Effect of Sintering Temperature on Microstructure and Densification of La and Ta Doped $BiFeO_3$

Takian Fakhrul, Ahmed Sharif

Abstract*— The role of codoping by La & Ta and sintering conditions on the densification, phase and microstructure of $BiFeO_3$ (BFO) ceramic have been investigated in this study. Single phase $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (BLFTO) ceramics with x = 0.0, 0.01, 0.03 and 0.05 were synthesized by the conventional solid-state reaction method. The BLFTO dried pellets were calcined at 800°C for 2 h and sintered at temperatures in the range of 875-975°C for 4h. Percent theoretical density (%TD) as high as 96.8% was attained in this research. Phase analysis by X–ray diffraction (XRD) indicated that a possible structural transition from rhombohedral to tetragonal occurred in the BLFTO ceramics. Moreover, microstructural investigation using the field emission scanning electron microscope (FESEM) showed that an increase in Ta^{5+} doping content to 0.05 mole fraction reduces the grain size from 6 µm in $Bi_{0.8}La_{0.2}FeO_3$ to 0.8 µm in $Bi_{0.8}La_{0.2}Fe_{0.95}Ta_{0.05}O_3$ when sintered at 975°C for 4h.

***Index Terms*— Bismuth Ferrite, Sintering, Densification, Microstructure, Doping.**

I. INTRODUCTION

Multiferroics are rare multifunctional materials that exhibit more than one ferroic order in the same phase. In recent years, multiferroics have been drawing the attention of researchers due to their unique behavior of coupling between two or more properties of ferroelectricity, ferromagnetism and ferroelasticity and also because of their prospective applications in devices in spintronics, information storage, sensing and actuation [1-3]. Ferroelectricity and ferromagnetism tend to be mutually exclusive and attaining both orders in a single compound is a rare phenomenon because the requirement of transition metal ions with partially filled d electrons for magnetism is not compatible with the requirement of empty d orbitals for ferroelectricity [4, 5]. This evident incompatibility can be overcome in $BiFeO_3$ which shows a large magnetoelectric coupling in single phase thus still being the only established multiferroic having ferroelectric transition temperature (T_C~1103K) and antiferromagnetic transition (T_N~643K) above the room temperature, a key requirement for most of the applications [6-8].

At room temperature, bulk BFO has a rhombohedrally distorted perovskite structure belonging to the R3c space group. The magnetic moments Fe^{3+} cations in BFO are coupled ferromagnetically within the pseudocubic (111) planes and antiferromagnetically between adjacent planes, showing G-type antiferromagnetic order. The magnetoelectric (ME) coupling results in canting of the antiferromagnetic sublattices, leading to a weak local net magnetization. However, the possible weak ferromagnetism is cancelled by the spiral spin structure with a period of 62 nm, which inhibits the observation of the linear ME effect [7-9]. Although BFO is one of the most widely studied multiferroic materials, leakage current (due to oxygen vacancies created for charge compensation owing to the reduction of Fe^{3+} to Fe^{2+}), low sintered density and the persistent appearance of impurity phases is the major problem in BFO [8-11]. These problems limit the use of BFO for fabrication of multifunctional devices. Many authors confirmed that doping [12-15] with lone-pair active ions (especially rare earth ions e.g. La^{3+}, Nd^{3+}, Sr^{3+}) at A-sites and magnetic transition metals (e.g. Mn^{4+}, Nb^{5+}, Ta^{5+}) at B-sites reduce the leakage current in BFO and improve the multiferroic properties. Enhancement in the multiferroic properties of the doped samples are observed as doping changes cycloidal spin structure of BFO to a canted spin structure [15] thus releasing latent magnetization and resulting in significant improvement in ME interaction. Doping also increases electrical resistivity by filling of oxygen vacancies, consequently reducing leakage current in BFO. A-site (Bi-site) substitution by lanthanide ions La^{3+}has been used to enhance the multiferroic properties of BFO by many authors [16-18]. The substitution of Bi^{3+} by $La^{3+}$is favorable for stabilizing the perovskite phase due to the similar radii values of Bi^{3+} (1.030) and La^{3+} (1.032), and La doping at the Bi site enhances the ferromagnetic property of BFO [19, 20].Addition of La also significantly reduces the volatilization of bismuth oxide and hence improves oxygen ion stability in the lattice [21].On the other hand, partial substitution of $Fe^{3+}$by higher valence ions, such as Nb^{5+}or Ta^{5+}, can decrease the charge defects and increase the electrical resistivity of BFO thus allowing ferroelectricity to be determined at room temperature [22]. A-site and B-site codoping is a good way to improve the multiferroic properties of BFO, both in films and ceramics [22].

