

# Preparation and characterization of high $T_c$ $(1-x)$ $\text{BiScO}_3-x\text{PbTiO}_3$ ceramics from high energy ball milling process

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Published online: 18 August 2007  
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**Abstract**  $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$  powders were synthesized from a mixture of the oxides  $\text{Bi}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{PbO}$  and  $\text{TiO}_2$  using a Fritsch P4™ vario-planetary ball milling systems. The pure perovskite structure of BS-PT powder can well be obtained and the crystallite size of the powders was greatly reduced to 18–25 nm after milling 4 h. The rhombohedral–tetragonal phase boundary was observed for the ceramics sintered at 1,000–1,100 °C when  $x$  was around 0.64 and 3–7  $\mu\text{m}$  grain size was obtained, which is smaller than traditional method. High Curie temperature ( $T_c$ ) and high dielectric constant can be obtained at the morphotropic phase boundary (MPB). As  $\text{PbTiO}_3$  contents increased from 60 to 68 mol%, the Curie temperature  $T_c$  shifted toward higher temperature and the maximum dielectric constant increased. The experimental results demonstrate that the high-energy ball milling process is a promising method to prepare BS-PT materials.

**Keywords** BS-PT · High-energy ball milling · Morphotropic phase boundary · Dielectric properties

## 1 Introduction

For many years, ceramics based on the perovskite  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) have been the best choice for various piezoelectric applications [1]. Recently, Bismuth perovskites have been attracting attention as a family of piezoelectric ceramics in place of the widely used PZT

system. The dielectric and piezoelectric properties of the  $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$  (BS-PT) perovskite system have previously been reported [2, 3]. Enhanced electric properties for compositions near the MPB ( $x=0.64$ ) between rhombohedral and tetragonal phases were found to be comparable to the soft PZT.  $T_c > 450$  °C is 100 °C higher than that of commercial PZT, which makes this material a promising candidate for high temperature and temperature-stable actuators and transducers.

Very recently, a mechanical activation synthesis (MAS) technique (i.e., high-energy ball milling) has successfully been used to synthesize nano-crystalline ferroelectrics and other alloys [4, 5]. MAS offers several advantages over the other methods and is indeed superior over the high-temperature solid-state reaction technique and wet chemical process because they lower the calcinations and sintering temperature due to their atomic or molecular scale homogeneity of the synthesized nano-crystalline powders [6]. MAS is a very useful and low-cost method to synthesis lead-based ceramic PZT, PZN and PMN-PT powders because effectively alleviating the loss of  $\text{PbO}$  [7]. Considering the advantages above, especially there are two materials  $\text{Bi}_2\text{O}_3$  and  $\text{PbO}$  volatilization simultaneously, we have synthesized nano-crystalline  $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$  by high-energy ball milling, on which not much work have been reported so far. In this study, the powder characteristics during milling process and sintering behavior were investigated in details; also electrical properties were discussed.

## 2 Experimental

Solid solutions powders of  $(1-x)\text{BiScO}_3-x\text{PbTiO}_3$  ( $x=0.60$ – $0.68$ ) were prepared using high energy ball milling.

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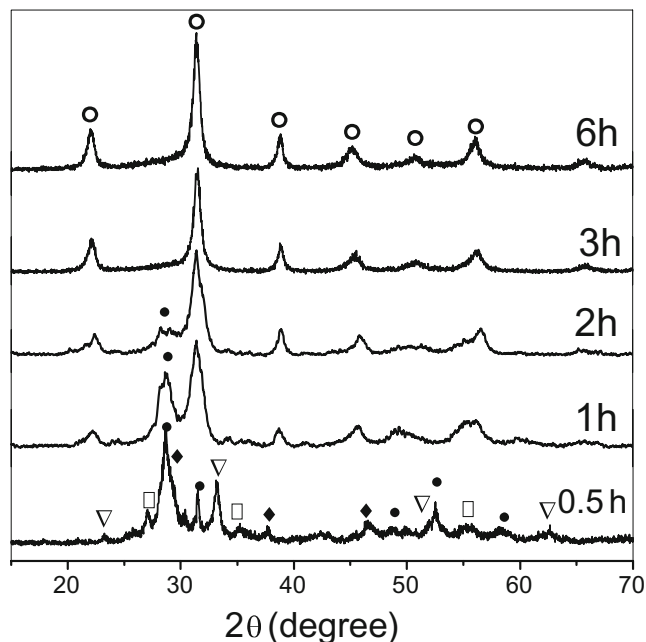
Reagent grade oxides  $\text{Bi}_2\text{O}_3$  (99%),  $\text{Sc}_2\text{O}_3$  (99.99%),  $\text{PbO}$  (99.9%) and  $\text{TiO}_2$  (99.6%) were used as the starting materials. The milling operation was carried out in a Fritsch Pulverisette 4™ vario-planetary high-energy ball milling system. A 225-ml tungsten carbide vial and 50 tungsten carbide balls with diameter ( $D_B$ ) of 10 mm were used as a milling medium. The milling speed of main disk was set at 400 rpm and the speed of each pair was set at  $-800$  rpm, which means that the rotation speed ratio (R-ratio)  $-2.0$ . The ball mass to powder mass ratio ( $M_B/M_P$ ) was 20:1. Pellets were pressed into disks 12 mm in diameter and 1–2 mm in thickness at 200 MPa, and sintered in sealed crucibles at temperatures between 1000–1150 °C for 2 h.

