Chapter - 4
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SYNTHESIS AND CHARACTERIZATION OF BiFeO₃ MULTIFERROIC NANOCERAMIC COMPOSITES

4.1 OBJECTIVE

- Preparation of polycrystalline samples of BiFeO₃ and to be synthesized at low temperature using sol-gel technique.
- Study of samples to know the characterization such as crystallite size and strain in the crystallite using XRD, homogeneity and grain size using SEM, Ferroelectric to para-electric transition temperature (Tₓ) by using DTA analysis etc.

4.2 EXPERIMENTAL PROCEDURE

As discussed in the chapter-2, in this section, the properties of BiFeO₃ phases are studies and extrapolated to set the properties of the pure compound. An attempt is made to estimate the effect of sintering temperature on electrical and structural properties of BiFeO₃ ceramics prepared using sol-gel technique.

BiFeO₃ is made by solgel technique. All reagents are in the analytical grade. Fe(NO₃)₉H₂O (Ferric nitrate), Bi(NO₃)₅H₂O (bismuth nitrate), citric acid and ethylene glycol are used as starting materials (Plate:4.1 & 4.2). In the first step, in the distilled water, an aqueous solution of citric acid is made. Then bismuth and ferric nitrates are
added to this solution with thoroughly mixing at 60-70°C. This is a mention to get a homogeneous mixture and to avoid precipitation. Thus a brown color citrate mixture is obtained with clear solution and without precipitation.

Plate: 4.1 Ferric Nitrate and Citric acid.

Plate: 4.2 Bismuth Nitrate and Ethylene Glycol.
Then the citric acid/ethylene glycol in the ratio of 60:40 is added to the solution. Subsequently the solution is heated at 600°C for 5 hours. Initially this solution was started to swell and filled the beaker by producing a foamy precursor. This foam contains light and homogeneous flakes of tiny particles. The formation of BiFeO$_3$ is checked by XRD technique with Cu K$_\alpha$ radiation ($\lambda=0.15418$ nm), using a BRUKER D8 XRD system spectroscope. The surface grain distribution and composition analysis of BiFeO$_3$ samples were studied using Field Emission Scanning electron micrographs (FESEM), Quanta 200 attached with Energy dispersion X-ray spectrometer (EDAX). Thermo-gravimetric (TG) and differential thermal gravimetric analysis are conducted and checked the stability and phase transformation in the samples. To study ferroelectric hysteresis behavior, a modified Sawyer–Tower circuit is used.

**4.3 RESULTS AND DISCUSSION**

BiFeO$_3$ is the rhombohedrally indistinct perovskite material. This is belong to the space class $R3c$, with rhombohedral lattice parameters $a_R=5.63$ Å and $\alpha_R=59.35^\circ$. In other words it has hexagonal parameters $a_{\text{hex}}=5.58$ Å, $c_{\text{hex}}=13.87$ Å [151-153]. Preparation of phase-pure BiFeO$_3$ is difficult because of its narrow temperature range of phase stabilization. Different impurity phases are reported, mainly Bi$_2$Fe$_4$O$_9$,
Bi$_{12}$(Bi$_{0.5}$Fe$_{0.5}$)O$_{19.5}$ and Bi$_{25}$FeO$_{40}$, since BiFeO$_3$ is metastable with respect to Bi$_2$Fe$_4$O$_9$ (mullite phase) and Bi$_{25}$FeO$_{39}$ (sillenite phase) [154, 155].

The presence of these impurities results in leakage current in BiFeO$_3$. It results in poor ferroelectric property and thus causes to be this material is not suitable for practical applications. The available methods, for formation of phase-pure BiFeO$_3$ with improved multi-ferroic properties are (a) forming solid solution of BiFeO$_3$ with other ABO$_3$ type of perovskites like PbTiO$_3$ [156,157] (b) calcinations of stoichio-metric mixture of Bi$_2$O$_3$ and Fe$_2$O$_3$ followed by discharging with nitric acid [158] and (c) rapid liquid phase sintering of BiFeO$_3$ [159,160].

Selbach et al., on the basis of thermodynamics have suggested that isovalent substitution with a larger cation on the A site or a smaller cation on the B site would increase the stability of BiFeO$_3$ relating to the binary oxides and possibly also relating to the Bi$_2$Fe$_4$O$_9$ mullite and Bi$_{25}$FeO$_{39}$ sillenite phase [161,162]. Substitution of a more acidic cation on the B site or a more basic cation on the A site is also expected to stabilize the perovskite phase. They also reported that La$^{3+}$ is about the same size as Bi$^{3+}$, and although the space group changes with high substitution levels, perovskite phase is obtained with up to 40% La$^{3+}$. Rare earth ions are smaller than Bi$^{3+}$, but more basic cations, hence the stable solid solutions prepared at ambient pressure have been reported up to 15-20% substitution [163-166].
Fig. 4.1 shows the XRD patterns of BiFeO₃, sintered at 650, 700, 750, 800, 825 and 850°C. From the XRD pattern, it is noted that the major peaks of all sintered samples belong to rhombohedrally fuzzy perovskite BiFeO₃ (R-phase), although tiny amounts of Bi₂O₃ were detected due to excessive Bi used for compensating volatilization during synthesis. Moreover, the formation of BFO (R-phase), the formation of the minor impure phases, like Bi₄₆Fe₂O₇₂ (non perovskite paramagnetic phase shown by * symbol) was detected from the XRD analysis. BiFeO₃ is a metastable composite and because of its chemical kinetics of formation. It is always associated with some impurities which do not contribute for the observed magnetic and dielectric properties, as reported by several research scholars [167, 168].

