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EFFECT OF CHELATING AGENTS, SINTERED TEMPERATURE AND HEAT TREATMENT DURATION ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF $BiFeO_3$

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ABSTRACT: A multiferroics $BiFeO_3$ (BFO) samples are prepared by co-precipitation and sol-gel methods. Various combinations of chelating agent, sintering temperature and heat treatment durations tried to prepare single phase $BiFeO_3$ samples. Sol-gel method is found more suitable to synthesize phase pure $BiFeO_3$ samples. The samples were characterized by XRD, SEM, EDX, Electrical resistivity and optical reflectivity measurements. The distorted rhombohedral perovskite structure R3c has been confirmed. The grain size and lattice constant of the samples are also calculated using XRD patterns. The resistivity of the samples is measured at room temperature. The resistivity is found to increase on changing the chelating agent from Tartaric acid to Tartaric acid plus Ethylene glycol. The resistivity reveals the semi conductivity behavior of the BFO samples. The measurement of infrared reflectivity of BFO samples at room temperature reveals optical phonons. The resonant frequency of the phonon modes is determined and reported.

Key words: X-ray diffraction; Scanning Electron Microscopy (SEM); Energy dispersive spectroscopy (EDS); Fourier Transform Infrared Spectroscopy (FTIR).

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INTRODUCTION

Multiferroics was first time introduced by Schmid in 1994; it has three types of ferroic order i.e. ferroelectricity, ferromagnetism and ferroelasticity which occur in the same phase (Kamrul Haque Bhuiyan, 2016) (Kamrul Haque Bhuiyan, 2016) The term utilized for such type of material exhibit a long-range magnetic ordering along with spontaneous polarization. Multiferroism often refers to a combination of ferroelectricity and magnetism (ferromagnetism, antiferromagnetism) in one particular material (Kamrul Haque Bhuiyan, 2016). Multiferroics are materials where electric and magnetic fields are combined in a single phase material. Ferroelectric materials are used for ferroelectric memories. A memory element made of a multiferroic material can be in one of four possible states instead of two in a traditional memory element, its means that it has the ability to store information twice as much can be stored per cell. Multiferroic memories have another benefit that they support in fast low-power electrical write and non-destructive magnetic read operation. This would remove the disadvantage of the destructive read process currently associated with ferroelectric memories(Scott, 2007) (Kamrul Haque Bhuiyan, 2016). A multiferroic which connects ferromagnetic and ferroelectric properties would be a multifunctional material which could help create non-volatile memory for computers, resonators and power control devices such as transformers, filters, magnetic field sensors, gas sensors, and many other applications. In Multiferroic memory technologically, one also needs a material with room temperature ferroelectric and ferromagnetic behavior. It is difficult to find a room temperature single-phase multiferroic having large magnetoelectric coupling effect. A material possessing both characteristics of a ferroelectric and ferromagnetic, it should satisfy the broken inversion symmetry in case of ferroelectric whereas broken time-reversal symmetry in the case of ferromagnets (Mostovoy, 2006). Ferroelectrics are insulators whereas ferromagnets are usually metals where spins of electrons of partially filled d shells magnetically order (Hill, 2000). Some materials do exhibit ferroelectricity and ferromagnetism simultaneously in spite of these criteria, they either have a weak magnetoelectric coupling (for example, $BiFeO_3$), or their critical temperatures, or electric polarizations are very low (Nan, Bichurin, Dong, Viehland, & Srinivasan, 2008). It is difficult to find a single phase multiferroic that has been expanded to include other long-range orders, for instance antiferromagnetism. Thus, any material that combines more than one of these properties is described as multiferroic. The classification of multiferroics has been extended to antiferroic ordering. However, it has become a trend to use the term multiferroics to mean the materials which have both spontaneous magnetic and electric ordering simultaneously (Nan *et al*., 2008). There are a number of ideas for device applications based on multiferroic materials. One of the more popular ideas is that multiferroic bits may be used to store information in the magnetization and the polarization. Such a memory does not require the coupling between ferroelectric and magnetism; a cross coupling would be even disastrous. If magneto-electric coupling is present, device applications could be realized where information is written magnetically, but stored in the electric polarization, leading to non-volatile memory. Multiferroics bits could also be used to increase the magnetic anisotropy and the decay time for magnetic storage. Other applications include magnetically field-tuned capacitors with which the frequency dependence of electronic circuits could be tuned with magnetic fields, or multiferroic sensors which measure magnetic fields through zero-field current measurements. Bismuth ferrite a well known inorganic material possesses a perovskite structure. It is one of the most promising lead-free piezoelectric materials by exhibiting multiferroic properties at room temperature. $BiFeO_3$ samples were synthesized by co-precipitation & sol-gel method. The present work concludes Tartaric acid as a good chelating agent to prepare single phase BFO by sol-gel method by sintering the gel at 500 ^oC for 1 hr.

