

# Synthesis and characterization of pure BiFeO<sub>3</sub> using various complexing agents by Sol-gel method

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## Abstract

Pure BiFeO<sub>3</sub> (BFO) nanoparticles were prepared using various complexing agents like citric acid, malonic acid, succinic anhydride and tartaric acid by sol-gel method annealed at different temperatures (400 °C, 500 °C, 600 °C). X-Ray diffraction pattern of various samples show the degree of formation of required phase. Particle size of pure phase BFO has been shown using TEM image. Scanning Electron Microscopy studies for different samples give detailed study of morphology of samples. Ferroelectric and magnetic studies of best prepared samples show their comparative multiferroic properties. Dielectric analysis also shows the variation in dielectric loss, real and imaginary part of permittivity versus frequency at room temperature. Copyright © 2018 VBRI Press.

**Keywords:** BiFeO<sub>3</sub>, Multiferroic, Complexing agents, Ferroelectric, Magnetic.

## Introduction

A ferroelectric and magnetic crystal exhibits the stable, switchable electric polarization and magnetization respectively. The multiferroic materials that exhibit both of these properties are very few but magneto-electric coupling of magnetic and electrical properties is a more general and widespread phenomenon. Due to long term technological aspirations in this field, a lot of research work has been reported. The surge of interest in multiferroic materials over the past 15 years has been driven by their fascinating physical properties and huge potential for technological applications. They are highly interdisciplinary covering a wide range of topics and technologies, like solar cell devices, data storage recording technologies and random access multi state memories etc. [1-4].

So, there has been the search for a particular material to fulfill the requirement to be a good multiferroic material. Ramesh *et al.* reported the enhancement of polarization and related properties in hetero-epitaxially constrained thin films of the ferro-electromagnet BiFeO<sub>3</sub>. The film displays a room temperature spontaneous polarization (50-60  $\mu\text{C}/\text{cm}^2$ ) almost an order of magnitude higher than that of the bulk (6.1  $\mu\text{C}/\text{cm}^2$ ) [5]. This paper is the landmark in functional materials leading to enthusiasm for multiferroic research. Since, multiferroics are the compounds which show the ferroelectric and a magnetic

order simultaneously. In this respect, BiFeO<sub>3</sub> is the good candidate for a single phase multiferroic material since it is ferroelectric and antiferromagnetic material simultaneously at room temperature. The Curie temperature (T<sub>c</sub>) and Neel temperature (T<sub>N</sub>) of BFO are 1103 K and 673 K due to which it act as a good multiferroic material at room temperature [6]. Subhash Sharma *et al.* reported the comparative studies of pure BiFeO<sub>3</sub> prepared by sol-gel method versus conventional solid-state-reaction method. This group found that sol-gel method is better as compared to solid state method for preparing pure phase of BFO at low temperature [7]. Magnetic, electric properties are studied by A. K. Pradhan *et al.* and found BFO to be a good ferroelectric material [8]. Also the ME coefficient of BFO determined 6.5 mV/cmOe for applied magnetic field [9]. So, there is the requirement of thorough study of preparation of pure phase of BFO using sol-gel method [10]. So, there is the requirement of thorough study of preparation of BFO by using various complexing agents by sol-gel method and annealing at different temperatures.

In this work, the strategy of sol-gel preparation of pure phase bismuth ferrite using various complexing agents like citric acid, malonic acid, succinic anhydride and tartaric acid followed by annealing at 400 °C, 500 °C, 600 °C has been adopted. Then structural, electric and magnetic characterization of the samples has been discussed in detail.