While solid state synthesis still remains the most widely used method for the preparation of BFO since the discovery of polycrystalline BFO in the late 1960s [23], throughout the years, various processes such as mechanochemical powder synthesis, [24] wet chemical processes, [25] and leaching out of second phases from sintered samples with HNO_3 [26] have been attempted.

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Although some of these attempts have partially succeeded in improving the ferromagnetic or ferroelectric properties (or both) of BFO, many studies have faced issues of coarse grain formation and porous microstructure evolution, which are possible causes for the deterioration of the collective properties. Hence, synthesis of single phase bulk BFO, which has a narrow stability range, still remains a challenging task [23]. It is difficult to synthesis BFO without impure phases (like Bi_2O_3, Fe_2O_3, Bi_2FeO_4 and $Bi_{25}FeO_{39}$) due to its reaction kinetics and the volatility of Bi_2O_3 [10, 27]. These impurities change its stoichiometry by creating oxygen vacancies and converting Fe^{3+} ions to Fe^{2+} ions that causes leakage currents which as mentioned limit practical use of BFO. Doping reduces defects related to oxygen vacancies by charge compensation mechanisms [28] and significantly modifies the microstructure during sintering. Considering the significance of microstructural modification in improving the ferroelectrical properties of some perovskite ceramics, proper understanding of the microstructure development in doped BFO ceramics synthesized using conventional solid-state reactions and sintering is required. However, studies on the microstructural evolution in BFO ceramics are rare in the literature. Probable reasons for the limited number of studies of microstructural evolution are the formation of coarse powder during calcinations [27, 29] and the very rapid grain growth during sintering, which increases the difficulty of controlling the microstructure using the sintering variables [29, 30].

In the present work, $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) bulk ceramic samples were prepared by standard solid-state synthesis and the effect of sintering conditions and codoping by La^{3+} (substituting B site), Ta^{5+} (substituting Fe site) on the densification and microstructure of BFO was studied. In order to improve the sinterability and to control the grain growth, a simple, cost effective ball milling route was employed prior to the sintering process. The percentage of densification and grain growth behavior were studied by sintering of the ball milled fine powders at different temperatures for a fixed time interval. The samples prepared under optimized sintering conditions demonstrated a significant improvement in relative density, up to 96.8%.

II. EXPERIMENTAL

Single phase $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ bulk ceramics (x = 0.0, 0.01, 0.03 and 0.05) were prepared by standard solid state reaction method. High purity (99.9%), nano sized powders of Bi_2O_3, Fe_2O_3, La_2O_3 and Ta_2O_5 (all supplied by Inframat, USA) were used as starting materials. These powders were carefully weighed in stoichiometric proportion, mixed thoroughly in an agate mortar, before dissolving in acetone followed by milling in a ball-milling machine for 24 hours. Next, the dried powder mixtures were grounded again and pelletized with an organic binder into pellets having 15 mm diameter and 2 mm thickness. Then, the dried pellets were calcined at 800°C for 2 hours. The final sintering of the pellets was done in the temperature range of 875-975 °C for proper densification. After sintering, the samples were characterized using X-ray XRD to confirm proper phase formation. The theoretical density was calculated from the molecular weight and lattice parameters derived from XRD using the Archimedes method. The microstructure of the samples were observed using field emission scanning electron microscope (FESEM: JEOL JSM 7600F) with the intention to investigate the effect of doping parameters and sintering temperatures on the densification of $BiFeO_3$ samples.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns at room temperature of BLFO and BLFTO samples sintered at 875°C indicating that distorted rhombohedral R3c structure was formed without any second phase. The slight splitting of the peaks in the XRD pattern suggest a possible phase transition from rhombohedral to tetragonal, which has also been reported in La, Nd, or Ba doped bulk $BiFeO_3$ in earlier studies. [8, 18, 31]

