Sintering BFO targets for sputtering

G. Orr,* A. Goryachev and G. Golan

Ariel University, Ariel, 40700 Israel

Abstract

Ceramic BiFeO$_3$ samples were prepared by rapid sintering at 880°C. Two compositions were examined. A 56/44 Bi$_2$O$_3$/Fe$_2$O$_3$ mole% composition and a 56Bi$_2$O$_3$·44Fe$_2$O$_3$ + 6.5wt% NaCl composition. The samples were heat treated at different times up to 8 minutes and the phase content was examined as a function of the time using XRD measurements and analysis. It was demonstrated that using both compositions, maximum BiFeO$_3$ phase content is obtained after 3.5 minutes. In the former approximately 50% of the material transformed to BiFeO$_3$ while in the latter 98.5%.

1 Introduction

BFO has regained much interest in recent years due to its multiferroic nature [1]. It is one of the few known materials which simultaneously possess both ferroelectric and ferromagnetic ordering at room temperature. It has promising applications in photovoltaics, and due to the magneto-electric coupling between the electric and magnetic polarization providing for new device design. As such, the material shows much promise in realizing spintronic devices, sensors and multistate memory devices [1,2]. It has been demonstrated [3] that impurities will result in additional phases, the more common and stable ones being the Bi$_2$Fe$_4$O$_9$ (mullite) and Bi$_{25}$FeO$_{40}$ (sillenite) with a relatively short lived phase of BiFeO$_3$ (BFO). Of the two variants (BiFeO$_3$, Bi$_2$Fe$_4$O$_9$) much work has been done in sintering ceramics composed of the variety of phases with the aim of obtaining materials which are composed mostly of BiFeO$_3$ nano crystallites. This is required for fabricating experimental devices based on deposition of thin films such as spintronics based components and sensors. BiFeO$_3$ sintered ceramic disks may be used as targets for the thin film deposition process.

While all three phases appear at different ratios within the sintered material we can expect that those phases with the greater change in Gibbs energy will be more stable. Based on experimental work, Phapale et al. [4] evaluated the heat capacity and derived the standard Gibbs energy of formation for the above compounds from room temperature up to 640°C. Selbach et. al. expanded this work demonstrating that at the temperature range of 447 ~ 767°C Gibbs energy of formation of BiFeO$_3$ is a metastable compound which would be the first to nucleate but would eventually transform into Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$. But above 767°C increasing to the proximity of the peritectic temperature at 930°C, or below it is a stable compound. Carvalho et. al. [5] using

*gilad.orr@ariel.ac.il
sol-gel combustion to create ceramic samples of $BiFeO_3$ have also demonstrated similar results to Selbach’s work. They further demonstrate that at a temperature of 600°C the $BiFeO_3$ transforms into the more stable mullite phase $Bi_2Fe_4O_9$ over many hours. This is the reasoning behind the short period heating and rapid cooling techniques for obtaining BFO ceramics [6, 7, 8]. Using ultra pure starting materials Lu et. al. [3] tested the stability as a function of the crucible type (gold or aluminum oxide) and the process from which the compound was synthesized. The processes consisted of solid state reaction of the starting materials without reducing parasitic phases using $HNO_3$, solid state reaction of the materials followed by parasitic phase reduction and crushed crystals. Composition stability was tested at 850°C for 24 and 48 hours and 855°C for 24 hours. Both temperatures are above 767°C so we should expect them to form the more stable $BiFeO_3$ phase. After 48 hours at 850°C both the phase reduced (alumina crucible) and the crushed crystal (gold crucible) did not decompose, while after 24 hours 44% of the non reduced compound decomposed. At 855°C after 24 hours, 7% of the crushed crystals in gold crucible, 26% of the parasitic phase reduced in gold crucible, and 87% of the parasitic phase reduced in alumina crucible decomposed. Evidently, and as expected at 850°C BFO is the stable phase, at the same temperature the material without parasitic phase reduction decomposed considerably. The important point to consider is that the $HNO_3$ treatment dissolves every compound but the $BFO$ and the $Bi_2Fe_4O_9$, thus without such a treatment, some phase impurities and not necessarily only the sillenite phase exist resulting in an increased decomposition. At 855°C the volatility of bismuth comes into play. Lu claims it is a phase transformation but we doubt it as no one has observed a phase transformation at that temperature, and that includes the DSC results that they present in the mentioned article. It is more likely a compositional change due to bismuth evaporation. Considering the parasitic reduced phase in the alumina crucible, something totally different is happening. According to the published phase diagrams [9, 10, 11, 3] we should not expect the mullite phase unless we exceed 930°C or if we suffer from considerable evaporation of bismuth. Hence, we are drawn to suspect that the existence of the mullite phase in areas which it is not a favorable phase is indicative of impurities. In order to test this assumption we will compare a $Bi_2O_3$ saturated composition against the same $Bi_2O_3$ saturated composition but with $NaCl$ as an impurity.