## Experimental

Sol-gel method has been used to prepare the pure phase of  $\text{BiFeO}_3$  using various complexing agents. The precursors used are  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and distilled water. Complexing agent like citric acid in 1:1 molar ratio of metal ions was added in stoichiometric solution of above precursors with constant stirring. On complete dissolution, the resultant solutions were then evaporated at  $\sim 80^\circ\text{C}$  on a hot plate with constant stirring and dried after taking the magnetic bead out of beaker with stirring off. The mesoporous solid structure swollen with liquid (gel) was then converted to xerogel powders corresponding to different complexing agents. The xerogel powders were grounded in agate mortar and then annealed all as prepared samples at  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$  [11]. Same steps were reported with other complexing agents (malonic acid, succinic anhydride, tartaric acid) for the preparation of  $\text{BiFeO}_3$ . The annealed powders at  $600^\circ\text{C}$  were subjected to a hydraulic press (10t) after mixing them with PVA solution. The well dense pallets (diameter  $\sim 8$  mm and thickness  $\sim 1$  mm) thus obtained were sintered at  $600^\circ\text{C}$ . The pellets were silver coated for the electric characterization.

## Results and discussions

### Structural analysis

Fig. 1 shows the X-Ray Diffraction patterns of bismuth ferrites samples prepared by using sol-gel method with various complexing agents like citric acid, malonic acid, succinic anhydride and tartaric acid and annealed at  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ . The diffraction spectra are matched with the  $\text{BiFeO}_3$  (JCPDS card no. 82-1254) file which exhibits the perovskite structure only.

These sol-gel prepared samples start to show the formation of peaks corresponding to various planes at  $400^\circ\text{C}$ ,  $500^\circ\text{C}$  but pure phase or all required peaks corresponding to various planes of bismuth ferrite formed at  $600^\circ\text{C}$ . The JCPDS card no. 82-1254 of pure  $\text{BiFeO}_3$  shows that the diffraction from the planes (012), (104), (110), (006), (202), (024), (116), (122), (018), (214), (300), (208), (220) for the formation of pure phase of bismuth ferrite. The peaks for the samples annealed at  $400^\circ\text{C}$  are not for all the required planes and these some of the peaks can be seen just for one or two samples like BFO (Citric Acid), BFO (Succinic Anhydride) and for most of the samples it is just the amorphous nature. But for the  $500^\circ\text{C}$  annealed samples, there is appearance of peaks corresponding to various planes for almost all the samples but the required intensity of various peaks is not matched well as required according to the above mentioned JCPDS card for BFO. For the  $600^\circ\text{C}$  annealed samples the appearance of peaks for various planes and their required intensity for almost all the samples approaches the required criterion but the sample which match well with JCPDS card is Bismuth ferrite prepared using the citric acid. This sample is in the rhombohedral perovskite structure. Hence, we can observe that the pure phase of bismuth ferrites is

obtained at  $600^\circ\text{C}$ . Even impurity phase of  $\text{Bi}_2\text{Fe}_4\text{O}_7$  is obtained due to kinematics of reaction [12].

