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Characterization of $BiFeO_3$ nanopowder obtained by mechanochemical synthesis

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Abstract

Bismuth ferrite nanopowders have been obtained by mechanochemical synthesis. The materials were characterized by high resolution electron microscopy, X-ray diffraction and NIR Raman scattering. The XRD pattern of the powder consists of reflections, characteristic of $BiFeO_3$ perovskite structure, superimposed on broad maxima that can be ascribed to an amorphous/disordered phase. The analysis of the two broad bands at low 2θ angle yields mean distances of about 3 and 1.8 Å which may be related to Bi—O and Fe—O bonds, respectively. The powder consists of loosely packed grains with a broad distribution of sizes between a few nm and 45 nm. The grains of sizes larger than about 30 nm exhibit well-developed crystalline structure.

Keywords: $BiFeO_3$; Milling; Electron microscopy; X-ray method

1. Introduction

Multiferroic materials are characterized by a coexistence of at least two various kinds of long range ordering: ferroelectric (or antiferroelectric), ferromagnetic (or antiferromagnetic), which in addition can be combined with ferroelastic properties. Under an external magnetic field, such materials would switch electric polarization while an external electric field would change magnetization, depending on the coupling between the various characteristic order parameters. Those materials were proposed by Pierre Curie more than 100 years ago and attracted a great attention during the 1960s and 1970s due to the interest in the understanding of some fundamental physics.[1,2] Recently, multiferroism is the subject of intensive investigation because multiferroic materials potentially offer a whole range of new applications, including the emerging field of spintronics, new data-storage media, and multiple-state memories. A great attention has attracted bismuth ferrite, which shows ferroelectric and antiferromagnetic properties at room temperature. Its phase transition temperatures are high ($T_N = 370\,°C$ and $T_C = 810\,°C$), which makes it very attractive from application point of view. Moreover, enhancement of polarization and related properties in heteroepitaxially constrained films of $BiFeO_3$ has been reported recently.[3]

Bismuth ferrite has perovskite structure and this group usually is fabricated by convention solid state reaction at high temperatures. Other preparation routes need also high temperature treatment during or after deposition. Recently, several attempts have been made in order to prepare nanosized $BiFeO_3$.[4–6] However, it is still a challenge to prepare it at room temperature. This issue is even more important for compounds contenting volatile elements at high temperature like bismuth. Recently, it was demonstrated that simple perovskite compounds (like $BaTiO_3$, (K, Na)NbO_3, $PbTiO_3$) can be obtained at room temperature via mechanochemical synthesis.[7–10] However, no such work has been reported for $BiFeO_3$. Formation of the product phase in solid state reaction proceeds usually at the interfaces of the reactant and the growth of the product phase requires a diffusion of reactant phases atoms through a product barrier layer that prevents further reaction.[9] High energy milling reduces the particle sizes (increases in the contact area of reactant particles) and the reaction can proceed without the diffusion trough the product layer, i.e. during mechanochemical synthesis the solid state reaction occurs at lower temperatures.

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This work was focused on preparation of $BiFeO_3$ nanopowder at room temperature. Mechanochemical synthesis was successfully applied for fabrication of perovskite phase without any additional thermal treatment. Structural investigations of the nanograins were done by XRD, high resolution electron microscopy, as well as Raman spectroscopy.

2. Experimental

Commercially available oxides (Bi_2O_3 and Fe_2O_3 purchased from Aldrich, 99% purity) were used as starting materials. Mechanochemical synthesis was performed under normal atmosphere using a SPEX 8000 Mixer Mill. The starting oxides in stoichiometric ratio were milled for different period between 5 and 120 h. The crystallographic structure of obtained material was proved by X-ray powder diffraction. XRD were performed using an X-ray powder diffractometer with Co Kα radiation. The detailed XRD analysis was done on the diffractogram obtained with a Siemens D-500 diffractometer with Cu Kα radiation using DHN-PDS-1995 program for data reduction. Further investigations were done by high resolution electron microscopy (HREM), and Raman scattering. The structure of the powder was studied by TEM with Philips CM-20 TEM working at the accelerating voltage of 200 kV. Raman spectra were recorded with Horiba Jobin Yvon spectrometer in backscattering geometry. The samples were excited with 632.8 nm light from an He–Ne laser. Power of the incident beam was 12 mW. $BiFeO_3$ samples in the form of nanopowder were used in the experiment. All Raman spectra were obtained at room temperature.

