

Cubic Shape Cobalt Substituted Bismuth Ferrite Prepared By Hydrothermal Method

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Abstract

Single crystals of Co substituted Bismuth Ferrite (BCFO) were prepared by using low temperature hydrothermal synthesis route. Effects of KOH concentration, reaction temperature and duration time on the phase evolution, the particle size and morphologies of BCFO crystallites were investigated systematically. The size of BCFO single crystals increased with reaction temperature and growth duration. Powder X-ray diffraction results indicated that BCFO formed as skin layer over the sillenite-type of $\text{Bi}_{25}\text{FeO}_{40}$ single crystals. Scanning electron microscopy observation revealed a cubic shape morphology of the crystals and the EDAX measurement shows the expected stoichiometry. Raman scattering spectra of bulk BCFO single crystals have been measured.

1. Introduction

Recently, much interest was directed towards the multiferroic materials, because of their versatile applications. Multiferroic materials possess coexistence of ferroelectric and magnetic order parameters. Their physical properties lead them as potential material in electrical and electronic sectors, especially, information storage, spintronics, sensors and optoelectronic devices [1-2].

Among the variety of materials specifically perovskite bismuth ferrite (BiFeO_3) is one of the emerging materials, which has the only single phase multiferroic property, that simultaneously possesses both magnetic and ferroelectric order at and above room temperature with an antiferro-magnetic Neel temperature of $T_N = 643$ K and a ferroelectric Curie temperature of $T_C = 1103$ K [3]. BiFeO_3 perovskites could only stabilize within a narrow ranged temperature. Subsequently, other methods have been developed to prepare BiFeO_3 , such as ferrioxalate precursor method [4], sol-gel process [5-6], co-precipitation [7], spray pyrolysis method [8] and hydrothermal method [9-10]. Of all these methods, the

hydrothermal method is one of the wet chemical methods, and is the most extensively used in the synthesis of advanced inorganic materials which are difficult to obtain by oxide precursor method [11] which has many advantages in comparison with other techniques such as low processing temperature high degree of crystallinity, well-controlled morphology, high purity and narrow size distribution. During the synthesis, BiFeO_3 crystals usually exist in multiphase due to the effect of the formation kinetics. It is strenuous to prepare phase pure and high quality single crystals of BiFeO_3 and to evaluate its physical properties. There are no reports so far on Co substituting BiFeO_3 crystals. In the present paper, for the first time we report the results of our attempts to grow cobalt substituted single crystals with molecular formula $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.1$). Device quality $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ single crystals of lattice parameter $a=8.817$ were grown by hydrothermal method and the results are presented.

2. Experimental Procedure

$\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.1$) samples were prepared by hydrothermal method [9]. All the chemical reagents used in the work were high purity analytical grade Bismuth Nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), Cobalt Nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Iron Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Potassium Hydroxide (KOH) and Hydrogen Peroxide (H_2O_2). All the chemicals were analytical grade purity and were used as received without further purification. At first equimolar mixer of two starting materials and KOH dissolved in 40 ml of double distilled water. The PH of the solution was adjusted with KOH, which also served as a mineralizer. The solution was well stirred using the magnetic stirrer, until the brown precipitate was formed. After the precursor solution was made, little amount of H_2O_2 was added and finally the solution was transferred into a Teflon-lined steel autoclave. The autoclave was sealed and then heated to a reaction temperature ranging from 200 to 240°C and the reaction period was kept for 2-10 days. The solid products were filtered and washed with de-mineralized

water in order to remove the soluble salt and heated at about 50-60°C in air. The BCFO crystals were grown by hydrothermal method at 240°C. Significantly, the powder sample and the big size crystals were separated by decantation with distilled water and ethanol. At last crystals and powders were dried at 100°C. The well grown crystals under the above conditions were x-ray analysed by an X-ray powder diffraction using monochromated CuK α radiation. The morphology of the crystals was observed using the scanning electron microscopy (SEM) equipped with an EDX spectrometer. Raman scattering was observed by using Ar-ion laser 514.5 nm for excitation by microscopic observation, the results are presented.

3. Characterization

The crystals grown under ideal conditions were analysed by an X-ray diffractometer (XRD, Bruker-D8 ADVANCE INSTRUMENT), using monochromated CuK α radiation. The morphology of the crystal was observed using a scanning electron microscope (EVO 40 EP of Carl Zeiss) with most advanced LN2 free energy-dispersive X-ray spectrometer of Bruker make (EDX, X Flash 4010 SDD X-ray detector). In addition, the Raman spectrum was recorded by RENISHAW InVia Raman Microscope.

