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Synthesis and piezoelectric properties of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics prepared by sol–gel auto-combustion method

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Abstracts In this study, $NaNO_3$, $Bi(NO_3)_3{\cdot}5H_2O$, $Ba(NO_3)_2$, $Ti(OC_4H_9)_4$ and citric acid were successfully introduced to fabricate lead-free piezoelectric $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ [NBBT] nanopartical powders by a novel modified sol–gel auto-combustion method. The resultant products were characterized by the X-ray diffraction analysis and transmission electron microscope method. $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3 + Mn(NO_3)_2$ [NBBTM] can be sintered by the traditional solid-state reaction, and the effects of NBBT doped different amounts of $Mn(NO_3)_2$ at various sintering temperatures upon phase formation, microstructure as well as piezoelectric properties were further studied. The experimental results show that it was helpful to control their chemical ingredients and microstructure to prepare nanocrystalline single phase NBBT powders. Where is the X-ray diffraction result of the corresponding ceramics to prove the existence of the mixing between rhombohedral and tetragonal phases at the MPB compositions. Doping 0.015 mol% $Mn(NO_3)_2$ into NBBT at 1,090 °C, piezoelectric constant (d_{33}) and relative dielectric constant (ε_r) reach the superior value of 159pC/N and 1,304, respectively, and dielectric loss (tan δ) and electromechanical coupling factor (K_t) are 2.5% and 65%, respectively.

Introduction

Bismuth Sodium Titanate $(Na_{1/2}Bi_{1/2})TiO_3$ (NBT)[1–4] which is a kind of perovskite structure with superior piezoelectric properties[5] has been studied for the increasing demand on environmental friendly materials and manufacturing processes. It has been investigated that NBT-based compositions modified with a small amount of additives such as $BaTiO_3$, $NaNbO_3$, $BiFeO_3$, $Bi_2O_3{\cdot}Sc_2O_3$ or La_2O_3 [6–10] had been reported improved piezoelectric properties comparing with pure NBT ceramics. Among these materials, $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ system has attracted considerable attention. MnO has been used as an additive for several NBT-based ceramics, including NBT [11] and $(Na_{0.5}Bi_{0.5})_{0.92}Ba_{0.08}TiO_3$ [12]. The material constants of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics doped various amounts of $MnCO_3$ have been evaluated by Kaewkamnerd et al. with respect to the application of the material in Lamb wave devices [13].

Research efforts have been devoted to the preparation of the material by various wet chemical methods, such as citrate method [14], hydrothermal process [15] and stearic acid gel route [16]. In continuation of our research on piezoelectric properties of NBBT ceramics prepared by a sol–gel method, $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ ceramics doped various amounts of $Mn(NO_3)_2$ were prepared by the sol–gel method and the effects of $Mn(NO_3)_2$ on the structure, sinterability and piezoelectric and dielectric properties were examined in this work.

Experiment

Preparation of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ powders

The powders with the nominal composition of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ were prepared by a sol–gel method. Sodium nitrate, bismuth nitrate pentahydrate, barium nitrate, manganese nitrate, tetrabutyl titanate and citric acid

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were used as starting materials. Their aqueous solutions were mixed together with 1:1(molar:ratio) of nitrates to citric. Appropriate amount of citric acid as a chelating agent was dissolved into 60 mL deionized water. A small amount of ammonia was doped by drop-wise to adjust the pH value of 7, keeping stirring the solution simultaneously. Then, tetrabutyl titanate diluted in ethanol was slowly doped and a yellowish two-layer liquid that was a transparent aqueous solution with an oil-like liquid on the top layer, was obtained. The homogeneous aqueous solution was separated from the mixing liquid by a separalory funnel. Various nitrates were doped into the solution according to the nominal composition, stirring at 60 °C for 1 h to form a transparent, yellowish precursor solution. The pH value of the final solution was approximate 8. The precursor solution was dehydrated in an oven at 100 °C for 12 h. As the viscosity of solution rose, and on further dehydration, a gel started to form. Subsequently the temperature was increased to 120 °C until dried gel obtained. At 210 °C, the dried gel auto-combusted and swelled, releasing a large amount of gases. After reheating at 600 °C for 1 h, the powders can be obtained.

Characterization

The phase identification and structure analysis of the thermally treated powders were carried out by the X-ray diffraction analysis and transmission electron microscope method. The morphology of the resultant samples was examined by transmission electron microscope method. The powders were further pressed into disk and sintered at 1,050–1,130°C for 2 h in air. Silver paste was applied to the top and bottom surfaces of the samples as electrodes. The specimens for piezoelectric measurements were poled in a stirred silicone oil bath at 120 °C under a field of 3.5 kV mm^{-1} for 15 min. The capacitance (C) and dielectric loss (tan δ) of the prepared samples were measured at room temperature (Automatic LMN Meter 4225, Japan). The relative dielectric constant was calculated by the capacitance and specimen dimension. The electromechanical coupling factor (K_t) was obtained by a resonance–antiresonance method using a low-frequency impedance analyzer (HP4192A). The piezoelectric constant (d_{33}) was measured by the quasi-static method (Model ZJ-3A, China).