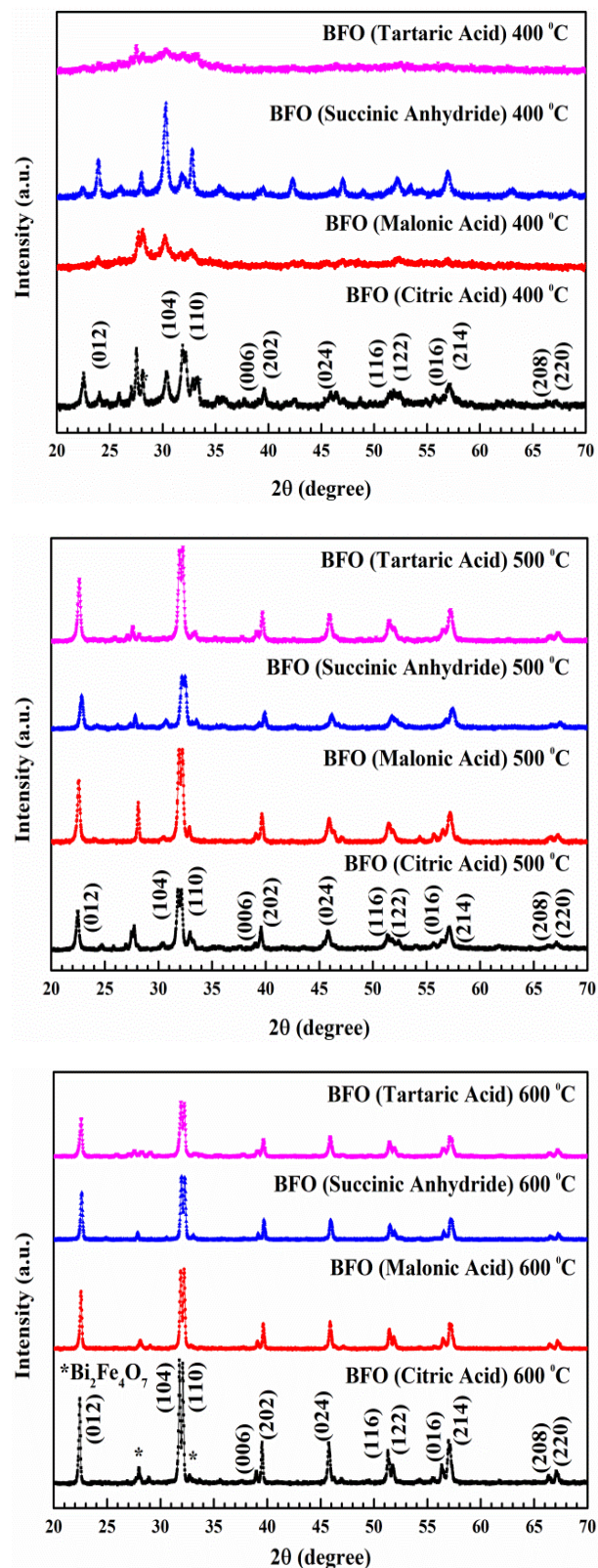
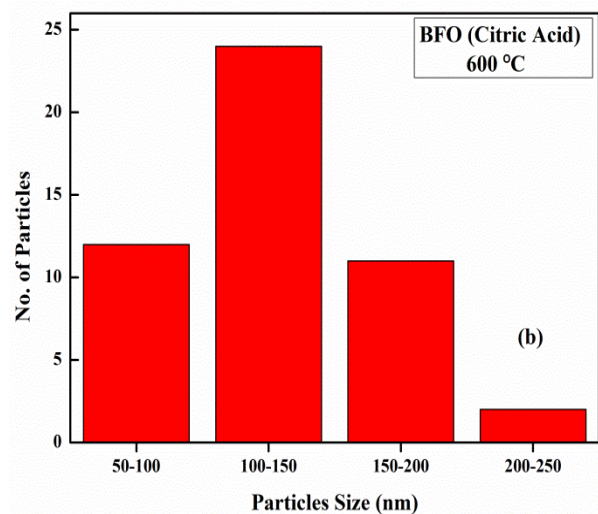
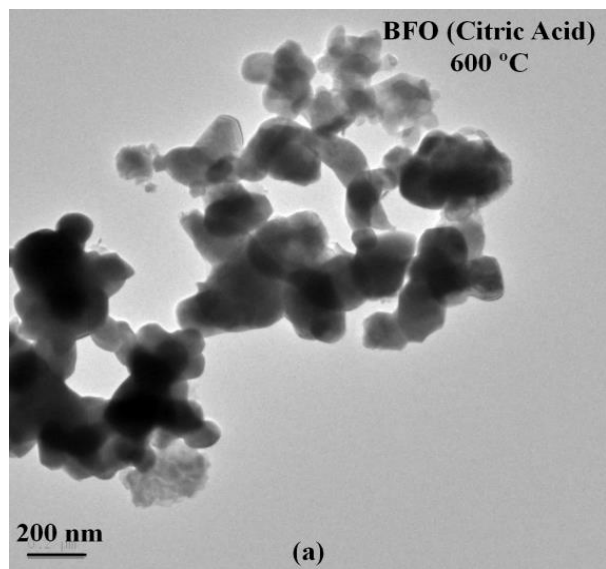


