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Multiferroic bismuth manganite prepared by mechanochemical synthesis

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Abstract

Multiferroic bismuth manganite ($BiMnO_3$) is known as a material that exhibits both ferromagnetic and ferroelectric properties making it interesting for various technological applications. Unfortunately, preparation of $BiMnO_3$ is not possible by a conventional solid-state reaction and it can form only from mixture of oxides at high pressures (>40 kbar).

In this work single-phased $BiMnO_3$ was prepared for the first time by mechanochemical synthesis in a planetary ball mill. A mixture of Bi_2O_3 and Mn_2O_3 was intensively milled in air atmosphere, using stainless steel vials and balls. According to analysis of XPRD results $BiMnO_3$ obtained after milling for 240 min has a tetragonal structure with lattice parameters $a = 3.9230$ Å, $c = 3.920$ Å and a crystallite size of 16.8 nm. The cumulative energy introduced into the system during milling for 240 min was 401 kJ/g. It was found that the obtained powders were agglomerated. Corresponding agglomeration factors were calculated from the results of BET and particle size distribution analysis.

Keywords: Milling; Structure; X-ray methods; $BiMnO_3$

1. Introduction

Recently, there has been much interest in materials that have multiple functionalities, such as multiferroic magnetoelectrics, i.e. materials that are both ferromagnetic and ferroelectric in the same phase. As a result, they have a spontaneous magnetization that can be switched by an applied magnetic field but also a spontaneous polarization that can be switched by an applied electric field.[1] Very few multiferroics exist in nature or have been synthesized in a laboratory, and one of them is $BiMnO_3$. This is a compound that has been intensively studied, both theoretically and experimentally. It displays a ferromagnetic transition temperature (T_C) at around −168.15 °C and a ferroelectric transition temperature (T_E) at 476.85 °C.[2] Unfortunately, preparation of $BiMnO_3$ powder is not possible by a conventional solid-state reaction. According to our best knowledge single-phase $BiMnO_3$ has been synthesized from a mixture of oxides only at high pressures (>40 kbar).[1,3]

The aim of this work was to synthesize $BiMnO_3$ (BMO) without additional heating or application of high pressures. The goal was reached by mechanochemical synthesis of BMO in iron milling media. Mechanochemical synthesis usually refers to solid-state reactions initiated by intensive milling in high-energy ball mills. The main characteristic of solid-state reactions is that they involve the formation of product phase(s) at reactant interfaces. Intensive milling increases the contact area between the reactant powder particles due to reduction in particle size and allows fresh surfaces to come into contact. Another important feature of mechanochemical synthesis is that a reaction is initiated through impacts between the powder and balls, thus containing both important conditions for BMO synthesis: heat and pressure. As a consequence, reactions that normally require high temperatures and pressures can occur at lower temperatures during mechanochemical synthesis without any externally applied field.

Finally, complete structural and microstructural analyses of synthesized BMO powders were performed and properties obtained were compared with the literature data for powders obtained by other methods.

2. Experimental procedure

According to the chemical formula of $BiMnO_3$ (BMO), appropriate amounts of starting oxides Bi_2O_3 (Aldrich, p.a.

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99.9%) and Mn_2O_3 (Alfa Aesar, p.a. 98%) were weighed, mixed and further dry milled in planetary ball mill (Fritsch Pulverisette 5). Milling conditions were the following: stainless steel jars ($V = 500\,cm^3$, 100 mm in diameter, 80 mm in height) and balls (32 balls of approximately $d = 12$ mm, $\rho = 7.874\,g/cm^{-3}$), ball-to-powder weight ratio was 30:1, air atmosphere, basic disc rotation speed was 325 rpm, rotation speed of discs with vials was 400 rpm, milling time was 60–720 min.

The powders were characterized using X-ray powder diffraction analysis (XRD) on a Philips PW 1050 device, and microstructural data were obtained through the Le Bail method using the Topas-Academic software.[4] Powders were also characterized using the following methods: DT and TG analysis (SDT Q-600) in the temperature interval from 20 to 800 °C and with a heating rate of 10 °C/min, SEM (SEM TESCAN Vega TS 5130MM), EDS analysis (Oxford Instruments, model: INCA PentaFETx3), particle size analysis (HORIBA LA-920 laser scattering particle size distribution analyzer), and measurements of specific surface area (BET method, Micromeritics Flow Sorb II 2300).

