J Mater Sci (2006) 41:6146–6149
DOI 10.1007/s10853-006-0572-z

LETTER

Synthesis of $(Na_{0.5}Bi_{0.5})TiO_3$ and $(Na_{0.5}Bi_{0.5})_{0.92}Ba_{0.08}TiO_3$ powders by a citrate method

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Received: 1 December 2003 / Accepted: 11 April 2006 /

At present, lead zirconate titanate (PZT) based ceramics are most widely applied piezoelectric materials because of their superior electrical properties. However, the evaporation of toxic lead during the fabrication of the ceramics causes an environmental problem. Therefore, there is an increasing interest of investigating lead-free piezoelectric materials to replace PZT based piezoelectric ceramics. Sodium bismuth titanate, $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), is a kind of perovskite-type ferroelectric with a relatively large remnant polarization ($P_r = 38\ \mu C/cm^2$) at room temperature and a relatively high Curie temperature ($T_c = 320$ °C) [1]. For its strong ferroelectricity at room temperature, NBT has been considered to be a promising candidate material for lead-free piezoelectric ceramics. However, it is difficult to pole NBT ceramic due to its large coercive field ($E_c = 73$ kV/cm), making it unsuccessful in obtaining desired piezoelectric properties. To solve this poling problem, various NBT based solid solutions have been developed [2–7]. Among these solid solutions, NBT–$BaTiO_3$ (NBT–BT) system has attracted a great deal of attention. Compared with NBT, the NBT–BT compositions near the rhombohedral–tetragonal morphotropic phase boundary (MPB) showed substantially improved poling behavior and piezoelectric properties [2, 6, 7].

It has been confirmed that preparation process has a great influence on NBT and NBT based solid solutions in terms of stoichiometry, lattice distortion and electrical properties [8–10]. Therefore, the synthesis and preparation of NBT and NBT based materials is an intriguing subject of significant importance. NBT and NBT based ceramics were usually made from powders prepared by the traditional solid state reaction method. By comparison, the synthesis of NBT or NBT based powders by alternative methods [11–13] was seldom reported. It has been found that the NBT ceramic made from the powder synthesized by a sol-gel method exhibited an improvement in sinterability, poling process and piezoelectric properties [13]. The citrate method is a kind of sol-gel method using citric acid as a complexing agent. The complexing of metal cations by free carboxyl groups allows molecular level mixing of reactants and consequently leads to uniform, fine powders with high purity at relatively low temperatures. In this work, we report the synthesis of NBT and $(Na_{0.5}Bi_{0.5})_{0.92}Ba_{0.08}TiO_3$ (abbreviated as NBT–BT8) powders by the citrate method.

Reagent grade $NaNO_3$, $Bi(NO_3)_3{\cdot}5H_2O$, $Ba(NO_3)_2$, tetrabutyl titanate and citric acid were used as starting materials. A weighed amount of citric acid was first dissolved into deionized water in a beaker. An appreciate amount of aqueous ammonia was dripped to adjust the pH value of the solution to 6–8. Then a designed amount of tetrabutyl titanate was slowly added under a stirring at 60 °C. After stirring at the temperature for 1 h, a yellowish two-layer liquid was obtained, comprising a transparent aqueous solution in addition to an oil-like liquid on the top layer. The aqueous solution was separated from the mixing liquid. Various nitrates were added into the solution according to nominal composition of the two powders, followed by a stirring at 80 °C for 1 h to generate a

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transparent, yellowish precursor solution. The pH value of the solution was about 6. The precursor solution was dehydrated in an oven at 100 °C to form a sol. Subsequent heating at a higher temperature of 160 °C yielded a gel. The gel was pulverized and then calcined at 500–650 °C for 1 h in air.

Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) analysis of the gel were performed by a simultaneous thermal analyzer (Netzsch, STA449C) at a heating rate of 2 °C min^{-1} in air. The crystalline structure of calcined powders was examined by a X-ray diffractometer (Rigaku, D/MAX-RB) using Cu K$_\alpha$ radiation. The morphology of calcined powders was analyzed by a scanning electron microscope (SEM, Jeol, JSM-5610LV) and a transmission electron microscope (TEM, Philips, JEM-100CX II). The specific surface area of calcined powders was measured by the Brunauer-Emmett-Teller (BET) method using liquid nitrogen as an adsorbent.

It was found that the mole ratio of citric acid to total metal cation content (abbreviated as C/M) was the main contributing factor to the formation of the sol and gel, while calcining temperature significantly influenced the crystalline structure and morphology of the calcined powders. When the C/M of the precursor solution was less than 1.0, white precipitate appeared in the sol and gel. It is presumably attributed to the hydrolysis of free metal cations in the aqueous solution, originating from the insufficient complexing of metal cations by citrate acid due to its low concentration. For the precursor solution with a C/M above 1.5, white crystalline-like grains were formed during the heating at 160 °C to generate a gel. It is probably due to the crystallization of excessive citric acid with the loss of solvent. It was ascertained that C/M in the range of 1.0–1.5 produced homogeneous, transparent sol and gel.