Results and discussion

Characterization of NBBTM powders

Figure 1 displays the X-ray diffraction patterns for NBBTM calcined at 600 °C in the 2θ range of 20° to 70°. The powders of Mn-doped NBBT present a single phase of perovskite structure with a rhombohedral symmetry and a small amount of impurity compared to that of pure NBBT and NBBT + 0.015%molMn without any detectable secondary phase. These powders exhibit an average particle size of 25–65 nm according to Scherrer's formula. In addition, it was noted that the color of NBBT powder is yellowish, whereas NBBTM powders became black yellowish with increasing a amount of $Mn(NO_3)$. The average grain size of NBBTM becomes larger than that of pure NBBT. Considering perovskite structure and impurity, the X-ray diffraction patterns reveal that the existence of Mn^{2+} has influenced on the composition of Mn-doped NBBT.

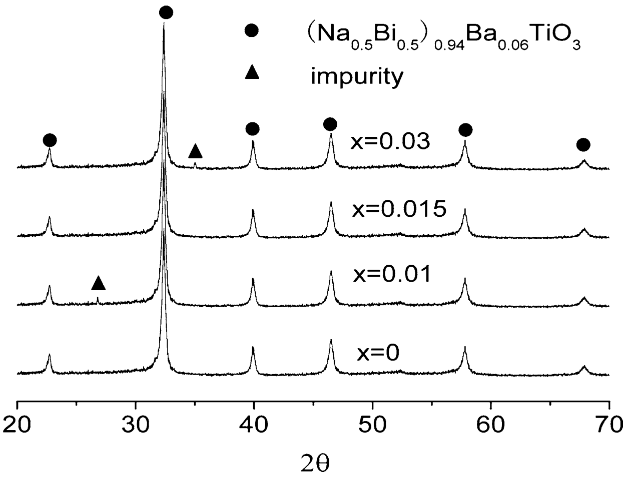


Fig. 1 X-ray diffraction diagrams of the NBBT + Mn (*x*.mol%) powders

Figure 2 shows TEM image of nanocrystalline $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ powders synthesized at 600 °C for 1 h. It indicates the particles are cubic morphology and have uniform distribution. The diameters of the particles are in the same range as measured in using X-ray diffraction method. And then, the nanocrystalline powders are separated well. It is because that the as-burnt powder by the sol–gel method does not require calcination at high temperature to make the dried gel transform into final powder with expected crystal structure. It prevents aggregation, which is detrimental to the sintering of powder. Thus, the synthesized ferrite powder is highly active and can be sintered at relative low temperature.

Microstructure of NBBTM ceramics

Figure 3 displays typical microstructure of NBBT doped different amount of $Mn(NO_3)_2$ ($x = 0.01$, 0.015, 0.03 mol%). The SEM observation confirms that grain size first increases then decreases with the increase of $Mn(NO_3)_2$ concentration. Grains of the sample doped with 0.015 mol% $Mn(NO_3)_2$ exhibit the largest size and homogeneous distribution. Furthermore, all resultant

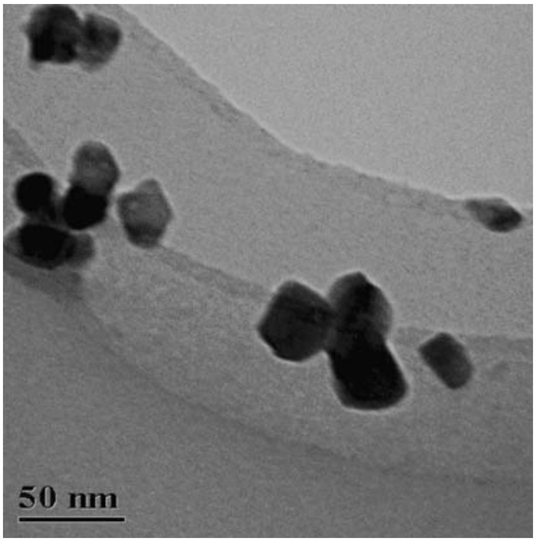


Fig. 2 TEM image of NBBT powders synthesized at 600 °C for 1 h

samples have high density around 5.42–5.76 g cm^{-3}, about 95% of theoretical density. Homogeneously growing grains were obtained due to the components lying in MPB when 0.015 mol% $Mn(NO_3)_2$ was introduced into NBBT. A consective increase of $Mn(NO_3)_2$, the growth of grains was significantly inhibited by the excessive content of $Mn(NO_3)_2$ segregating at grain boundaries and thus exerted a drag force against the grain boundary movement.