3. Results and discussion

XRD results obtained for powders milled from 60 to 720 min are shown in Fig. 1. In the first 60 min of milling almost complete amorphisation occurred and only the two most intensive peaks of Mn_2O_3 were still visible. After 120 min of milling the first peaks of the BMO phase appeared at $2\theta \approx 22.9°$ and 32.4°. Further prolongation of milling resulted in the formation of an apparently single phase BMO after 240 min of milling. According to the model derived by Burgio et al.[5] we calculated the ball-impact energy ($\Delta E_b^* = 81$ mJ/hit) and the cumulative energy ($E_{cum} = 401$ kJ/g) introduced to the system during milling until the BMO phase was formed. This value is higher than the values obtained for some other perovskite phases prepared by mechanochemistry. The XRD pattern obtained for the powder milled for 360 min is almost the same as the pattern obtained for 240 min of milling. 720 min of milling resulted in the appearance of several new peaks besides the main BMO phase. These peaks at $2\theta = 27.7°$, 29.3°, 30.9°, 41.9° and 50.9° can be identified as minor non-stoichiometric phases, such as $Bi_2Mn_4O_{10}$ – JCPDS card 74-1096, $Bi_{1.83}Mn_{0.17}O_{3.08}$ – JCPDS card 50-0370, $Bi_{1.69}Mn_{0.31}O_{2.85}$ – JCPDS card 49-0738, and $Bi_{12}MnO_{20}$ – JCPDS card 74-1096, some of them have the most intensive peaks at very close angles. These phases were probably also present in samples milled for 360 and 240 min, but were hidden in the amorphous part of the pattern around $2\theta = 30°$. After prolonged milling for 720 min, the amount and crystallinity of these phases increased and they became visible on the diffractogram. This conclusion is in good agreement with the literature data. In most articles reporting on BMO synthesis using other methods, the presence of impurity phases was confirmed, either non-stoichiometric Bi–Mn–O phases or bismuth oxy-carbonate ($Bi_2(CO_3)O_2$).[6]

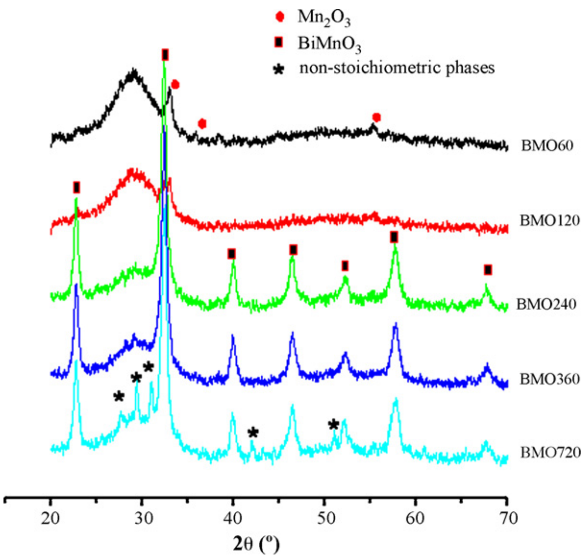

Fig. 1. XRD pattern for the Bi_2O_3–Mn_2O_3 mixture milled from 60 to 720 min.

Most literature data suggest the monoclinic (JCPDS card number 89-4544)[7,8] or triclinic (JCPDS card number 53-0766)[9]crystal structure for the room temperature BMO phase, but also the existence of several polymorphs, that could be identified during high-temperature XRD analysis.[6,9] It seems that during heating BMO undergoes several polymorphic transitions. According to Montanari et al.[6] there are five polymorphs transforming successively one into another with temperature increase from room temperature to 600 °C. The last two polymorphs, signed IV and V, are considered to be oxidized, cation-deficient phases – $Bi_{1-x}MnO_3$, whose formation is always followed by segregation of Bi-rich impurities and a higher Mn^{4+} content. According to Montanari et al.,[6] these phases preserved a distorted triclinic perovskite structure. Phase IV can be easily distinguished from the phases formed at lower temperatures because it has relatively broader peaks and multiplets typical for triclinic or monoclinic structures are not noted. BMO formed in our investigation shows this type of XRD pattern and one can suppose that a similar structure was obtained.

