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Short communication

Solid state metathesis synthesis of $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$

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Abstract

A solid state metathesis approach has been applied to synthesize perovskite oxides such as $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$, these were characterized by powder XRD, IR and energy dispersive spectra (EDS). Potassium titanium oxalate and metal chlorides are used as the starting materials. X-ray analysis shows the formation of a single phase with tetragonal structure for $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and a monoclinic structure for $Na_{0.5}Bi_{0.5}TiO_3$. The Infrared spectra of these compounds show the characteristic band due to Ti–O octahedron for all the compounds. The EDS spectra show the relative ratio of the metal ions. The morphology of synthesized compounds was obtained from SEM measurements.

Keywords: B. X-ray methods; D. $BaTiO_3$; D. Perovskites; Metathesis

1. Introduction

Perovskite oxides of general formula ABO_3 (for example, $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ etc.) have attracted considerable attention due to their outstanding applications in various devices [1–6]. The conventional solid state reaction between reactant oxides requires repeated cycles of milling and calcinations at high temperatures of ≈1400 °C to obtain phase homogeneity. The powders obtained from solid state reactions are characterized by agglomerated grains of unequal size and contaminated with impurities. Solution routes such as hydrolysis and sol–gel methods provide molecular level mixing of reactants, homogeneous distribution of dopant ions and control over the particle size of the product at temperatures lower than those employed in solid state reactions. Although, sol–gel method has many advantages, reactions which give homogeneous products at lower temperatures employing inexpensive reactants are still interesting and require considerable attention. For instance, materials such as $BaTiO_3$, $La_{0.5}Ba_{0.5}MnO_3$ [7,8], $Na_{0.5}Bi_{0.5}TiO_3$ [9], $Pb(Zr_{0.5}Ti_{0.5})O_3$ and $PbZrO_3$ [10,11] have been prepared by solvo/hydrothermal and sol–gel methods. Solid state metathesis (SSM) reactions have been used to synthesize different types of materials at relatively low temperatures and with better purity [12–14]. In the present investigation, we report the preparation of $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ (here after referred as BT, PT, KBT and NBT respectively) employing potassium titanium oxalate as one of the reactant by SSM reactions at relatively low temperatures than reported [5,15–17].

2. Experimental

Potassium titanium oxalate, $BaCl_2$, $PbCl_2$, NaCl (all SD Fine Chemicals-99%) and $Bi(NO_3)_3$ (Merck-99%) were used as starting materials as received. For the preparation of BT sample, stoichiometric amounts of Potassium titanium oxalate and barium chloride were ground thoroughly using spectral grade acetone. The resultant material was heated in a muffle furnace at 650 °C for 14 h and furnace cooled. The product thus obtained was washed with double distilled water several times to remove KCl and then dried on a hot plate. PT, KBT and NBT were prepared in similar way. In the preparation of KBT and NBT, $BiCl_3$ was prepared by dissolving $Bi(NO_3)_3$ in

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concentrated HCl and evaporated to dryness to expel excess HCl. NaCl was used as reactant during the preparation of NBT.

The X-ray diffractograms of the washed out powders were recorded at room temperature on a Siemens D-5000 powder X-ray diffractometer using Ni filtered monochromatic Cu-Kα radiation of wavelength 1.5406 Å. The scan rate was 5.4°/min in the range $2\theta = 10–80°$. Infrared spectra were recorded in the form of KBr pellets in the wave number range 1500–400 cm^{-1} using JASCO IR-5300 spectrometer. SEM-EDS images were recorded on the HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM). Transmission electron microscopy (TEM) images were recorded on a TECNAI FE1 FE12 transmission electron microscope.

3. Results and discussion

3.1. Powder XRD

The powder XRD patterns of products obtained before and after dissolving in distilled water were recorded. In the case of BT sample, the powder XRD of the product obtained before dissolving in distilled water was characterized by d-lines belonging to BT and KCl. Similarly, the powder XRD of PT, KBT and NBT samples before dissolving in distilled water were characterized by d-lines of corresponding target samples and KCl. The high lattice energy by-product (KCl) facilitates the formation of the target product in a metathetic pathway. Fig. 1 shows the powder X-ray diffractograms of products after washing with distilled water. The d-lines of BT, PT, KBT and NBT were found to be similar to those reported earlier and free from undesirable crystalline phases. The powder XRD patterns of all the samples were examined with corresponding JCPDS data [18]. A comparison of the powder patterns of investigated samples with the corresponding phases of each material suggest that BT, PT and KBT samples crystallize in tetragonal lattice where as NBT sample crystallizes in monoclinic lattice. The powder XRD patterns of KBT and NBT samples look similar in spite of their different crystal structures. A close examination of powder patterns of these two samples shows that the 1 0 2 and 1 0 1 lines of NBT appear together as one line while the 1 0 1 and 1 1 0 lines of KBT were well separated [JCPDS File Nos.

