The Influence of BTO-BHF Different Composition on its Ferroelectric Properties

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Abstract. Barium Titanat and Barium Hexaferrite composite was synthesized by sol-gel method in different composition and holding sintering time. The crystallographic property was characterized by x-ray diffraction and analysed by GSAS program, the saturation and remanent electrical polarisation were measured using Sawyer Tower circuit. The best composition for multiferroic candidate is BTO:BHF 1:1 at 5 hours sintering time.

1. Introduction

As individual material, both Barium Titanat ($BaTiO_3$) and Barium Hexaferrite ($BaFe_{12}O_{19}$) are well known respectively as ferroelectric [1,2,3] and ferromagnetic [4,5] materials, however their combination is rarely looked at as multiferroic materials. Already known, these materials possess more than onetype of ferroic order such as ferromagnetic, ferroelectric, ferroelastic andferrotoroidics. This class of materials finds promisingapplications in nonvolatile memory, memory-cellcapacitor, electromagnetic-interference filter, sensorsand so forth [6,7].

In this paper we present our current work on synthesizing BTO - BHF and exploring the possibility of having them as multiferroic devices. We prepared BTO-BHF composant by sol-gel method in our laboratory at Physics Department, University of Indonesia. The specimen was then analyzed by x-ray diffraction and quantitatively by GSAS program. We further explored its electrical polarisation saturation and remanent to seek the possibility BTO-BHF composant as multiferroic materials.

2. Experiment Method

By using regular route, the BHF-BTO composite are synthesized by using sol gel technique[5,8]. We start to synthesized BHF and followed by BTO synthesized. The starting materials for BHF were iron nitrate $Fe(NO_3)_3.9H_2O$, barium nitrate $Ba(NO_3)_2$, citric acid ($C_6H_7O_8$) and ammonia solution (NH_4OH), all of with the analytical purity (99.0%) from Merck KGaA Chemicals, Damstadt, Germany. The appropriate amount of $Fe(NO_3)_3.9H_2O$ and $Ba(NO_3)_2$ in molar ratios of Ba^{2+}/Fe^{3+} of 1:12 and 1:11.5 were dissolved in a minimum amount of deionized water to get a clear solution. Citric acid was added into the prepared aqueous solution to chelate Ba^{2+} and Fe^{3+}, stirring for a few minutes until turning into the solution. Then ammonia solution was added to adjust the pH of 7 until the mixed solution getting into brown. The solution was evaporated to dryness by heating at 80-90^{o}C on a hot plate with continuous stirring. As the water evaporated, the solution became viscous and finally it formed a very viscous brown gel then kept it in oven at 150^{o}C for 5 hours. Most of the moisture in the viscous brown gel was evaporated and formed dried gel after heating at 450^{o}C for 24 hours. After grinding in the mortar, the dried gel was sintered at 850^{o}C for 10 hours respectively.

The starting materials for BTO were barium nitrate $Ba(NO_3)_2$, Titanium Oxide (TiO_2), citric acid ($C_6H_7O_8$), ammonia solution (NH_4NO_3), and nitric acid (HNO_3). The appropriate amount of $Ba(NO_3)_2$, TiO_2, were reacted by NH_4NO_3. Citric acid ($C_6H_7O_8$) were add into result compound with ratio $C_6H_7O_8$:NH_4NO_3 (1:1 and 2:1). The solution was evaporated to dryness by heating at 80-90°C on a hot plate with continuous stirring for 5 hours. As the water evaporated, the solution became viscous and finally formed a very viscous brown gel then kept it in oven at 100°C for 1 hours. Most of the moisture in the viscous brown gel was evaporated and formed dried gel after heating at 500°C for 12 hours. After grinding in the mortar, the dried gel was sintered at 700°C for 2 hours respectively.

