PMN-PSMNT ceramics fabricated using the twin-crystal mixed co-firing method

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Abstract

$(1-w)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.67}\text{Ti}_{0.33}\text{O}_3]-w[\text{Pb}_{1-1.5x}\text{Sm}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_y\text{Ti}_{1-y}\text{O}_3]$ ((1- w)PMN- w PSMN-PT) piezoelectric ceramics were prepared using the newly proposed twin-crystal mixed co-firing method in which two pre-sintered precursor powders were mixed and co-fired with designated ratios ($w = 0.3, 0.4, 0.5, 0.6$). X-ray diffraction results show that all the samples presented a pure perovskite structure. The grains were closely packed and the average size was $\sim 5.18 \mu\text{m}$ from the observations of scanning electron microscopy images, giving the high density of ceramics to be 97.8% of the theoretical one. The piezoelectric, dielectric, and ferroelectric properties of the ceramic samples have been investigated systematically. It was found that the performance of ceramics was significantly enhanced when compared to the ceramics fabricated using the conventional one-step approach. Outstanding piezoelectric coefficient d_{33} of 1103 pC/N and relative dielectric permittivity ε_r of 9154 could be achieved for the ceramics with $w = 0.5$.

1 Introduction

Perovskite $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT), one of the typical ferroelectrics among perovskite-type ferroelectrics, tungsten bronze type ferroelectrics, bismuth-layer-type ferroelectrics, and pyrochlore-type ferroelectrics, features excellent piezoelectric properties. The dipole alignment caused by the movement of A-site and B-site ions plays a critical role in ferroelectricity. In detail, the A-site ions are occupied by Pb^{2+} ions and located at eight vertices of the cube, while the B-site ions are dominated disorderly by Mg^{2+} and Nb^{5+} in the center of the cube, presenting a disordered distribution macroscopically^[1]. PT is also a normal ferroelectric with a perovskite-type structure in which the B-site lattice is occupied by Ti^{4+} . The mechanism of relaxor ferroelectrics could be explained as follows: 1. Due to the difference of ionic radius and the repulsion against the adjacent electron clouds, the arrangement of ions is loosely bonded. 2. Under the external electric field, the disordered B-site lattice favors larger ions such that smaller ions retain more free space, assisting the movement in oxygen octahedrons easily^[2-4].

The relaxor ferroelectrics exhibit excellent dielectric, pyroelectric and electrostrictive properties^[5, 6] due to their unique crystal structure. For PMN-PT, when the PT content reaches 33% – 35% in mole, the crystal structure is a mixture of the pseudo-cubic phase and tetragonal phase in the vicinity of phase boundaries, denoting a morphotropic phase boundary (MPB)^[7]. Besides, it is generally recognized that the PMN-PT ceramics exhibit outstanding piezoelectric properties due to the synergistic effect from both the MPB feature and local structural heterogeneity (induced by the disordered arrangement of B-site heterovalent cations (Mg^{2+} and Nb^{5+})^[1, 6, 8-10]). Previous studies have also shown that this disordered structure in the nanoscale plays a key role in excellent dielectric and piezoelectric properties for relaxor-PT-based ferroelectric materials^[11-15]. To further enhance the heterogeneity, Li Fei et al. manipulated the interfacial energy of PMN-PT materials with a rare-earth element, Sm. The d_{33} reached as high as 1500 pC/N and 3400–4100 pC/N for doped-PMN-PT ceramics^[16] and single crystals^[17], respectively. Due to the

unexpectedly high piezoelectric response in Pb-based ferroelectrics, Sm^{3+} has recently attracted great attention on modifying piezoelectric ceramics^[18–26].