4. Result and Discussion

Crystals of dimension up to 0.5 x 0.5 x 0.5 mm³ were obtained after a period of 2-10 days. Fig.1 shows the micrographs of BiFe_{1-x}Co_xO₃ (x=0.1) crystals and the results suggest that all the crystals are perfectly cubic in shape. The inset Fig.1 illustrates an enlarged image of the clear cubic shaped crystal.

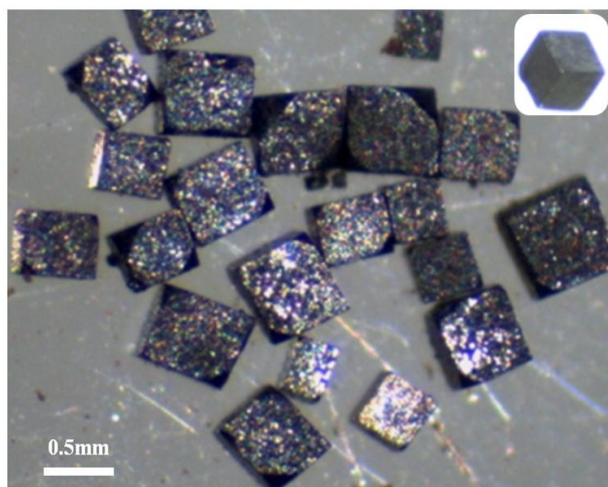


Fig. 1. Micrographs of BiFe_{1-x}Co_xO₃ (x=0.1) crystals

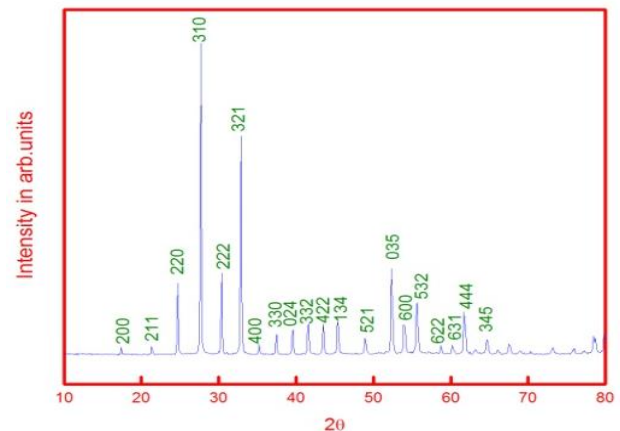


Fig.2. XRD pattern of BCFO graph

The grown BCFO crystals have been analysed on XRD-Bruker-D8 advance instrument using monochromated CuK α radiation. The X-ray powder diffraction patterns of BCFO crystals synthesized under the condition of Bi/K molar ratio range of 15-20 at 240°C showed a single phase of sillenite-type compound as shown in Fig. 2. It can be seen that the XRD refinements fits well with data of Bi₂₅FeO₄₀ only. The XRD pattern are indexed according to the JCPDS 00-046-0416 and it is clear that no impurity phase such as cobalt oxides is detected from Fig. 2. This indicates that Co substituted BiFeO₃ formed as skin layer single crystals over the Bi₂₅FeO₄₀ single crystals. From a systematic investigation of crystal morphology and structure, Cai et al have shown that in the beginning of hydrothermal reaction Bi₂₅FeO₄₀ nucleation occurs which finally converts into BiFeO₃ [12]. This revealed that BiFeO₃ crystallites had the pure perovskite structure belonging to the polar R3m space group, the XRD pattern is in good agreement with the reported values [13-14]. It is concluded that the BCFO enlarged since large radius of Co²⁺ cations with respect to Fe³⁺ cations [15]. But energy dispersive X-ray (EDX) pattern checked from the results clearly shows the existence of Co in the hydrothermally grown crystals (Fig.3). From the XRD results, it is reasonable to consider that substituted Co ions have been effectively incorporated into the crystal structure of BCFO. In addition, the increase of reaction temperature and KOH concentration result in a remarkable increase in the thickness and decrease in the edge length of the crystals. The EDX Spectrum showed that all crystals are equal stoichiometric ratio of Both Bismuth and Iron and small amount of cobalt (Co).

Scanning electron microscopy (SEM) images reveal all the crystal morphologies were observed as the cubic in nature shown in Fig. 4. In the beginning of the hydrothermal treatment, crystallites with irregular

shape and relatively rough surfaces then the reaction time was prolonged up to 2-10 days rough and irregular crystallites start to transform into cubic crystals.

