

Synthesis and Characterization of BaBiO₃ Perovskite through Chemical Route

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Abstract

BaBiO₃ (perovskite) polycrystalline semiconducting material was synthesized by sol-gel chemical method. Structure of the sample was characterized by X-Ray Diffraction (XRD). Grain, Grain boundary topography and chemical composition of the sample studied by using Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectrometry (EDS). Fourier transform-infrared spectroscopy (FT-IR) was used for the study of band structure. The result of XRD characterization was indicated as the BaBiO₃ is monoclinic perovskite and crystalline size is 85 nm. SEM image of the BaBiO₃ showed the grain size of 85 nm. The FT-IR spectroscopy study showed that, the BaBiO₃ has absorbent peak at 1420 cm⁻¹.

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INTRODUCTION

The BaBiO₃ which belong to the crystallographic family called perovskite (Robert M. Hazen, 1998) is known by its charge distortion i.e. Bi occupies two distinctive sites, having bond length of Bi (1) – O = 2.28Å and Bi (2) – O = 2.12Å (Sven Larsson, 1996). This differences in distance are the reason for the charge disproportionation occurred in the way that 2Bi⁺⁴ = Bi⁺³ + Bi⁺⁵, which results in the insulating property in this compound. The cubic BaBiO₃ has an odd number of electrons in each unit cell and it is expected to be a metal, from simple electronic band model because the mean valence of Bi is 4+, i.e. valence band mainly composed of Bi 6s orbital should be half-filled, however BaBiO₃ shows semiconducting temperature dependence of electrical conductivity, experimentally (Takuya Hashimoto *et al.*, 2008). But, A or B site doping suppresses the charge density waves to produce the metallic superconducting phases (Shen *et al.*, 1990) which means that semiconducting property should be changed to semi-metallic or metallic by modification of crystal structure to higher symmetry with single Bi site. One of the probable methods is a partial cation substitution to BaBiO₃. It has already been reported that K substitution of Ba site or Pb one of Bi site causes variation of crystal structure to higher symmetry accompanied by semiconductor–metal transition and that superconducting transition is also observed in Ba_{0.6}K_{0.4}BiO₃ and BaPb_{1-x}Bi_xO₃ (x ¼ 0.1–0.35). It can be concluded that chemical state of Bi was affected by the cation substitution resulting in variation of crystal structure and electrical conduction property (Takuya Hashimoto *et al.*, 2008). The high temperature super conductivity of the K-doped in the Ba site and Pb-doped in the Bi site made this compound very interesting. The mechanism of the high-temperature superconductivity in Ba_xK_xBiO₃ is still the open question. This material has a rather high critical

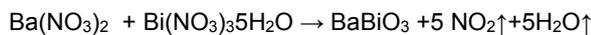
temperature T_c ≈ 30K (x ≈ 0.4) for a system without a layered structure in contrast to CuO planes in cuprates (Dm. M. Korotin, 2013). More than two decades ago it was found that the superconducting transition temperature T_c of Ba_{1-x}K_xBiO₃ is close to 30 K (for x = 0.4), one of the highest among materials without copper or iron. Unlike copper- and iron based superconductors, Ba_{1-x}K_xBiO₃ is nonmagnetic and its electrons are likely paired by a more conventional electron-phonon coupling mechanism (Timur Bazhrov *et al.*, 2013). Super conductivity in Ba(Pb,Bi)O₃ over a composition range 0.1 < x < 0.3 was discovered in 1975 by Sleight *et al* with a maximum T_c of 13.5K. Superconductivity in the (Ba,K)BiO₃ was discovered in 1988 by Mattheis and his colleagues (Grumann *et al* 1994).

The crystal structure of BaBiO₃ was determined to be monoclinic at room temperature in 1976, 1979 by Cox and Sleight using powder neutron diffraction. This result was supported by neutron diffraction studies and x-ray absorption studies (Akhtar *et al.*, 1993). In this compound, two different BiO₆ octahedral are connected alternatively by edge-sharing mode along the crystallographic directions. One octahedron is tilted from the vertical c-axis and the next one is tilted in opposite direction to construct a zigzag structure with the angle of 159.9⁰ (Dongwoon Jung *et al.*, 1999).

