Microstructural properties of lead free BiMnO$_3$ ceramic prepared by mechanochemical synthesis

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Abstract. The present paper reports the synthesis of BiMnO$_3$ (BMO) using Bi$_2$O$_3$ and Mn$_2$O$_3$ as initial powder mixture through mechanochemical synthesis route by a planetary ball milling. The powder mixture was intensively milled in atmospheric temperature to achieve crystalline powder of BiMnO$_3$ (BMO). For structural analysis of the sample the X-ray diffraction (XRD) and Scanning electron microscopy (SEM) investigation was carried. The XRD analysis clearly shows the single phase perovskite structure having monoclinic symmetry with lattice parameter $a=5.883\,\text{Å}$, $c=7.525\,\text{Å}$ and space group P121/C1. SEM images confirm the achievement of polycrystalline morphology of BMO ceramic with visible grain boundary. It is also found that the presence of agglomerated structure was reduced as the milling time increases. The particle size of starting BMO was somewhat proportional to the grain size. The enhancement in the values of relative density from 90% to 97% of the resulting ceramics was recorded when the sample milling time increases from 1h to 20h. Eventually, the dielectric characteristics of the BMO sample were studied. The dielectric behaviour at room temperature to a temperature of 200°C has been reported. The properties of the prepared ceramic powder signify for potential application as a multiferroic material with simultaneous control over piezoelectric and dielectric characteristics.

1. Introduction

Multiferroic and piezoelectric ceramics possesses a perovskite structure remains the focus of attention of researchers as the material exhibiting the ferromagnetism and ferroelectricity in the polycrystalline single phase structure. The most interesting characteristics of this material that their spontaneous magnetization and polarization can easily be changeable by applying magnetic and electric field respectively [1, 2]. These switchable properties have attracted significant attention towards the possibility of commercial application of this class of materials in development of new memory devices [3, 4]. Nevertheless, current challenge in the development of perovskite ceramic based piezoelectric and ferroelectric material is the search of alternatives for replacement of toxic lead content in the ceramic compounds [3]. In this context less toxic Bismuth [Bi] containing perovskite have emerges as great alternative to replace lead [Pb] part in the oxide. Since the Bi$^{3+}$ ions have the active $6s^2$ lone pair of electrons that probably causes off-cantering of Bi$^{3+}$ ion in the Bi-based perovskite compounds. It is likely that thus Bi$^{3+}$ cater the role of Pb$^{2+}$ that provoke the piezoelectric and ferroelectric properties in perovskite ceramics [5].
The Bi-based Perovskite compounds are studied more than decades. Few recent theoretical and experimental studies indicated that Bi$_2$MO$_3$ ceramics are promising materials for high performance ferroelectric and piezoelectric [6]. For example BiFeO$_3$ [4], BiCrO$_3$ [7], BiScO$_3$ [8], BiCoO$_3$ [9], BiNiO$_3$ [10], BiAlO$_3$ [11], BiInO$_3$ [12] and BiMnO$_3$[13] are to name a few. BiMnO$_3$ has been found to be a unique compound in the group because it exhibit high resistivity, orbital degrees of freedom and low leakage current which is excellent combination for promising multiferroic materials.

In the solid solution, PbTiO$_3$-BiMnO$_3$ [14, 15], PbTiO$_3$-BiScO$_3$ [16], BaTiO$_3$-BiFeO$_3$ [17] etc. were extensively studied with reduction of toxic lead. The synthesis technique is also plays an important role in determining the phase stability, density and properties of the resultant ceramics. Many synthesis techniques have been implemented, such as conventional solid state reaction, wet chemical, co-precipitation, combustion, hydrothermal and mechanochemical etc. However, the mechanochemical route is found to be cost-effective and simple method for preparation of multiferroic ceramic material [18]. The synthesis of BMO has been attempted by many different routes. V. Samuel et al. attempted to synthesize by sol gel method at 100°C and atmospheric pressure. They observed the formation of ultrafine particles of BiMnO$_3$ with the average particle size of 90 nm. Also formation of amorphous structure of BMO has been recorded and attributed the formation of the phase due to presence of some unknown impurities in the sample [19]. Another experimental study carried out by W. Prellier et al, to synthesize the BMO. The reported ferromagnetic transition temperature (T$_{F}$) and ferroelectric temperature (T$_{E}$) in this work was -168.15°C and at 476.85°C respectively [20]. The difficulty experienced in this conventional solid state approach is requirement of very high pressure of more 40kbar [19]. P. Toulemonde a et al, grows the orthorhombic single crystal BMO by in situ HP-HT at 4.5GPa using fluxing technique [21]. As reported in the literature, many other approaches are also attempted for formation BMO with the aim to tailor the multiferroic properties of the materials even at low pressure and low temperature.

