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IMPEDANCE SPECTROSCOPIC STUDIES ON $LaGd_{0.1}B_{4.9}Fe_2Ti_3O_{18}$ CERAMIC

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ABSTRACT

Bismuth-layered structure ferroelectromagnetic (BLSFEM) compounds of Auruvillius family are found to be interesting because of their crystallographic anisotropic nature. Compound of this family, such as Lanthanum bismuth-iron titanate (LaBi5Fe2Ti3O18) has attracted much attention due to its magnetic and ferroelectric nature. These materials have a tendency to grow in the ab-plane, keeping this background, double rare earth dopants were added for Bi-site to obtain dense and promising magneto-electric ceramics. In the present investigation, polycrystalline sample of LaGd0.1Bi4.9Fe2Ti3O18 was prepared, using solid-state reaction method. XRD analysis indicated the formation of a single-phase orthorhombic structure. Cole-Cole plots revealed the presence of grain boundary and its interface effects. In the conductivity analysis, DC conductivity plot is found to be a characteristic-probe, for double rare earth dopants.

Keywords: LGBFT, double rare earth dopants, magnetoelectric, polycrystalline, Cole-Cole plots, Dc-conductivity.

1. INTRODUCTION

Bismuth-layered structure ferroelectromagnetic (BLSFEM) compounds of Auruvillius family have attracted much attention due to their magnetic and ferroelectric coupling properties[1,2]. The BLSFEM compounds crystallize in the orthorhombic structure and are characterized by $(Bi_2O_2)^{2+}$sheets interleaved with perovskite layers of$(A_{n-1}B_nO_{3n+1})^{2-}$. In the above formula n represents the number of perovskite layers in the compound. Quite a good number of compoundswith the substitution of Bi^{3+} with rare earths have been reported [3-6]. Earlier we have reported that $LaBi_5Fe_2Ti_3O_{18}$ (LBFT) showed a kind of superparamagnetic behaviour at room temperature [6]. In view of this, highmagnetic moment rare earth ion (Gd) was substituted in place of bismuth ion. Since these compounds have a tendency to grow in ab-plane, and to reduce the significant percentage of porosity, Gadolinium substituted LBFT compound namely ($LaGd_{0.1}B_{4.9}Fe_2Ti_3O_{18}$) was prepared in the present investigation. The present work is an attempt to study the role of different rare earth ions (La and Gd) on electrical properties. Detailed impedances analysis and dc conductivity is presented.

2. Materials and Methods

$LaGd_{0.1}B_{4.9}Fe_2Ti_3O_{18}$ (LGBFT) was prepared by conventional solid state reaction method. AR-Grade of La_2O_3,Gd_2O_3, Bi_2O_3, TiO_2 and Fe_2O_3 were taken in stoichiometric ratios. Using agate mortar and pestle the reactants were mixed thoroughly. The mixture was then pre-sintered at 850°C for 2 h. Requisite amount of polyvinyl alcohol was added as a binder before making into pellets. Circular disc shaped pellets were made by pressing the powder. Finally, pellets were sintered at 950°C for 4 hours.XRD patterns of the powder sample were obtained at room temperature, using Cu-Kα radiation(1.54A^o). The data was collected, with a scan rate of 2^o/min. Microstructure characterization of sintered ceramic was performed by Scanning electron microscope. Impedance measurements were carried out employing impedance analyser HP 4192A as a function of frequency within the range of 1kHz to 1MHz at different temperatures (RT–550°C). DC conductivity measurements were made, by using conventional two-probe method, using 610C Keithleyelectrometer.AC

conductivity data was extracted from the impedance data, using the standard relation: $\sigma_{a.c.} = Y'(t/A)$, where Y' is the real part of admittance, t and A are the thickness and area of the samples, respectively.