MATERIALS AND METHODS

The sol–gel method widely used to produce nano crystalline BaBiO₃ powders and films. This process involved dissolving the metal-containing compounds in the solvent, hydrolyzing to polymeric condensation, drying the resulting solution into various gels, and, finally, annealing

the gels at high temperature to form BaBiO₃ nano crystals (Sreenu *et al.*, 2014) In this process, the choice of starting materials, concentration, pH value, and heat treatment schedule had a strong influence on the properties of the BaBiO₃ nanoparticles. However, the different rates in the hydrolysis and condensation of Ba and Bi precursors often led to chemical component segregation in the obtained gels. The stoichiometric amounts of barium nitrate (Ba(NO₃)₂) (Merck 99%) is taken in aqueous solution and Bismuth nitrate (Bi(NO₃)₃·5H₂O) is added to the solution. The mixture is slowly heated on a hot plate and citric acid is added. The pH value is adjusted to desired value by adding ammonium hydroxide solution. Ethylene glycol is added to the mixture and heated till precursor is obtained. The precursor is burned at 600°C for 5 hours. Finally calcinated at 800 °C in furnace of oxygen atmosphere then the resultant powder was crushed and pressed into circular pellets of 10 mm diameter and ~ 1mm thickness. The possible chemical reactions are as follows:



The crystalline structure of the prepared samples was analyzed with X-ray diffraction. The microstructure of the samples was investigated by using scanning electron microscope (Hitachi N3400 Japan). The FTIR patterns were acquired by using BRUKER OPTICS, Germany Model TENSOR 27 FTIR spectrometer from 4000 cm⁻¹-400cm⁻¹, using KBr pellet as a reference material.

RESULTS AND DISCUSSION

In nature everything has got its own uniqueness so to be identified from one another they have to be characterized. Characterization is a wonderful method for identifying one sample from other because same time we

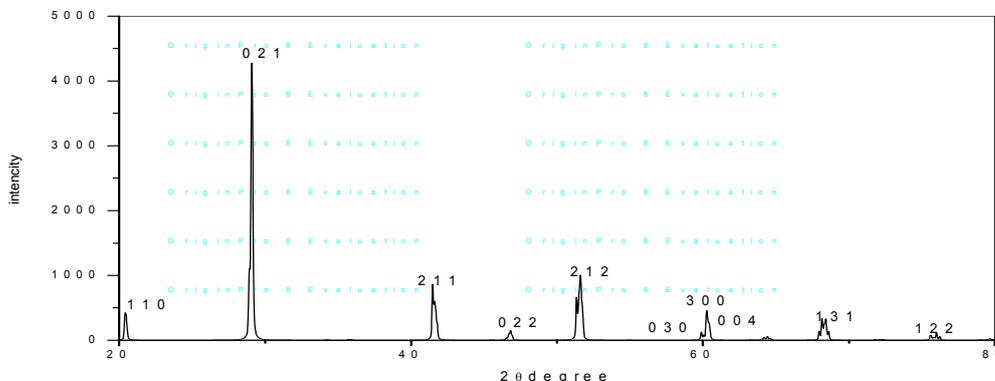


Figure 1: XRD pattern of BaBiO₃

Micro Structural Properties of BaBiO₃ Ceramics

The close observation at the micrograph of BaBiO₃ figure 2 taken from SEM showed large grain size at the boundary this is expected to be due to existence Bi ions in the sample (Sreenu *et al.*, 2014) with same porosity and scratches. The grain size was around 4 μm in uniform as calculated using line intercept method.

Compositional Distribution Study

An interaction of an electron beam with a sample target produces a variety of emissions, including x-rays. An energy-dispersive (EDS) detector is used to separate the characteristic X-rays of different elements into an energy spectrum, and EDS system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. EDS can be used to find the chemical composition of materials down to a spot size

are not able differentiate samples by their texture, color, odor and the like. Therefore, a BaBiO₃ sample was characterized by x-ray diffraction, Scanning Electron Microscope, Energy Dispersive x-ray Spectroscopy and Fourier Transform Infrared Spectroscopy.