MATERIALS AND METHODS

The chemicals used in the synthesis were Fe $(NO_3)_3$. $9H_2O$, HNO_3, NH_3, Bi_5O (OH) $_9(NO_3)_4$. The aqueous solution of Fe (NO_3) $9H_2O$ was prepared in the deionized water. The solution of Bi_5O $(OH)_9$ $(NO_3)_4$ was made in 20% dilute HNO_3 because it is insoluble in H_2O. The solutions of Bi_5O (OH) $_9(NO_3)_4$ and Fe (NO_3) $9H_2O$ were mixed in stoichiometric ratio of 1:1. These solutions were stirrer separately for 10 minutes. When temperature reaches up to 60 ^oC, NH_3 was added drop by drop to maintain pH. Addition of NH_3 was stopped when pH reaches up to 10. Heating process continued until sample was dried completely. Finally the sample was washed with the deionized water. Methanol was added to stop the further reaction. The sample was dried in the oven at 200 ^oC and then finally grinded. At the end sample was sintered at 550 ^oC for 1hr. Finally the resulting material is grinded to get fine powder sample. The chemicals used in the synthesis of samples were Fe $(NO_3)_3$. $9H_2O$, Bi_5O $(OH)_9$ $(NO_3)_4$, HNO_3, NH_3, Citric acid, Tartaric acid. The aqueous solutions of iron nitrate non-hydrated, citric acid were made in deionized water. Aqueous solution of Bismuth sub nitrate was made in 20% dilutes HNO_3 because it is insoluble in water. Bismuth sub nitrate and iron nitrate were mixed in stoichiometric ratio of Bi/Fe = 1:1. Both solutions were stirred for 15 mints separately to make a homogeneous solution before mixing. The resultant solution was transparent, blackish red and clear. The heating was started when temperature reaches up to 60 ^oC, then NH_3 was added drop wise to maintain pH. When pH reached up to 8 then addition of NH_3 was stopped. The sample was dried up to 140 ^oC , finally gel was obtained to be grinded. The sample was pre-heated at 400^oC for 5^oC/ minutes after this sintering is done at 500 ^oC for 1 hr. The final sample was washed for several times with deionized water and dried at 80 ^oC. Finally the resulting material is grinded to get fine powder sample. The bismuth ferrite can be synthesized by different methods such as solid state route(Nan *et al*., 2008) , co-precipitation(Xu, Ke, Jia, Wang, & Zhou, 2009) , sol-gel (Nan *et al*., 2008) etc. Among these methods, the sol-gel synthesis seems to be easy and reliable method to prepare bismuth oxide. In the solid-state route, nitric acid leaching was required to eliminate the impurity phases such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ after the calcinations of mixed bismuth and iron oxide(Ianoş & Lazău, 2009) (Ianoş & Lazău, 2009), which resulted in the formation of coarser powders and the process suffered from the poor reproducibility. In the present work BFO is prepared by co-precipitation method. BFO is reported to be synthesized using co-precipitation method by many researchers. It requires low thermal conditions and gives higher purity.