Besides the effect of doping element, the fabrication method plays a key role in the performance of ceramics. The common issue of preparing PMN-PT-based materials using the conventional one-step mixed oxide sintering method is the formation of pyrochlore phase. Generally, the pyrochlore phase could be easily induced by the doping of lanthanide elements (such as Sm, La) in the PMN-PT system^[23, 26, 27] due to the high melting point of Sm_2O_3 ^[28] and the poor diffusion ability of Sm^{3+} at high temperature. In this study, a twin-crystal mixed co-firing method^[29] is proposed to prepare $(1-w)\text{PMN}-w\text{PSMN-PT}$ (PMN-PSMNT) ceramics with the same chemical composition but in different mixing ratios, w . The major merit of this newly proposed method is the accurate control of the crystal phase proportions for reducing or even preventing the formation of the pyrochlore phase and subsequently forming a local heterostructure in ceramic grains, resulting in the enhancement of piezoelectric and dielectric properties. It was found that the overall performance of PMN-PSMNT ceramics prepared using the proposed method was significantly improved when compared to those prepared by the conventional method.

2 Materials And Methods

2. 1 Ceramics preparation

In order to avoid the formation of pyrochlore phase, niobium and titanium compounds (Nb_2O_5 , TiO_2) with poor sintering activity were mixed with $\text{Mg}_2(\text{OH})_2\text{CO}_3$, and a small amount of lead oxide was used as a diffusion promoter to synthesize two kinds of pre-sintered powders in advance. Analytical purity chemicals, Pb_3O_4 , Sm_2O_3 , TiO_2 , $\text{Mg}_2(\text{OH})_2\text{CO}_3$, and Nb_2O_5 , were used as raw materials to synthesize $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.67}\text{Ti}_{0.33}\text{O}_3$ (Component A) and $\text{Pb}_{1-1.5x}\text{Sm}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_y\text{Ti}_{1-y}\text{O}_3$ (Component B, B_1 : $x = 0.0833$, $y = 0.8367$; B_2 : $x = 0.0625$, $y = 0.795$; B_3 : $x = 0.05$, $y = 0.77$; B_4 : $x = 0.0417$, $y = 0.7533$) ceramic powders. In Component B, $\text{Mg}_2(\text{OH})_2\text{CO}_3$, Nb_2O_5 , Sm_2O_3 , partial Pb_3O_4 , and TiO_2 were ground evenly and pre-sintered at 880 °C for 4 h, then crushed and added with residual Pb_3O_4 pre-sintered again.

$\text{Pb}_{0.9625}\text{Sm}_{0.025}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ piezoelectric ceramics with the nominal composition were prepared by mixing Component A and Component B according to the chemical formula of $(1-0.025/x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.67}\text{Ti}_{0.33}\text{O}_3]-0.025/x[\text{Pb}_{1-1.5x}\text{Sm}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_y\text{Ti}_{1-y}\text{O}_3]$ ($0.025/x = 0.3, 0.4, 0.5, 0.6$), followed by ball milling, granulation, molding, and sintering processes. The process flow chart is shown in Fig. 1. To simplify the analysis, we denote w as $0.025/x$. The sintering condition was 1250 °C for 1.5 h. After ground and polished, the silver paste was coated on the two surfaces, and the silver electrode was formed by calcinating at 650 °C for 30 min. The ceramic discs were poled at 3 kV/mm for 1 min at room temperature, aged and short-circuited for 24 h, then the electrical properties were measured. For comparison, $\text{Pb}_{0.9625}\text{Sm}_{0.025}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3$ were prepared by the traditional mixed oxide sintering process as a reference sample.

