

The effect of ball-milling solvent on the decomposition properties of $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$

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Abstract

$\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ compound, which exhibits perovskite structure is a superconducting material. It can be a useful material for resistor when x value equals 0. The conducting behavior of BaPbO_3 is liable to be affected during aqueous processing. In contrast, the phenomenon is not found in $\text{Ba}(\text{Pb}_{0.8}\text{Bi}_{0.2})\text{O}_3$. The milling solvents of water and ethanol have different effect on the stability of perovskite phase. The decomposition of BaPbO_3 into BaCO_3 and PbO_2 is found when CO_3^{2-} ion exists. The partial substitution of Bi^{3+} stabilizes the perovskite phase. The stabilization and decomposition of perovskite phase explain the resistivity change with different milling solvents. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$; Perovskite; Solvent; Decomposition

1. Introduction

The structure of BaPbO_3 is cubic perovskite at room temperature which was reported by Hoppe and Blinne [1], Wagner and Binder [2,3], and Nitta et al. [4], who determined the lattice parameter $a = 4.27, 4.265$ and 4.267 \AA , respectively. Shannon and Bierstedt [5] reported that BaPbO_3 was found to be pseudocubic, with a unit cell and space group similar to those of the orthorhombic perovskites CaTiO_3 , CdSnO_3 and SrZrO_3 . Despite the fact that this is a normal valence compound, BaPbO_3 exhibits metallic conduction, with a room-temperature resistivity of $8.3 \times 10^{-4} \Omega \text{ cm}$ and a positive temperature coefficient from 70–420 K [4,6]. Wagner and Binder [2,3] found that BaPbO_3 was formed below 1000°C and decomposed into Ba_2PbO_4 and other compounds above 1000°C . BaPbO_3 ceramics are useful as a resistor of small temperature coefficient in resistivity [6].

Sleight et al. [7] first discovered superconductivity in $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ while studying the metal–semiconductor transition in the pseudo-binary system $\text{BaPbO}_3\text{–BaBiO}_3$. $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ was the first high temperature superconductor found which contains no transition metals. The semiconductor–metal transition occurred at $x = 0.35$, with T_c decreasing from 13 K at this composition

to 9 K at $x = 0.05$. Khan et al. [8] have investigated a semiconductor–metal phase transition in the $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ system with X-ray diffraction, magnetic induction and infrared absorption. Superconducting $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ can also be prepared by RF sputtering. Gilbert et al. [9] reported that a superconducting film was obtained by annealing the amorphous film made by sputtering.

In the present experiment, we study the effect of ball-milling solvent (water and ethanol) on the electric properties of $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ and the stability of BaPbO_3 phase. Water and ethanol are the popular solvents for ball-milling and grinding in fabricating ceramics. From the results of this experiment, use of different solvents (water and ethanol) will result in different electric properties of BaPbO_3 ceramics. The phenomenon is connected with the decomposition of BaPbO_3 phase. In contrast, the phenomenon is not found in $\text{Ba}(\text{Pb}_{0.8}\text{Bi}_{0.2})\text{O}_3$.

2. Experimental procedures

Raw materials of BaCO_3 , PbO_2 and Bi_2O_3 with purity higher than 99.5% were used. Both BaPbO_3 (composition A) and $\text{Ba}(\text{Pb}_{0.8}\text{Bi}_{0.2})\text{O}_3$ (composition B) were weighed according to the composition formula with an extra 5 mol% PbO_2 added for each composition. Milling process was conducted by yttrium stabilized ZrO_2 balls with either water or

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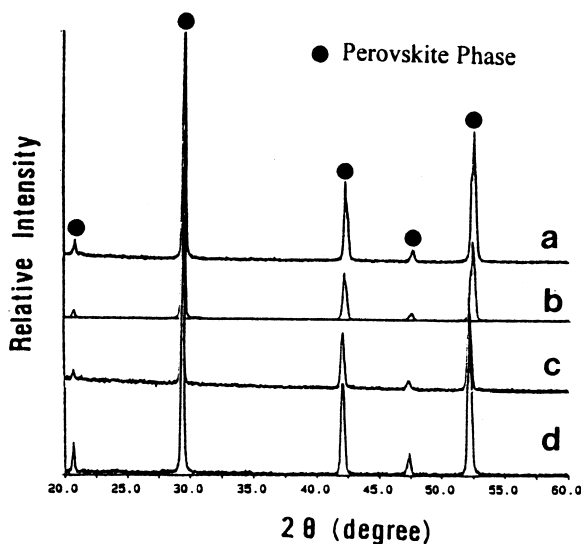