Fig. 1. X-Ray Diffraction pattern of BFO using various complexing agents at  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$

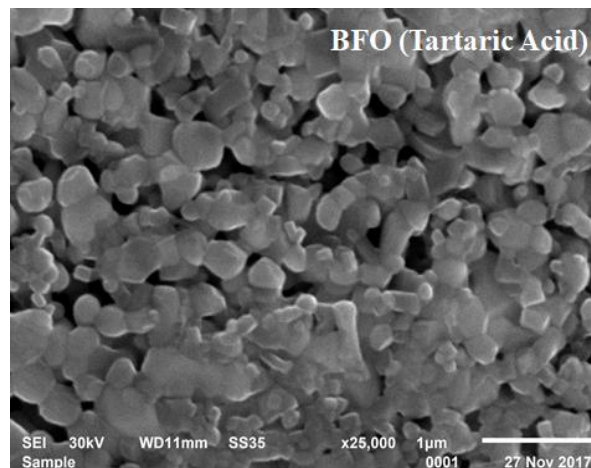
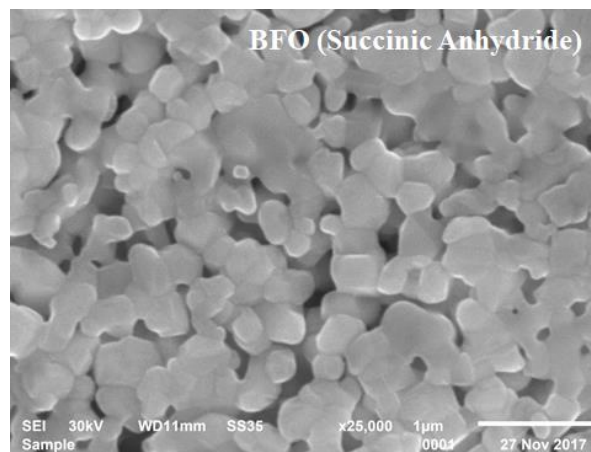
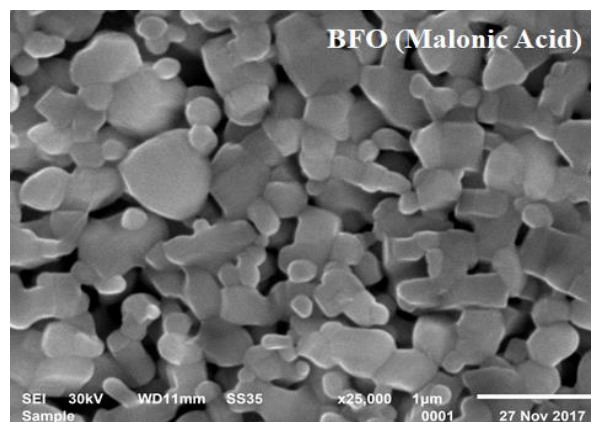
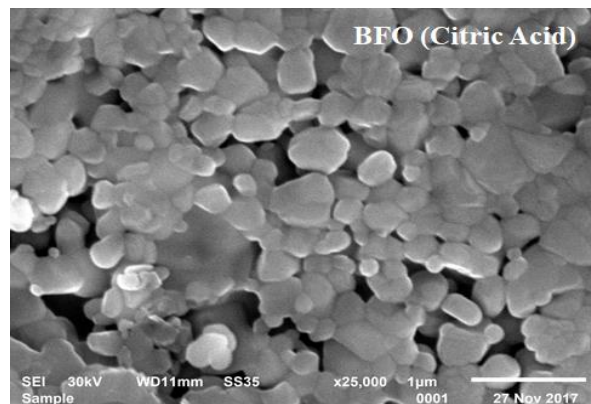
### Morphological Analysis

**Fig. 2** shows the tunnelling electron micrograph (TEM) of pure BFO prepared using citric acid as complexing agent and annealed at 600 °C. The average particle size was calculated by using *image j* software. It was observed that the average particle size of BiFeO<sub>3</sub> is 110 nm and this is compatible with XRD results of this particular sample and it can be generalized that the same results will be expected from the remaining samples of bismuth ferrite annealed at 600 °C.