Numerical data of the effect of single stage sintering on percent theoretical density (%TD) of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ ceramics (x = 0.0, 0.01, 0.03 and 0.05) sintered at 875°C are tabulated in Table 1.

Table 1. shows that for $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ samples sintering was moderate at 875 °C for 4 hours and resulted in 85.4 % TD. However, the %TD deteriorated with increasing additions of Tantalum. Fig 2 shows the microstructures of the $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ ceramics sintered at 875°C.Addition of Ta inhibited the densification process and resulted in porous ceramics of reduced compactness. From Figs.2 (b), 2(c) and 2 (d) it is clearly evident that sintering for 4 hours at 875°C was

Table 1. Percent theoretical density (%TD) of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ ceramics (x = 0.0, 0.01, 0.03 and 0.05) sintered at 875°C for 4 hours

Sl No.	Sintering Temperature (°C)	Holding Time (hours)	Composition	Percent Theoretical Density (%TD)
1	875	4	$Bi_{0.8}La_{0.2}FeO_3$	84.2
			$Bi_{0.8}La_{0.2}Fe_{0.99}Ta_{0.01}O_3$	57.3
			$Bi_{0.8}La_{0.2}Fe_{0.97}Ta_{0.03}O_3$	53.1
			$Bi_{0.8}La_{0.2}Fe_{0.97}Ta_{0.05}O_3$	52.6

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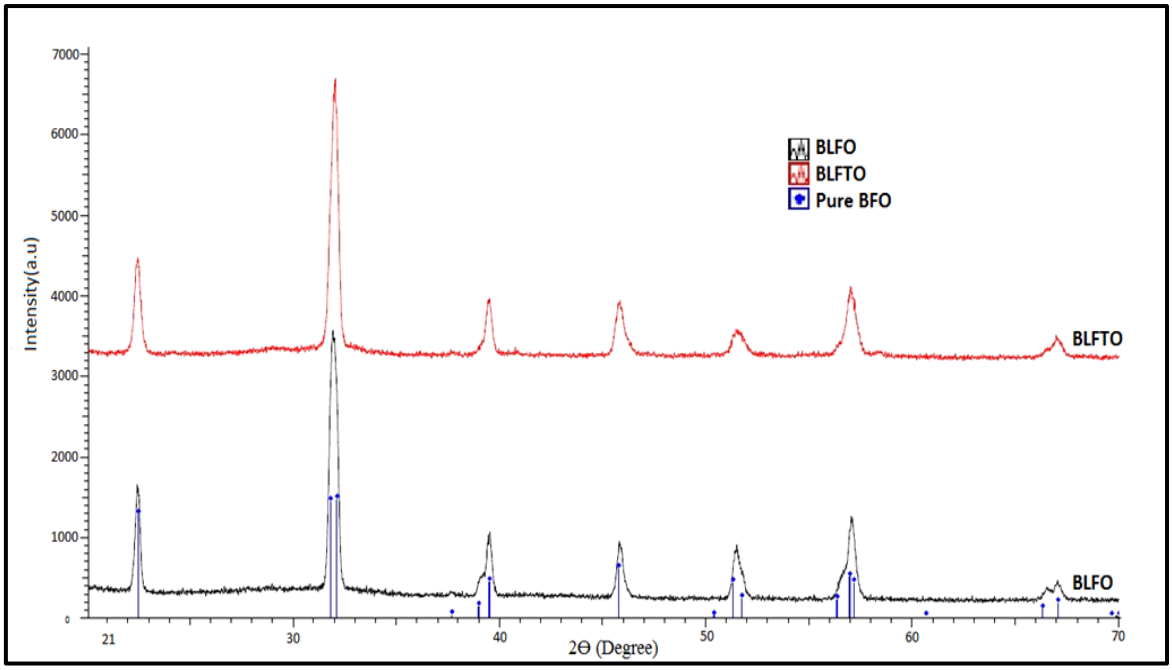


