparing pyrochlore phase-free PMN ceramics and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) ceramics [25–29]. The PMN powder synthesized by Gupta and Kulkarni via the partial oxalate route exhibits high reactivity, based on which the sintered PMN ceramics present single-phase and good dielectric properties [25]. The PMN-PT ceramics prepared by our group via the same method exhibit excellent dielectric, piezoelectric and pyroelectric properties brought by the rather pure perovskite structure and densified microstructure morphology [27–29].

In this work, the high-T_C $0.15Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.38PbHfO_3$-$0.47PbTiO_3$ (0.15PMN-0.38PH-0.47PT) ceramics were prepared by the partial oxalate route via the B-site oxide mixing method [20,27–29] to increase the perovskite phase content and improve the electrical properties. Such composition was chosen since it locates around the morphotropic phase boundary (MPB) composition in the 0.15PMN-xPH-(1-x)PT system and presents excellent piezoelectric properties confirmed by our previous work [30]. The influences of partial oxalate route and ceramic processing conditions on crystal phase structure, microstructure morphology, ferroelectric phase transition features, the MPB effect, and electrical properties of the PMN-PH-PT ceramics were investigated.

2. Experimental procedure

The 0.15PMN-0.38PH-0.47PT (abbreviated as PMN-PH-PT) ceramics were prepared by the partial oxalate route via the B-site oxide mixing method [20,27–29]. $Pb(CH_3COO)_2{\cdot}3H_2O$ (99.0%), MgO (98.0%), Nb_2O_5 (99.5%), HfO_2 (99.9%), TiO_2 (98.0%), and $H_2C_2O_4{\cdot}2H_2O$ (99.8%) were used as starting materials. First, the columbite precursor $MgNb_2O_6$ (abbreviated as MN) was synthesized by the calcination of the well-mixed stoichiometric mixture of MgO and Nb_2O_5 at 1000 °C for 2 h. Next, stoichiometric HfO_2 and TiO_2 were reacted with the synthesized MN particles by calcining at 1100 °C for 2 h, to form the B-site compound $(Mg_{1/3}Nb_{2/3})_{0.15}Hf_{0.38}Ti_{0.47}O_2$ (abbreviated as MNHT). Then, the required amount of lead acetate solution (1.5 mol/L) was dripped slowly into the MNHT suspension, formed by dispersing the MNHT powder into the oxalic acid (OA) aqueous solution (2 mol/L), to form the lead oxalate precipitation-coating under magnetic stirring. In this method, the molar ratio of oxalic acid to lead acetate was 1.5:1. Finally, the clean-washed precipitated powder was calcined at 675–825 °C for 2 h, which was determined based on the simultaneously thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis (TG-DSC, SDT Q600 Simultaneous Thermal Analyzer, TA Instruments, USA) as discussed in the Supplementary Information (Fig. S1), and then sintered at 1205–1255 °C for 2 h to synthesize the PMN-PH-PT ceramics. Sufficient Pb-rich atmosphere was produced by covering $PbZrO_3$ powder to minimize the evaporation of lead during sintering.

The precursor powder before calcination was undertaken TG-DSC analysis under a heating rate of 10 °C/min from room temperature to 1300 °C in air (Supplementary Information, Fig. S1). The Zetasizer Nano ZS90 nano laser particle size and zeta potential analyzer (Malvern Instruments Ltd., UK) was used to measure the particle size (Z-average-diameter D_z) with its distribution (intensity PDI) of the calcined PMN-PH-PT powders. Temperature dependent Raman spectra (20–320 °C) was collected using the Horiba LabRAM HR Evolution Raman spectrometer equipped with a Linkam THMS600 heating/cooling stage. Crystal structure of the calcined PMN-PH-PT powders and sintered PMN-PH-PT ceramics was determined by SmartLab X-ray Diffractometer and Rigaku D/max-2500/PC X-ray Diffractometer (XRD, Rigaku Corp., Japan), respectively. The Zeiss Supra™ 55 Sapphire Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Group, Germany) was used to observe the microstructure morphology of the calcined powders and the sintered ceramics. For electrical performance tests, electrode was formed by coat-painting and firing at 650 °C for 30 min. Detailed dielectric, ferroelectric and piezoelectric properties measurement procedures were reported elsewhere [23,29]. Besides, the TF 2000 Ferroelectric Analyzer (aixACCT Systems GmbH, Germany), along with a laser interferometer, was used to measure the strain-electric field (S-E) curves under 1.5 kV/mm at 10 Hz.

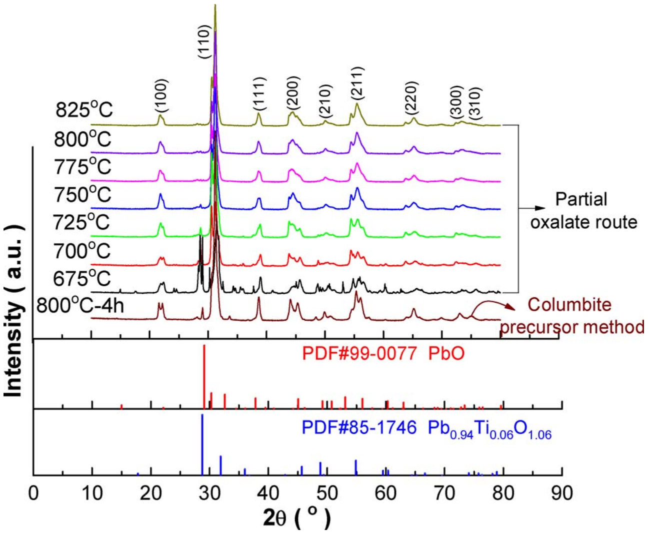

Fig. 1. XRD patterns of the PMN-PH-PT powders calcined at different temperatures for 2 h prepared by the partial oxalate route and calcined at 800 °C for 4 h prepared by the columbite precursor method.

3. Results and discussion

According to the TG-DSC analysis (Fig. S1), the solid-state reaction and the initial crystallization occur at 650 °C for the precursor powder prepared by the partial oxalate route. Considering the evaporation of PbO at high temperatures also, the calcining temperatures for synthesizing perovskite PMN-PH-PT powder are determined ranging from 675 °C to 825 °C. Fig. 1 displays the XRD patterns of the PMN-PH-PT powders prepared via the partial oxalate route and prepared by the columbite precursor method for comparison. At the lowest calcining temperature of 675 °C, main perovskite structure is formed although some impurity phases PbO and $Pb_{0.96}Ti_{0.06}O_{1.06}$ exist. The formation of these impurity phases can be attributed to the relatively low calcination temperature, therefore, PbO can not be reacted completely and residues slight content, and $Pb_{0.94}Ti_{0.06}O_{1.06}$ is formed via short-range ion migration without needing too high activation energy [31,32]. With increasing calcination temperature, these impurity phases decrease gradually since sufficiently high energy is provided for stabilizing perovskite structure and enhancing crystallinity, with the splitting of diffraction peaks weakening progressively and the diffraction peaks merging gradually accompanied by sharpening and symmetry improvement. When the calcining temperature increases up to 725 °C, the structure and crystallinity of the PMN-PH-PT powder prepared by the partial oxalate route are similar to the counterpart synthesized by the columbite precursor method and calcined at 800 °C for 4 h. The decrease of calcining temperature and time is the result of the enhanced activity of the PMN-PH-PT precursor powders induced by the partial oxalate route.

Particle size (Z-average-diameter D_z) with its distribution (intensity