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Synthesis and characterization of Lanthanum doped Bismuth Ferrite

ABSTRACT

$B_{1-x}La_xFeO_3$ ($x = 0.0, 0.025$) crystallites were prepared by chemical solution route. XRD analysis confirmed the phase formation of the materials. Thermal characterization was done by DSC-TGA to confirm crystallization and thermal behavior for phase development. Morphological studies by FESEM showed the agglomerated nature of the ferrite and EDX analysis confirmed the degree of doping. FTIR studies were done to determine the molecular signature of both undoped and doped sample.

Keywords: Lanthanum doped Bismuth Ferrite; Nanocrystalline; Solution route; DTA-TGA; FESEM; EDX; FTIR.

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INTRODUCTION

Multiferroics are the class of materials which possess at least two of the properties among ferroelectricity, ferromagnetism, ferrotoroidicity and ferroelasticity. Magnetoelectrics are a type of multiferroics possessing simultaneous existence of ferroelectric and ferromagnetic properties. Bismuth ferrite (BFO) is a unique material because of its room-temperature ferroelectric and weak antiferromagnetic (G-type ordering) properties, it has evoked much interest among the material scientists in the last few years. It has got tremendous potential for application in the field of ferroelectric memories and being non-toxic in nature is advantageous over conventional lead containing ferroelectrics like PZT. The material has got problems of high conductivity and leakage due to oxygen vacancies in the structure. Device fabrication using BFO as materials needs these properties to get modified. Over the last few years attempts have been made to improve its electrical and magnetic properties by doping. Studies of doped BFO samples and thin films have shown much improved multiferroicity than polycrystalline form. It has been seen that when pure BFO is doped with rare earth transition metals (Gd, Eu, La, Tb, Dy), the Bi site is occupied by the dopant ions and observed the change in the structure of the doped BFO [1].

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This structural change is dependent upon the route of sample synthesis. Pulsed laser deposition of BFO and lanthanum (La) doped BFO thin films on Pt/TiO₂/SiO₂/Si substrate have given monoclinic, orthorhombic and tetragonal structures of the doped samples [2-4]. On the contrary, no structural change was observed in case of La doped samples prepared by hydrothermal route [5-9]. Chen et al. prepared yttrium (Y) doped BFO samples through sol-gel method and found a structural change of doped BFO from rhombohedral R3c to orthorhombic Pnma and found 15 times increase in remnant magnetization [10]. Doping BFO crystallites with Y has also decreased the band gap, which have made BFO suitable for photocatalytic phenomenon [11, 12].

The objective of this research is to synthesis La doped BFO and to see the effect on the structure, property and morphology of the material prepared through chemical solution route.

EXPERIMENTAL

Stoichiometric amounts of analytical grade bismuth (III) nitrate pentahydrate (Merck, India) and anhydrous iron(III) nitrate (Merck, India) in equimolar proportions were taken in a beaker. 2 moles of citric acid monohydrate (Merck, India) was added to the solution of equimolar proportion of the nitrate salts. Then 10 ml. of double distilled water was added to it and the solution was stirred for 15 mins. Ethylene glycol (Merck, India) was then added to the mixture maintaining nitrate solutions in the volumetric ratio of ethylene glycol to citric acid (60:40) and stirred for 1hr. The mixture was then heat treated in an auto-combustion chamber at 317°C to form an amorphous structure followed by annealing at 450°C for 1 hr to get crystalline bismuth ferrite. To prepare La doped BFO samples, stoichiometric amount of analytical grade lanthanum(III) nitrate solution (2.5 wt%) was added to the mixture such that the total number of moles of bismuth nitrate and lanthanum nitrate be equal to that of iron nitrate. After preparation, the samples were ground in an agate mortar for characterization. DTA-TGA (Perkin Elmer, Diamond analyzer) analysis was done to ascertain the thermal characterization and crystallinity formation of the samples. The phase

identification was done by XRD (Cu K α = 1.54Å, Rigaku ultima III) to identify the phases and to calculate crystallite size. The morphological studies were done by FESEM and EDX (Hitachi, S-4800) to study the effect of doping of the sample. Finally, the existence of various bond formations was evaluated by FTIR (IR Prestige-21, Shimadzu) studies.