Both result compound were mixed with weight fraction BTO:BHF (1:1, 1:2, 1:3) and heated at 925°C for 5, 10 and 15 hours in sintering process. XRD and General Structure Analysis System (GSAS)program were used for crystallographic properties andelectrical properties were characterized to know their ferroelectric properties [5,8,9].We have utilized Sawyer Tower circuit to measure these electrical properties. The circuit is conected to our home made instrument (Fig. 1) which consists of voltage attenuators, an adjustable HVPS, a DAQ card and a PC.

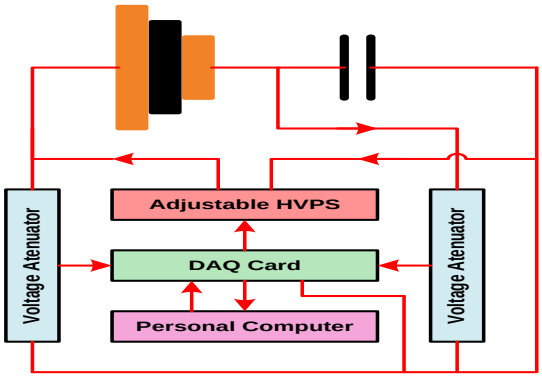


Figure 1. Electrical Hysterisis Loop Measurement

3. Result and Discussion

For three different composition of BTO:BHF and three different sintering temperature, we have examined the crystallographic property and the real composition by using x-ray diffraction (XRD). The results for 5 hours sintering at different weight fraction are shown in Fig 2 and the results for different sintering time at weight fraction of 1:1 are shown in Fig.3.