Structural Studies

Many techniques are used to characterize the solids. Among them, the most important is x-ray diffraction studies, which gives information about the phase formation of the compound, lattice parameters, theoretical density. X-ray patterns were taken on the pre-sintered and final sintered samples. By comparing the powder diffraction of the samples with standard patterns given in JCPDS (Joint Committee on Powder Diffraction standards, USA), lattice parameters were evaluated using the powd software, which is based on the least square minimization procedure. The x-ray powder diffraction may also be used to measure the average crystal size from the peak broadening using the Scherer formula.

As shown in figure 1 the XRD detector reads both angle (2θ) of x-ray diffraction and the intensity of diffracted X-ray which resulted in a two dimensional pattern called characteristic pattern of BaBiO₃ ("finger print of BaBiO₃"). The materials were examined by x-ray powder diffraction for phase purity and hence it showed single phase of BaBiO₃.

From powd program it was found that each respective parameters to be a = 6.33Å, b = 6.12Å, c = 8.62 Å and with β = 90.171. This confirms that BaBiO₃ has monoclinic structure at room temperature. The calculated crystalline size using the Scherer formula was 85nm as well. And its XRD density was 6.13gcm⁻³.

of a few microns, and to create element composition maps over a much broader raster area.

In figure 3 each energy peak of the EDS pattern corresponds to elements in the sample i.e. Ba, Bi and Au. The showing up of gold in the pattern is because the sample was coated with gold before its characterization of SEM.

The EDS does not only tell us the elemental composition of the sample but also shows the relative abundance of each chemical element in the sample (Table 1).

Table 1: elemental weight of BaBiO₃

Elements	O	Ba	Bi	Au
Weight	11.81	21.07	49.78	12.33

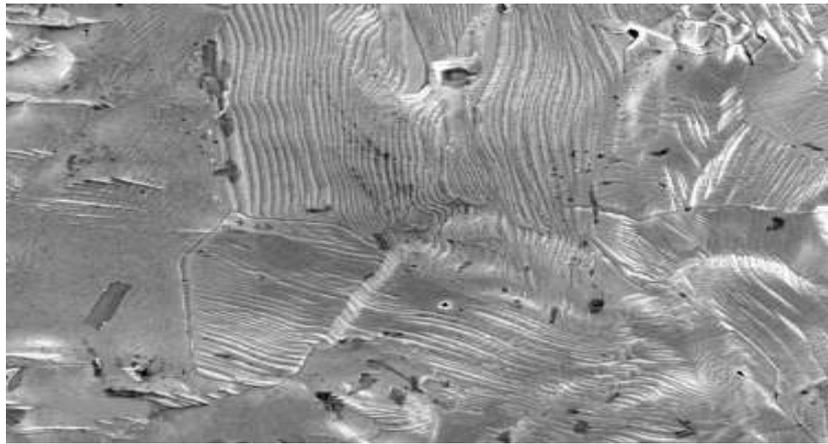


Figure 2: the micrograph of BaBiO₃ taken by SEM

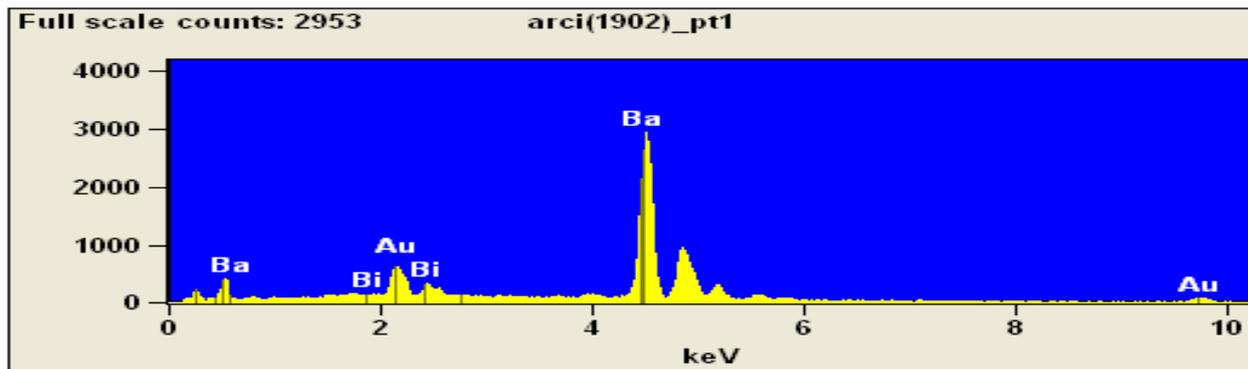


Figure 3: EDS pattern of BaBiO₃

Fourier Transform Infrared Spectroscopy (FTIR)