3. Results and discussion

The XRD pattern of LGBFT is shown in figure 1. The lattice parameters of LGBFT was obtained on the basis of parent compound ($Bi_6Fe_2Ti_3O_{18}$), abbreviated as BFT. The maximum intensity was observed approximately at 30°of 2θvalue, corresponding to (1, 1, 11) reflection, which was also observed in the parent compound. However, a shoulder peak was observed near 33^0 of 2θ angle. Since this reflection (0 0 18) is considered to be one of the characteristic reflection for orthorhombic structure, the sample [GBFT] is once again sintered (annealed) at 500°C for 4 hours. This compound is found to be a single-phase material, since no extra peaks were observed, when compared to the BFT (shown in the fig 1). The lattice parameters, orthorhombic distortion (b/a), inter layer distance (c/a) and density values of LGBFT are given in table 1.

Table 1. Lattice parameters of LGBFT

Lattice parameters (A˚)	a=5.49 b=5.50 c=52.83
Orthorhombic distortion (b/a)	1.0018
Interlayer distance (c/n)	10.566
X-ray Density (gm/c.c)	7.16
Experimental Density (gm/c.c)	7.15
Relative density (%)	99

Table 2: Atomic and weight percentages of the constituent elements.

Element	Atomic Percentage EDS	Atomic Percentage Theoretical
La	2.56	3.00
Bi	16.30	16.80
Gd	0.71	0.34
Fe	5.38	6.80
Ti	10.85	10.34
O	65.08	62.06