RESULTS AND DISCUSSIONS

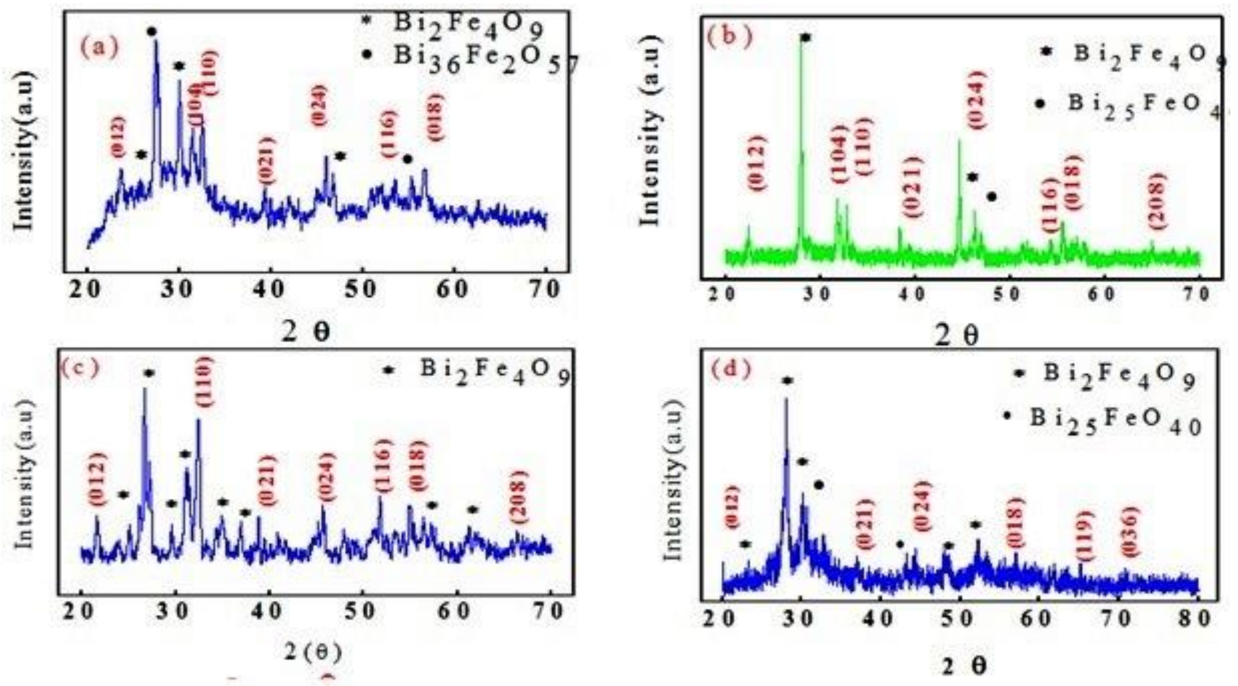
X-ray diffraction (XRD) studies were made to determine the crystalline structure of nano crystalline BFO prepared by wet chemical methods. The XRD patterns were recorded using a computer controlled diffractometer (XPERT-PRO) which was operated at 30 kV and 30 mA, using CuK_α (λ = 1.5418 Å) radiations and the data was collected in the range of $2\theta = 20^o$- 70^o with a step of 0.01^o and having a total no of steps equal to 5000. X-ray diffraction patterns of different samples prepared under different synthesis environment are shown in Figure 1(a-j). The synthesis parameters are also tabulated in the Table. I. Fig. 1(a) shows the XRD pattern of BFO prepared by co–precipitation method sintered at 550 ^oC for 1 hr. All the major peaks are indexed to $BiFeO_3$ with a rhombohedraly distorted perovskite structure belonging to R_3C space group using JCPDS Cards (141018). It is found that majority of the observed peaks has been indexed leaving only few peaks, which remained un-indexed. These un-indexed peaks reveal the presence of impurity phases. However, as it could be seen in the EDX pattern that the sample contains only Bi, Fe and O elements. Thus, impurity phase may be the secondary phases of BFO. These secondary phases, which appear quite often along with the primary phase of BFO and extensively found in literature as well, are $Bi_2Fe_4O_9$ and $Bi_{36}Fe_2O_{57}$. The few un-indexed peaks are attributed to these secondary phases. Since these peaks appear with a quite high intensity as compared to the indexed peaks, it seems as these secondary phases are quite strong in this sample. The increase in sintering temperature may help in removing these phases. The similar impurity phases were observed in the literature for sample prepared at 500 ^{o}C and for 550 ^{o}C 1 hr(Ianoş & Lazău, 2009; Jia, Xu, Ke, Wang, & Zhou, 2009). Thus another sample was prepared by co-precipitation method by sintering the powder at a bit higher temperature i-e., 650 ^{o}C at 1 hour. The XRD pattern of this sample is shown in Fig. 1(b). Relatively sharp diffraction peaks can be seen in this pattern. However, the extra peaks are still present manifesting the presence of impurity phases. Nevertheless, the high intensity of the indexed peaks indicates the dominance BFO phase. Since increasing the sintering temperature above 650 ^{o}C could produce deficiency of Bi due to its volatility at high temperature, it was not increased and rather synthesis method was changed to sol-gel to prepare single phase samples. Fig. 1(c) shows the XRD pattern of BFO prepared by sol-gel method sintered at 550 ^{o}C for 1 hr using citric acid as chelating agent. Majority of the peaks have been indexed to BFO but some peaks remained un-indexed. The un-indexed peaks present the impurity phases. These secondary phases of BFO are also reported in literature such as $Bi_2Fe_4O_9$ (Jia *et al.*, 2009). The intensity of secondary phases is small as compared to indexed peaks; only one un-indexed peak has high intensity. It is also clear that the sample which was prepared by co-precipitation method have secondary phases with high intensity as compared to that which is prepared by sol-gel method. This indicates that sol-gel method may result in phase pure BFO. Fig. 1(d) shows the XRD pattern of BFO prepared by sol-gel method sintered at 500 ^{o}C for 1 hr using tartaric acid as chelating agent. Some peaks of other phases are obtained which are $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$, which shows that BFO is multi-phase. The change of chelating agent shows that the intensity of extra peaks is decreased. Majority peaks are indexed to BFO. As compared to the last sample in which Citric acid and NH_3 was used as chelating agent, the intensity of secondary phases is very small. Fig. 1(e) shows the XRD pattern of BFO prepared by sol-gel method sintered at 550 ^{o}C for 10 hr using Ethylene glycol as base. It is found that majority of the peaks are indexed, only few peaks remained un-indexed. These un-indexed peaks represent to some impurity phases. These secondary phases which appear along with the primary phase of BFO and extensively found in literature are $Bi_2Fe_4O_9$, $Bi_{46}Fe_2O_{72}$ and $Bi_{24}Fe_2O_{39}$. Since these peaks appear with a quite high intensity as compared to the indexed peaks, it seems as this secondary phases are quite strong in this sample. The increase in sintering temperature decreases the number of secondary phases. Fig. 1(f) shows the XRD pattern of BFO prepared by sol-gel method sintered at 1 hr which is attributed to the decomposition of $BiFeO_3$ phase at high temperature(Kamba *et al.*, 2007). It 500 ^{o}C for 3 hr using tartaric acid and E.G as chelating agent. Relatively sharp diffraction peaks are present. However the extra peaks is also present which indicate the presence of secondary phases. Only two un-indexed peaks of $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ are intensity of impurity phases increases. Fig. 1(i) shows present but the intensity of the impurity phases is extremely large as compared to the indexed peaks, which shows that the secondary phases are quite strong in this sample as shown in Table. I, that the sample which is prepared at 500 ^{o}C for 1 hr has three extra peaks with very small intensity. In this sample the sintering temperature is same, as time is increased; the intensity of the peaks is increased. Hence it is concluded that the increment in time is not favorable. Fig.1 (g) shows the XRD pattern of BFO sintered at 600 ^{o}C for 1 hr using tartaric acid and E.G as chelating agent. All major peaks are indexed but some peaks remained un-indexed. The intensity of the un-indexed peaks is quite large as compared to the indexed peaks. The n-indexed peaks indicate the presence of secondary phases of primary phase BFO and extensively found in literature are $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$. The high intensity of the secondary phases represent that the impurity phases are strong in the sample. The intensity of extra peaks is low as compared to sintered at 600 ^{o}C for 2 hr, which indicates that increase in sintering time have no effect on the impurity phases. The same extra peaks were obtained for the sample sintered at 600 ^{o}C for 1 hr by wet chemical method (Kamba *et al.*, 2007). Fig. 1(h) shows the XRD pattern of BFO prepared by sol-gel method sintered at 600 ^{o}C for 2 hr, relatively sharp diffraction peaks can be seen in this pattern. However, the extra peaks are also present manifesting the presence of impurity phases. The intensity of the indexed peaks is relatively high, indicating that the BFO phase is high. Since by increasing the sintering time indicates that the intensity of the impurity peaks is increased. The secondary phases which appear along with the primary phase of BFO and extensively found in literature are $Bi_2Fe_4O_9$. These secondary phases represent that the BFO of multi-phase is obtained. The intensity of the extra peaks is increased as compared to the sample sintered at 600 ^{o}C for 1 hr. It showed that by increase the XRD pattern of BFO prepared by sol-gel method sintered at 700 ^{o}C for 1 hr using tartaric acid as chelating agent. All the major peaks are indexed to rhombohedral BFO, but some extra peaks of small intensity are obtained such as $Bi_2Fe_4O_9$. The intensity of the peaks is very small which shows that the BFO phase is high. It is clear that at higher temperature the impurity phase decreases. In literature the same extra phase was also obtained for the sample sintered at 700^{o}C for1 hr which is attributed to the decomposition of $BiFeO_3$ phase at high temperature(Kamba *et al.*, 2007) {Kamrul Haque Bhuiyan, 2016 #448} has been reported that a second phase compound, $Bi_2Fe_4O_9$ is formed above 675 ^{o}C (Kamba *et al.*, 2007).