A molecule absorbs radiation at certain frequency, which cause a quantum change in its energy. The IR radiation has correct frequency to cause a quantum jump in the vibration energy of the molecule. The vibrations of a molecule absorb the radiation of IR radiation, which the oscillations cause a change in the dipole moment. The frequency at which the absorption takes place is equal to frequency of oscillations of the dipole and falls in the region. IR spectra of all the samples are recorded in the range 4000-400 cm⁻¹ (Figure 4). From this FTIR pattern it is seen that pure BaBiO₃ shows as absorption at 1420cm⁻¹ which are considered to be a characteristic feature of the

sample and are attributed to Ba-O band bending vibrations. Even though some ions are different, the absorption peak in the vicinity of 540 cm⁻¹ is assigned to the vibration of O-M (M=ion at B-site) bond i.e. O-Bi (Table 2).

Table 2: Infrared band positions (cm⁻¹) of BaBiO₃

Band position	Wave No(cm ⁻¹)
Ba-O	1420
Bi-O	702
	520

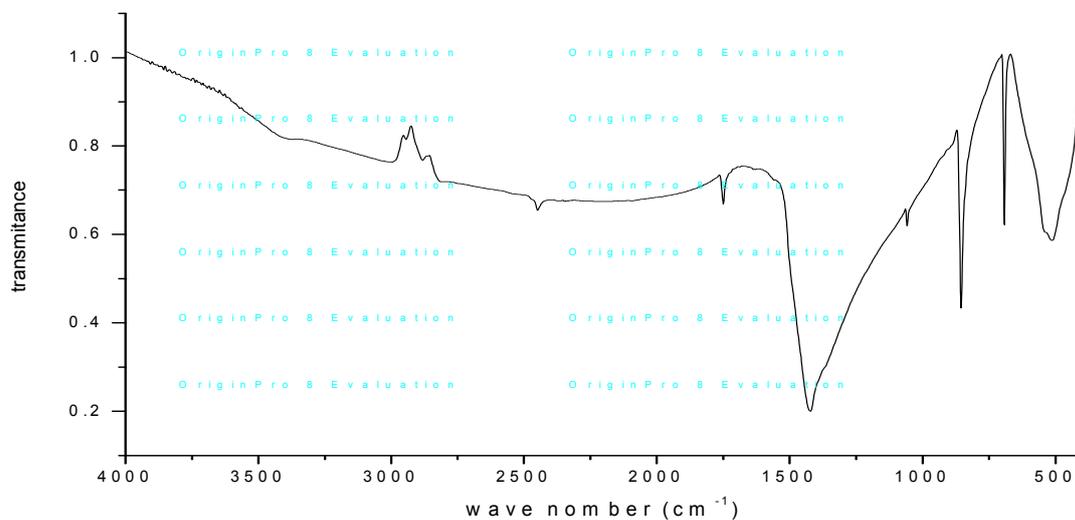


Figure 4: Infrared spectra of barium bismuthate

CONCLUSIONS

BaBiO₃ polycrystalline material is synthesized by sol-gel method having the crystallite size of 85nm and the xrd characterization with lattice parameters $a = 6.33\text{\AA}$, $b = 6.12\text{\AA}$ and $c = 8.62\text{\AA}$ and unit volume is 334cm^3 indicates that BaBiO₃ is monoclinic perovskite at room temperature with percentage of density 94 (gm/cm^3). SEM results reveal that the grain size is large because of the Bi-ion. The EDS analyze of sintered pellet of BaBiO₃ revealed that the sample was pure. From the detailed FTIR spectra analysis, it was observed that the pronounced peak at 1420cm^{-1} , where a metallic bond is observed, considered being a characteristic feature of BaBiO₃.

Conflict of Interest

Conflict of interest none declared.

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