2.2 Characterization

D/max-2500/PC X-ray diffraction (XRD, Rigaku, Japan) with Cu K α radiation and JSM-6510 scanning electron microscopy (SEM, JEOL, Japan) were performed to characterize the crystal structures and morphologies of the samples, respectively. The Raman spectra were measured using the DXR2 laser confocal microscopy Raman spectrometer (Raman, ThermoFisher, USA) with an argon ion laser excitation line of 532 nm and a laser power of 1 mW. The identification of the phase was performed using the JADE software. The piezoelectric coefficient d_{33} was measured by the quasi-static d_{33} tester (ZJ-6A, Chinese Academy of Science, China). The relative dielectric permittivity ϵ_r , dielectric loss $\tan\delta$, the resonance and anti-resonance frequencies of the samples were acquired using a precise impedance analyzer (HP4294A, Agilent, USA). The temperature-dependent dielectric characteristics were measured by a high-temperature dielectric measurement system (DMS-1000, Partulab, China). The electric hysteresis loop and field-induced strain of the samples were also investigated with the Radiant Precision Premier ferroelectric material test system (LC8000, Radiant, USA).

3 Results And Discussion

3.1 Structure and morphology

XRD patterns are shown in Fig. 2(a) for Component A, Component B, (1- w)PMN- w PSMN-PT ($w = 0.3, 0.4, 0.5, 0.6$) samples, and the reference sample. As expected, the pyrochlore phase Pb₂Nb₂O₇ (PDF card no. 40-0828) was formed with the featured diffraction peaks at 14.32° and 30.36° in the reference sample. Component A exhibited a pure perovskite tetragonal phase structure with no obvious impurities. However, a traceable pyrochlore phase in Component B with a rhombohedral structure was detected. And with increasing w , pyrochlore phase first decreases and then increases, indicating the challenge to completely eliminate the pyrochlore phase, though the contents were still far below from the reference sample. The samples prepared by the twin-crystal phase mixed co-firing method displayed higher crystal purity (99.62–99.89% perovskite structure), which is much better than the samples prepared by the conventional sintering method (98.64% perovskite structure). In this study, niobium oxide, magnesium oxide, titanium oxide, samarium oxide, and partial lead oxide were pre-sintered at 880 °C for 4 h, promoting the homogenization of the system and minimizing the pyrochlore phase induced by the local excessive samarium concentration^[16].

By fitting the diffraction peaks of the (1- w)PMN- w PSMN-PT at 44°–46°, Fig. 2(b) shows that the overlapping degree of diffraction peaks increased gradually with w . With the increment of w , the tetragonal phase Component A decreased and the rhombohedral phase Component B increased such that the samples would gradually transform from tetragonal phase to rhombohedral phase. Consequently, double diffraction peaks of (002) and (200) transformed to a single peak of (200). When $w = 0.6$, (002) and (200) diffraction peaks overlapped completely. Rietveld refinement was performed for (1- w)PMN- w PSMN-PT ($w = 0.3, 0.4, 0.5, 0.6$) samples by GSAS software^[30] and the results are shown in Figs. 2(c)–(f). Comparing the diffraction patterns of (1- w)PMN- w PSMN-PT samples and Component A, the symmetry of the diffraction peaks of (1- w)PMN- w PSMN-PT ceramics samples became worse in the

tetragonal phase (111) at $2\theta = 31.44^\circ$. To avoid excessive grain growth, the sintering time at 1250°C was only 1.5 h such that Component A with the tetragonal phase and Component B with the rhombohedral phase cannot be completely homogenized, resulting in the distortion of diffraction peaks to some extent^[16, 23]. During the mixed sintering of tetragonal Component A and rhombohedral Component B, the green body was gradually densified with the movement of grain boundary. As different grain sizes were involved in the mixture, some grains retained their original composition in the sintering process. The lattice parameters, cell volume, and density of Component A, Component B, and $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples are shown in Table 1. It can be seen that with the increment of w , the cell parameters a and b of the samples decreased first and then increased, while the corresponding c exhibited the opposite trend. The phenomenon could be explained as follows: (1) the chemical composition of crystal particles had a gradient change when the ceramic samples with the identical chemical composition and different mixing ratios were prepared by the twin-crystal mixed co-firing process, resulting in the change of cell parameters; (2) the cell parameters a and b of the samples with more pyrochlore content ($w = 0.3$ and $w = 0.6$) were relatively large, which indicates that the generation of pyrochlore phase would deviate the chemical composition of the main phase, resulting in the change of crystal lattice. In addition, the c/a ratios of $(1-w)\text{PMN}-w\text{PSMN-PT}$ ($w = 0.3, 0.4, 0.5, 0.6$) ceramics were 1.0033, 1.0033, 1.0028, 1, respectively. It can be seen that the c/a of the samples was closer to 1 with higher w because the phase structure of the samples tended to the cubic phase, which agreed well with the overlapping degree of diffraction peaks in Fig. 2(b). Compared with Sm-doped $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (Sm-PZT) ceramics, the c/a of Sm-PMN-PT ceramics was much closer to 1^[23, 25] such that the internal stress caused by domain switching is smaller, the octahedral gap formed by oxygen atoms is relatively loose, and the micro-displacement of B-site ions is relatively easy.