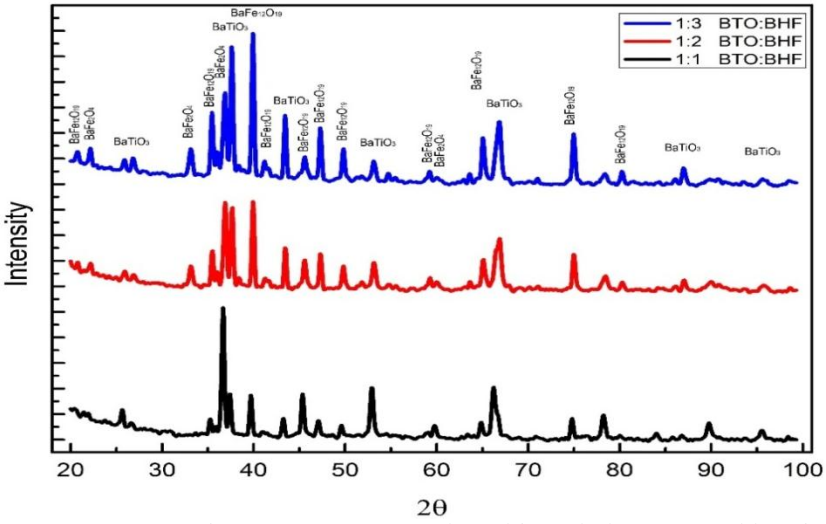


Figure2. XRD pattern of BTO-BHF composite with variation composition for 5 hours

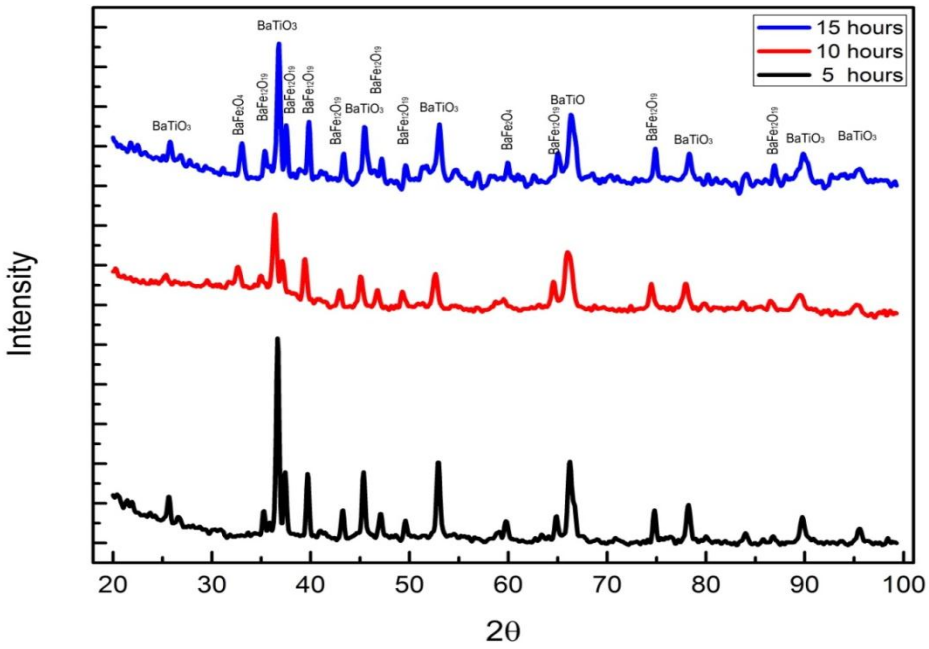
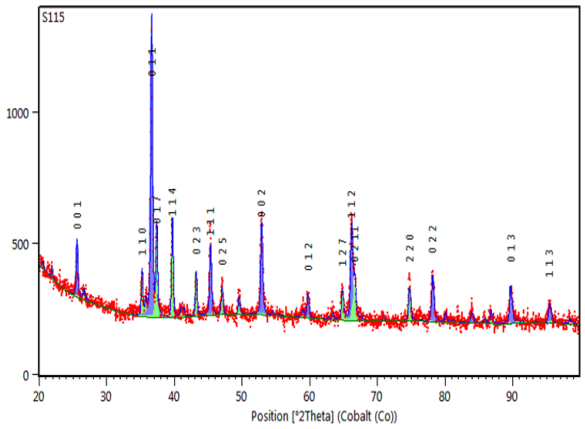
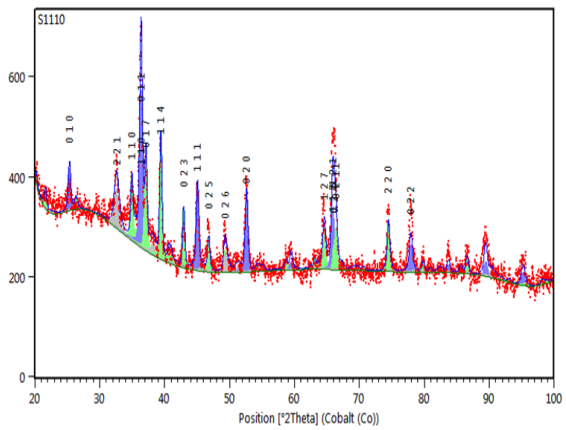


Figure 3. XRD pattern of 1:1 composition with temperature variation of BTO-BHF composite