3. Results and discussion

Fig. 1 shows the θ–2θ XRD patterns of the starting oxides and mixture after various time of milling. After 10 h milling, almost all of the XRD peaks of the staring materials have disappeared. After 70 h of synthesis, several relatively sharp diffraction peaks appear. They correspond to the perovskite structure of $BiFeO_3$. The appearance of these diffraction peaks prove that $BiFeO_3$ can be grown at room temperature without any additional crystallization step.

The direct synthesis of perovskite materials from respective oxides by mechanical milling yields an asymmetric distribution of grain sizes with the mean size being dependent mainly on the milling time. For detailed characterizations, powders obtained after 120 h of milling have been chosen. Their detailed analysis of XRD (see Fig. 2) has shown that the relatively sharp diffraction reflections are superimposed on two broad maxima. All reflections are characteristic of perovskite structure of $BiFeO_3$. The broad bands can be ascribed to an amorphous/disordered phase. The additional scattering appears distinctly in two ranges of the 2θ angle (about 25–35 and 40–60°) and the analysis of the two broad bands yield mean distances of about 3 and 1.8 Å. The spacings may be related to Bi–O and Fe–O bonds, respectively.[11]

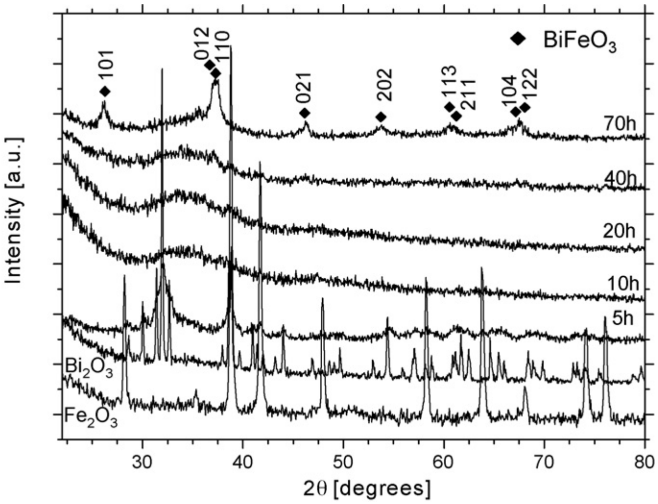

Fig. 1. XRD patterns (Co Kα) of starting oxides and $BiFeO_3$ nanopowder after different stages of synthesis.

Fig. 3 presents TEM images of the 120 h milled sample. The powder forms irregular agglomerates with lateral size of 100–150 nm. Detailed analysis made at high resolution showed that these grains are built as loosely packed structures composed of nanocrystallites. $BiFeO_3$ nanograins exhibit core/shell structure. The inner part of the grains has well-developed crystalline structure. For oval grains, it is difficult to specify the direction of the incident electron beam with respect to the basic translation vectors of the lattice. Therefore, we analyzed the spacing of sets of parallel fringes due to the imaging of various crystallographic planes. The calculated spacing corresponds to the (0 0 1) crystallographic planes of the perovskite structure (see Fig. 3). All crystallites are surrounded by thin layer of 1–2 nm thickness which does not posses crystallographic order. This structurally disordered (or amorphous) shell with broken bonds and/or different electron densities on the ions is apparent as broad bands in the XRD spectrum of the nanopowder (Fig. 2).

Fig. 4 has presented a Raman spectrum for nanopowder of $BiFeO_3$ obtained after 120 h synthesis. According to factor group analysis, rhombohedral R3*c* structure gives 13 Raman active modes: $4A_1 + 9E$.[12,14] Our Raman spectrum contains

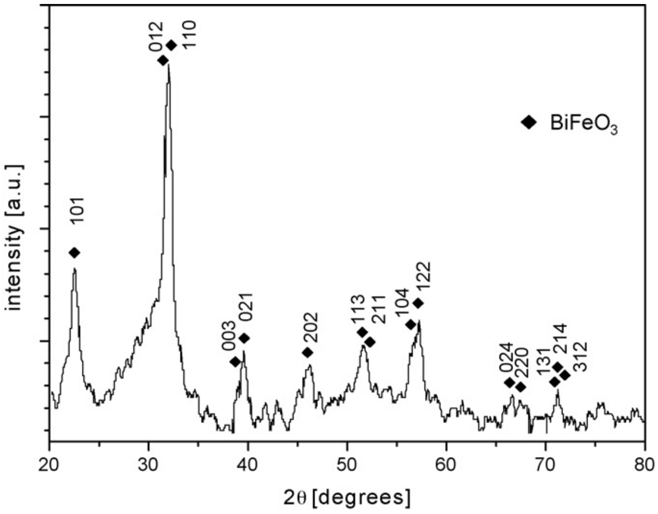

Fig. 2. XRD patterns $BiFeO_3$ nanopowder, after 120 h of mechanochemical synthesis, obtained with Cu Kα radiation.