The Raman peaks of lead-based ferroelectric materials with the ABO_3 perovskite structure are divided into three categories: The Raman mode with the wavenumber less than 150 cm^{-1} belongs to Pb-BO_6 stretching mode, the one between 150 cm^{-1} and 500 cm^{-1} is a mixture of B-O-B bending mode and O-B-O stretching mode, and the one between 500 cm^{-1} and 800 cm^{-1} is related to B-O-B stretching mode^[31, 32]. According to the lattice dynamics, group theory, and Raman studies of other ferroelectrics with the ABO_3 structure, the number of Raman modes can be used to determine the phase structure of ferroelectrics. The rhombohedral phase (R3m) has seven Raman active modes and the tetragonal phase (P4mm) has eight Raman active modes^[33]. The room-temperature Raman spectra of the $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples and the deconvolution of multiple Lorentzian/Gaussian peaks are shown in Fig. 3, in which the fitting results agree well with the measured Raman spectra. Among the vibrational bands, the mode located at $\sim 800\text{ cm}^{-1}$ can be assigned to the stretching vibration of Nb-O-Mg and B-site cations; the band at 580 cm^{-1} is originated from the oxygen bending vibration; the band 500 cm^{-1} is attributed to the stretching vibration of Nb-O-Nb ; the band at 433 cm^{-1} arises from the stretching vibration of Mg-O-Mg mode; and the most intense band at 270 cm^{-1} is contributed by B site ions against O stretching vibration inside the octahedron^[34]. The Raman spectra of samples with $w = 0.3$ and $w = 0.4$ can be deconvoluted into 7 Raman modes using the Lorentzian/Gaussian fitting in the wavenumber range of

180 cm^{-1} –840 cm^{-1} , while the samples with $w = 0.5$ and $w = 0.6$ have 6 Raman modes, which is related to the ratio of tetragonal Component A and rhombohedral Component B in the samples. Based on the characteristics of Raman spectra, the samples with $w = 0.3$ and $w = 0.4$ were with the tetragonal phase, while those with $w = 0.5$ and $w = 0.6$ samples were with the rhombohedral phase. Due to the detection limit of our Raman spectrometer, the Raman modes below 99 cm^{-1} could not be accurately evaluated.

The ceramic samples were polished and etched at 1100 °C for 1 h before the morphological characterizations. Figure 4 shows that the grain size was relatively uniform in the range of 4 – 6 μm , with an average size of 5.18 μm . The SEM images of the fresh section of the sample show both transgranular fracture and intergranular fracture mechanisms. This may contribute to the comparative bonding strength between grains and grain boundaries. Besides, the grain boundaries are angular, revealing that no glass phase remained. The grains of the samples were closely packed with very few pores, which agree with the high density (95.4%–97.8%) of the samples listed in Table 1.