RESULTS AND DISCUSSION

DTA-TGA analyses

Figure 1(a) and 1(b) show the result of DTA-TGA analyses of the two samples. The endothermic peaks around 100°C and 450°C, found in both the samples, are due to the dehydration, chelate and compound formation respectively. In case of pure BFO, an endothermic peak is observed at around 330°C with a corresponding decrease in weight. For undoped bismuth ferrite, weight change observed was less than La doped bismuth ferrite, while heat flow curve of both were also distinctly different. This can be attributed to the antiferromagnetic Néel temperature of BFO (643K). In 2.5% La doped BFO this peak slightly shifts towards left, although the decrease in temperature is not much pronounced. To conclude the effect of doping on antiferromagnetic Néel temperature further study of various doping percentages is required. However, the decrease in antiferromagnetic Néel temperature is in correspondence to the previous studies [8, 10, 14]. Deep trough of endothermic curves was observed from room temperature to 300°C for undoped bismuth ferrite, while in contrast to La doped one the trough extends only upto 180°C. For both, weight changes in the range of 330°C to 450°C were observed. Heat treatment temperature was selected for both samples to be around 450°C for proper phase development and stabilization.

XRD analyses

Figure 2 shows the XRD plot of pure and 2.5% La doped BFO. It was found that in the both the samples most of the peaks were indexed to rhombohedral BFO (JCPDS No.- 86-1518). It was found that orthorhombic Bi₂Fe₄O₉ was also present in both the samples and upon doping the intensity of the peak increased a bit. The Bi₂₅FeO₄₀ peak seen

in the pure BFO sample was absent in the La doped sample. However, no separate peak was found due to La doping which is indicative of the fact that the La^{3+} ions completely diffused into the Bi^{3+} ions sites. The effect of doping on the structure of the BFO crystallites as previously reported was not seen due to the lower weight percentage of dopant [13].

The particle sizes were calculated using the Scherrer's formula. For pure BFO, it was found to be around 38.95nm and that for La doped BFO was about 50.04nm. The larger size of the doped sample could be due to the greater ionic radius of La^{3+} ions as compared to Bi^{3+} ions.

Morphological analyses

Figure 3(a) and 3(b) give the FESEM micrographs of pure and La doped BFO. The particles formed were of polyhedral structure with interconnected network amongst them in both the cases. The average crystallite sizes in both the cases were found to be comparable to the crystallite size calculated by the Scherrer's formula. The average size was for pure BFO was found around 40nm and that for La doped BFO was around 50nm. For both samples, extensive agglomeration tendency was also observed. Segregations of polyhedral particulates were observed more distinctly for La doped sample.