The purpose of present work is to synthesize BiMnO$_3$ (BMO) by mechanochemical synthesis route at room temperature and absence of high pressures. Mechanochemical synthesis usually referred as solid state reaction initiated with milling in high energy planetary ball mill. The method is adopted for the preparation of BiMnO$_3$ perovskite ceramic starting from a mixture of Bi$_2$O$_3$ and Mn$_2$O$_3$. The results of structure of synthesized powder has been analysed by XRD and SEM investigation. The dielectric properties and the relative density of the BMO has been evaluated and discussed in this article.

2. Materials & Methods

2.1 Materials

In this work BiMnO$_3$ (BMO) is synthesized by mechanochemical route starting with the powder mixture of Bi$_2$O$_3$ and Mn$_2$O$_3$. The Bi$_2$O$_3$ and Mn$_2$O$_3$ powders were procured from standard supplier with purity level of 99.9 and 98.0 percent. The estimated amount of powder mixture was weighted, used for solid state reaction using ball milling.

2.2 Experimental Procedure

The BiMnO$_3$ (BMO) was synthesised through solid state reaction by high energy planetary ball mill (Retsch: PM-400, Germany) with starting reagent powders milled in toluene environment with tungsten balls. The milling parameters were maintain as tungsten jars (V=500cm$^3$, 100mm in height and 75mm in diameter) and balls (13mm in diameter and 7.67 in weight), ball to powder ratio 10:1, with rotation speed 250 rpm. After milling, the powder was dried in air for 2hrs followed by compaction by hydraulic press applying 12 ton load and sintered at 650°C in a tubular furnace. The phase identification and structural characterization was carried out by XRD (PANalytical X’Pert Pro diffractometer with CuKa, λ=1.5406 A$^\circ$ radiation source) analysis. Subsequently the sample surface morphology was investigated via Scanning Electron Microscopy (Zeiss EVO 18, Germany). The bulk density of sintered samples was obtained by Archimedes method. Eventually the dielectric property of
the sample was studied using LCR meter (Hioki 3533) in a temperature range of room temperature to 200°C.

3. Results and Discussions

3.1 X-Ray Diffraction Studies

Figure 1 represents the XRD profile of the ball milled oxide mixture ceramic powder. The XRD patterns of the synthesized powders have been studied as against the time of milling with a maximum milling time of 20 hours. Samples were taken for XRD analysis at 1 hour, 5 hours, 10 hours, 15 hours and 20 hours. The XRD of initial stage of milling clearly depicted that no alloying has been taken place as the starting powders Bi$_2$O$_3$ and Mn$_2$O$_3$ peaks are prominent. As the time of milling increases the peaks of Bi$_2$O$_3$ and Mn$_2$O$_3$ powders are suppressed that clearly signifies the alloying of the powders. The XRD profile of 10 hours sample shows that the starting of alloying of the powder mixture and that of 15 hours shows the signature of complete alloying as the peaks of reagent powders are vanishes and new set of peaks are appeared in XRD profile. The obtained structural XRD data of 15 hours sample has been analyzed that reveal a single perovskite structure with no trace of any other additional phase formation. The observed pattern declare miscellaneous diffraction peaks noticeable by different crystallographic planes. As we can see that highest diffraction intensity of BiMnO$_3$ achieved at 31.5° that appears to be from the plane (020). The others peaks are identified and confirmed with the ICSD database. The analysis of the diffraction data allowed computing the cell parameters and it was recorded as: a = 5.883Å, c = 7.525Å and α = β = γ = 90°. The cell parameters calculated from XRD data revealed that the observed parameters are closely matching with the monoclinic crystal structure (space group-P121/c1). It is worthy to note here that recorded structure and the parameters are in good agreement with the previously reported work [22]. In a similar work carried out by Z. H. Chi et al. reported the monoclinic crystal structure of the BMO synthesized by HT-HP [23].