Fig. 1(j) show the XRD pattern of BFO prepared by sol-gel method sintered at 700 ^{o}C for 2 hr. It is found that the majority of peaks are indexed to BFO leaving only few peaks which remained un-indexed. These un-indexed peaks represent the presence of impurity phases, the peaks of small intensity are such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$. From the XRD pattern it is clear that the BFO phase is high. It is also clear that multi-phase BFO is obtained. The extra peaks are shifted to higher angle and have high intensity. So, it is concluded that by increasing sintering time at the same temperature have no effect to decrease impurities, but the impurity level is increased. Fig. 1(k) shows the XRD pattern of BFO prepared by sol-gel method sintered at 500 ^{o}C for 1 hr using tartaric acid as chelating agent. All the peaks are indexed to BFO; only three peaks of two different phases namely $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ are obtained. However, it can be seen that the intensity of extra peaks is very small as compared to that of diffraction peaks of primary phase, i-e., BFO. Thus this can be regarded as almost pure sample. It is interesting to note in the present work, it is very difficult to prepare completely pure phase of BFO.

It is found that purity of the phase is very much sensitive to the synthesis conditions such as chelating agents, sintering temperature and duration etc (Kamrul Haque Bhuiyan, 2016). The present work concludes Tartaric acid as a good chelating agent to prepare single phase BFO by sol-gel method by sintering the gel at 500 ^{o}C for 1 hr.

Table 1. Different samples of $BiFeO_3$ (BFO) prepared under various synthesis environments. T.A stands for Tartaric acid and E.G for Ethylene Glycol..