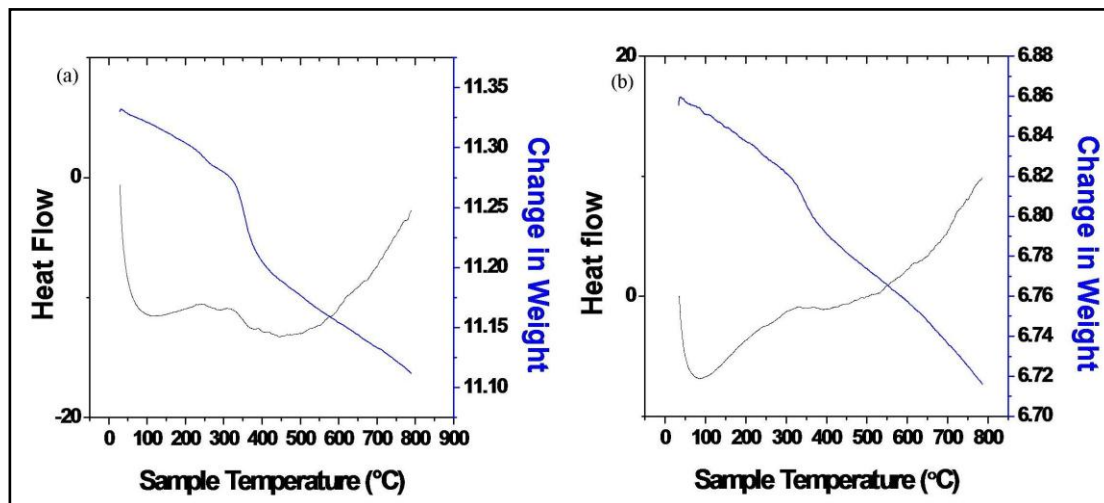


Fig. 1. DTA-TGA of (a) bismuth ferrite and (b) 2.5wt% La doped bismuth ferrite

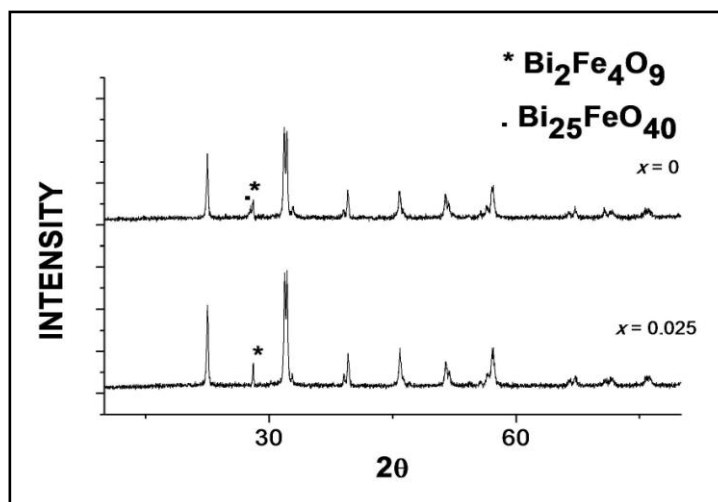


Fig. 2. XRD pattern of $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0, 0.025$) crystallite samples

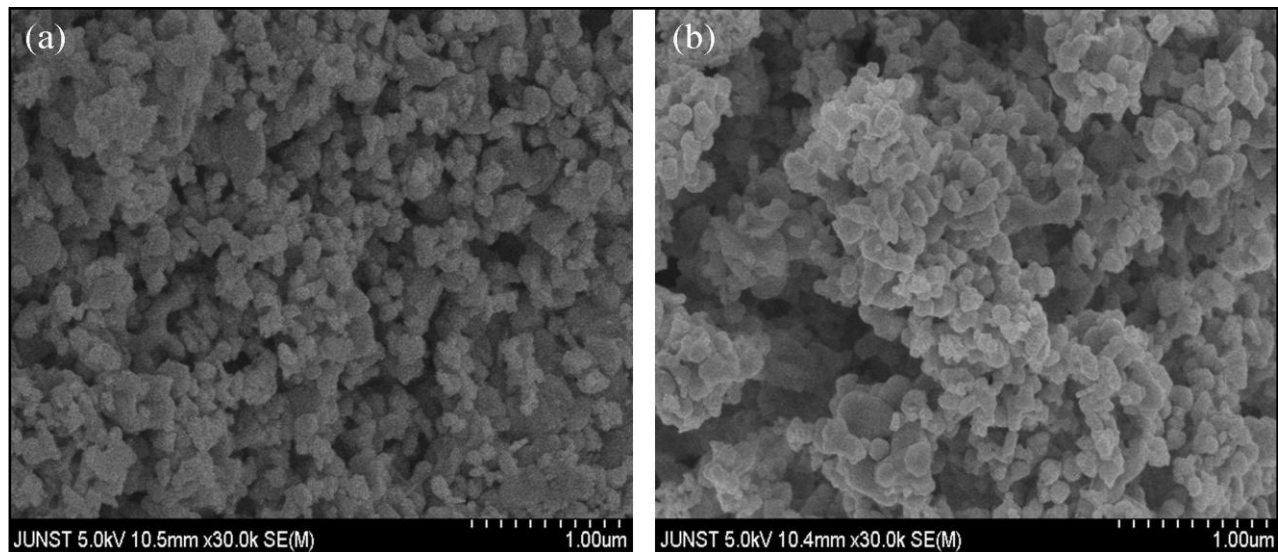


Fig. 3. FESEM micrograph of (a) $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0$) and (b) $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0.025$) crystallite samples

EDX analyses

Figure 4(a) and 4(b) illustrates the EDX analysis of the samples. The figures clearly show that the presence of bismuth, iron and oxygen as element in the pure sample and these along with lanthanum as element in appropriate ratio in the doped sample confirming La^{3+} substitution at Bi^{3+} site of pure bismuth ferrite.