Fig. 1. XRD patterns of compositions A and B after calcining at 850°C for 2 h: composition A using (a) water and (b) ethanol as milling solvent, composition B using (c) water and (d) ethanol as milling solvent.

ethanol for 20 h. The mixture was dried and calcined in covered Al_2O_3 crucible and O_2 atmosphere at 850°C for 2 h. The calcined body was ground into powder by ball milling with solvent of water or ethanol. The purity of the ethanol is 95%. After drying, disk type sample of 5 mm diameter and 4 mm thickness was formed by pressing with 50 MPa pressure. The sample was sintered in a closed Al_2O_3 crucible at 900–1100°C for 30 min. Ohmic contact was made with Ag paste (SR5083, Namics Corporation, Japan) which was fired at 580°C for 10 min. Multimeter,¹ XRD² and SEM³ were used for resistance measurement, phase identification and microstructure observation, respectively.

3. Results and discussion

3.1. The effects of ball-milling solvent

Perovskite phase was formed after calcining at 850°C for 2 h for both composition A (BaPbO_3) and B ($\text{Ba}(\text{Pb}_{0.8}\text{Bi}_{0.2})\text{O}_3$), as shown in Fig. 1, where either water or ethanol was chosen as milling solvent. The resistivity of sintered body is shown in Fig. 2 for both compositions. The sintering conditions were at 900–1100°C for 30 min. The resistivity of composition B remains almost unchanged despite the kind of solvent used. In contrast, the resistivity of composition A increases to a relatively high value when water is used as milling solvent. Furthermore, the pressed disk melted when sintering was done at temperatures higher than 1050°C. These results indicate that the use of water produce phase

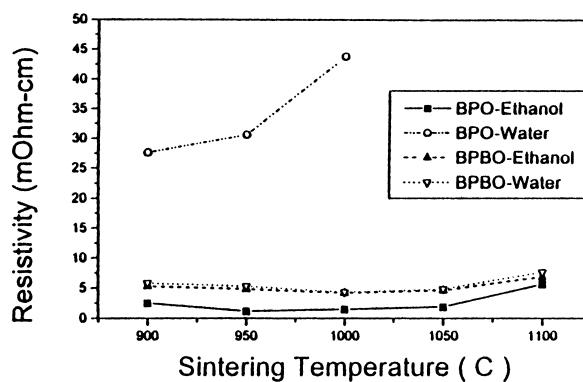


Fig. 2. The resistivity of sintered body for both compositions with different milling solvent (water and ethanol).

changes in composition A. The evidence can be found in the XRD patterns of specimens sintered at 1000°C for 0.5 h (Fig. 3). Composition B exhibits pure perovskite phase no matter what milling solvent was used. However, composition A possesses PbO and BaCO_3 phases in addition to perovskite when water was used as milling solvent. The existence of these second phases may explain the increase of resistivity as shown in Fig. 2. Fig. 4 shows the microstructures of specimens sintered at 1000°C for 0.5 h. The second phases render different microstructures as observed in Fig. 4(a) and Fig. 4(b). The EDS results of Fig. 4(a) are shown in Fig. 5(a) and Fig. 5(b). Fig. 5(a) is the EDS peaks of the segregation of PbO (point P) in Fig. 4(a), and Fig. 5(b) is the EDS peaks of matrix (point M) in Fig. 4(a). The PbO is liable to segregate when water is used. This phenomenon demonstrates that water has certain effect on the phase formation and electrical conductivity of composition A. The effect cannot be found when Pb is partially substituted by Bi (the composition B).