Figure 1 shows the TG–DSC curve of the NBT–BT8 gel derived from the precursor solution with a C/M = 1.3 The faint endothermic peak at 82.8 °C is attributed to the evaporation of residual nitric acid and water, corresponding to a small weight loss of 6.94%. The exothermic peak at 276.1 °C was caused by the decomposition of excessive citric acid, resulting in a weight loss of 15.81%. There are two successive exothermic peaks at 478.0 and 549.6 °C, accompanied by the weight losses of 27.61% and 14.08%, respectively. The exothermic peak at 478.0 °C is associated with the thermal decomposition of the citrate complex, and the exothermic peak at 549.6 °C is assigned to the combustion of remaining organic components. No further DSC peak or weight loss can be seen thereafter. A rather similar thermal decomposition process was observed for the NBT gel derived from the precursor solution with a C/M = 1.3, indicating that its thermal decomposition was also completed below 600 °C.

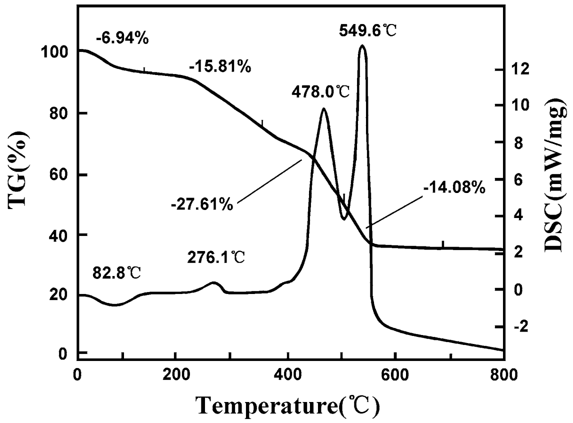

Fig. 1 TG–DSC curve of NBT–BT8 gel derived from the precursor solution with a C/M = 1.3

Figure 2 shows the XRD patterns of NBT powders calcined at different temperatures. The powders were derived from the precursor solution with a C/M = 1.3. After calcining at 500 °C, a perovskite structure was detected together with a tiny amount of intermediate phase, attributed to a bismuth titanate compound ($Bi_4Ti_3O_{12}$). The increase of calcining temperature promoted the development of the perovskite structure. A pure perovskite structure was identified for the powders calcined at 600 and 650 °C, respectively. Fig. 3 shows the SEM micrographs of NBT powders (C/M = 1.3) calcined at different temperatures. The powders calcined at 500 and 550 °C, respectively, consist of homogeneous, fine particles. Raising the calcining temperature to 600 °C did not cause significant change in particle morphology. Further elevation of the calcining temperature to 650 °C increased particle size and particle agglomeration. With respect to the phase development and morphological evolution of

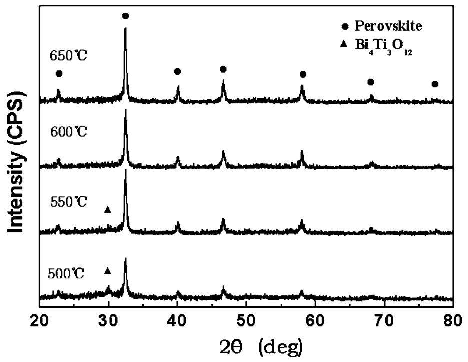

Fig. 2 XRD patterns of NBT powders (C/M = 1.3) calcined at different temperatures