![Figure 1. XRD patterns of BiMnO$_3$ milled from 1hr-20hr.](image-url)
Table 1 presents the calculated crystallite size and cell parameters of the ball milled samples milled for 1, 5, 10, 15 and 20 hours. The calculated crystallite size \( t \) is obtained with the broadening of major peaks. The average crystallite size \( t \) has been computed with the help of Debye-Scherer’s formula [24] as shown in equation 1.

\[
t = \frac{0.9\lambda}{\beta \cos(\Theta)}
\]  

Where, \( \lambda \) represents wavelength of X-Ray used, \( \Theta \) represents Braggs angle and \( \beta \) represents full Width half Maximum (FWHM). Further milling (20 hours), do not show any significant change in XRD profile except some further refinement of structure increment in the crystallinity as apparent in Table 1.

|                | a[Å]  | c[Å]  | Crystallite size[nm] |
|----------------|-------|-------|----------------------|
| BMO 1hr        | 5.850 | 7.510 | 25.95                |
| BMO 5hr        | 5.883 | 7.525 | 20.90                |
| BMO 10hr       | 5.890 | 7.528 | 16.28                |
| BMO 15hr       | 5.883 | 7.525 | 14.209               |
| BMO 20hr       | 5.892 | 7.529 | 11.52                |

3.2 Microstructure studies

Figure 2 (a)-(e) shows the typical micrograph of synthesized and compacted sintered BiMnO3 samples. From the SEM images it is clear evident that the grain size becomes finer with increasing milling time and their distribution becomes more homogeneous with little agglomeration. The presence of agglomeration can be attributed as due to vicinity of strong inter-particle bond across the aggregates. The similar phenomenon has been noticed by Z. Brankovic et al. [25]. The density of the sample pallets has been recorded between 5.59–5.62 g/cm3. The Figure 3 plotted the relative density against the milling time. The SEM images has also confirm that in all the cases sample have dense microstructure and average grain shape become more spherical with increase in milling time.

![Figure 3. Relative Density with respect to milling hours.](attachment:image.png)
Figure 2. The SEM images of BiMnO$_3$ samples a) 1hr b) 5hr c) 10 hr d) 15 hr e) 20hr

3.3 Dielectric Studies

Figure 4 shows the frequency dependant dielectric behavior of BiMnO$_3$ investigated for the sample milled for 15 hours. The dielectric constant has been recorded in the temperature range of room temperature (RT) to a temperature of 200°C with an interval of 50°C. The frequency range was kept in the range of 5kHz to 0.1MHz. As we can see in Figure 4 that at low temperature the material exhibits high dielectric constant and at high temperature the dielectric constant decreases. At RT, the dielectric constant ($\varepsilon'$) shows the sharp decrement towards high frequency region. At higher temperature the dielectric constant reduces even at the low frequency range (see green line in Figure 4). As reported in S. Hanif et al. the electronic and ionic polarizations dominate the dielectric constant at high frequency field, while in the case of low frequency filed dipolar and space charge polarization Strongly influence the dielectric constant [26].

The observed results here in the case BMO are in good agreement with reported phenomena. The sharp decrement of dielectric constant of the BMO sample at high temperature in low frequency field can be attributed following the explanation reported by Ghulam ali et al [27]. They mentioned that dielectric relaxation governs the reduced dielectric constant values. That means in the case of present BMO the space carriers miss to respond the necessary alteration in the time duration in which applied field changes. This time duration is frequently referred as the relaxation time in literature. Usually the grain size is one of the important factors that significantly influence the dielectric properties [28]. As can be seen in SEM images of 15 hours and 20 hours sample that with high milling temperature there
is significant chance for improvement of grain refinement and avoid the agglomeration formation. Therefore, it is apparent that further increasing the milling time with considering higher temperature for measurement of dielectric properties it is possible to develop BMO with further improved dielectric constant materials.

![Frequency dependent Dielectric Constant at RT to 200°C.](image)

**Figure 4.** Frequency dependent Dielectric Constant at RT to 200°C.

### 4. Conclusions
Mechanochemical synthesis method has been successfully employed for synthesis of single phase polycrystalline BiMnO$_3$ with monoclinic perovskite structure by ball milling at room temperature and atmospheric pressure. The proposed method can achieve the homogeneous distribution of grain with good densification of BiMnO$_3$ ceramic with 97% of relative density in a 15 hours milled sample from the starting powder mixture of Bi$_2$O$_3$ and Mn$_2$O$_3$. The developed BiMnO$_3$ exhibit a dielectric constant of 4x10$^4$ in a frequency range 5 kHz at temperature of 200°C. Exploring the possibility of further improvement of microstructure as well as the dielectric properties at higher temperature remain beyond the scope of the present study.

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