Sample No:	Chelating agent	Base	Pre-heating	Sintering temp	PH	D(nm)
1	_	NH_3	Uncontrolled 400^{0}C	550 ^{o}C for 1hr	10	11
2	_	NH_3	Uncontrolled 400^{0}C	650 ^{o}C for 1 hr	10	39
3	Citric acid	NH_3	Uncontrolled 400^{0}C	550 ^{o}C at 1hr	7-8	40
4	T.A	NH_3	Uncontrolled 400^{0}C	500 ^{o}C for 1hr	7	71
5	_	E.G	Uncontrolled 400^{0}C	550^{o}C for 10hr	6-7	68
6	T.A	E.G	Uncontrolled 400^{0}C	500 ^{o}C for 3hr	6	5
7	T.A	E.G	Uncontrolled 400^{0}C	600 ^{o}C for 1hr	6	44
8	T.A	E.G	Uncontrolled 400^{0}C	600 ^{o}C at 2hr	6	16
9	T.A	E.G	Uncontrolled 400^{0}C	700 ^{o}C for 1hr	6	67
10	T.A	E.G	Uncontrolled 400^{0}C	700 ^{o}C for 2hr	6	17
11	T.A	E.G	Uncontrolled 400^{0}C	500 ^{o}C for 1hr	6	12



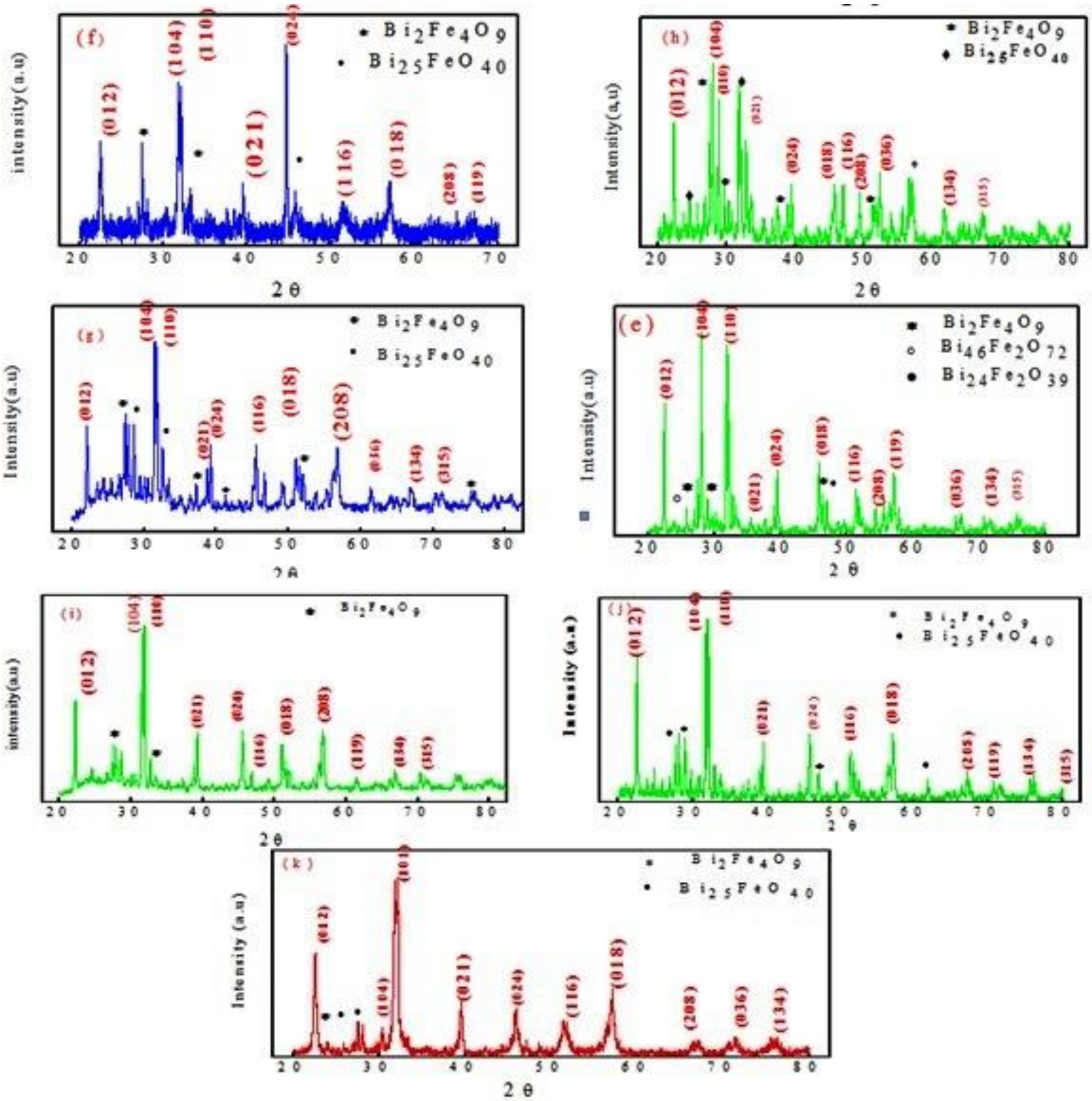


Fig. 1. X-ray diffraction pattern of BFO (a) sintered at 550 °C (b) sintered at 650°C for 1 hr by co-precipitation method (c) sintered at 550 °C for 1 hr by sol-gel method (d) sintered at 500 °C for 1 hr. All the peaks were indexed to crystalline BFO JCPDS 71-2494. (e) Sintered at 550°C using Ethylene glycol as a base, (f) Sintered at 500 °C for3 hr, (g) Sintered at 600 °C for 1 hr and (h) Sintered at 600 °C for 2 hr. (i) Sintered at 700 ⁰C at 1 hr, (j) Sintered at 700 °C for 2 hr and (k) Sintered at 500 °C for 1 hr.