The phase analysis is carried out by taking into account the hexagonal BFO unit cell. This unit cell of BFO system consist two formula pseudocubic units cells of BiFeO₃. The lattice parameters for rhombohedral unit cell of BiFeO₃ are calculated from the indexed XRD pattern for BFO samples sintered at 850°C as shown in Fig. 4.1. Using 2θ values from the XRD graph and (hkl) values from the standard JCPD-86-1518 card the lattice parameters for the unit cell are generated. The calculated values of the lattice parameters for the hexagonal unit cell of BiFeO₃ matched well with the values reported in the literature [152-153].
Fig: 4.1 XRD patterns for BiFeO$_3$ at different sintering temperature [where (*) Bi$_2$O$_3$].

Fig: 4.2 Variation of Lattice parameter ‘$a_R$’ with sintering temperature plot for BiFeO$_3$. 
The variation of lattice parameter ‘$a_R$’ with sintering temperature is given in Fig.4.2. From the plot of lattice parameter, it is found that with increasing sintering temperature the lattice parameter ‘$a_R$’ decreases for BiFeO$_3$.

In this research work the Williamson–Hall approach is used for de-convoluting crystallite size and strain contribution to the X-ray line broadening ($\beta_{1/2}$) in the present materials since the Scherrer’s formula does not take the strain contribution into account. According to this approach, the X-ray line broadening is a sum of the contribution from small crystallite size and the broadening caused by the lattice strain present in the material [169], i.e.

$$\beta_{1/2} = \beta_{\text{size}} + \beta_{\text{strain}}$$

(4.1)
where $\beta_{\text{size}} = \lambda/L \cos \theta$ (from Scherrer’s formula) and $\beta_{\text{strain}} = 4\eta \tan \theta$; where $\eta$ is strain

Therefore Eq.4.1 becomes

$$\beta_{1/2} = \frac{\lambda}{L} \cos \theta + 4\eta \tan \theta$$  \hspace{1cm} (4.2)

$\beta_{1/2} \cos \theta/\lambda = 1/L + T \sin \theta/\lambda$, where $T = 4\eta$, is a measure of strain present in the lattice. Hence by plotting $\beta_{1/2} \cos \theta$ vs. $\sin \theta$, it is found that the crystallite size from the intercept of the line at $x = 0$. The lattice strain and crystallite size is calculated from Fig.4.3 using the above explained expression (eq.4.2) for BiFeO$_3$ sintered at different temperatures. The variation of crystallite size and strain with different temperature are plotted in Fig.4.4 (a) and (b) respectively.

![Graphs showing variation of crystallite size and strain with sintering temperature](image)

**Fig: 4.4(a)** variation of Crystallite size with temperature and (b) Variation of Strain with sintering temperature plot for BiFeO$_3$.

From the plot of crystallite size verses sintering temperature, it is found that with increasing sintering temperature crystallite size
increases and strain decreases. Fig. 4.5 shows the FESEM micrographs of BiFeO$_3$ sintered at different temperature. The microstructures of the sintered BiFeO$_3$ pellets specified spherical grains, which are uniformly and homogeneously distributed. These microstructures also reveal that the sintered pellets are reasonably dense. Also, it was found that the edges of the grains are not sharp, which shows melting like behavior resembling liquid phase sintering.

*Fig: 4.5 SEM images of BiFeO$_3$ sintered pellets (a) 800°C, (b) 825°C and (c) 850°C*
The Fig. 4.6 is shown the variation of grain size with sintering temperature. Grain size measurement is complicated by a number of factors. First, the three-dimensional size of the grains is not constant and the sectioning plane will cut through the grains at random. Thus, on a cross-section it is observed a range of sizes, none larger than the cross section of the largest grain sampled. Grain shape also varies, particularly as a function of grain size. So the intercept approach is applied for measuring grain size.

In this method, one or more lines are superimposed over the structure at a known magnification. The true line length is divided by the number of grains intercepted by the line. This gives the average length of the line within the intercepted grains. This average intercept length will
be less than the average grain diameter but the two are interrelated. Grain size was observed to increase with increase in sintering temperature. This happens because as the sintering process continues at higher temperatures, the individual powder particles lose their identity completely and grain boundaries move across prior particle boundaries. Larger grains replace the original fine particle structure which influences the dielectric and electrical properties of the samples.

![Fig: 4.7 DTA analysis curve](image)

In order to observe the phase transition temperature, the DTA curve of BFO is shown in Fig.4.7. Ferroelectric to paraelectric transition temperature ($T_c$) was detected by DTA analysis, which shows that the Curie temperature of pure BiFeO$_3$ is 814°C which is very close to the ideal value (827°C) found by dielectric measurement [170].
4.4 SUMMARY

In summary, it is concluded that the synthesis of BiFeO₃ at low temperature using sol-gel technique is possible. From the XRD pattern it is observed that crystallite size increases with increase in sintering temperature. It is also seen from the XRD pattern that the strain in the crystallite reduces with increase in sintering temperature. As the crystallite size increase with increase in temperature, then the lattice parameter decreases. SEM micrographs reveal that the samples are homogeneous. It is also confirmed from the SEM micrographs that the grain size increases with increase in sintering temperature. Analyzing a SEM micrograph it is concluded that the particle size follows the Gaussian distribution. The DTA analysis shows that the Curie temperature of pure BiFeO₃ is 814°C and this is close to the ideal value 827°C found by dielectric measurement.