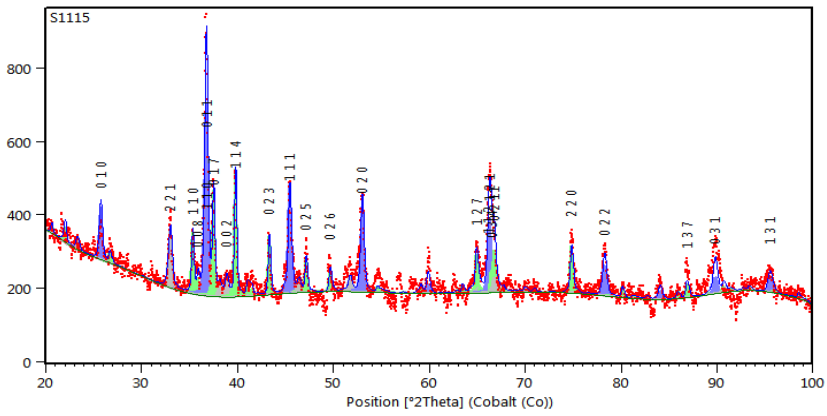
The ICDD database running on PCPDFWin is utilized to get the crystal structure, space group and lattice parameters. The search-match found the existence of $BaTiO_3$, $BaFe_{12}O_{19}$ as well as one satelite phase $BaFe_2O_4$. The peaks increase or decrease in accordance with the prescripted composition. There is no residual phase $BaFe_2O_4$ in weight fraction of 1:1 at 5 hours sintering. The XRD data is further examined deeply by refinement with HighScore Plus Software to know the exact composition, crystallographic parameters and crystallite size. However, what we concern the most is their composition. Figure 4 showsrefinement results for BTO:BHF with 1:1 intended composition respectivelly at 5, 10 and 15 hours sintering hold time. Figure 5 shows refinement results for BTO:BHF with 1:2 intended composition respectively at 5, 10 and 15 hours sintering hold time and Fig 6. Shows the similar case for BTO:BHF with 1:3.



(a).

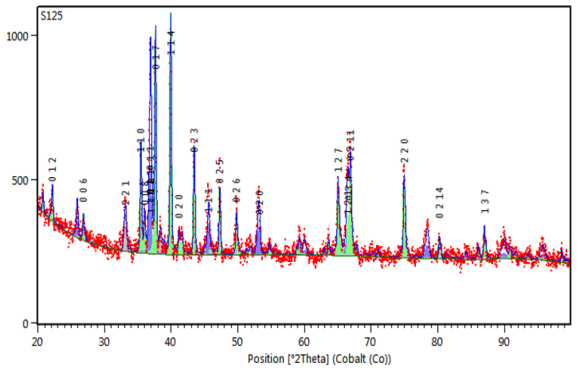


(b).

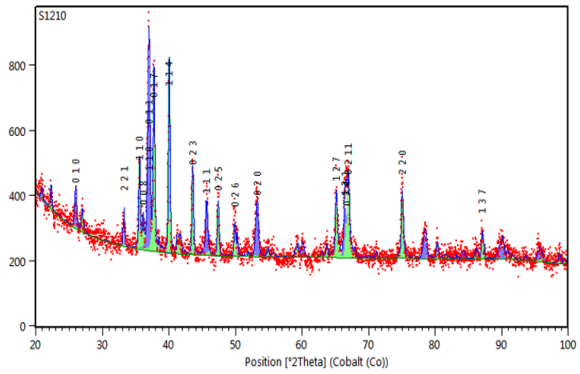


(c).

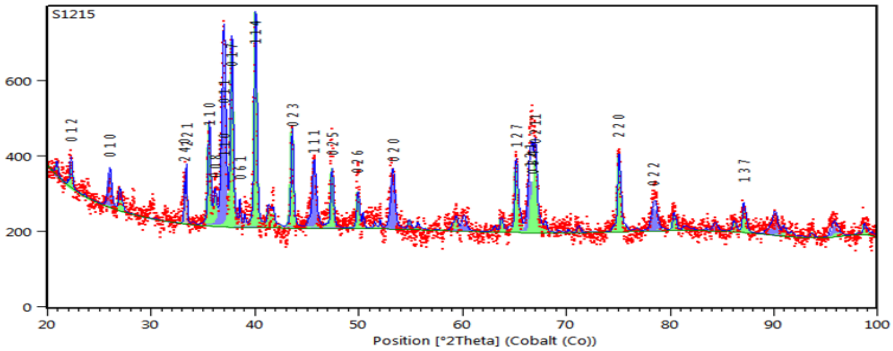
Figure 4. Refinement Results for BTO:BHF 1:1 (a) t = 5 hours (b) t=10 hours (c) t=15 hours