**Fig. 2.** (a) TEM image of BFO (Citric Acid), (b) Particle Size of BFO (Citric Acid) at 600°C.

The scanning electron micrographs (SEM) of bismuth ferrite pellets, sintered at 600 °C, are shown in **Fig. 3**. These micrographs show the dense picture of grains in the materials of nearly uniform grains having clear and small grains as well as grain boundaries. The grains of BFO sample using citric acid are comparatively better as compared to other samples. The grains of samples are rectangular in shape and the type of structure is rhombohedral [13].



**Fig. 3.** SEM images for pure BFO at 600 °C using different complexing agents.

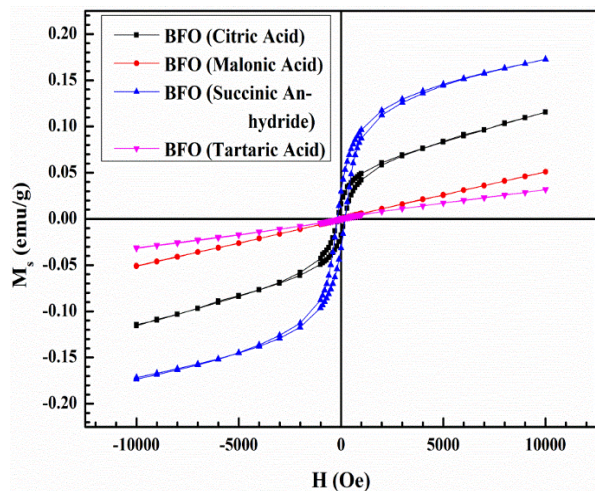


Fig. 5. M-H Loops of BFO using different acids at 600 °C

### Ferroelectric analysis

Polarization versus electric field loops of bismuth ferrite annealed at 600 °C using various complexing agents like citric acid, malonic acid, succinic anhydride and tartaric acid were measured under a maximum applied field of ~35 kV/cm (50Hz) at room temperature are shown in Fig. 4. Breakdown field was not observed within the applied electric field for any samples.

From the Fig. 4 it is found that the observed saturation polarization ( $P_s$ ), remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ) are higher for BFO (Citric acid) as compared to rest of the samples. Its values are -  $P_s = 0.37 \mu\text{C}/\text{cm}^2$ ,  $P_r = 0.12 \mu\text{C}/\text{cm}^2$ ,  $E_c = 10.58 \text{ kV}/\text{cm}$ . So, bismuth ferrite prepared using citric acid is a good candidate as a ferroelectric material. The reason for this particular sample to be a good ferroelectric material as compared to other one is that it will attain the rhombohedral perovskite structure which is the indication of good ferroelectric material as shown by the BFO (Citric Acid) sample [11].

### Magnetic analysis

M-H loops of sol-gel prepared bismuth ferrite using various complexing agents and annealed at 600 °C are shown in the Fig. 5. Parameters such as saturation magnetization ( $M_s$ ), retentivity ( $M_r$ ), coercivity ( $H_c$ ) were determined from M-H loops of the samples for maximum applied magnetic field of 1 T. BFO (Citric Acid) have good magnetic properties but rather smaller as compared to BFO (Succinic Anhydride). So, as a multiferroic material our concentration will be on the citric acid prepared bismuth ferrite. Saturation magnetization ( $M_s$ ), retentivity ( $M_r$ ) and coercivity ( $M_c$ ) for BFO (citric acid) are 0.11 emu/g, 0.016 emu/g and 170.58 Oe respectively.