The grain or particle size for each sample was calculated from XRD patterns by using the well known Scherer formula given as $D = K.\lambda / \beta \cos\theta$, where K = 0.9, λ = 1.5418 Å, β is the full width at half maximum (FWHM) and θ is the Bragg's angle. The calculated values for grain size are presented in Table. I. It is observed that the grain size increases by increasing sintering temperature. However, it is found to decrease in grain size by increasing sintering time (Kamrul Haque Bhuiyan, 2016). The grain size calculated for synthesized BFO is in the range of 11 to 71 nm for sintering temperature ranging from 500 °C to 700 °C. Therefore, the grain size increases by increasing the sintering temperature, in consistent with the change in grain size observed in the literature (He & Gao, 2009).

For a fixed sintering temperature, the grain size is also found to vary on varying chelating agent. For example, for a sample sintered at 500 °C for 1 hr, the grain size decreases from 71 nm to 12 nm on changing the chelating agent from T.A + NH_3 to T.A + E.G as seen in the Table. Thus, using T.A + E.G as a changing chelating agent not only improves the quality of the samples but also decreases the grain size. So, it may be also concluded that the combination of T.A and E.G may be suitable to use as chelating agent to minimize the grain size of the crystallites in BFO (He & Gao, 2009).

Fig. 2 shows the SEM of $BiFeO_3$ synthesized at various temperatures. Here Fig. 2 (a) shows the result of SEM which was prepared at 500 °C, Fig. 2 (b) shows the SEM of the sample which was prepared at 600 °C and Fig. 2 (c) shows the SEM of the sample which was prepared at 700 °C. SEM is used to determine the surface morphology of the material. It was reported that the average particle size increases by increasing temperature. It is also revealed from the SEM results that the sample comprises grains of various sizes ranging from 200 nm to 1000 nm. Thus, the values of grain size calculated from the Scherer formula are under estimated as compared to that found from the SEM patterns. The particle size is slightly greater than the crystalline size obtained by the Scherrer formula because of agglomeration of the particles. As reported in literature $BiFeO_3$ has average length and width of 400 and 200 nm respectively(Haumont, Kreisel, Bouvier, & Hippert, 2006)

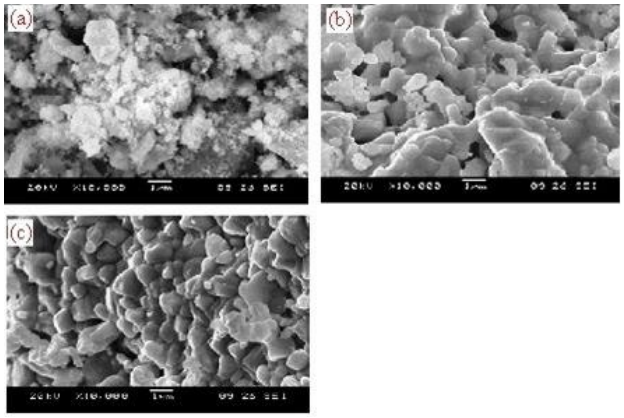


Fig. 2. Scanning Electron Microscopy (SEM) of $BiFeO_3$ synthesized at sintering temperature (a) 500 °C, (b) 600 °C and (c) 700 °C.

Energy dispersive spectroscopy (EDS) provides information regarding presence of the constituent elements in a material as well as their relative amount. In order to confirm the presence of Bi and Fe in $BiFeO_3$ and to observe whether these elements are present in 1: 1 combination, which is considered an ideal ratio for pure $BiFeO_3$, we have employed EDX on $BiFeO_3$ sample. Fig. 3(a-c) show EDX pattern obtained on three $BiFeO_3$ samples synthesized respectively at 500, 600 and 700 °C. It has been observed from these patterns that only Bi and Fe are present in the prepared samples, leading us to conclusion that there is no elemental impurity present in these samples. However, our samples do not show the required 1: 1 ratio of Bi and Fe. The best ratio obtained was Fe: Bi = 43: 57 which is close to 1: 1, for the sample prepared at 500 °C as shown in Fig. 3. The deviation from 1: 1 ratio increases from 500 °C to 600 °C (Fe: Bi = 35: 65) and 700 °C (Fe: Bi = 30: 70). So it can be concluded that pure phase of $BiFeO_3$ could be obtained by sintering the powder around 500 °C.