.**(a).**

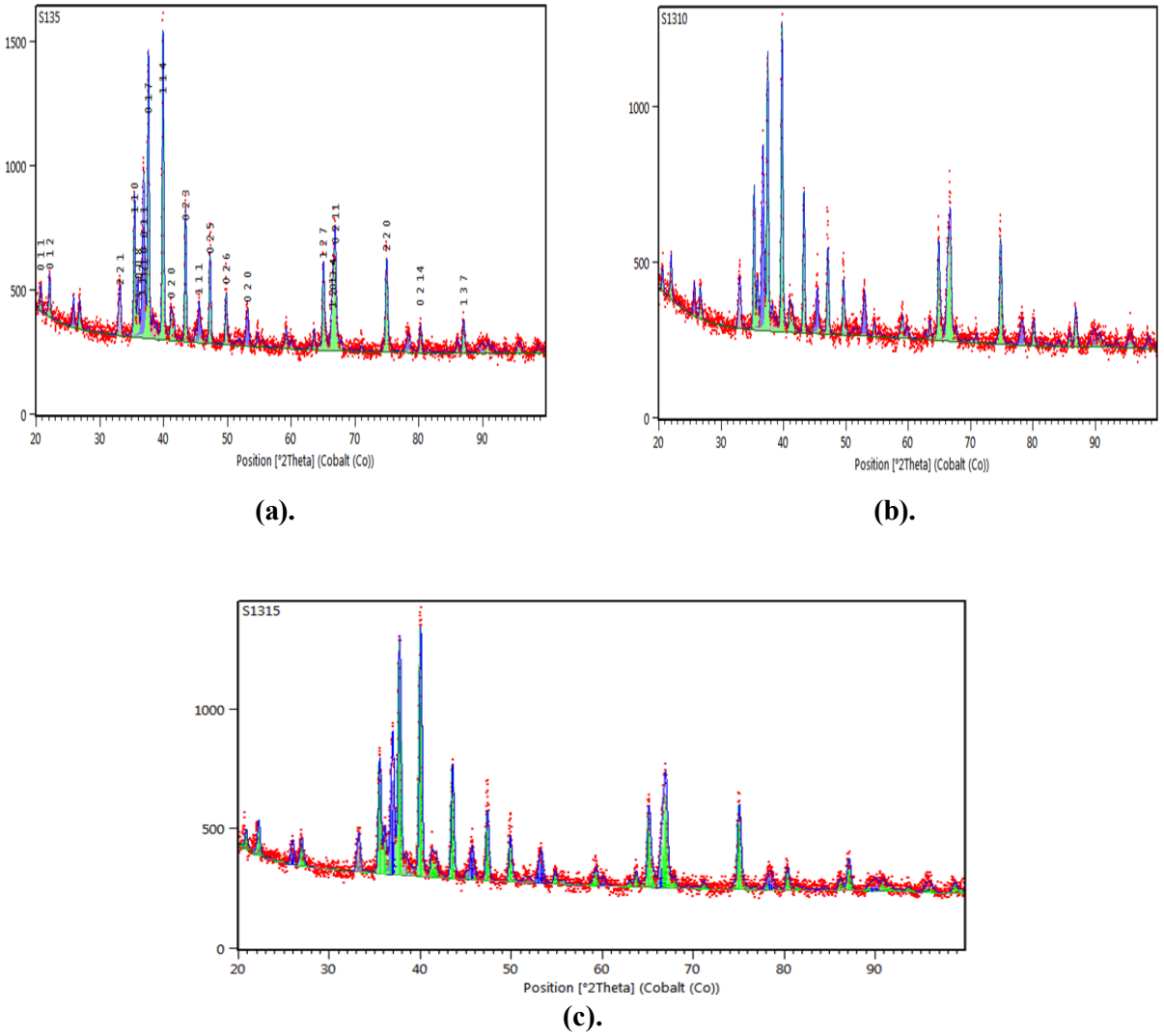


(b).