2 Experimental

2.1 Material synthesis and sintering

The starting materials for the samples which were sintered are based on the what was found to be the optimal composition by Bush et. al and Gabbasova et. al [12] for growing BFO macroscopic crystals from the melt. The melt composition is 75.6 weight% $Bi_2O_3$, 17.9 weight% $Fe_2O_3$, and 6.5 weight% $NaCl$. Disregarding the NaCl that provides the sodium as a spectator ion, this translates to 56 mole% $Bi_2O_3$ and 44 mole% $Fe_2O_3$. We regard the above material as the material with controlled impurities. This was compared to results obtained with a composition of 78.85 weight% $Bi_2O_3$ and 21.15 weight% $Fe_2O_3$, considered the material without controlled impurities. It gives ample room for study without the system shifting into a different phase system during the study due to mass loss. A recent article [13] illustrates this mass loss using DTA/TGA curves stating that above 400°C and up to 800°C approximately 2.5% Bi evaporation occurs. This corresponds to approximately a 1 mole% decrease in Bi content. Based on [3] we can assume that at 855°C it increases to 7 mole% over a period of 24 hours. As shall be seen, the above compositions will
assist us in evaluating dynamics and evolution of the different compounds in the sintered samples. The constituents were mixed and milled, followed by calcination at 800°C for 4 hours in alumina crucibles. The furnace was heated at a rate of 100 degrees per hour with the material inside until it reached the target temperature. After 4 hours of calcination it was cooled to room temperature at a rate of 100 degrees per hour. The calcinated material was ground for 2 hours using a ball grinder and sieved through a 50µm mesh. Approximately 0.6g was pressed uniaxially into 12.7 mm disks with a pressure of approximately 100MPa. Pressed disks were inserted into a muffle furnace set at 880°C for a certain period of time set in minutes and were extracted followed by quenching in air.

2.2 Evaluation of the calcined materials

The resulting calcined materials and sintered samples were recorded visually using a metallurgical microscope, followed by XRD and SEM analysis. The XRD measurements were conducted on a Rigaku SmartLab using the SmartLab Studio II software for analysis. One of the most important aspects for comprehending the optical microscope images is the ability to distinguish the morphology of at least one of the phases. As we shall see from the XRD analysis, the three obtained crystalline phases important to us, are BiFeO$_3$, Bi$_2$Fe$_4$O$_9$ and Bi$_{25}$FeO$_{40}$. Based on the Gibbs energy of formation [14] during the initial stages of nucleation, and for a relatively short time a metastable BiFeO$_3$ compound prevails over the Bi$_2$Fe$_4$O$_9$ and the Bi$_{25}$FeO$_{40}$. It means as well, that the metastable compound will prevail at a lower temperature range. In the longer time span we expect the more stable compounds as are described by the Bi$_2$O$_3$ − Fe$_2$O$_3$ phase system. For the 56/44 mole% Bi/Fe composition we expect either BFO or sillenite. We begin by analyzing the compounds after calcination. Figure 1 illustrates an x100 optical microscope image of fragments of crushed calcinated material before grinding.

![Figure 1](image_url)

Figure 1: Fragments of crushed material after calcination prior to grinding. Much of the material has crystallized into its distinguishable phases.

The figure illustrates that during the calcination process some of the constituents may be separated for analysis. In the example illustrated in the figure two phases are distinguishable, the metallic colored orthorhombic Bi$_2$Fe$_4$O$_9$ and the orange tinted brown rhombohedral BiFeO$_3$. 
Crystal phases developed due to the calcination process were analyzed by crushing some of the calcinated compounds rinsing them in $HNO_3$ and washing them in water. This procedure dissolved all the different phases but the $Bi_2Fe_4O_9$ and $BiFeO_3$. The two remaining crystals were manually separated and were analyzed with XRD. Figure 2 illustrates an example of separated $Bi_2Fe_4O_9$ crystals.