The magnetic hysteresis loops of BFO show the linear magnetic field dependence of magnetization which suggests that it is antiferromagnetic material and is reported to be G-type antiferromagnetic due to local spin ordering of  $\text{Fe}^{3+}$  at room temperature [14].

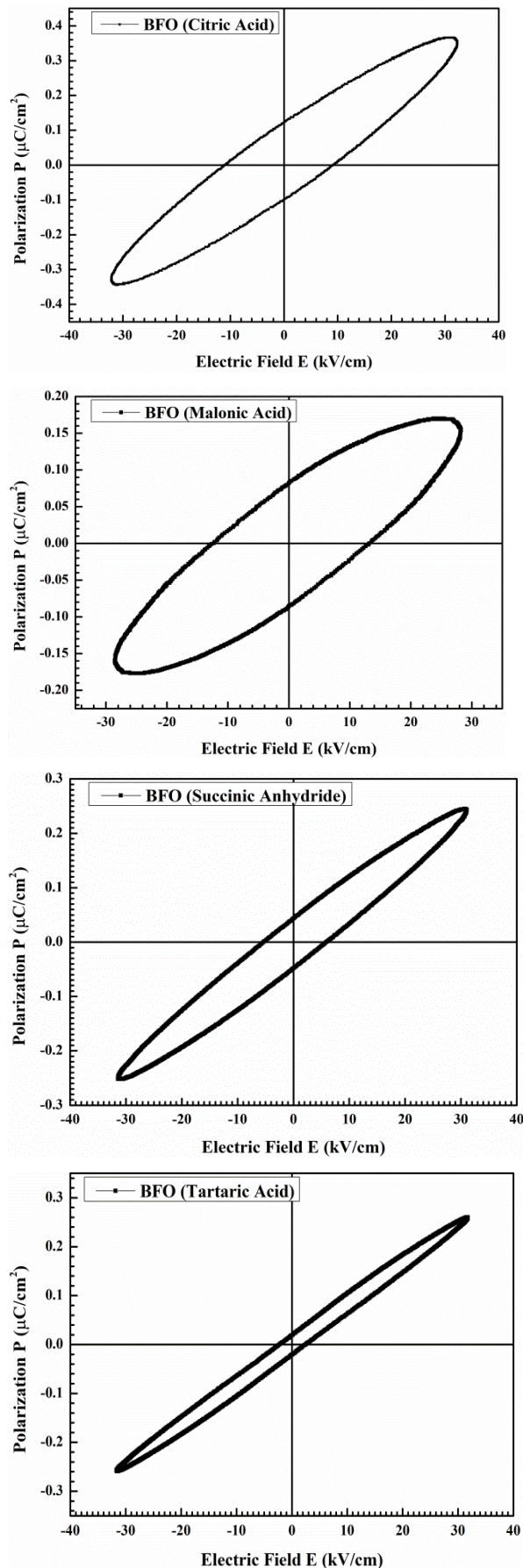
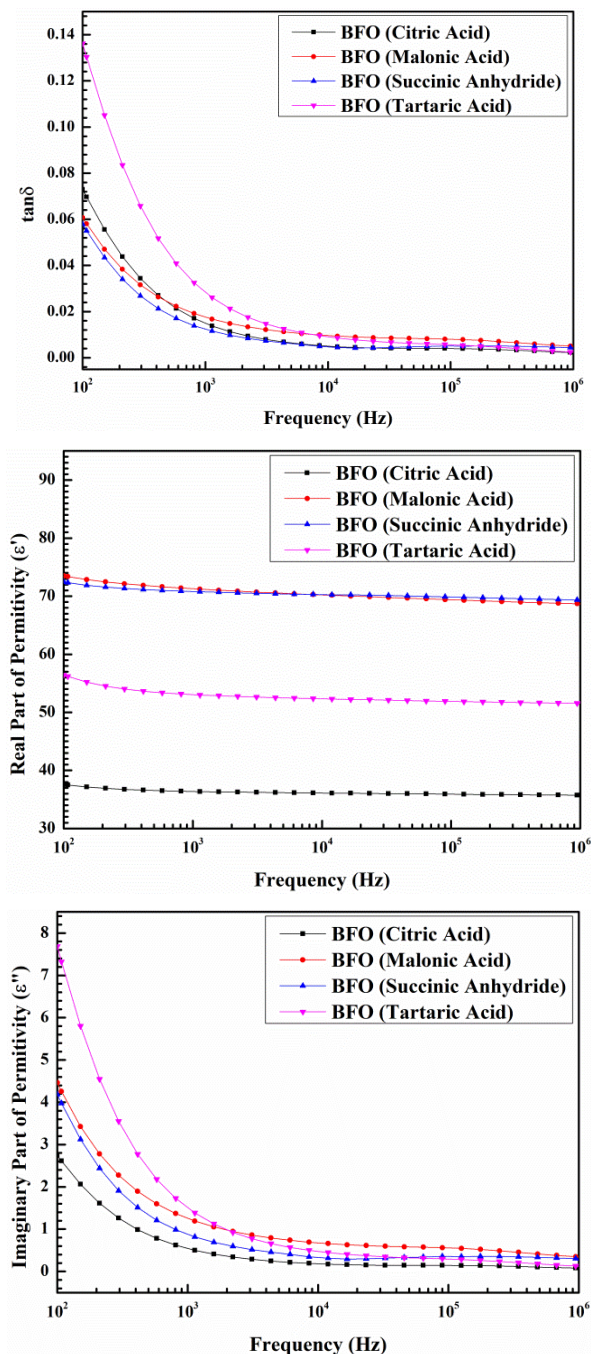