FTIR analyses

Figure 5 shows the FTIR spectra of both the crystallite samples. The peaks around 430cm^{-1} -

443cm^{-1} and 555cm^{-1} - 570cm^{-1} in both the samples were due to the bending and stretching vibrations of Fe-O bond, which signifies the presence of the FeO_6 octahedral in the structure. The peaks around 848 - 852cm^{-1} can be attributed to the presence of carbonates and the peaks around 1392cm^{-1} and 1035cm^{-1} were due to the presence of nitrate ions [6, 12]. The peak around 2353cm^{-1} can be attributed to the nitrile formation, which is found disappeared on doping.

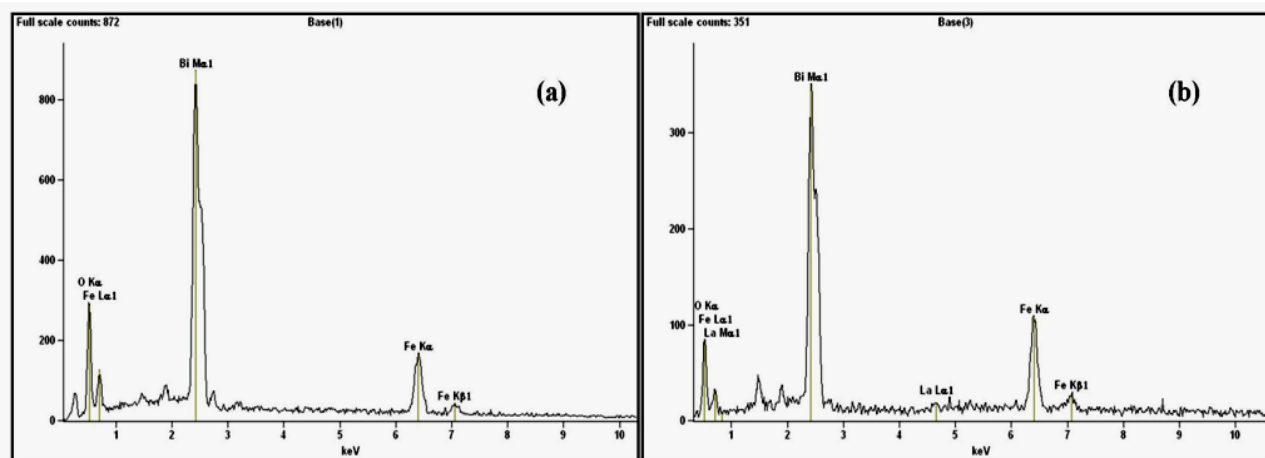


Fig. 4. EDX spectra of (a) $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0$) and (b) $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0.025$) crystallite samples

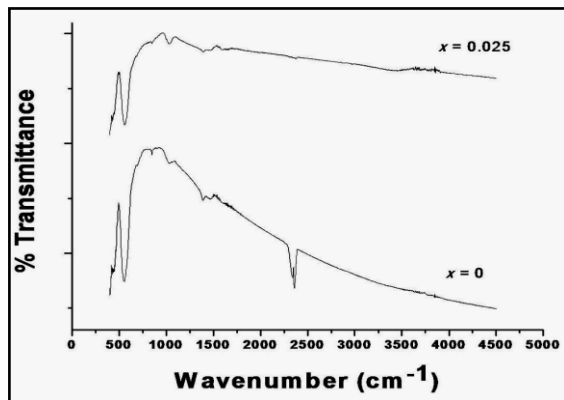


Fig. 5. FTIR spectra of $\text{Bi}_{1-x}\text{La}_x\text{FO}$ ($x = 0, 0.025$) crystallite samples

CONCLUSIONS

BFO and 2.5 % La doped BFO nanocrystals were successfully synthesized by chemical solution route. The amount of impurity in the doped sample was less than that in the undoped one. DTA-TGA showed the slight decrease in the antiferromagnetic Néel temperature of La doped bismuth ferrite with respect to pure bismuth ferrite. FESEM studies showed interconnected polyhedral structure of the prepared samples along with agglomeration, while efficacy of the doping via chemical synthesis route was established by EDX analysis. FTIR studies further exhibits the presence of the necessary bonds in the prepared samples.

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