In accordance with XRPD data $BiMnO_3$ phase formation occurred after 240 min of mechanical activation. However, the obtained product crystallizes in a form differing from the originally proposed highly distorted triclinic structure[10] or the recently reported monoclinic C2 superstructure.[8] Indexed diffraction lines fit well with the tetragonal phase observed by Faqir et al.[9] during heating of triclinic $BiMnO_3$. According to Faqir a structural phase transformation was detected at 490 °C in air, and is found to be irreversible. During milling crystallization of the new phase appears due to close particle contact in the collision points where the temperature is high enough to provoke such phase transitions. Starting from published data,[9] refinement of the crystal unit cell from a powder diffraction scan was done through Le Bail fitting assuming the space group *P*4*bm* and using the Topas-Academic software.[4] Calculated values of the crystallite size, microstrain and lattice parameters are shown in Table 1. After milling for 1 h (sample BMO360) the proposed structure stays stable ($a = b = 3.9223(6)$; $c = 3.916(1)$). The crystallite size grows along with the microstain increase. Further increase of the milling time (sample BMO720) induces

Table 1
Results of structural analysis of the tetragonal BMO phase in powders milled 240 and 360 min.

Sample	*a* [Å]	*c* [Å]	Crystallite size [nm]	Microstrain [%]
BMO240	3.9230(5)	3.920(1)	16.8(5)	0.85(8)
BMO360	3.9223(6)	3.916(1)	22(1)	1.31(8)

$BiMnO_3$ phase decomposition resulting in multiphase sample generation.

In conclusion, the fact that the high-temperature polymorphs of BMO form during mechanochemical synthesis is logical if one considers that the main properties of mechanochemical synthesis are local generation of very high temperatures due to impacts. The obtained results can also be confirmed by DTA analysis (Fig. 2). Most authors reported of two endothermic peaks on the DTA curve connected with phase transformations.[7,9,11] In our investigation these peaks were not found, because we already have a high-temperature phase. On the DTA curve of the sample milled for 240 min only two exothermic peaks in the temperature interval from 500 to 650 °C were detected, which are probably connected with completion of BMO synthesis and crystallization and are not present in the repeated heating–cooling cycle.

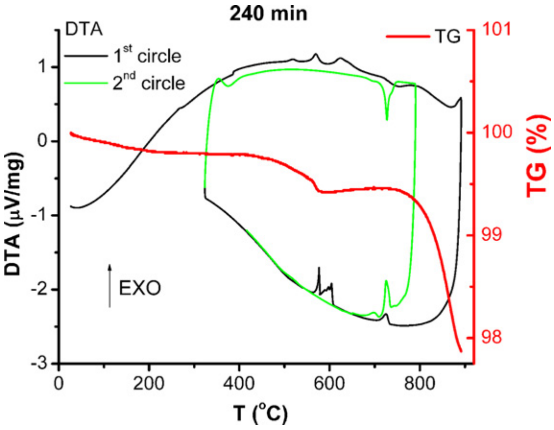

Fig. 2. DTG results for BMO formed after 240 min of milling.