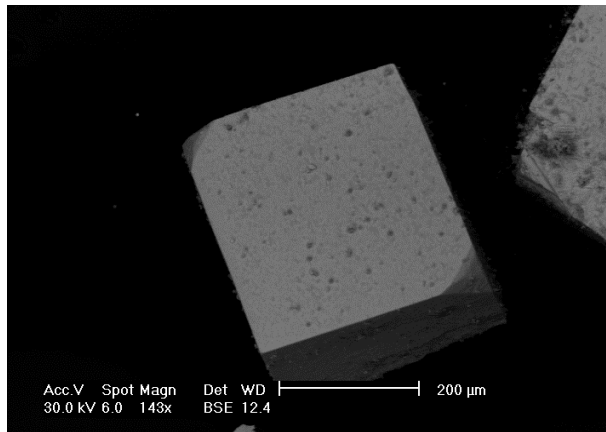


Fig. 4. SEM image of BGFO

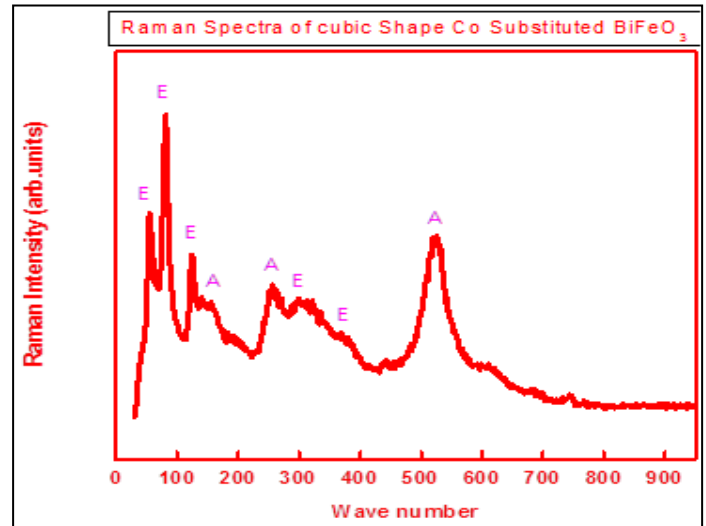


Fig. 5. Raman spectrum of BCFO

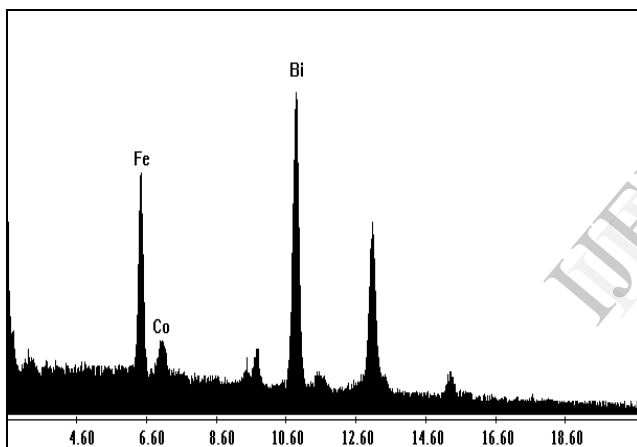


Fig. 3. EDX data of BCFO

BCFO crystal growth should take place through a dissolution / recrystallization mechanism. It is known that the size and morphology of the well grown crystals strongly depend on crystal nucleation and crystal growth [11]. The Raman scattering spectrum of BCFO is shown in Fig.5. The spectrum of bulk BCFO single crystals are measured using Ar ion laser of excitation wavelength 514.5 nm, where the probe laser was focussed to diameter (~1μm) at the crystals surface. All the raman active phonon modes observed to be A1 (symmetry longitudinal-optical) and E (transverse optical) modes are raman and IR active modes [16,17]. Some A1 modes did not completely disappear by crossed polarization probably because the observed area contained neighbouring domains with different polarization directions [18].

5. Conclusions

Good quality BCFO crystals were successfully synthesised by hydrothermal method by optimising the growth parameters. A long 10 days of growth duration at 240°C yielded doped cubic shaped $\text{Bi}_{25}\text{FeO}_{40}$ single crystals of perovskite phase though different phases were reported for different growth parameter. The doping was confirmed from the EDAX and the XRD results and no impurity domination was observed. From the Raman spectrum the A1 and E modes are found to be active. The authors are thankful to the XSGCS of IGCAR Kalpakkam for providing the facilities to carry out the work.

6. References

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