(c).

Figure 5. Refinement Results for BTO:BHF 1:2 (a) t = 5 hours (b) t=10 hours (c) t=15 hours



(a). **(b).**

(c).

Figure 6. Refinement Results for BTO:BHF 1:3 (a) t = 5 hours (b) t=10 hours (c) t=15 hours

From the results of refinement from Fig. 4, 5 and 6, it could be seen that almost of all samples have residual phase $BaFe_2O_4$ in plane (221) except at weight fraction of 1:1 for 5 hours sintering time. The figures also show that longer sintering time and higher sintering temperature, the amount of $BaFe_2O_4$ phase getting increase as shown in Table 1.

Table 1. Composition (Wt%) of BTO-BHF Composite for several sintering temperature variaton

BTO:BHF	t : 5 hours			t : 10 hours			t : 15 hours		
	BTO	BHF	$BaFe_2O_4$	BTO	BHF	$BaFe_2O_4$	BTO	BHF	$BaFe_2O_4$
1:1	44.2%	55.8%	0%	27.5%	49.5%	7.02%	35.2%	48.6%	11.38%
1:2	25.4%	49.4%	5.25%	23.1%	42.1%	8.56%	22.8%	38.1%	16.24%
1:3	20.2%	70.5%	6.92%	23.5%	69.5%	9.16%	23.6%	65%	22.98%

If the sintering process getting longer and higher, it will hapen the decomposition of $BaFe_{12}O_{19}$ whereas Ba^{2+} ion with Fe_2O_3 will form the third phase $BaFe_2O_4$ in plane (221).We summarized the prescripted and real composition in Table 1. The table also shows the variation condition for several sintering times.

After we convinced the existence of BTO and BHF, we examine the electrical polarization saturation and remanent. The some results of electrical characterization are shown in Fig 7,8 and 9 as an electrical hysteresis loop.