According to TGA results only small mass loss was detected (<0.5%), probably due to decomposition of carbonate, which is always present in small amounts. The endothermic peak at 727 °C, which is partially masked in the first heating, but

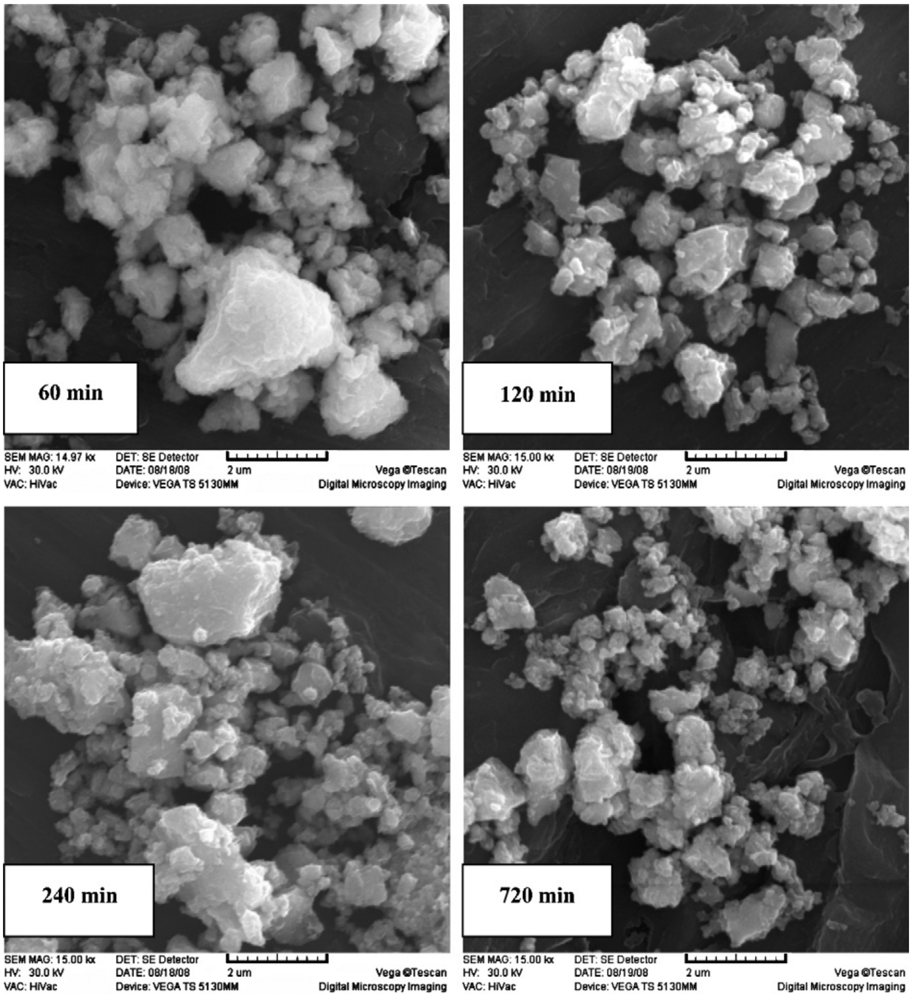

Fig. 3. SEM micrographs of the powders milled from 60 to 720 min.

Table 2
Results of measurements of specific surface area and particle size distribution.

Sample	Dv_{10} [μm]	Dv_{50} [μm]	Mean [μm]	Mode [μm]	Dv_{90} [μm]	D_{BET} [μm]	Fag	Sp [m^2/g]
BMO60	1.4240	7.6849	9.7650	12.3604	21.4186	0.5548	13.85	1.455
BMO120	1.0678	6.1844	8.3301	10.7760	18.6483	0.4690	13.19	1.721
BMO240	1.1208	5.9781	7.7101	10.7747	16.7316	0.3537	16.90	2.282
BMO360	1.0246	5.2654	6.9684	9.4571	15.3456	0.3501	15.04	2.306
BMO720	1.1223	6.7221	7.8402	12.3026	16.4165	0.3558	18.89	2.269