3.2 Dielectric properties

Figures 5(a)–(d) show the temperature-dependent dielectric constant ε_r and loss tangent $\tan\delta$ of (1- w)PMN- w PSMN-PT samples. The characteristic temperatures T_m of (1- w)PMN- w PSMN-PT samples with $w = 0.3, 0.4, 0.5$ and 0.6 were 79 °C, 79 °C, 81 °C and 86 °C, respectively, and the corresponding peak values of ε_r were 23789, 30190, 30192, and 27656. Above T_m , both the dielectric and loss peaks shifted to high temperature along with the increasing frequency. The results show an obvious frequency dispersion characteristic, indicating the diffusive phase transition and the relaxor ferroelectric property. The dielectric spectra of the (1- w)PMN- w PSMN-PT samples and the reference sample at 1 kHz are shown in Fig. 5(e). The characteristic temperature of the reference sample was 82.2 °C, and the corresponding ε_r peak value was 19373. The sample prepared by the twin-crystal mixed co-firing process exhibited significantly improved ε_r . However, the Curie temperature of PMN-PT ceramics decreased when doped with Sm. $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) ceramics (from 385 °C to 335 °C^[21, 35]) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZ-PT) ceramics (from 230 °C to 184 °C^[22, 36]) also had this characteristics after doped with Sm. The dielectric behavior of ferroelectrics above T_m can be fitted by the quadratic law for the typical relaxor ferroelectrics and normal ferroelectrics.

$$1/\varepsilon = 1/\varepsilon_{\max} + (T - T_{\max})^\gamma / C^{[37]}$$

where γ is the degree of diffuseness, C is a constant. γ approaches 2 for an ideal relaxor ferroelectric, while γ approaches 1 for a normal ferroelectric^[38]. The dielectric behavior of (1- w)PMN- w PSMN-PT samples above T_m at 1 kHz were linearly fitted according to the quadratic law. An example of the sample with $w = 0.5$ sample is shown in Fig. 5(f). The relaxation indexes were 1.72, 1.74, 1.83, and 1.75, respectively, showing obvious relaxation.

3.3 Piezoelectric properties

The piezoelectric and dielectric properties of $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples are shown in Fig. 6 and Table 2. It can be seen that d_{33} , ε_r , electromechanical coupling factors k_p (planar vibration mode) and k_t (thickness vibration mode) increased along with w and reached maximum when $w = 0.5$. Compared to the reference sample, d_{33} and ε_r of $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples were greatly improved. Besides, the dielectric losses of all samples varied slightly while the mechanical quality factor dropped for the $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples. This could be attributed to the formation of Pb vacancy at the A-site after doped with Sm^{3+} such that the directional activation energy of the domain decreases. As the domain walls in the grains move easily, the coercive field reduces and makes the ceramics more easily polarized, thus improving the piezoelectric properties. At the same time, due to the easy movement of domain walls, the internal loss would inevitably increase, resulting in the decrease of mechanical quality factor Q_m and the increase of dielectric loss^[22].

3.4 Ferroelectric properties

The hysteresis loops and field-induced strain plots of $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples are shown in Fig. 7. It can be seen that the coercive fields E_c varied slightly among samples, giving ~ 2.3 kV/mm. The remanent polarization P_r reached the maximum value of $24.5 \mu\text{C}/\text{cm}^2$ when $w = 0.5$, which is consistent with the piezoelectric and dielectric performance. Similarly, the sample with $w = 0.5$ exhibited the largest field-induced strain of 0.25% as shown in Fig. 7(b). The butterfly curve is relatively thin, which indicates that the small field-induced strain hysteresis, good repeatability, and fast response of $(1-w)\text{PMN}-w\text{PSMN-PT}$ ceramics^[39]. This is very beneficial to the application of large displacement devices, such as atomic force microscopy, long-distance laser ranging calibration, submarine passive sonar, large displacement jacquard driver^[40], and so on.