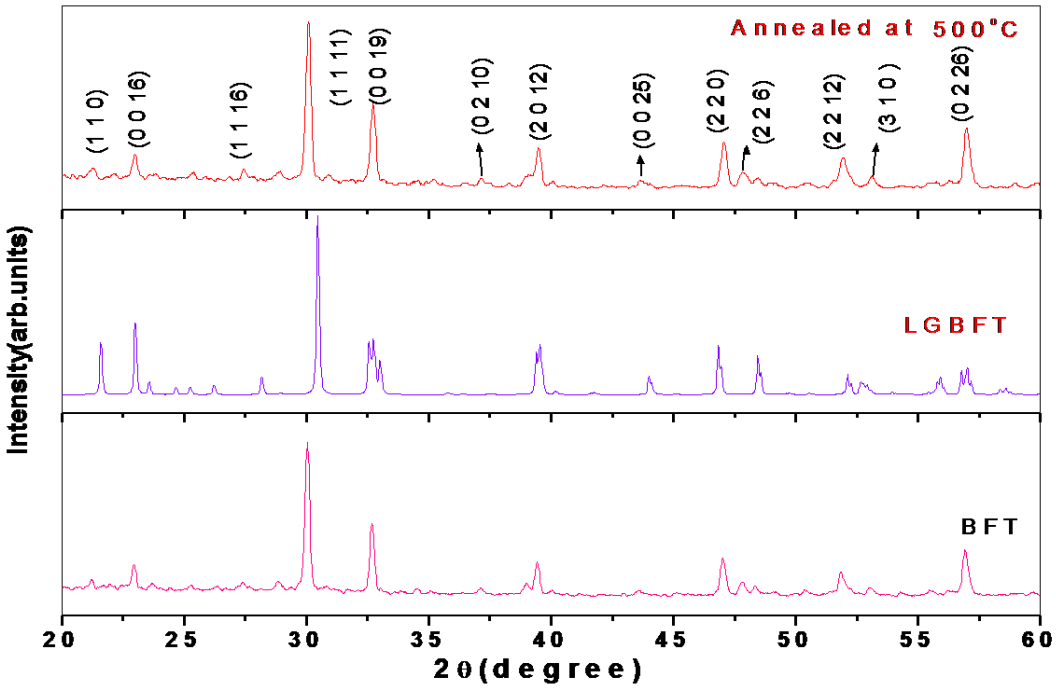

Figure1: XRD pattern recorded using PAN analytical (X'pert) diffractometer

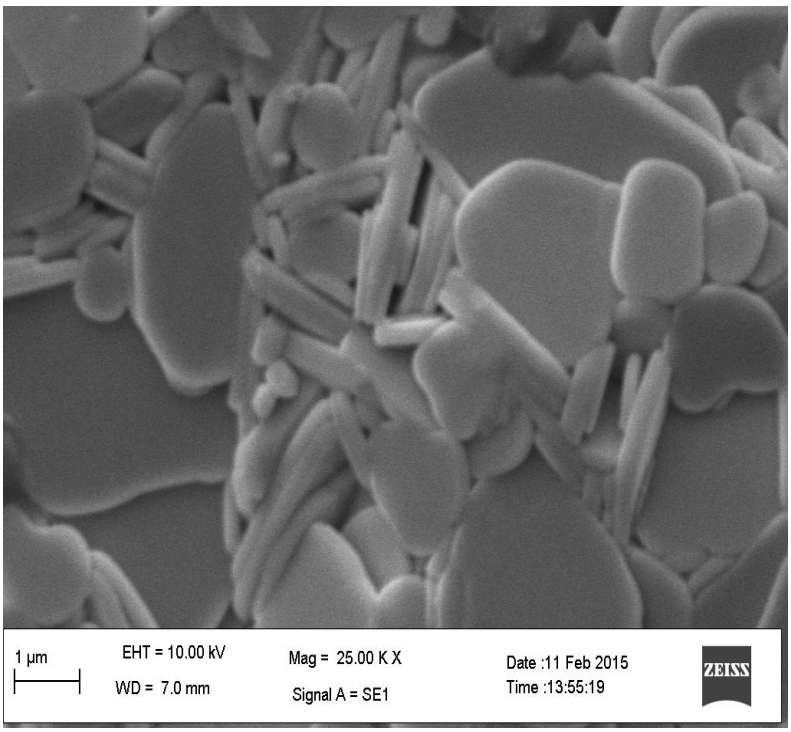

Figure2: SEM pictures of $LaGd_{0.1}B_{4.9}Fe_2Ti_3O_{18}$ ceramic

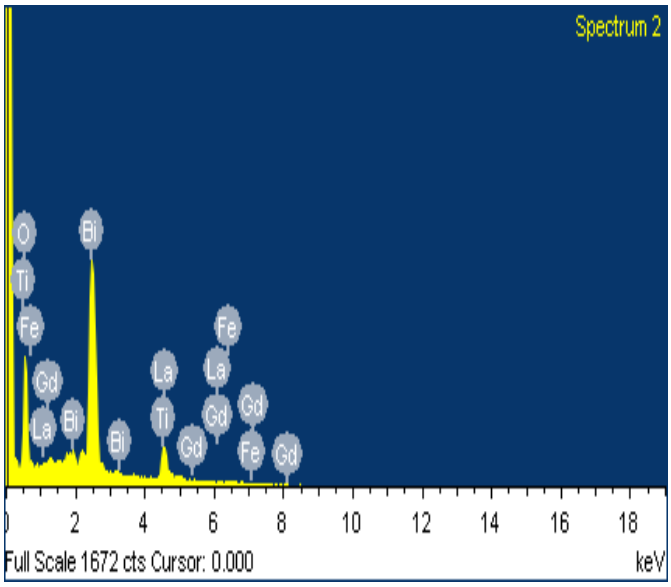

Figure3: EDS analysis of $LaGd_{0.1}B_{4.9}Fe_2Ti_3O_{18}$ ceramic

Figure 2 shows a mixture of both needle-like and plate like structures. The average size of the plate is found to be 1 – 2 µm. The density of gadolinium substituted compound is found to be more when compared to that of LBFT compound [6]. The experimental density of the sample is found to be 99% compared to that of theoretical density,which reveals that the porosity is very small and hence grain growth is enhanced[6,7].

Figure 3 shows the EDS photograph of LGBFT. Detailed EDS analysis is made and the results are summarised in the table 2. From the table, it is clear that the atomic percentage of final compound is well-agreement with the theoretical values, as mentioned in the table 2.

