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Synthesis and Characterization of $BiFeO_3$: La Nanoparticles

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Abstract: $BiFeO_3$: La nanoparticles were successfully synthesized by a citrate-gel method at a temperature as low as 80^0c. Then calcined at 600^0c for 3h. The Prepared samples were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), Diffusion Reflectance Spectra (DRS) and Dielectric Studies. From SEM studies the morphology of the nanoparticles are more or less spherical. The crystallographic structure of nanoparticles from XRD studies is well fitted to rhombohedral structure. The elemental composition analysis from EDAX spectra revealed small variations in target compositions around ±2%. The band gaps of nanoparticles were calculated from DRS and were increased with increasing La concentration 1.8 to 2.5ev.The conductivity values were calculated and were increased with increasing La concentration.
Keywords: $BiFeO_3$, Citrate-gel method, Multiferroics.

1. Introduction and Experimental procedure

In recent years, multiferroics, showing the coupling of at least two of the possible three order viz, ferromagnetic (or antiferromagnetic), ferroelectric (or antiferroelectric) and ferroelastic, have attracted a great deal of attention due to the fascinating fundamental physics and potential applications in data storage media, spintronics and multistatememories[1-5]. Bismuth Ferrite ($BiFeO_3$, also commonly referred to as BFO) is an inorganic chemical compound with perovskite structure, one of the most promising multiferroic materials. The room temperature phase of $BiFeO_3$ is classed as rhombohedral belonging to the space group R3c. Bismuth ferrite has very high ferroelectric transition temperature (Tc) of 1100K [6] and shows G-type antiferro magnetism with cycloidal spin structure with Neel temperature (T_N) of 650K [7]. The co-existence of ferroelectricity and ferromagnetism and their coupling with elasticity provide an extra degree of freedom in the design of new functional sensors and multistate devices. Due to its multiferroism, an electric field can induce change in magnetization and an external magnetic field can induce electric polarization. These phenomenons are known as the magneto electric effect and are called magneto electrics. Further proof of it being ferromagnetic is that it produces a hysteresis loop during ferroelectric characterization. The ability to couple to either the electric or the magnetic polarization allows an additional degree of freedom in device designs. One of the main obstacles to the technological applications of $BiFeO_3$ is the large leakage current problem caused mainly by nonstoichiometry, defects and impurities. The leakage current behaviour seriously affects the ferroelectric polarization and hence the magnetoelectric coupling. In order to overcome the leakage current problem and improve the multiferroic properties, much work has been devoted to the synthesis of high-quality $BiFeO_3$ samples, especially with nanostructures.

The samples with the composition $Bi_{1-x}La_xFeO_3$ (X=0.10, 0.15, 0.20) were prepared by Citrate-gel method. Appropriate quantities of materials were weighed in microbalance according to the stiochiometry to obtain 0, 0.1, 0.15, 0.2 of La^{+3} dopant concentrations. The compounds were dissolved in HNO_3 (are insoluble in water) with deionized water to make up 0.2 M solution. Then equimolar amount of citric acid is added to the solution. After thorough mixing the homogeneous solution was kept on hot plate at 80^{o}C for 14 hours and then evaporated, a gel was formed. Finally the powder was obtained. The obtained powder is calcined at 600^{o}C.

2. Results and Discussion

The XRD patterns of the as-synthesized and sintered (at 600 ^{0}C) $BiFeO_3$: La^{+3} nanoparticles were shown in Fig.1. The prominent peaks in XRD pattern of as-prepared nanoparticles are indexed to (012), (110), (111), (020), (120) and (112) planes of rhombohedrally distorted perovskite structure of BFO (JCPDS: 86-1518 R3c space group), indicating the formation of BFO. Besides these peaks some other peaks of low intensity were also observed in as synthesized nanoparticles. The literature survey of BFO synthesis relates these peaks to be that of Bi_2O_3, Fe_2O_3 and $Bi_2Fe_4O_9$ phases, however, the nanoparticles sintering at 600 ^{0}C resulted in the removal of these extra peaks and only prominent peaks of pure BFO phase were appeared in the spectra. This implies that a single phase of BFO:La^{3+} nanoparticles could be obtained only after sintering the as-prepared nano particles at 600 ^{0}C (Fig.1) for 3h. The intensities of the prominent peaks are found to decrease as the dopant concentrations of La are increased. Earlier workers also reported similar behaviour in La doped nanoparticles [8, 9]. The lattice parameters a and c were calculated. The decrease of lattice parameters as the doping level goes up, suggesting compressive strain in the lattice upon doping. Origin of compressive strain in the BFO samples could be a combined result of doping induced structural distortion and internal stresses in the particles as a result of crystallization during heat treatment [10].