3.5 Comparison

When compared to the reported properties of lead-based piezoelectric ceramics, as shown in Table 3, the proposed work has achieved great achievement on the significant improvement of piezoelectric and dielectric properties. This is attributed to the capability of controlling the crystal phase proportion of the twin-crystal mixed co-firing method, resulting in the enhancement of piezoelectric properties of ceramics. As the samples were with the pyrochlore phase, there is still room to further improve the properties especially when compared with the results reported by Li Fei et al.^[16]. Nevertheless, the work still shows the proposed twin-crystal mixed co-firing method is a promising approach to prepare high-performance piezoelectric materials.

4 Conclusions

The $(1-w)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.67}\text{Ti}_{0.33}\text{O}_3]-w[\text{Pb}_{1-1.5x}\text{Sm}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})_y\text{Ti}_{1-y}\text{O}_3]$ piezoelectric ceramics with the identical stoichiometric chemical composition and the pure perovskite structure were successfully prepared by the twin-crystal mixed co-firing process. The effects of mixing ratio w on the crystal structure, micro-morphology, piezoelectric, dielectric and ferroelectric properties of ceramics were studied. The results showed that:

(1) The aggregation of Sm is the main reason for the formation of the pyrochlore phase. The formation of the pyrochlore phase can be inhibited by pre-sintering the mixed oxide of Sm, Mg, Nb, and Ti to fully diffuse Sm^{3+} , and the main crystal phase could be formed by pre-sintering the mixture with the PbO.

(2) The electrical properties varied with w of Component A and Component B. When $w = 0.5$, the piezoelectric and dielectric properties reached the optimal level in which $d_{33} = 1103 \text{ pC/N}$, $k_p = 0.66$ and $\epsilon_r = 9154$.

(3) The symmetry distortion of the x-ray diffraction peak reveals that the Sm^{3+} in the ceramics prepared by the twin-crystal mixed co-firing process are likely to be distributed in gradient, resulting in local structural heterogeneity and the subsequent improvement of the piezoelectric properties. This process could also be applied to the synthesis of other series of piezoelectric ceramics.

Declarations

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Conflict of interest The authors declare that they have no conflict of interest.

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Tables

Due to technical limitations, Tables 1, 2, and 3 are only available as a download in the Supplemental Files section.

Figures

Figure 1

Experimental process flow chart for the synthesis of (1-w)PMN-wPSMN-PT samples.

Figure 2

(a) Original XRD patterns of Component A, Component B, $(1-w)\text{PMN}-w\text{PSMN}-\text{PT}$ samples, and the reference sample (the crystallographic index was calibrated according to the tetragonal phase); (b) Fitting peaks of $(1-w)\text{PMN}-w\text{PSMN}-\text{PT}$ samples at $2\theta = 44^\circ-46^\circ$; (c)–(f) Rietveld refinement results of $(1-w)\text{PMN}-w\text{PSMN}-\text{PT}$ samples.

Figure 3

(a) Raman spectra of (1-w)PMN-wPSMN-PT samples at room temperature; (b-e) Deconvolution of multiple Lorentzian/Gaussian peaks at 180 cm^{-1} -840 cm^{-1} of (1-w)PMN-wPSMN-PT samples.

Figure 4

SEM images of (a) surface and (b) cross-section of the 0.5PMN-0.5PSMN-PT sample.

Figure 5

Temperature-dependent dielectric spectra of (1-w)PMN-wPSMN-PT samples with (a) $w = 0.3$, (b) $w = 0.4$, (c) $w = 0.5$ and (d) $w = 0.6$; (e) Temperature dependent dielectric spectra of (1-w)PMN-wPSMN-PT and the reference samples at 1 kHz ; (f) Linear fitting of dielectric behavior of (1-w)PMN-wPSMN-PT sample with $w = 0.5$ at 1 kHz according to the quadratic law.

Figure 6

Piezoelectric coefficient d_{33} , electromechanical coupling factors k_p and k_t , and relative dielectric permittivity ϵ_r of $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples.

Figure 7

(a) Electric hysteresis loops and (b) field-induced strain plots of $(1-w)\text{PMN}-w\text{PSMN-PT}$ samples.

Supplementary Files

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