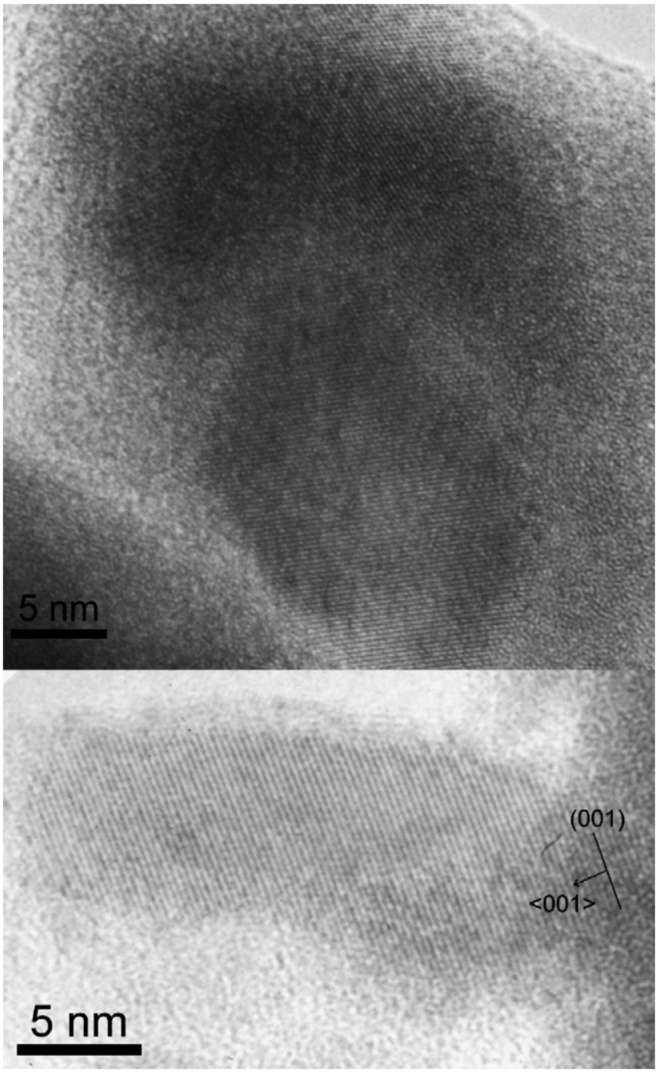

Fig. 3. TEM images of $BiFeO_3$ powder after 120 h of mechanochemical synthesis.

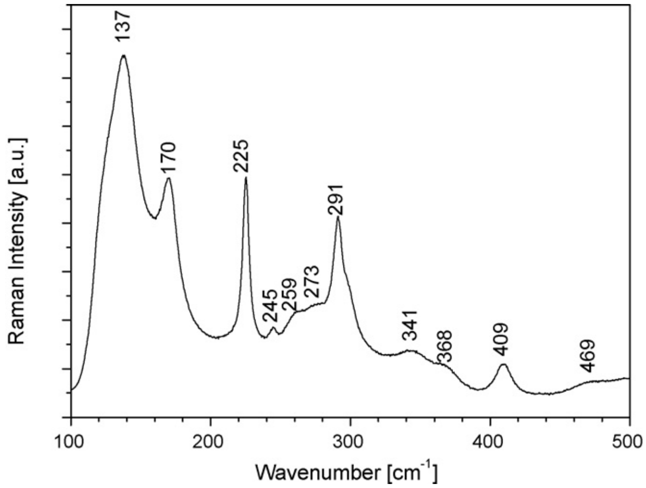

Fig. 4. Raman spectrum of $BiFeO_3$ nanopowders after 120 h of mechanochemical synthesis.

much less lines in comparison to spectrum of $BiFeO_3$ single crystal.[12] Besides, the lines are shifted to lower frequencies and some of them are broadened. There are two reasons which should be taken in account: possible strain existing in nanoparticles and relatively large amount of disordered/amorphous volume. Mechanochemical synthesis introduces usually strain,[13] which can be also present in $BiFeO_3$ nanopowders. The Raman spectra of $BiFeO_3$ nanopowder are more similar to those obtained recently for epitaxial films[14] than for single crystals. The thin films are deposited on substrates, and due to lattice and thermal mismatch, they are strained. On the other hand, presence of amorphous materials results usually in broadening of line widths or sometimes merging neighbour lines to broad band.