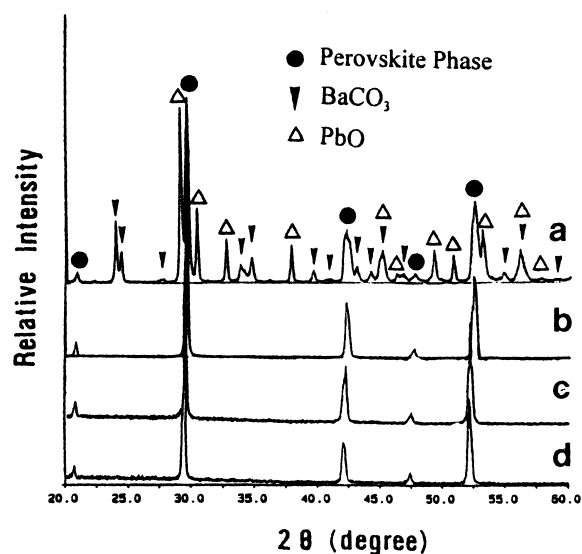


Fig. 3. XRD results of both compositions sintered at 1000°C for 0.5 h: composition A using (a) water and (b) ethanol as milling solvent, composition B using (c) water and (d) ethanol as milling solvent.

¹ 34401A Multimeter, Hewlett-Packard Company, USA.

² PW1700, Philips Electronic Instruments Co., Eindhoven, Netherlands.

³ Cam Scan, Cambridge Scanning Co., Cambridge, UK.

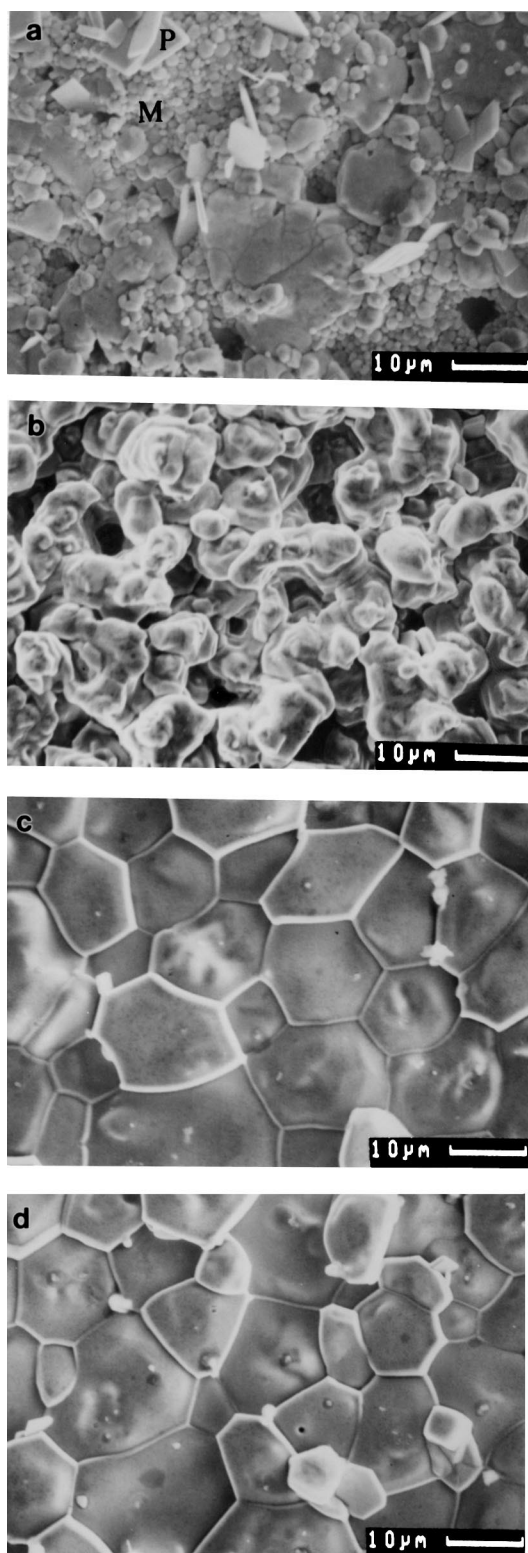


Fig. 4. Microstructures of both compositions sintered at 1000°C for 0.5 h: composition A using (a) water and (b) ethanol as milling solvent, composition B using (c) water and (d) ethanol as milling solvent.