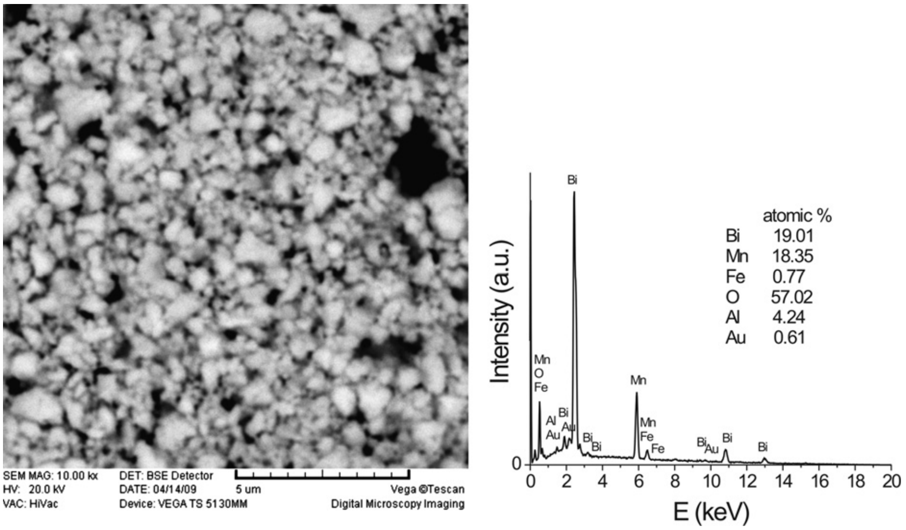

Fig. 4. SEM micrograph of the powder milled for 720 min (BSE mode), EDS spectra and results of quantitative analysis (data acquisition was done from the whole figure; Al peak refers to sample holder and Au peak refers to Au sputtered conductive layer).

is clearly visible in repeated heating, and also always has its endothermic equivalent in cooling cycles, can be related to melting, i.e. crystallization during the cooling process or to some reversible phase transformation. According to the phase diagram of the Bi_2O_3–Mn_2O_3 system at the temperature of 730 °C the phase transformation from monoclinic to cubic Bi_2O_3 occurs.[12]

The obtained powders have a similar particle size distribution. Their main characteristic was prevalence of large size particle fractions with the median particle size ranging from 5 to 8 μm (Table 2). Microstructural analysis showed that all powders were agglomerated (Fig. 3). Agglomeration was also confirmed by measurements of the specific surface area of the powders (Table 2). Very small values of the specific surface area, from 1.4 to 2.7 m^2/g are typical for highly agglomerated powders. From these results the corresponding agglomeration factors (Table 2) were calculated using the following equation $Fag = Dv_{50}/D_{BET}$.

The values of agglomeration factors are very high and suggest that the observed agglomerates should be considered as aggregates, with strong inter-particle bonds, actually chemical bonds, within each aggregate.

Since milling was performed in iron media, contamination of the powders was inevitable. Fe^{3+} and Mn^{3+} ions have very similar ionic radius values (difference less than 4%) and because of that Fe^{3+} can easily substitute for Mn^{3+}. XRD analysis did not reveal peaks from iron or iron oxides. In order to investigate the eventual presence of a second phase, SEM analysis in the BSE mode was performed. It was most important to prove that there was no isolated Fe or iron oxide grains. The results obtained for powders milled for 720 min are shown in Fig. 4. It was expected that this powder should contain the highest amount of iron due to the longest milling time. According to this analysis there are no other phases besides BMO. Additionally, EDS analysis was performed at several points, and also from the whole figure. It was found that Fe was homogeneously distributed in the sample and there is no significant difference in the composition between points. According to these results the presence of less than 0.5 wt.% of Fe was detected in the powder milled for 720 min. EDS results are also included in Fig. 4.

The main result of this work was successful synthesis of BMO without the use of high pressures. BMO was synthesized for the first time by mechanochemical synthesis. Nevertheless, it is necessary to further optimize the milling parameters and conditions, and to improve powder properties. This will be the aim of our future investigation.

4. Conclusions

$BiMnO_3$ powders were successfully prepared by mechanochemical synthesis in a planetary ball mill, after 240 min of milling. The BMO powders milled for 240 min were agglomerated with a mean particle size of 7.7 μm and specific surface area of 2.282 m^2/g. According to analysis of

XPRD results $BiMnO_3$ obtained after milling for 240 min has a tetragonal structure with lattice parameters $a = 3.9230$ Å, $c = 3.920$ Å and crystallite size of 16.8 nm.

Acknowledgment

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