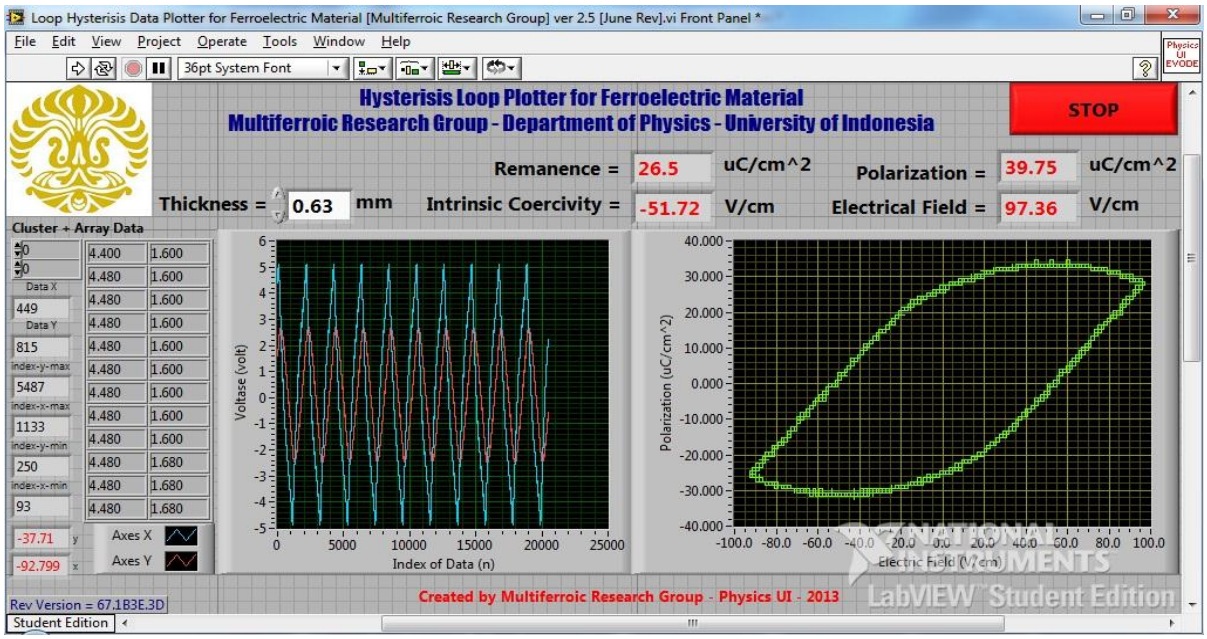


Figure 7. Hysteresis Loop of BTO:BHF 1:1 for 5 Hours Sintering Time

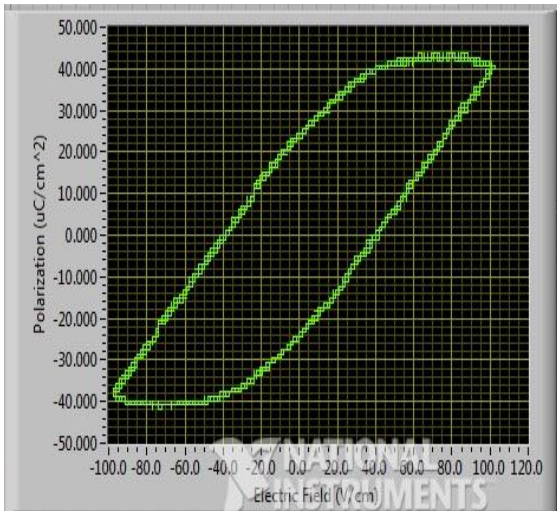


Figure 8. Hysteresis Loop of BTO:BHF 1:1 for 10 Hours Sintering Time

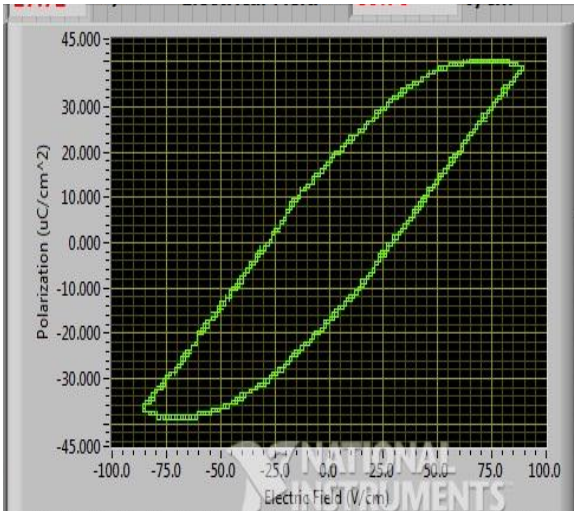


Figure 9. Hysteresis Loop of BTO:BHF 1:1 for 15 Hours Sintering Time

Clearly as indicated in the Fig. 7,8 and 9 that for all cases we found that all samples show a form of hysteresis loop with different value of electrical polarisation, coersive and remanent. The data could be converted in graph as shown in Fig 10, 11 and 12.