Fig.2 shows the EDAX spectrum of La doped $BiFeO_3$ nanoparticles. The appearance of La elements along with Bi, Fe and O revealed that La^{3+}ions successfully doped into BFO. However there are small variations in target compositions maximum of ± 2.0% compared to estimated composition due to limitation of the instrument.

From SEM analysis, all the sintered samples are having grains with size larger than a micrometer which may be due to the agglomeration of the particles as a result of annealing. The medium of interconnection of grains can be seen in the micrographs.

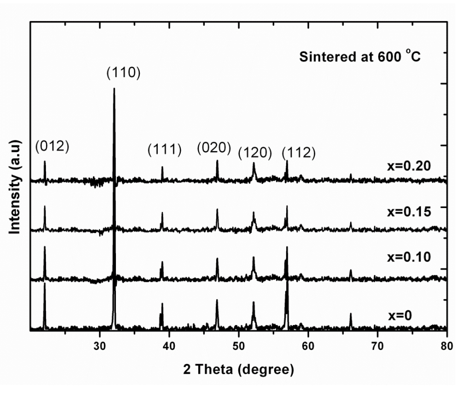

Fig.1.XRD spectra of $BiFeO_3$: La nanoparticles sintered at 600 ^{0}C

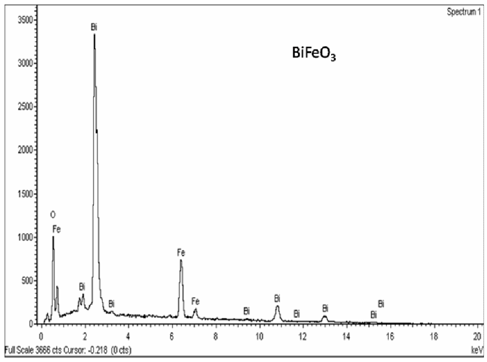

Fig.2. EDAX spectrum of $BiFeO_3$ nanoparticles

From DRS the direct band gap for all samples increases with the increase of La^{3+} concentration and varies from 1.8 to 2.5 eV as shown in Fig.3. The increase of band gap with the La concentration may be due to the decrease of lattice parameters with La doping.

In Dielectric studies the Dielectric Permittivity, Dielectric loss and AC Conductivity are studied in the frequency rage 1Hz-1MHz. It is observed that the dielectric constant ε'(ω) for all concentrations of La is decreased rapidly at lower frequencies and showed almost frequency independent behaviour at higher frequency region. It is the typical behaviour of ferrites [11,12]. It is observed that the dielectric loss ε''(ω) is also decreased by increasing frequency. Generally, the dielectric losses at high frequencies are much lower than those occurring at lower frequencies at specific temperature. This kind of dependence of ε''(ω) on frequency is typically associated with losses by conduction.

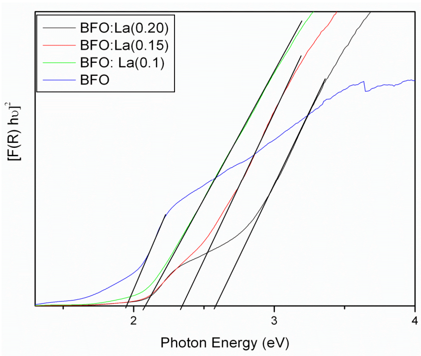

Fig.3. Kubelka–Munk plots of pure and La doped $BiFeO_3$ nanoparticles sintered at 600 ^{0}C

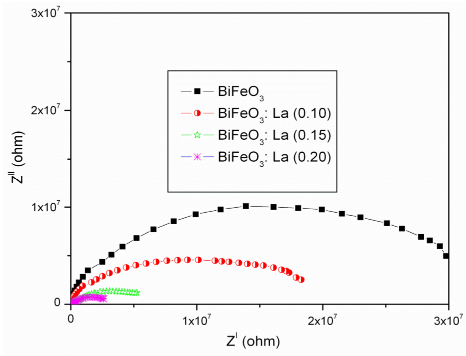

Fig.4. Cole-Cole plots of La doped $BiFeO_3$

The Cole-Cole plots for different concentrations of La doped $BiFeO_3$ were drawn. These plots give the information of scattering mechanisms with different relaxation time. As the radii of semicircle pattern is decreased with increasing La concentration, which indicates decrease in the total resistance of the sample. The conductivity values are calculated from the above relation and it is observed that the conductivity increases from 7.2 x 10^{-9} S/m to 6.1 x 10^{-8} S/m as the La concentration increased from 0.1 to 0.2.

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