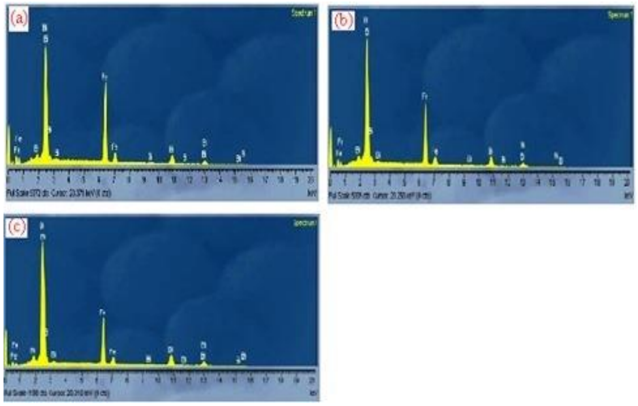


Fig 3. EDX of the $BiFeO_3$ synthesized at sintering temperature (a) 500°C, (b) 600 °C and (c) 700 °C.

Table 2. The weight percent ratio between Fe and Bi samples sintered at 500°C, 600°C and 700°C.

Weight Percent			Resistivity (ohm m)
Sintering Temp. (a) 500°C	Fe= 42.06	Bi =57.94	$2.79^{*}10^{10}$
Sintering Temp. (b) 600°C	Fe=35.35	Bi =64.65	$1.35^{*}10^{10}$
Sintering Temp. (c) 700°C	Fe=29.82	Bi = 70.18	$4.9^{*}10^{9}$

DC Resistivity Measurement of $BiFeO_3$: Fig 4 shows the current-voltage characteristic of $BiFeO_3$ sintered at 500 °C using tartaric acid as chelating agent annealed in air and current-voltage characteristic of $BiFeO_3$ in which annealing environment is changed from air to oxygen. The current increases linearly on increasing applied voltage. The resistance of the sample calculated from the V/I it is used to obtain the resistivity of the sample which is $2.79^{*}10^{10}$ Ohm- cm. Fig.5 show the current-voltage characteristic in which chelating agent is changed as tartaric acid + ethylene glycol. Also the resistivity is found to increase on changing the chelating agent from Tartaric acid to Tartaric acid + Ethylene glycol. The resistivity calculated from the I-V curves decreases on sintering the $BiFeO_3$ in oxygen environment. This is due to the fact that oxygen is absorbed by the sample in an oxygen environment and therefore, the increased number of defects / vacancies produced during the heat treatment is reduced. As a result, the resistivity of the sample is reduced as observed in the present work.

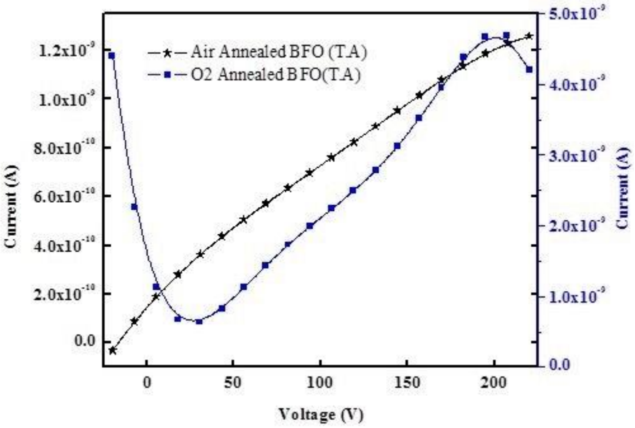


Fig. 4. I-V curve of $BiFeO_3$ using tartaric acid sintered at 500 ^oC annealed in air and O_2 environment.

Infrared (IR) optical reflectance spectroscopy is a nondestructive, versatile and a powerful technique to study the optical response of materials. In contrast to photoemission spectroscopy where cleaved and virgin surface of the samples are required and neutron scattering in which large size samples is generally required, the IR only requires small sized samples with the smooth surfaces for its characterization. Moreover, unlike electrical resistivity, no special contacts are required for measurements. IR reflectance provides information about the lattice vibration in a material. It is of fundamental importance to investigate the normal modes of vibration, herein after called the optical phonons, and their possible role involved in exhibiting different properties of materials. Since measurement of optical reflectance in the mid- IR and Near- IR frequency range provides information regarding the electronic excitation in a material, the complete IR spectrum is thus obtained to study the optical phonons, optical electronic excitations enabling one to determine the optical band gap, and the possible phonon-electron interaction. In case of multiferroics $BiFeO_3$, the IR spectroscopy may provide an understanding to the driving mechanism of the ferroelectric transition and its coupling to magnetic ordering (Kamrul Haque Bhuiyan, 2016). There have been few studies on $BiFeO_3$ using Raman scattering (Cazayous, Malka, Lebeugle, & Colson, 2007; Haumont *et al*., 2006) and infrared spectroscopy (Haumont *et al*., 2006). However, few issues are still unresolved, for example, regarding the phonon modes symmetry and the possible role, if any, of phonon softening in the ferroelectric transition. In the present work, IR reflectance is measured on two samples of $BiFeO_3$ sintered at a) 500 ^oC b) 600 ^oC, both in air environment. The measurements were made in the frequency range 30 - 7500 cm^{-1} at room temperature. Suitable combinations of light source, beam splitter and detector were used in the Fourier Transform Infrared Spectroscopy (FTIR) (VERTEX 80V) to cover the spectral range. One of the smooth surfaces of a disc-shaped sample was exposed to light and the spectrum was collected. Later, gold film, which was used as a reference, was replaced with the sample in the sample compartment and the reflectance spectrum was recorded with the same optical alignment. The absolute reflectance of the sample was calculated by the ratio % R= Reflectance of sample/ Reflectance of reference the reflectance so obtained is plotted as a function of frequency for two samples as shown in Fig 6. The sharp reflection peaks observed correspond to optical phonons in the IR range dictate that the spectrum is of a typical semiconductor. The semiconducting behavior is also predicted by the electrical resistivity measurements. The sharp peaks observed below 1000 cm^{-1} correspond to