Complex impedance analysis is a well-known and powerful technique, which is being used from long time on electro ceramics. In order to analyse the experimental data, it is essential to have a model of equivalent circuit that gives plausible grain and its interface parameters. Fig 4 shows the complex plot of LGBFT. From the plot, two semicircles were observed [8]. Using Zview software, the experimental data was fitted into equivalent RC circuit, shown as inset fig 4.The parameters like resistance (R) and capacitance (C) of grain (g) and grain boundary (gb) were summarized in the table 3. Sine grain resistance is more than grain boundary the defects get entrapped at grain boundary interfaces, as reported earlier [7].

Fig 5 shows the variation of ac-conductivity as a function of frequency at different temperatures. From the plot, it is clear that the ac-conductivity varying very slowly at lower frequency domain while at intermediate frequency domain it becomes frequency dependent. In the frequency dependent domain, the ac-conductivity obeys Jonscher's Universal power law, defined as $\sigma_{ac} = A\omega^n$. The exponent (universal parameter) n lies between 0.5 and 1. Based on this vale, one can explain the conduction mechanism on the basis of many body interaction models [8]. According to this model, the interaction between all the dipoles participating in the polarization process is characterized by the universal parameter (n). Here it should be noted that the unity value of universal parameter (n) impels Debye type, where the interaction between the dipoles is negligible and the conductivity is only on the basis of pure dc-resistance part. This phenomenon is normally observed in these materials, at lower temperatures. As the temperature increases, the dipolar interaction increases leading to decrease the paramour (n). This is clearly seen in the fig 5. At higher frequencies, the power law dependence of ac-conductivity is universal (global) nature, corresponding to the short range hopping of charge carriers through trap sites with various heights, as mentioned above. A small peak observed at higher frequency indicates that their exist a cooperative phenomenon of both long range and short range ordering on account of double rare earth dopants for Bi-site. Dispersion in the lower as well as intermediate frequency domain indicates thermally activated relaxation process, where conductivity is related to the relaxation time (τ) and therefore it might reflected as a hump at higher frequency region and this peak is found to be

disappeared at higher temperature. From this observation one can speculate that the double rare earth dopants for Bi site certainly shows non-smooth data curves. Activation energy values of the AC conductivity and relaxation of different contributions were in agreement with the reported values.

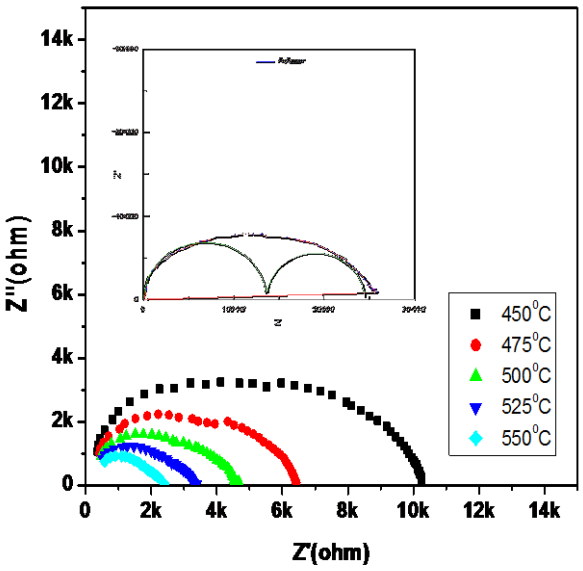

Figure 4 Cole-Cole plot of LGBFT (Inset fig Cole-Cole fitting)

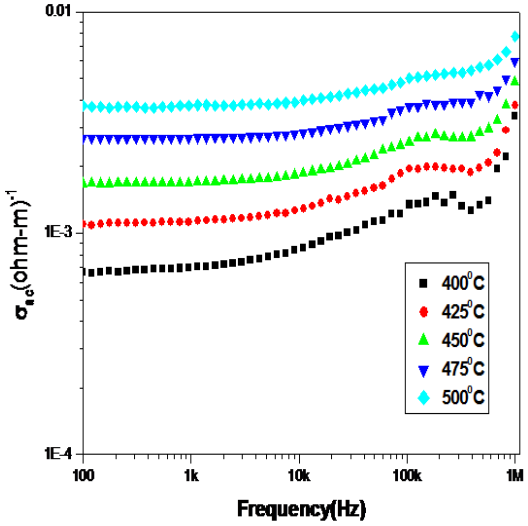

Figure 5 Variation of ac- conductivity with frequency.