![Image](image.png)

**Figure 2:** $Bi_2Fe_4O_9$ crystals extracted from the calcinated material with its XRD profile

For the above example using split pseudo-Voigt fitting of the diffraction peaks and fitting the peaks with the ICDD database. The lattice parameters were measured to be $a = 7.9947\,\text{Å}$; $b = 8.4599\,\text{Å}$; $c = 5.9254\,\text{Å}$.

We now compare the crystallized compositions of the two synthesized materials (with $Bi_2O_3$; NaCl flux and $Bi_2O_3$ flux) after calcination and grinding. Figure 3 illustrates the ground material with 6.5 weight% $NaCl$. 


Figure 3: An optical microscope image of the synthesized and ground material with 6.5 weight% NaCl prior to sintering. An example of the various phases that can be observed are pointed to using arrows.

X-ray diffraction measurements of the ground material with NaCl in the flux show the following weight fraction of the crystalline phases (Table 1).

| Compound      | Weight fraction [%] | \(a\) [Å] | \(b\) [Å] | \(c\) [Å] | \(\alpha\) [°] | \(\beta\) [°] | \(\gamma\) [°] |
|---------------|---------------------|-----------|-----------|-----------|---------------|---------------|---------------|
| Bi\(_2\)Fe\(_4\)O\(_9\) | 27.4                | 7.96623   | 8.43444   | 5.99638   | 90.000        | 90.000        | 90.000        |
| Bi\(_{22}\)Fe\(_2\)O\(_36\) | 26.3               | 10.13167  | 10.13167  | 10.13167  | 90.000        | 90.000        | 90.000        |
| Bi\(_{25}\)FeO\(_40\) | 24.4                | 10.15868  | 10.15868  | 10.15868  | 90.000        | 90.000        | 90.000        |
| BiFeO\(_3\)   | 14.6                | 5.63427   | 5.63427   | 13.78349  | 90.000        | 90.000        | 120.000       |
| \(\alpha\) − BiFeO\(_3\) | 7.3                | 5.62267   | 5.62936   | 5.62796   | 59.330        | 59.350        | 59.380        |

Table 1: Weight fraction of crystalline phases in calcinated BFO Bi\(_2\)O\(_3\); NaCl based flux

As we can expect, we see that the prevailing phases are the mullite (27.4%) and sillenite (24.4%). An additional, less commonly reported compound Bi\(_{22}\)Fe\(_2\)O\(_36\), was observed as well. This compound was suggested by Mel’Nikova et al. [15] who developed a method of determining the composition of sillenites using XRD data. Murakami [16] working on BaTiO\(_3\) − BiFeO\(_3\) compounds, reports detecting the compound but does not dwell on the subject. We assume that it is one of the metastable phases which is attained due to the existence of the sodium ions, acting as spectator ions. A smaller fraction (14.6%) of rhombohedral BiFeO\(_3\) phase exists with an additional 7.3% (2:1 ratio) of the triclinic (P1) \(\alpha\) − BiFeO\(_3\). The \(\alpha\) − BiFeO\(_3\) results obtained, corresponds with the lattice parameters reported by Wang et al. [17]. It is interesting to notice that even though the NaCl did not react with the material displaying obvious segregation it was found to be in an amorphous state.

Figure 4 displays an optical microscope image of the second calcinated and ground Bi\(_2\)O\(_3\) based flux.
Figure 4: Optical microscope image of the calcinated and ground $Bi_2O_3$ based flux

while the orthorhombic mullite structure is hardly observed in the figure, one can easily notice
the considerable increase in the metallic gray areas signifying the sillenite compound. Table 2
displays the weight fraction of the crystalline phases of the calcinated flux materials that do not
include the sodium chloride.

| Compound     | Weight fraction [%] | $a$ [Å]  | $b$ [Å]  | $c$ [Å]  | $\alpha$ [°] | $\beta$ [°] | $\gamma$ [°] |
|--------------|---------------------|----------|----------|----------|---------------|-------------|--------------|
| $Bi_{25}FeO_{40}$ | 68.9                | 10.15600 | 10.15600 | 10.15600 | 90.000       | 90.000      | 90.000      |
| $BiFeO_3$     | 25.7                | 5.57801  | 5.57801  | 13.86400 | 90.000       | 90.000      | 120.000     |
| $Bi_2Fe_4O_9$ | 5.39                | 7.97971  | 8.43282  | 6.00463  | 90.000       | 90.000      | 90.000      |

Table 2: Weight fraction of crystalline phases in calcinated BFO flux materials without sodium chloride

Table 2 shows a similar percentage of mullite to the material in which the parasitic phases were
not reduced (Lu [3]). In this molar ratio we do expect the sillenite to be much more abundant as
it is one of the two stable phases.