The sintered BS-PT ceramics were analyzed by Rigaku D/MAX-2400 X-ray diffraction with  $\text{Cu K}\alpha$  radiation. Microstructures were analyzed by scanning electron microscopy (JEOL JSM-5800). A HP4284A impedance analyzer in conjunction with a furnace was used to measure the dielectric constants as a function of temperature on heating at frequencies of 0.1 to 100 kHz. The P-E hysteresis loops were measured using TF analyzer 2000 FE-module system (AIXACCT).

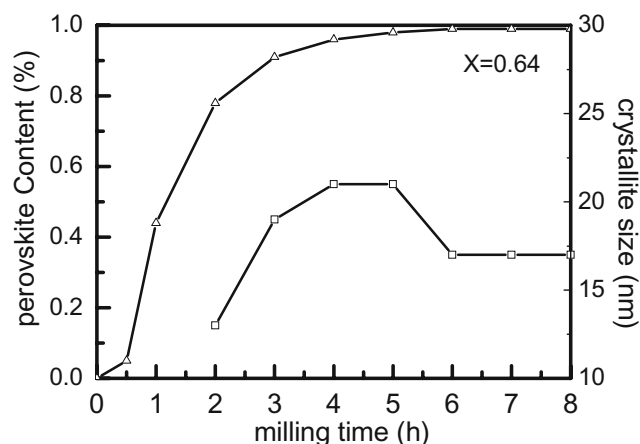
### 3 Results and discussion

#### 3.1 Powder preparation study

Figure 1 shows the XRD pattern of the  $x=64\%$  mixture milled powder with different milling time. The peak at



**Fig. 1** XRD patterns of  $x=0.64$  powder mixture treated for various times ranging from 0.5 to 6 h: (●)  $\text{PbO}$ , (□)  $\text{TiO}_2$ , (◆)  $\text{Bi}_2\text{O}_3$ , (▽)  $\text{Sc}_2\text{O}_3$ , (○) BS-PT



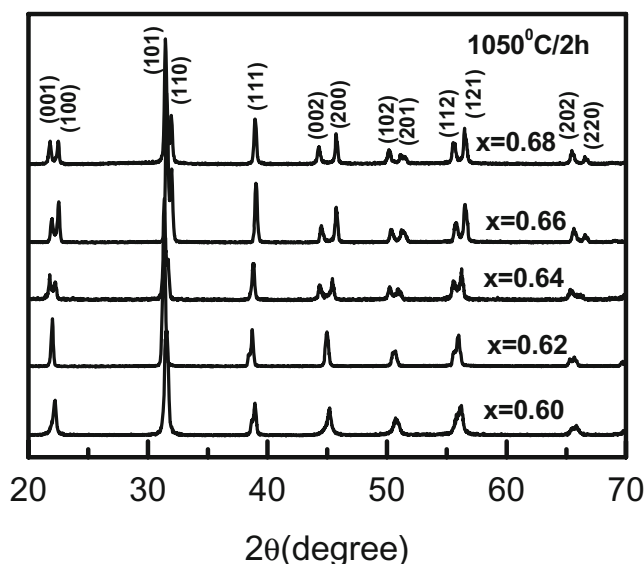
**Fig. 2** The relative amount of perovskite phase and crystallite size of powder with different milling times