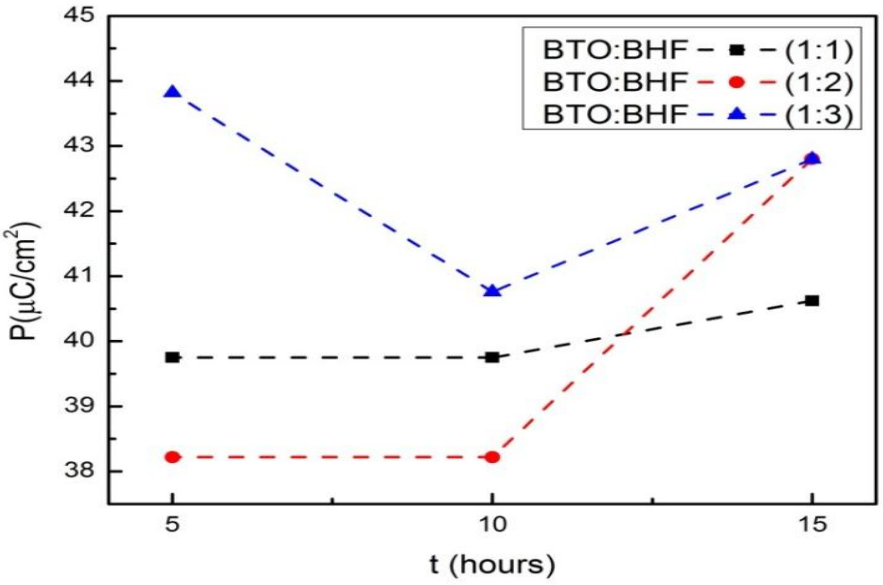


Figure 10. Electrical Saturation Polarisation for Several Sintering Process Duration

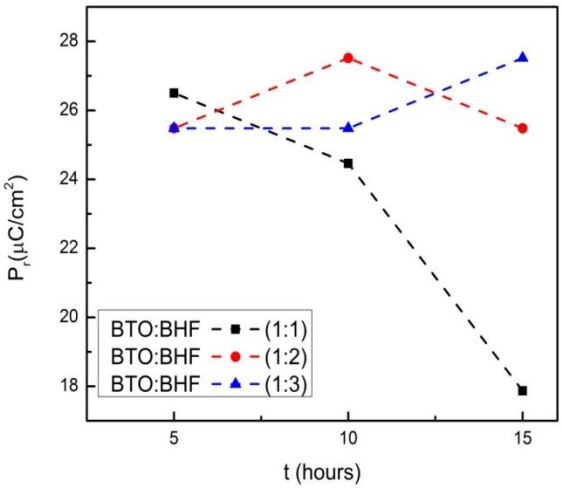


Figure 11. Electrical Saturation Polarisation for Several Sintering Process Duration

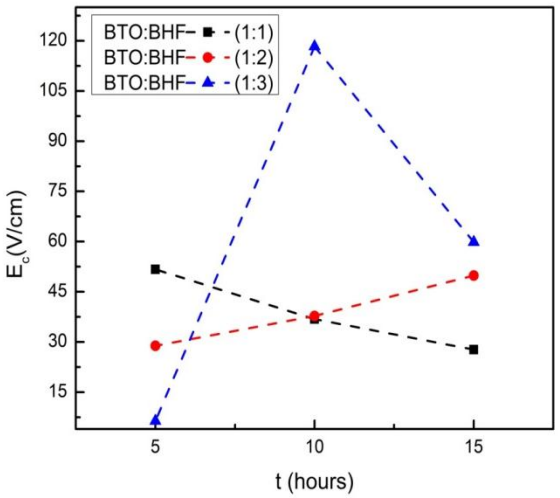


Figure 12. Coersive Electric Field of BTO-BHF Composite at different Composition

From Fig 10 it could be seen that the value of electrical saturation polarisation decreasesuntil 2 parts of weight fraction of BHF, but if the weight fraction of BHF exceeds from 2 parts (especially at ratio of 1:3) the value of electrical saturation polarisation increases. On theotherhand the Fig. 11 shows that the electrical remanent polarisation decreases as the BHF composition increases.We further examined the coersive field of the materials. Unfortunetely, the Fig. 12 indicates the strenght of the field is inconclusive if we compare with its composition, this is probably due to the unknown nature of the third phase, $BaFe_2O_4$.

4. Summary

We can conclude that BTO:BHF prepared by sol-gel method shows good crystalinity and the ferroelectric property is well observed. The composition 1:1 at 5 hours sintering time is the most stable and no residual phase, hence judging from its saturation and remanent electrical polarisation, it can be a good candidate for multiferroic devices.

5. Acknowledgment

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