4. Conclusions

Mechanochemical synthesis is a method in which the solid state reaction proceeds due to high mechanical energy impact. The method has the advantage over the conventional solid state synthesis since it occurs at room temperature and results in a product of particle size in nanometer scale. It was demonstrated that bismuth ferrite nanopowders can be successfully fabricated by this method directly at room temperature. The X-ray diffraction showed the perovskite structure of the powder. It was found that: (1) the powder consists of loosely packed grains with a broad distribution of sizes between a few nm and 45 nm, (2) the grains have core/shell structure and (3) grains of sizes larger than about 30 nm exhibit well-developed crystalline structure. Compared with traditional ceramics and single crystalline $BiFeO_3$, the core/shell structure of nanopowder has influence on its Raman spectra.

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References

1. Smolenskii, G. A., Bokov, V. A., Isupov, V. A., Krainik, N. N. and Nedlin, G. H., Magnetically ordered ferroelectrics. *Helvetica Physica Acta*, 1968, **41**, 1187–1198.
2. Smolenskii, G. A. and Chupis, I. E., Ferroelectromagnets. *Sov. Phys. Usp.*, 1982, **25**, 475–493.
3. Wang, J., Neaton, J. B., Zheng, H., Nagarajan, V., Ogale, S. B., Liu, B. *et al.*, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures. *Science*, 2003, **299**, 1719–1722.
4. Fruth, V., Berger, D., Matei, C., Ianculescu, A., Popa, M., Tenea, E. *et al.*, Preparation and characterization of $BiFeO_3$ nanopowders. *J. Phys. IV*, 2005, **128**, 7–11.
5. Ghosh, S., Dasgupta, S., Sen, A. and Maiti, H. S., Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route. *J. Am. Ceram. Soc.*, 2005, **88**, 1349–1352.
6. Cheng, J., Chen, C., Yu, S., Che, L. and Meng, Z., Hydrothermal synthesis of perovskite bismuth ferrite crystallites. *J. Cryst. Growth*, 2006, **291**, 135–139.
7. Van Hal, H. A. M., Groen, W. A., Maassen, S. and Keur, W. C., Mechanochemical synthesis of $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ dielectric ceramics. *J. Eur. Ceram. Soc.*, 2001, **21**, 1689–1692.
8. Rojac, T., Kosec, M., Malic, B. and Holc, J., Mechanochemical synthesis of $NaNbO_3$, $KNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$. *Sci. Sintering*, 2005, **37**, 61–67.

9. Stojanovic, B. D., Simoes, A. Z., Paiva-Santos, C. O., Jovalekic, C., Mitic, V. V. and Varela, J. A., Mechanochemical synthesis of barium titanate. *J. Eur. Ceram. Soc.*, 2005, **25**, 1985–1989.
10. Szafraniak, I., Połomska, M. and Hilczer, B., XRD, TEM and Raman scattering studies of $PbTiO_3$ nanopowders. *Cryst. Res. Tech.*, 2006, **41**, 576–579.
11. Kubel, F. and Schmid, H., Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite $BiFeO_3$. *Acta Cryst.*, 1990, **B46**, 698–702.
12. Haumont, R., Kreisel, J., Bouvier, P. and Hippert, F., Phonon anomalies and ferroelectric phase transition in multiferroic $BiFeO_3$. *Phys. Rev.*, 2006, **B73**, 132101–132111.
13. Fecht, H.-J., Nanostructured materials synthesized by mechanical means. *Dekker Encyclopedia of Nanoscience and Nanotechnology*. Marcel Dekker, New York, 2004, pp. 2583–2593.
14. Singh, M. K., Jang, H. M., Ryu, S. and Jo, M.-H., Polarized Raman scattering of multiferroic $BiFeO_3$ epitaxial films with rhombohedral R3c symmetry. *Appl. Phys. Lett.*, 2006, **88**, 042907.