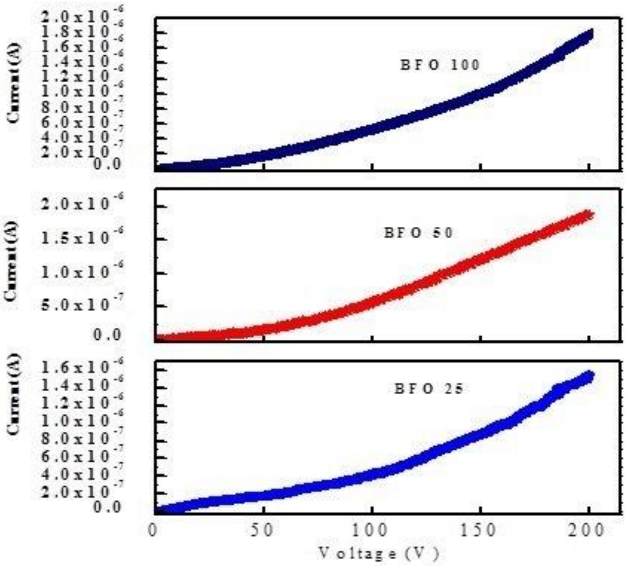


Fig. 5. I-V curve of $BiFeO_3$ using T.A + E.G sintered at 500 ^oC annealed in air optical phonons at frequencies 550, 440, 387, 285, 144, 65 cm^{-1} which appears due to vibration of ions or group of ions in the sample.

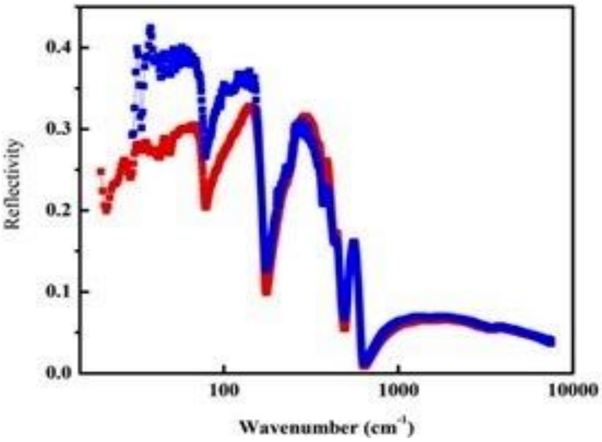


Fig. 6. Infrared reflectivity of $BiFeO_3$ sintered at temperature (a) 500 ^oC (b) 600 ^oC.

Below 80 cm^{-1}, noise appears due to the high signal to noise ratio and it is experimentally not possible to resolve optical phonons. Moreover, the limited range of source, beam splitter and detector combination used also restrict the observation of phonon at such a low frequency.

Conclusion: The multiferroics $BiFeO_3$ has been successfully synthesized by sol-gel method sintered at 500 °C. The almost pure phase of BFO was obtained using Tartaric acid and Ethylene glycol as a chelating agent sintered at 500 °C. It is found in this work that using Tartaric acid and Ethylene Glycol, the sample becomes more resistive as compared to the sample in which only tartaric acid is used. It was concluded that by increasing sintering time at the same temperature have no effect to decrease impurities, but the impurity level is increased. The present work concludes Tartaric acid as a good chelating agent to prepare single phase BFO by sol-gel method by sintering the gel at 500 °C for 1 hr. The grain size increases in the range of (11.448-70.832 nm) by increasing the sintering temperature (500 °C - 700 °C). Scanning Electron Microscopy (SEM) shows that grains are homogenous and well defined. It is found from EDX that the atomic ratio of Bi to Fe is close to 1:1 prepared at 500 °C. The observation of optical phonons in the reflectivity spectrum demonstrates the semiconducting of BFO, in consistent with the conclusion drawn from electrical resistivity measurements

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