Table 3: Resistance and Capacitance values of grain and grain boundary of LGBFT at different temperature

Temp °C	Rg (ohms)	Rgb (ohms)	Cg (F)	Cgb (F)
400	13645	10933	1.7E-7	2.4E-5
425	15007	9633	1.7E-6	2.4E-4
450	6668	3689	1.7E-9	3.2E-6
475	4120	2305	1.6E-9	4.2E-6
500	3278	1310	1.6E-10	2.9E-6

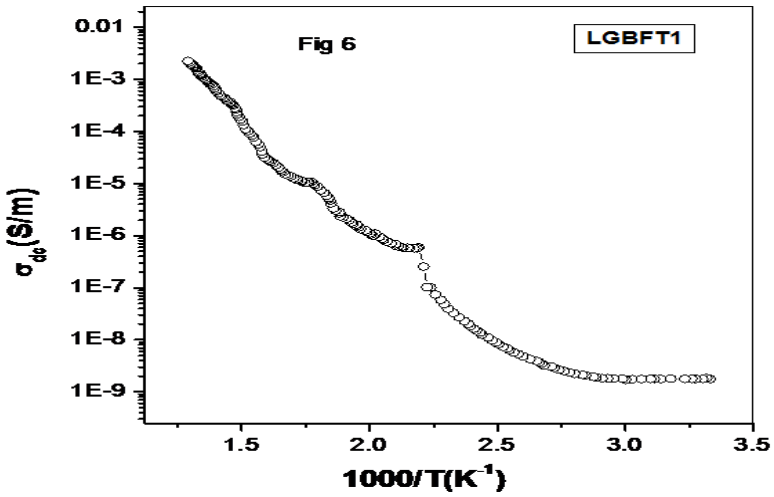

Figure 6: Variation of dc conductivity with inverse of temperature (K)

DC conductivity measurement is made in the present investigation to understand the typical oxide ion conductivity nature, where double rare earths doped for Bi site. Figure 6 shows the variation of dc-conductivity with inverse temperature. It has been globally accepted that oxygen-transportation process in the Bi-based materials is related to the dc-conductivity plot; therefore dc-conductivity plot is used to probe the effect of double earth dopants for Bi-site. More kinks observed in the dc conductivity plot (fig 6), unlike the parent compound [6] clearly confirms that the two rare earth ions were substituted for Bi site. Higher the unit cell volume, compared to the parent compound BFT has free volume and hence oxygen ions can diffuse easily in the present oxide-based conductors. Bismuth ion has a lone pair electrons located at oxygen sites and occupied a volume similar to that of oxygen anion. Therefore, rare earths doping for bismuth site increases the free volume of unit cell and cannot blocks the oxygen ions and hence sudden jumps were observed in the dc-conductivity data. Based on this analysis one can conclude that the double rare earth dopants for bismuth site can effectively enhances the ion conductivity and hence in application of materials at room temperature.

4. CONCLUSIONS

The following conclusions can be drawn keeping in view of above discussions:

1. LGBFT was prepared by conventional solid state reaction method

2.It is evident from the diffraction pattern that single phase LGBFT ceramic is in orthorhombic structure. The unit cell volume is found to be more, compared to the parent compound BFT.

3. Needle and plate like morphology of grains were observed in the SEM.

4. In the complex impedance plots, two semicircles were observed. Using Z-view software, the experimental data was fitted into equivalent RC circuit.

5. DC conductivity plot is used as finger print test for confirming the double rare earth dopants for bismuth site.

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