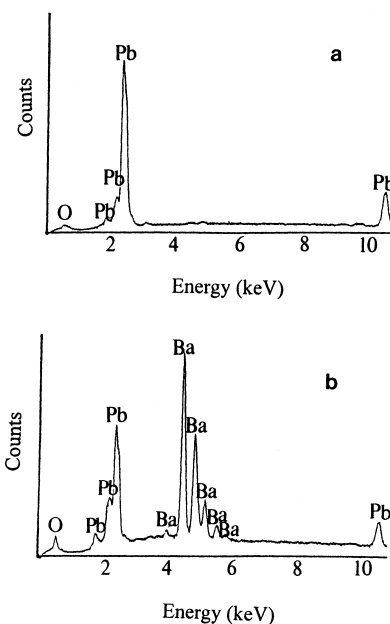


Fig. 5. (a) The EDS peaks of the segregation of PbO (point P) in Fig. 4(a); (b) the EDS peaks of matrix (point M) in Fig. 4(a).

After ball-milling in water, the calcined powder of composition A which has pure perovskite phase (Fig. 1) was changed to a combination of perovskite BaPbO_3 , BaCO_3 and PbO_2 as shown in Fig. 6(a). The decomposition of BaPbO_3 results in the high resistivity of the corresponding sintered specimens. In addition, the resulting PbO_2 phase

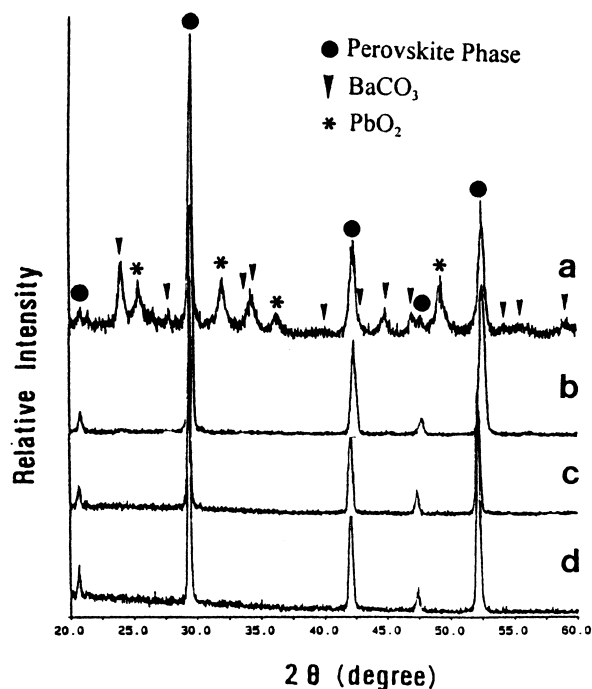


Fig. 6. XRD patterns of calcined powder after ball-milling with different solvent: composition A using (a) water and (b) ethanol as milling solvent, composition B using (c) water and (d) ethanol as milling solvent.

in the specimen transforms into PbO phase during sintering, which explains the melting of the sintered specimen when the sintering temperature is higher than 1050°C. The crystallization of PbO phase and its segregation on the surface after sintering causes the microstructure as shown in Fig. 4(a). When ethanol was used as milling solvent, no second phase was observed as was shown in Fig. 6(b). In the case of composition B, both water and ethanol solvent produce the same results. No obvious decomposition of perovskite phase was found. This implies that the substitution of Bi into Pb site stabilizes the perovskite crystal structure.