Piezoelectric, dielectric properties and density of NBBT doped 0.015 mol% $Mn(NO_3)_2$ ceramics at room temperature was measured respectively. The results are shown in Table 1. It can be seen that the piezoelectric, dielectric properties and density properties are superior to that prepared by a conventional solid-state reaction method except for dielectric loss. The resulting powders are traditionally prepared by conventional solid-state reaction method usually have a high agglomeration and inhomogeneous particle size as a result of the high-temperature treatment. In comparison with this technique, the sol–gel process has shown considerable advantages, including excellent compositional control and homogeneity on the molecular level due to the mixing of liquid precursors.

Figure 4 show the effects of piezoelectric constant (d_{33}) and dielectric loss (tan δ) of different Mn-doped compositions at different temperatures. It can be seen that piezoelectric constant (d_{33}) increases and dielectric loss (tan δ) decreases with the increase of the sintering temperatures. When the sintering temperatures exceed a high value (e.g., >1,090 °C), any addition of $Mn(NO_3)_2$ ceases to be beneficial for their properties. At the same time, compared with pure NBBT, piezoelectric constant (d_{33}) of NBBT + 0.015 mol% $Mn(NO_3)_2$ is improved remarkably from 142 to 159pC/N and dielectric loss (tanδ) decreases significantly from 3.3% to 2.5% at 1,090 °C.

Figure 5 shows the relative dielectric (ε_r) and dielectric loss (tan δ) as functions of NBBTM ceramics at 1,090 °C. It can be seen that the sample doped with 0.015 mol% $Mn(NO_3)_2$ exhibits higher relative dielectric ($\varepsilon_r = 1,304$) and lower dielectric loss (tan $\delta = 2.5\%$) than that doped concentration of 0.01 mol%, 0.02 mol% and 0.03 mol%. This result is related to the domain wall motion contribution, which causes energy loss because of the interaction of domain walls with other domain walls, domain walls crystallites, and domain walls with defects. Figure 6 shows that the values of piezoelectric constant (d_{33}) and electromechanical coupling factor (K_t) increase as increasing $Mn(NO_3)_2$ fraction up to 0.015 mol% with the maximum value of 159pC/N and 65%, respectively, then decrease. Obtaining optimum values may result from the densification of the composition and the reduction of the microstructural discontinuity. The piezoelectric properties decrease rapidly due to excessive $Mn(NO_3)_2$ which may result in inhibiting grain growth, the existence of secondary phase and poor microstructural homogeneity.

The appropriate amount of $Mn(NO_3)_2$ can lead to sufficient densification, maintain controlled grain growth, and achieve optimum piezoelectric properties. This can be ascribed to the introduction of Mn^{2+} ions, remarkably influencing the piezoelectric propertities and sinterability during the sintering process. A small amount of $Mn(NO_3)_2$ into NBBT resulted in improvement of piezoelectric and dielectric properties it is supposed that Mn^{2+} ion has a cationic radius (0.8 Å) larger than that of Ti^{4+} (0.68 Å),

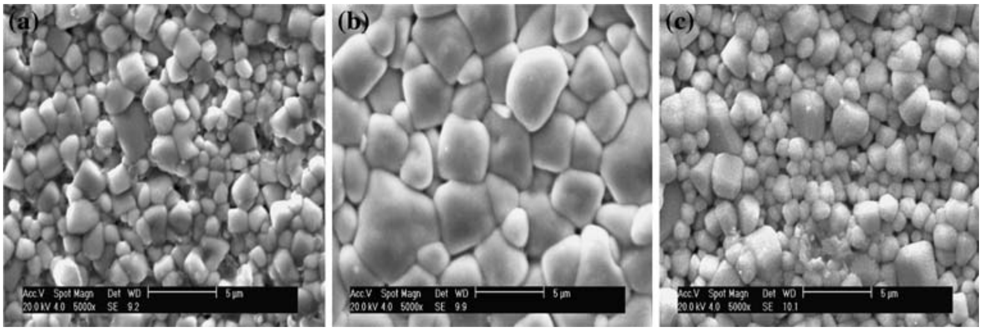
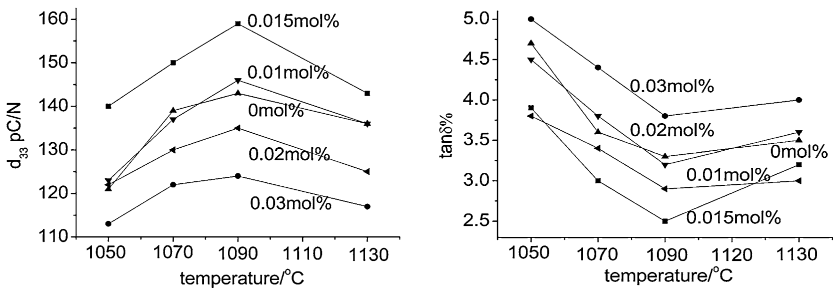