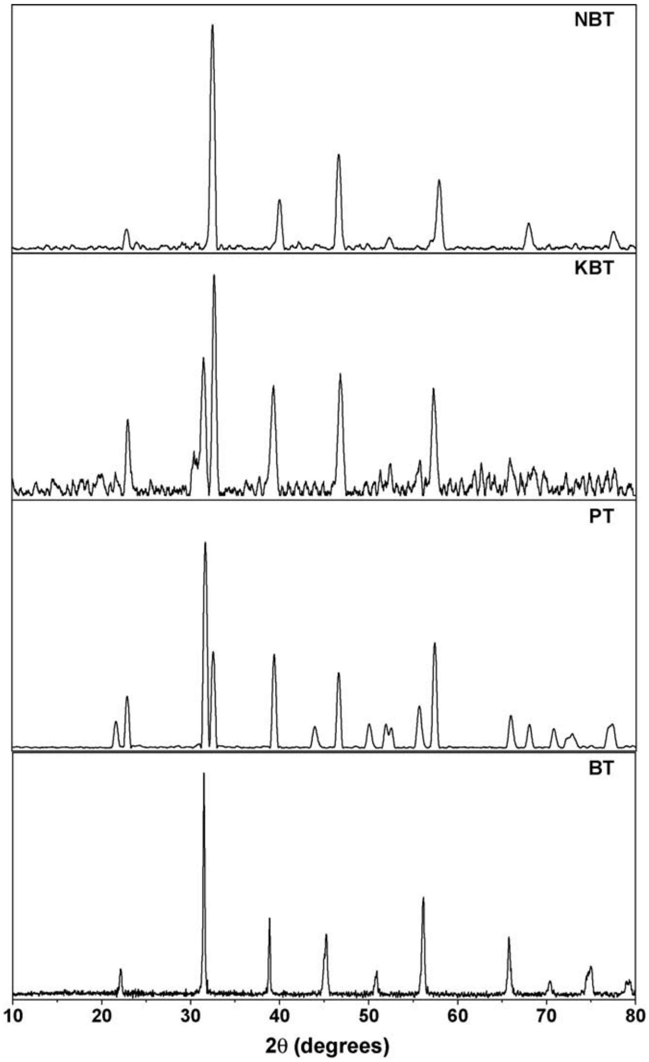

Fig. 1. Powder XRD patterns of BT, PT, KBT and NBT.

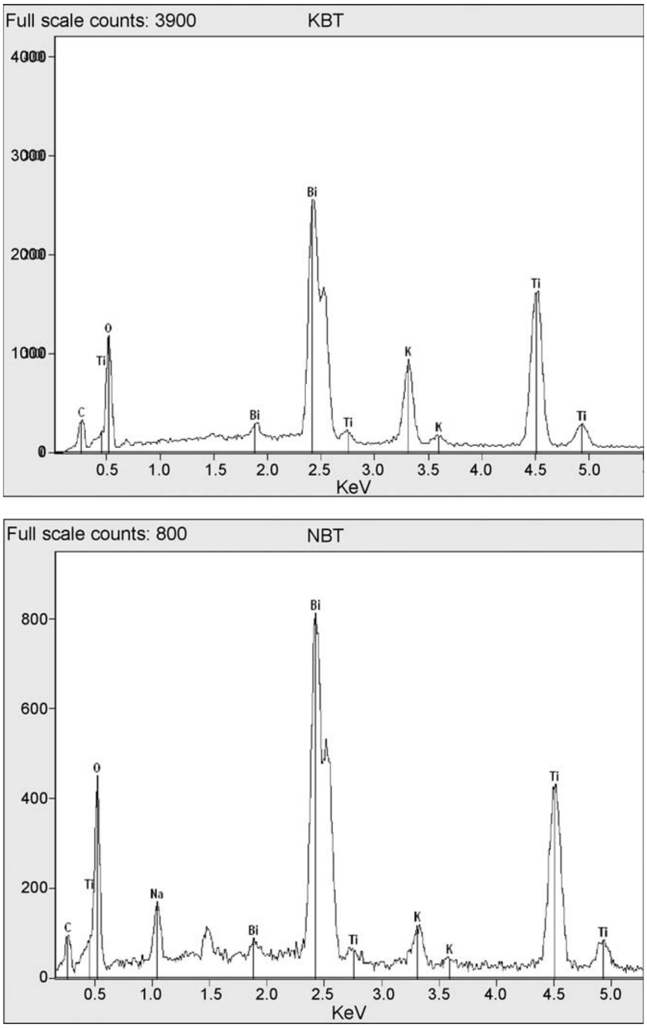

Fig. 2. EDS spectra of KBT and NBT.