2.3 Sintering

Prior to sintering and in order test the stable phases, the materials were placed for 16 hours at
$600^\circ C$ thus increasing the stable phases at that temperature range, i.e. the mullite and sillenite
phases. The reaction trend gives us a better indication which are the stable phases. As the various
articles using rapid sintering [6, 7, 8] reported placing the pressed disks within the furnace between
400 and 450 seconds, the samples were placed in the furnace up to 8 minutes and then rapidly
cooled by extracting them from the furnace and letting them cool on a piece of ceramic at room
temperature. Figure 5 illustrates the results obtained from the 56/44 mole% $Bi_2O_3 – Fe_2O_3$ solid
state compounds based on XRD measurements.
Figure 5: Weight fraction of the different compounds resulting from the solid state reaction of the quenched disks at 880°C based on the reaction time.

At this specific $\text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio, the two expected phases that are known to coexist are the BFO phase and the sillenite phase. The results show that up to approximately 3.5 minutes the $\text{BiFeO}_3$ phase increased to about 50% at the expense of both the $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases, after which it experiences a fast decline to undetectable levels. After 3.5 minutes while the BFO decomposes the level of the mullite increases slightly and the sillenite becomes the dominant stable phase. This does not correspond with the accepted phase diagram and hints that some impurities from the crucible may have altered the composition or that at 880°C $\text{Bi}_{25}\text{FeO}_{40}$ is the dominant phase.

We repeated the process described above, with the $\text{Bi}_2\text{O}_3 − \text{Fe}_2\text{O}_3 − \text{NaCl}$ composition. The weight fraction of the different compounds obtained by the system as a function of time is described in figure 6.
Figure 6: Weight fraction of the different compounds obtained by the 56Bi$_2$O$_3$·44Fe$_2$O$_3$ + 6.5wt% NaCl composition heated and quenched disks at 880°C based on the reaction time.

Figure 6 demonstrates the process in which the NaCl (Melting point 801°C) slowly, dissolves the constituents and between 3-4 minutes suppressing the mullite and sillenite phases while the BiFeO$_3$ temporarily dominates. At this composition, the material is beyond the peritectic which for longer periods will result in a liquid + Bi$_2$Fe$_4$O$_9$ similar to the transition, for the 56/44 mole% composition above 934°C.

3 Discussion

Based on the accepted phase diagram [18, 9, 10, 11, 3], and Gibbs energy of formation [14], during the synthesis of materials and solid state reactions above 767°C the Bi$_2$Fe$_4$O$_9$ phase, should not be a stable phase. This is true as long as the Bi$_2$O$_3$/Fe$_2$O$_3$ molar ratio is above 1:2. Contrary to what has just been stated, experience has shown that for long enough periods of time the mullite phase does form as a stable phase. As a result, rapid heating and cooling techniques are a common practice for obtaining a high weight fraction of BFO ceramics. Lu et. al. have shown that for highly controlled compositions in gold crucibles at a temperature of 850°C, BFO is the prevalent stable phase. Given impurities it will slowly decompose to other phases primarily to mullite. At temperatures above 855°C even the highly controlled compositions tend to decompose over a long period of time. This has to be taken into account if one attempts to grow bulk crystals even for highly controlled environments, one is limited below 850°C for bulk BFO crystal growth. As the goal of this work was sintering targets for sputtering machines, we were interested in BFO phase stability and the adequate sintering time during the sintering process. We compared a 56:44
mole% $Bi_2O_3 - Fe_2O_3$ composition to a $56Bi_2O_3 \cdot 44Fe_2O_3 + 6.5wt% NaCl$ composition. We demonstrated that at 880°C after 3.5 minutes in the composition which does not include NaCl only approximately 50% of the material has transformed into BFO. At the same time using the composition that includes NaCl as a flux, 98.5% of the material was in the BFO phase totally suppressing any other phase. The importance of this finding is that it is relatively simple to remove the NaCl from the sintered disk. This is done by rinsing the disk in water. One drawback of this method is that it leaves the disk with pitting and cavities.