$2\theta \approx 29.1^\circ$  corresponds to the  $\text{PbO}$  (111) peak is visible from 1–2 h. The pure perovskite phase has been obtained after milling 3 h. The relative amount of perovskite phase was determined using the formula (Eq. 1):

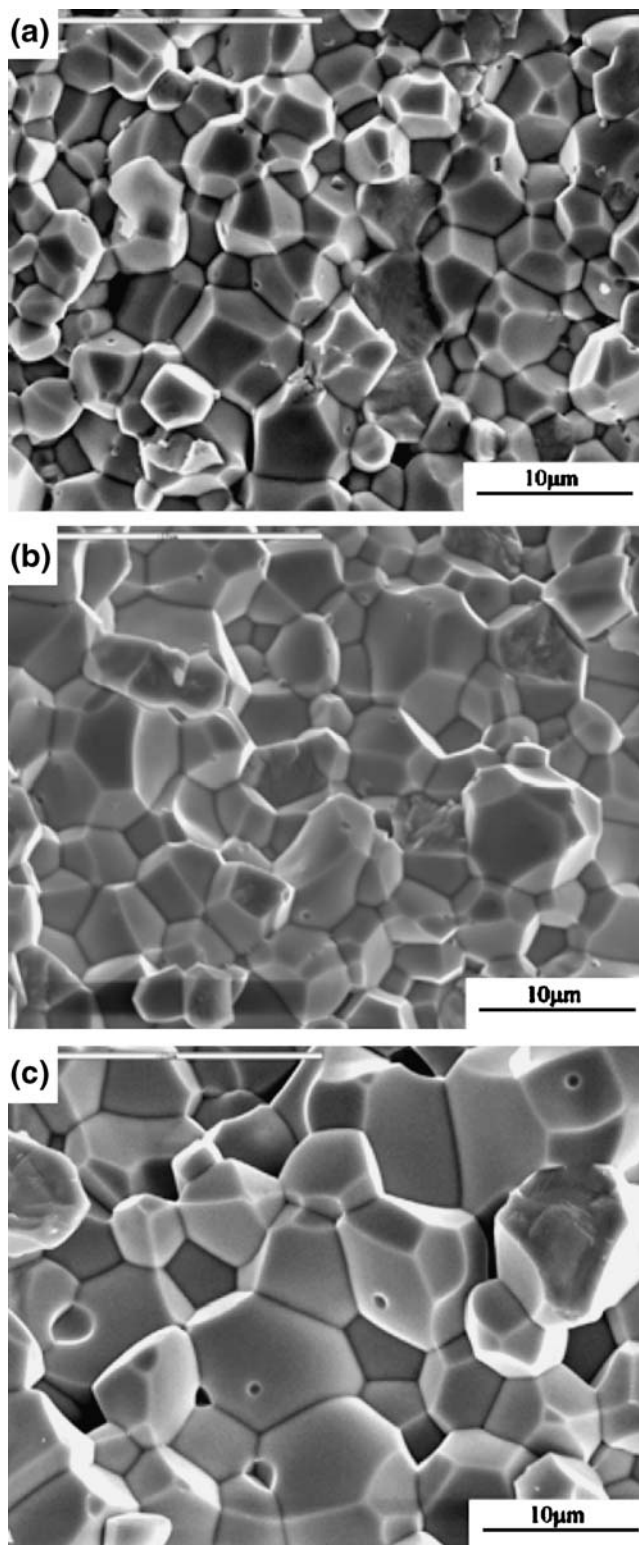
$$\text{perovskite}(\%) = \frac{I_{\text{perov}(110)}}{I_{\text{perov}(110)} + I_{\text{others}}} \times 100 \quad (1)$$

Figure 2 shows the relative amount of perovskite phase with those subjected to different times of milling. From Figs. 1 and 2, these results indicate that high-energy milling process is simple and effective in producing pure perovskite BS-PT ceramics. After milling 4 h, the relative amount of perovskite phase is more than 90%.