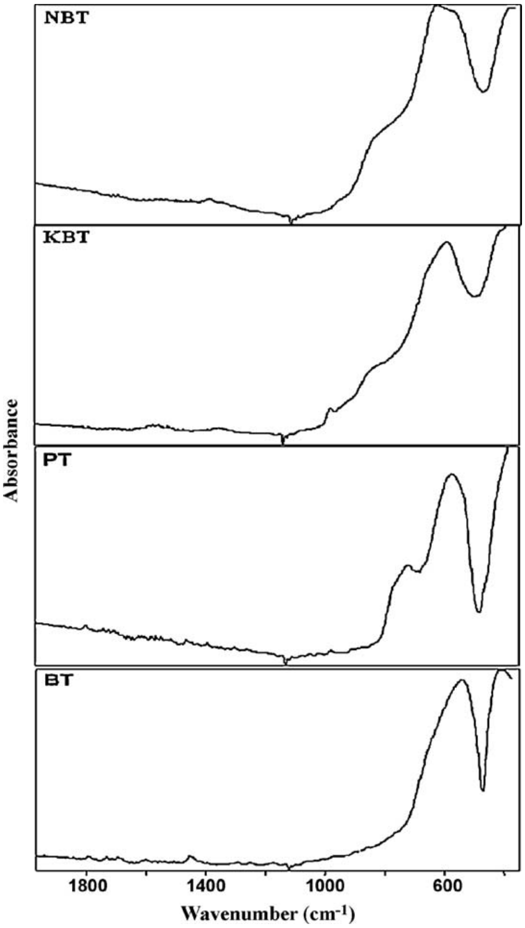

Fig. 3. IR spectra of BT, PT, KBT and NBT.

36-0339, 46-0001]. The observed powder XRDs of NBT and KBT were in accordance with this observation (Fig. 1). Further confirmation on the composition of these materials was obtained from EDS analysis. The reported temperatures of preparation of BT, PT, KBT and NBT by conventional solid state method were 1150, 800, 1000 and 1150 °C respectively [5,15–17]. Mandal et al. have reported the preparation of BT and PT samples in two steps. The precursor Li_2TiO_3 was first prepared by solid state method using Li_2CO_3 and TiO_2 at 1000 °C for 24 h. This precursor was treated with $BaCl_2$ (at 900 °C/24 h) and $PbSO_4$ (at 810 °C/12 h) to obtain BT and PT in a metathetic pathway [12]. In the present investigation we have prepared BT, PT, KBT and NBT samples in a single step by metathesis reaction at much lower temperature than reported using potassium titanium oxalate as precursor. The XRD patterns of all the compounds were least square fitted to deduce the unit cell parameters. The unit cell parameters thus obtained were very close with corresponding JCPDS data [18].

3.2. EDS

Energy dispersive spectra (EDS) were recorded for all the products obtained after washing with double distilled water. From these spectra, the ratio of Ba or Pb to Ti was found to be 1 for BT or PT samples. In the case of KBT, the ratio of K:Bi:Ti was found to be 0.5:0.5:1. However, in the case of NBT sample, a small peak corresponding to K was observed. The ratio of K:Na:Bi:Ti in NBT sample was found to be 0.06:0.44:0.5:1.0. This impurity of K was due to the incomplete exchange of sodium ions with