Fig. 3 SEM images of different Mn-doped compositions: (**a**) $x = 0.01$ mol%, (**b**) $x = 0.015$ mol%, (**c**) $x = 0.03$ mol%

Table 1 Piezoelectric, dielectric properties and density of NBBT doped 0.015 mol% Mn(NO$_3$)$_2$ ceramics compared by sol–gel method and conventional solid-state method at 1,090 °C

	d_{33} (pC/N)	ε_r	Tan δ%	K_t %	ρ(g.cm^{-1})
Sol–gel method	159	1,304	2.5	64	5.82
Conventional solid-state method	128	1,110	0.4	56	5.69

Fig. 4 Effect of temperature on piezoelectric constant of different Mn-doped NBBT ceramic



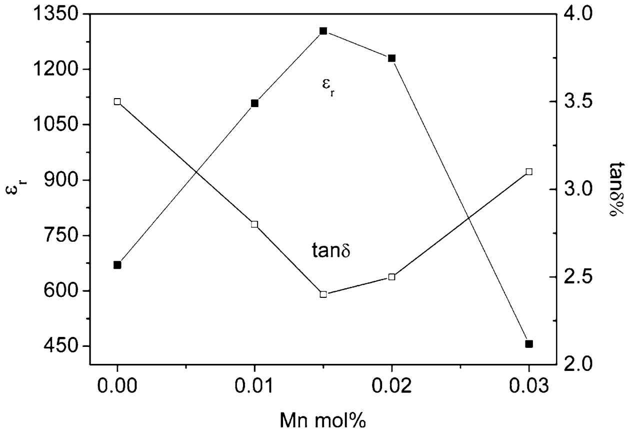


Fig. 5 Relative dielectric constant ε_r, dielectric loss tan δ as functions of NBBTM ceramics

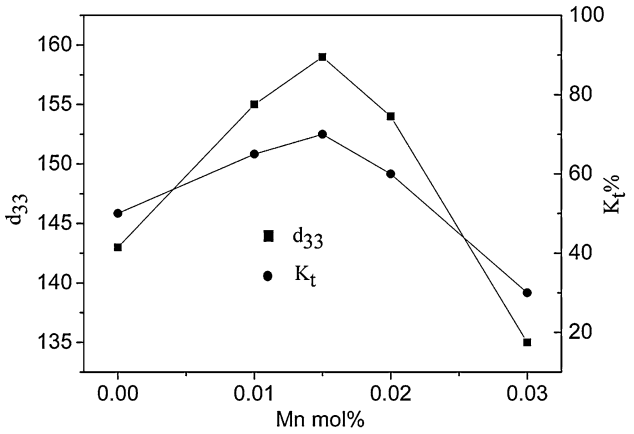


Fig. 6 Effect of Mn(NO$_3$)$_2$ on piezoelectric constant of NBBTM ceramic at 1,090 °C

bringing A-site vacancies and aberration of lattice, which spur to lower the potential barrier of electric domains and benefit the spontaneous polarization. But an immense amount of Mn(NO$_3$)$_2$ into NBBT deteriorated piezoelectric properties due to the excessive Mn^{2+} segregating at grain boundaries. Considering the versatility of Mn in valence state as a transitional metal element [17–20], an amount of Mn^{2+} ions were possibly transformed into Mn^{4+} ions during sintering in air. With a relatively smaller radius (0.6 Å) of Mn^{4+} ions, the corporation of Mn^{4+} ions into the B-site of the structure can generate a different influence on spontaneous polarization in contrast to Mn^{2+} ions according to their relative radius. Despite this possibility, the effect of the versatility Mn as a transitional metal element in valence state of Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{7+}, on piezoelectric property seems to be considered in the present work.

Conclusion

A novel modified sol–gel auto-combustion method is an effective route to synthesize NBBTM powders, which can be sintered more effectively than solid-state method. The effects of NBBT doped a different amount of Mn(NO$_3$)$_2$ near the MPB of NBBT with perovskite structures at various temperatures upon single phase formation, homogeneous microstructure, higher piezoelectric and dielectric properties were further studied in this work. For NBBT + 0.015 mol% Mn(NO$_3$)$_2$ ceramics at 1,090 °C, piezoelectric constant (d_{33}) and relative dielectric constant (ε_r) reach the superior value of 159pC/N and 1,304, respectively, and dielectric loss (tan δ) and electromechanical coupling factor (K_t) are 2.5% and 65%, respectively, which can improve the temperature ability of NBBTM ceramics.

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