The variety of powder size with the milling time is also shown in Fig. 2. The crystallite size calculated from the



**Fig. 3** XRD profiles of BS-PT ceramics with  $x=0.60$ – $0.68$  sintered at 1050 °C for 2 h

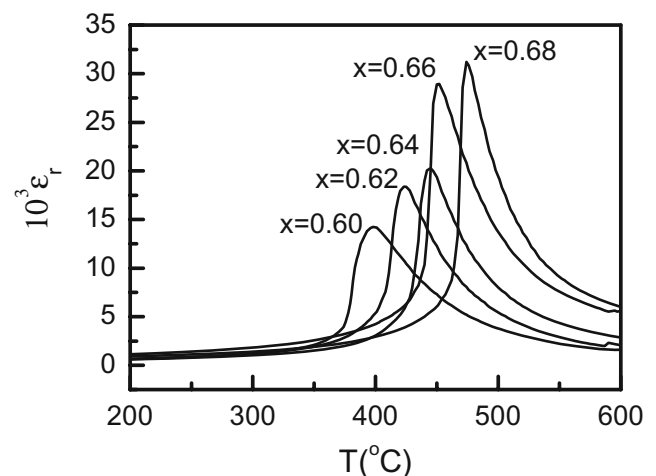


**Fig. 4** SEM photographs of the fresh fracture surface of ceramics sintered at (a) 1000 °C, (b) 1050 °C and (c) 1100 °C for 2 h

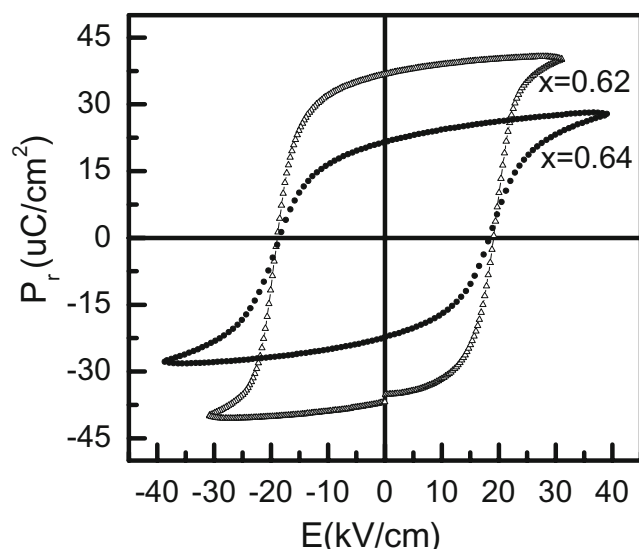
broadening of XRD peaks is 18–25 nm using Sherrer equation (Eq. 2):

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (2)$$

$\lambda$  is the wavelength of X-ray (1.5418Å),  $\theta$  is the Bragg angle.  $B$  is the line broadening, by reference to a standard, so that  $B^2 = B_M^2 - B_S^2$ , where  $B_M$  is the (full width at half-maximum) of BS-PT (110) peak and  $B_S$  is the FWHM of standard material in radians. Before 2 h, it is a dramatic refinement in particle size and some degree of amorphization of mixed oxides at the initial stage. We calculate the crystallite size of powder starting from 2 h because the Perovskite phase has been formed obviously. The time from 2 to 4 h is the period of the growing of crystallite and the size steadily increased, because solid-state reaction in the activated matrix leads to the formation of a crystalline phase under mechanical activation. From 4 to 6 h, the perovskite has been formed and the effect of fragmentation and refinement is greater, so that the dominant factor is to minimize crystallite size by collision and friction. Considering the increase of the surface defects, the trend is to make the crystallite's energy more stable by refinement. Prolonged mechanochemical treatment, up to 7 h, resulted in little further refinement in the average size. Because the milling time was much longer enough, the effect of impact was weakened and refinement reaches the limit result in the crystallite size was no longer decreased. In this process, localized heating at the points of collision may be a contributing factor, which may be sufficient to trigger a solid-state reaction on a nanometer scale, although this is not easily monitored [5]. Also the effects of high-pressure impact and internal stress at the collision points may have an important role in facilitating the reaction. All these



**Fig. 5** Variation of dielectric constant with temperature under 100 kHz for BS-PT for 60, 62, 64, 66 and 68 mol% PbTiO<sub>3</sub> ceramics sintered at 1050 °C for 2 h



**Fig. 6**  $P$ - $E$  hysteresis loops at room temperature for  $x=0.62$  and  $0.64$  of BS-PT

factors may be involved in the formation of the Perovskite BS-PT phase via the mechanochemical treatment.