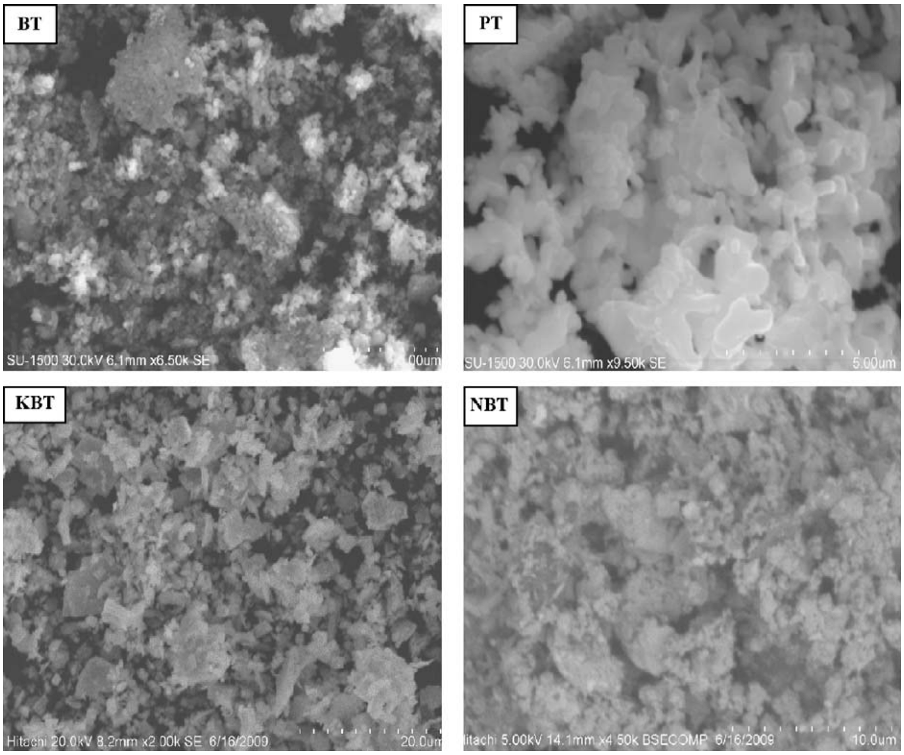

Fig. 4. SEM micrographs of BT, PT, KBT and NBT.

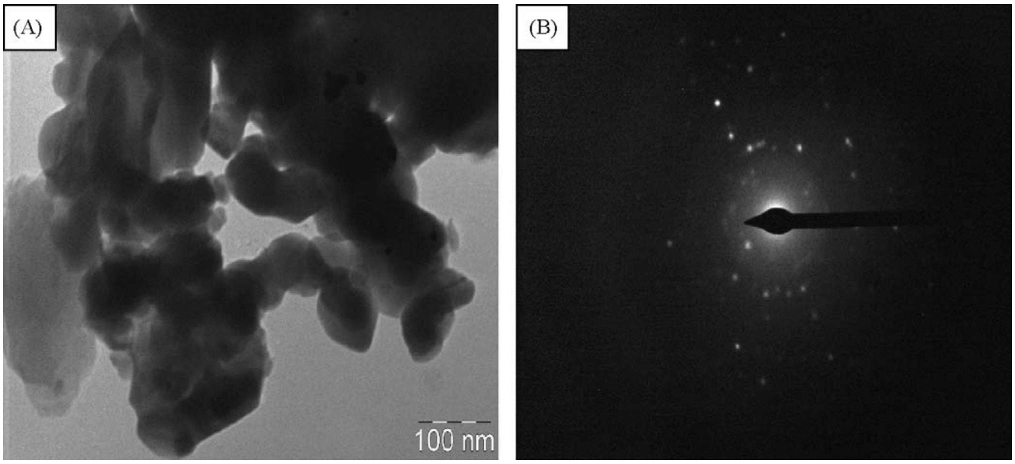

Fig. 5. (A) Low magnification TEM image of BT and (B) SAED pattern of BT.

potassium ions. The EDS spectra of NBT and KBT are shown in Fig. 2.

3.3. IR spectra

The infrared spectra of all the synthesized compounds have been recorded in the range 4000–450 cm^{-1}. The compounds did not exhibit any bands above 1000 cm^{-1} (Fig. 3). A single broad band was observed for all the compounds in the range 540–610 cm^{-1}. A band centered at 545, 600, 580 and 600 cm^{-1} was observed for BT, PT, KBT and NBT compounds respectively which characterizes the stretching vibration of Ti–O [19,20].

3.4. SEM and TEM

The surface morphology of all the prepared compounds was studied by SEM measurements. All the SEM diagrams exhibit agglomerated particles of different sizes. Fig. 4 shows the SEM micrographs of all the compounds. It is seen clearly that the aggregate particles of BT sample consists of many small spherical particles whereas the aggregate particles of PT, KBT and NBT samples consists of many small particles of different shapes. Fig. 5 shows the TEM image and SAED pattern of BT sample. The TEM image of BT sample also support the agglomeration of particles with particle size lying in the range of 50–80 nm.

4. Conclusions

Phase pure BT, PT, KBT and NBT have been successfully synthesized by solid state metathesis reaction at lower temperature compared to the ceramic method. From X-ray diffraction, it was observed that BT, PT and KBT samples crystallize in tetragonal lattice where as NBT sample crystallize in monoclinic lattice. The infrared spectroscopy gave a single broad band corresponding to Ti–O octahedron. SEM and TEM measurements of the morphology of the synthesized samples showed agglomeration.