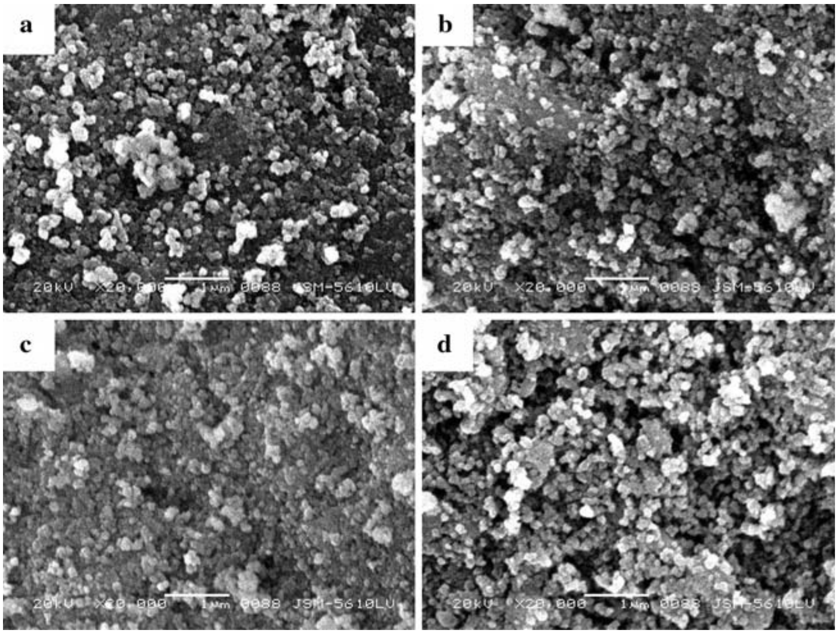

Fig. 3 SEM micrographs of NBT powders (C/M = 1.3) calcined at (**a**) 500 °C, (**b**) 550 °C, (**c**) 600 °C and (**d**) 650 °C

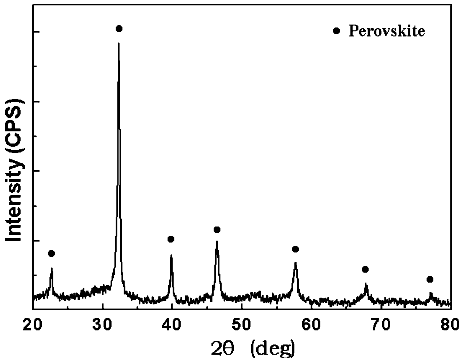

Fig. 4 XRD pattern of NBT–BT8 powder (C/M = 1.3) calcined at 600 °C

NBT powder (C/M = 1.3) during the calcining process, it was concluded that the preferred calcining temperature for NBT powder (C/M = 1.3) is 600 °C. The variation in crystalline structure and particle morphology with calcining temperature for NBT–BT8 powder (C/M = 1.3) is almost identical to that for NBT powder (C/M = 1.3). The preferred calcining temperature for NBT–BT8 powder (C/M = 1.3) was also ascertained to be 600 °C. Fig. 4 shows the XRD pattern of NBT–BT8 powder (C/M = 1.3) calcined at 600 °C, certifying the formation of a pure perovskite phase.

Figure 5 shows the TEM micrographs of NBT and NBT–BT8 powders (C/M = 1.3) calcined at 600 °C. A soft agglomeration of particles was observed for the two powders. The particle size of NBT powder (C/M = 1.3) is primarily in the range of 40–60 nm. The particle size of NBT–BT8 powder (C/M = 1.3) is relatively larger than that of NBT powder (C/M = 1.3), exhibiting an average particle size around 80 nm. BET measurement indicates that the specific surface areas of NBT and NBT–BT8 powders (C/M = 1.3) calcined at 600 °C are 19.0 and 12.9 $m^2 g^{-1}$, respectively. The difference in specific surface area between the two powders is consistent with that in particle morphology observed by TEM.

In summary, the citrate method was proved to be a feasible and convenient route to prepare NBT and

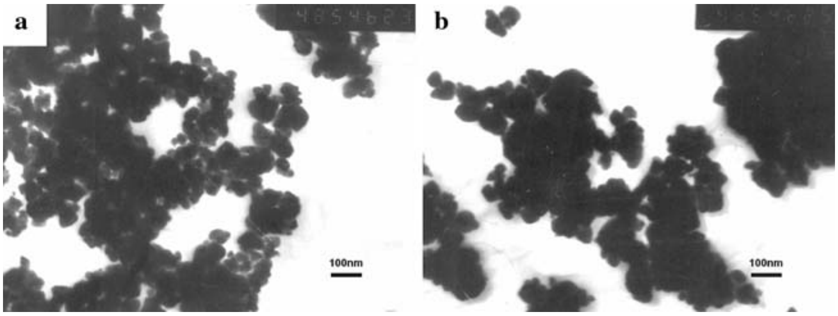

Fig. 5 TEM micrographs of powders (C/M = 1.3) calcined at 600 °C. (**a**) NBT and (**b**) NBT–BT8

NBT–BT8 powders. It was found that C/M in the range of 1.0–1.5 resulted in homogeneous, transparent sol and gel. When the C/M was 1.3, the preferred calcining temperature for NBT and NBT–BT8 powders was ascertained to be 600 °C with respect to the phase development and morphological evolution of the powders during calcining process. The specific surfaces areas of NBT and NBT–BT8 powders (C/M = 1.3) calcined at 600 °C are 19.0 and 12.9 $m^2 g^{-1}$, respectively. It is considered that the citrate method used herein for synthesizing NBT and NBT–BT8 powders can also be potentially adopted to prepare NBT–BT powders with other compositions.

Acknowledgements This work was financially supported by the Natural Science Foundation of China (Grant No. 5027044), the Natural Science Foundation of Hubei Province (Grant No. 2002AB076) and Nippon Sheet Glass Foundation for Materials Science and Engineering.

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