### 3.2 Ceramics phase and microstructural study

Figure 3 shows the BS-PT ceramics XRD patterns of  $x=0.60\sim 0.68$  sintered at  $1050\text{ }^{\circ}\text{C}$  for 2 h. As  $x$  increased, the crystal symmetry of the perovskite cell changed from rhombohedral to tetragonal phases. The MPB, i.e., the rhombohedral–tetragonal phase boundary, was observed when  $x$  was in the vicinity of 0.64 and this results is in agreement with the study by Eitel et al. [3].

SEM photomicrographs are illustrated for each sintering condition for BS-PT with  $x=0.64$  in Fig. 4. Grain size determination for BS-PT with  $x=0.64$  resulted in average grain sizes of  $2\text{ }\mu\text{m}$ ,  $4\text{ }\mu\text{m}$  and  $7\text{ }\mu\text{m}$  for sintering temperatures of  $1000\text{ }^{\circ}\text{C}$ ,  $1050\text{ }^{\circ}\text{C}$  and  $1100\text{ }^{\circ}\text{C}$ , respectively. The grain size increased apparently with sintering temperature and uniform grain-size growth was observed. As compared with PS-PT ceramics prepared by E.Eitel. et al. [2], using traditional solid solutions, whose grain size is  $6\text{--}15\text{ }\mu\text{m}$ . Because of high-energy milling, the grain sizes of our ceramics were reduced so small and were at a half or third of the sizes in corresponding temperatures respectively which produced by traditional solid solutions.

### 3.3 Electrical characterization

Figure 5 shows temperature dependence of  $\epsilon_r$  at 100 kHz for BS-PT ceramics. As  $\text{PbTiO}_3$  contents increased from 60 to 68 mol%, The Curie temperature  $T_c$  shifted toward higher

temperature and the maximum dielectric constant increased. The  $T_c$  of 36% $\text{BiScO}_3$ –64% $\text{PbTiO}_3$  is  $448\text{ }^{\circ}\text{C}$ ; these results are closed to those reported by Y. Shimjo et al. [3].

Figure 6 shows the  $P$ - $E$  hysteresis loops at room temperature for  $x=0.62$  and  $0.64$  of  $(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$  ceramics. The remnant polarization  $P_r$  is  $37\text{ }\mu\text{C}/\text{cm}^2$  and the coercive field  $E_c$  is  $19\text{ kV}/\text{cm}$  for  $x=0.62$  BS-PT ceramic, while these values are  $22\text{ }\mu\text{C}/\text{cm}^2$  and the coercive field  $E_c$  is  $18\text{ kV}/\text{cm}$  for  $x=0.64$  BS-PT ceramic, respectively. The hysteresis curves of  $x=0.62$  is taller than that of  $x=0.64$ , namely the coercive field the remnant polarization  $P_r$  increases.

## 4 Conclusions

$(1-x)\text{BiScO}_3$ - $x\text{PbTiO}_3$  powders were synthesized from a mixture of the oxides  $\text{Bi}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{PbO}$  and  $\text{TiO}_2$  using a Fritsch P4™ vario-planetary ball milling system. The pure perovskite structure of BS-PT powder can well be obtained and the crystallite size of the powders was greatly reduced to  $18\text{--}25\text{ nm}$  after milling 4 h. The rhombohedral–tetragonal phase boundary was observed for the ceramics sintered at  $1000\text{--}1100\text{ }^{\circ}\text{C}$  when  $x$  was around 0.64 and  $3\text{--}7\text{ }\mu\text{m}$  grain size was obtained, which is smaller than traditional method. High Curie temperature ( $T_c$ ) and high dielectric constant can be obtained at the morphotropic phase boundary (MPB). As  $\text{PbTiO}_3$  contents increased from 60 to 68 mol%, The Curie temperature  $T_c$  shifted toward higher temperature and the maximum dielectric constant increased. The experimental results demonstrate that the high-energy ball milling process is a promising method to prepare BS-PT materials.

**Acknowledgements** This work was financially supported by the Ministry of Sciences and Technology of China through 973-project (Grant No. 2002CB613307), and the Natural Sciences Fund of China (Grant No. 50472052), and Key Science and Technology Research Project from the Ministry of Education of China (Grant No. 03155).

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