3.2. The decomposition of BaPbO₃

Phase decomposition affects the properties of BaPbO₃. It is important to study the decomposition of BaPbO₃ in order to obtain good conductivity material. Massicot PbO is a metastable phase which can transform into the stable litharge phase during either ball-milling or uniaxial grinding [10,11]. According to the experimental results, use of ethanol as milling solvent during the calcined powder grinding does not affect the BaPbO₃ perovskite phase in the sintered bodies. In contrast, if water was used as milling solvent in grinding the calcined powder the sintered bodies consist of BaCO₃, PbO and BaPbO₃ phases. It can then be concluded that water plays an important role on the decomposition of BaPbO₃ into BaCO₃ and PbO₂.

To elucidate the decomposition process, three experiments were conducted. First, BaPbO₃ powder was placed in deionized water that had been boiled for 2 h and then cooled down. The mixture of water and BaPbO₃ powder was kept in vacuum for one month. After drying at 120°C, the crystal phase of the treated powder was determined using XRD analysis. The reason for boiling deionized water for 2 h and keeping the water in vacuum is to dry out CO₂ and to maintain the near zero CO₂ content in the water. The XRD result (Fig. 7(a)) shows that only the BaPbO₃ perovskite phase exists in the powder.

Secondly, BaPbO₃ powder was kept in CO₂ atmosphere (about 1 atm) at 120°C for one month. The XRD result shown in Fig. 7(b) also exhibits only one BaPbO₃ phase. Thirdly, BaPbO₃ powder was soaked in deionized water for two weeks in open air. During the soaking period, formation of white powder was observed. The crystal phases of the soaked powder were identified to be BaPbO₃, PbO₂ and BaCO₃ (Fig. 7(c)).

Based on these three experiments, coexistence of the water and CO₂ is concluded to be the reason of BaPbO₃ phase decomposition. Existence of either water alone or CO₂ alone did not produce decomposition of BaPbO₃. The decomposition may be expressed by the following reactions:

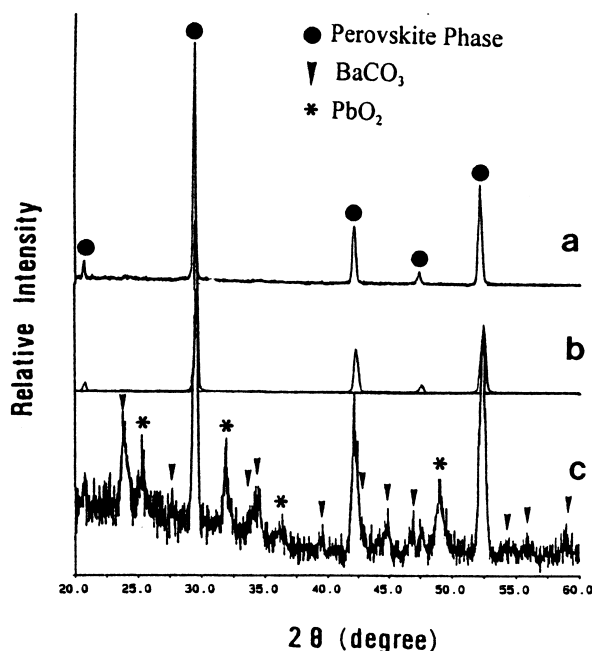
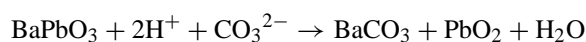
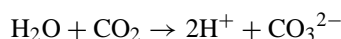


Fig. 7. (a) XRD pattern of BaPbO₃ after keeping in preheated water in vacuum for one month; (b) XRD pattern of BaPbO₃ after keeping in CO₂ atmosphere (about 1 atm) at 120°C for one month; (c) XRD pattern of BaPbO₃ after keeping in water for two weeks in air.

4. Conclusions

1. The resistivity of BaPbO₃ changes when water not ethanol is used as milling solvent. The partial decomposition of BaPbO₃ is the reason of the change of properties.
2. Ba(Pb_{0.8}Bi_{0.2})O₃ shows no change of the properties when either water or ethanol is used as milling solvent. The partial substitution of Bi into Pb site stabilizes the perovskite phase.
3. The decomposition of BaPbO₃ is attributed to the coexistence of water and CO₂. Either water or CO₂ alone will not produce the decomposition of the BaPbO₃ phase.

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