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References

[1] K. Uchino, Ferroelectric Devices, Marcel Dekker, Inc., New York, 2000.
[2] G.H. Haertling, Ferroelectric ceramics: history & technology, J. Am. Ceram. Soc. 82 (4) (1999) 797–818.
[3] D. Hennings, Barium titanate based ceramic materials for dielectric use, Int. J. High Technol. Ceram. 3 (2) (1987) 91–111.
[4] L.E. Cross, Relaxorferroelectrics: an overview, Ferroelectrics 151 (1) (1994) 305–320.
[5] Y. Li, W. Chen, J. Zhou, Q. Xu, H. Sun, M. Liao, Dielectric and ferroelectric properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3$-$K_{0.5}Bi_{0.5}TiO_3$ ferroelectric ceramics, Ceram. Int. 31 (1) (2005) 139–142.
[6] Y. Wang, G. Xu, X. Ji, Z. Ren, W. Weng, P. Du, G. Shen, G. Han, Room-temperature ferromagnetism of Co-doped $Na_{0.5}Bi_{0.5}TiO_3$: diluted magnetic ferroelectrics, J. Alloys Compd. 475 (1–2) (2008) L25–L30.
[7] R.I. Walton, Subcritical solvothermal synthesis of condensed inorganic materials, Chem. Soc. Rev. 31 (4) (2002) 230–238.
[8] J. Spooren, A. Rumplecker, F. Millange, R.I. Walton, Subcritical hydrothermal synthesis of perovskite manganites: a direct and rapid route to complex transition-metal oxides, Chem. Mater. 15 (7) (2003) 1401–1403.
[9] Y. Wang, G. Xu, L. Yang, Z. Ren, X. Wei, W. Weng, P. Du, G. Shen, G. Han, Hydrothermal synthesis and characterization of $Na_{0.5}Bi_{0.5}TiO_3$ microcubes, Ceram. Int. 35 (4) (2009) 1657–1659.
[10] C. Liu, B. Zou, A.J. Rondinone, Z.J. Zhang, Sol–gel synthesis of free-standing ferroelectric lead zirconate titanate nanoparticles, J. Am. Chem. Soc. 123 (18) (2001) 4344–4345.
[11] M. Panda, R. Seshadri, J. Gopalakrishnan, Preparation of $PbZrO_3$/ASO_4 composites (A = Ca, Sr, Ba) and $PbZrO_3$ by metathetic reactions in the solid state: metathetic exchange of divalent species, Chem. Mater. 15 (7) (2003) 1554–1559.
[12] T.K. Mandal, J. Gopalakrishnan, From rocksalt to perovskite: a metathesis route for the synthesis of perovskite oxides of current interest, J. Mater. Chem. 14 (8) (2004) 1273–1280.
[13] P. Parhi, V. Manivannan, Novel microwave initiated solid-state metathesis synthesis and characterization of lanthanide phosphates and vanadates, LMO_4 (L = Y, La and M = V, P), Solid State Sci. 10 (8) (2008) 1012–1019.
[14] V. Thangadurai, C. Knittlmayer, W. Weppner, Metathetic room temperature preparation and characterization of scheelite-type ABO_4 (A = Ca, Sr, Ba, Pb; B = Mo, W) powders, Mater. Sci. Eng. B 106 (3) (2004) 228–233.

[15] N. Vittayakorn, Dielectric properties of bismuth doped barium titanate ($BaTiO_3$) ceramics, J. Appl. Sci. Res. 2 (12) (2006) 1319–1322.

[16] G.B. Kumar, S. Buddhudu, Spectral analysis of $PbTiO_3$: Sm^{3+} or Dy^{3+} ferroelectric ceramics, Ferroelectrics 361 (1) (2007) 77–83.

[17] P.V.B. Rao, E.V. Ramana, T.B. Sankaram, Electrical properties of $K_{0.5}Bi_{0.5}TiO_3$, J. Alloys Compd. 467 (1–2) (2009) 293–298.

[18] JCPDS File Nos. 05-0626, 06-0452, 36-0339, 46-0001.

[19] J.T. Last, Infrared-absorption studies on barium titanate and related materials, Phys. Rev. 105 (6) (1957) 1740–1750.

[20] J. Liu, H. Wang, Y. Hou, M. Zhu, H. Yan, M. Yoshimura, Low-temperature preparation of $Na_{0.5}Bi_{0.5}TiO_3$ nanowhiskers by a sol–gel-hydrothermal method, Nanotechnology 15 (7) (2004) 777–780.