References

[1] Nicola A Spaldin, Sang-Wook Cheong, and Ramamoorthy Ramesh. Multiferroics: Past, present, and future. Physics Today, 63(10):38, 2010.

[2] Gustau Catalan and James F Scott. Physics and applications of bismuth ferrite. Advanced materials, 21(24):2463–2485, 2009.

[3] J Lu, LJ Qiao, PZ Fu, and YC Wu. Phase equilibrium of $Bi_2O_3 - Fe_2O_3$ pseudo-binary system and growth of bfeo3 single crystal. Journal of crystal growth, 318(1):936–941, 2011.

[4] S Phapale, R Mishra, and D Das. Standard enthalpy of formation and heat capacity of compounds in the pseudo-binary $Bi_2O_3 - Fe_2O_3$ system. Journal of nuclear materials, 373(1-3):137–141, 2008.

[5] TT Carvalho and PB Tavares. Synthesis and thermodynamic stability of multiferroic bfeo3. Materials Letters, 62(24):3984–3986, 2008.

[6] JAHAR L MUKHERJEE and FRANKLIN FY WANG. Kinetics of solid-state reaction of $Bi_2O_3$ and $Fe_2O_3$. Journal of the American Ceramic Society, 54(1):31–34, 1971.

[7] YP Wang, L Zhou, MF Zhang, XY Chen, J-M Liu, and ZG Liu. Room-temperature saturated ferroelectric polarization in $BiFeO_3$ ceramics synthesized by rapid liquid phase sintering. Applied Physics Letters, 84(10):1731–1733, 2004.

[8] MS Awan and AS Bhatti. Synthesis and multiferroic properties of bfo ceramics by melt-phase sintering. Journal of materials engineering and performance, 20(2):283–288, 2011.

[9] EI Speranskaya, VM Skorikov, E Ya Rode, and VA Terekhova. The phase diagram of the system bismuth oxide-ferric oxide. Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 14(5):873–874, 1965.

[10] A Maitre, M Francois, and JC Gachon. Experimental study of the $Bi_2O_3 - Fe_2O_3$ pseudo-binary system. Journal of Phase Equilibria and Diffusion, 25(1):59–67, 2004.

[11] R Palai, RS Katiyar, Hans Schmid, Paul Tissot, SJ Clark, Jv Robertson, SAT Redfern, GA Catalan, and JF Scott. $\beta$ phase and $\gamma$- $\beta$ metal-insulator transition in multiferroic $bifeo_3$. Physical Review B, 77(1):014110, 2008.

[12] ZV Gabbasova, MD Kuzuñin, AK Zvezdin, IS Dubenko, VA Murashov, DN Rakov, and IB Krynetsky. $Bi_{(1-x)}R_{(x)}FeO_{3}$ ($r$= rare earth): a family of novel magnetoelectrics. arXiv preprint arXiv:1008.1470, 1991.
[13] Piyush Sharma, PK Diwan, and OP Pandey. Impact of environment on the kinetics involved in the solid-state synthesis of bismuth ferrite. *Materials Chemistry and Physics*, 233:171–179, 2019.

[14] Sverre M Selbach, Mari-Ann Einarsrud, and Tor Grande. On the thermodynamic stability of BiFeO$_3$. *Chemistry of Materials*, 21(1):169–173, 2009.

[15] TI Mel’nikova, GM Kuz’micheva, NB Bolotina, and NV Sadovskaya. Development of methods of x-ray diffraction analysis for determining the composition and structure of selenite-family crystals. *Crystallography Reports*, 59(2):155–159, 2014.

[16] Shunsuke Murakami. *BaTiO$_3$ – BiFeO$_3$ based lead-free ceramics for actuator applications*. PhD thesis, University of Sheffield, 2018.

[17] Hui Wang, Chengxu Yang, Jun Lu, Meimei Wu, Jie Su, Kuo Li, Junrong Zhang, Guobao Li, Tounan Jin, Takashi Kamiyama, et al. On the structure of $\alpha$-BiFeO$_3$. *Inorganic chemistry*, 52(5):2388–2392, 2013.

[18] Hideo Koizumi, Nobukazu Niizeki, and Takuro Ikeda. An x-ray study on Bi$_2$O$_3$ – Fe$_2$O$_3$ system. *Japanese Journal of Applied Physics*, 3(8):495–496, aug 1964.