Fig. 4. P-E loops of BFO using different acids at 600°C.

### Dielectric analysis

Dielectric properties of various complexing agents prepared samples as a function of varying frequency has been measured in the range of frequency  $10^2$  Hz to  $10^7$  Hz. For various samples annealed at  $600^\circ\text{C}$  as shown in **Fig. 6**. It can be seen that the BFO (Citric Acid) has the lowest value of dielectric constant or real part of permittivity and this permittivity goes on rapidly decreasing on increasing frequency and becomes independent at higher frequencies. The decrement in  $\epsilon'$  is attributed to the dielectric relaxation. The dielectric relaxation can be explained by Koop's theory.



**Fig. 6.** Dielectric properties of BFO using different complexing agents.

According to this theory, the decrement in  $\epsilon''$  with increasing frequency is due to the fact that the atoms in the dielectric materials requires a finite time to align up in the direction of the applied field direction. As the frequency of the field increases at some point the charge carriers of the dielectric do not follow with the frequency of the applied field and the value of the  $\epsilon''$  decreases. As the frequency of the applied electric field increases again the polarization values do not attain some value but the field reverse its direction and it becomes independent of the applied electric field. Another important point for this behaviour of material with increasing frequency is related to hopping of electrons from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions. At higher frequencies electric field provide the enough energy to the electron and the hopping of the electron from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ions starts. Therefore conductivity of dielectric increases as the frequency is increased and hence a decrement occurred in  $\epsilon''$  [16].

Loss tangent variation with frequency in the same range as above are also shown in the **Fig. 6**. This loss is maximum for the citric acid used BFO but decreases upto smallest value for all the samples with increasing frequency.

### Conclusions

In summary, we successfully prepared the pure phase of bismuth ferrite using different complexing agents at  $600^\circ\text{C}$ . X-Ray diffraction pattern of various samples show the degree of formation of required phase. Particle size of pure phase BFO (citric acid) has been shown using TEM image and in agreement with XRD data. Morphology of samples in terms of particle's grains studied using Scanning Electron Microscopy. Ferroelectric and magnetic study of best prepared samples shows their comparative multiferroic properties. Dielectric analysis also shows the variation in dielectric loss, real and imaginary part of permittivity versus frequency at room temperature. It is observed that the complexing agents play an important role to control structural and physical properties of samples.

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