Fig 1: XRD pattern of BLFO ($Bi_{0.8}La_{0.2}FeO_3$) and BLFTO ($Bi_{0.8}La_{0.2}Fe_{0.99}Ta_{0.01}O_3$) ceramics, sintered at 875^{0}C for 4 hours, compared to pure BFO.

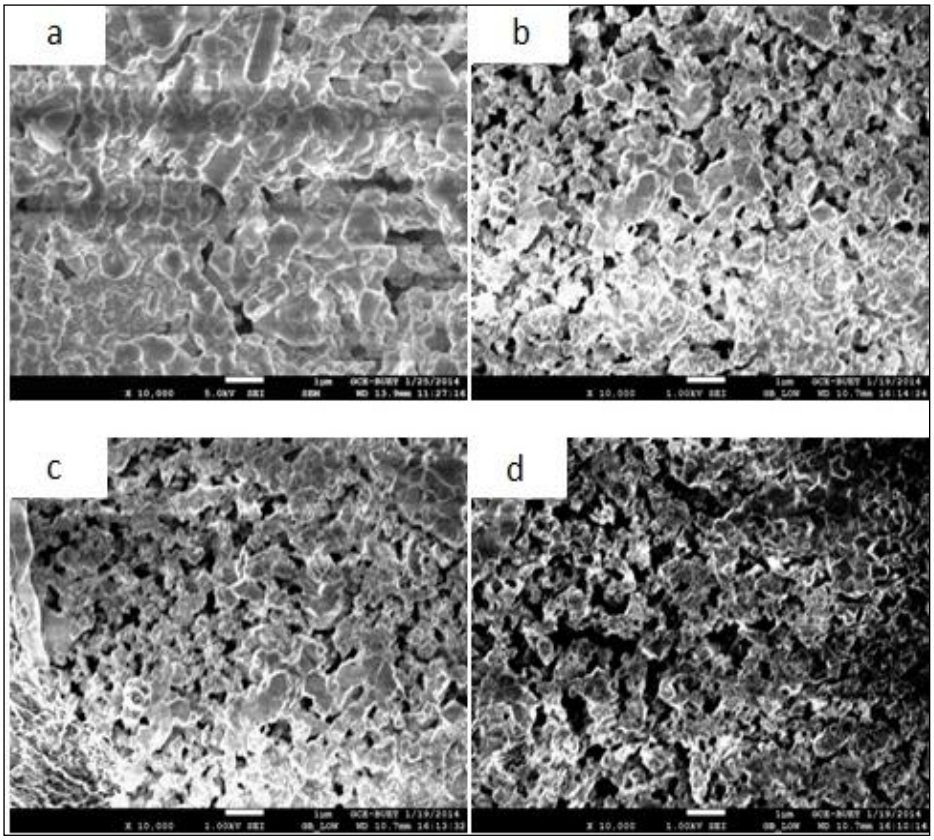


Fig 2: FESEM Micrograph of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics sintered at 875^{0}C for 4 hours

inadequate to offer sufficient energy for proper coalescence hence resulting in poor densification.

The FESEM images in Fig.2 clearly indicates the necessity for higher temperature of sintering in order to obtain proper densification, especially for $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ where the solute drag or pinning effect of Ta inhibits the densification process [32]. The %TD of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) sintered at 925, 950 and 975°C are tabulated in Table 2.

Table 2. Percent theoretical density (%TD) of $Bi_{0.8}La_{0.2}Fe_{1-x}TaxO_3$ ceramics (x = 0.0, 0.01, 0.03 and 0.05)

Sl No.	Sintering Temperature (°C)	Holding Time (hours)	Composition	Percent Theoretical Density (%TD)
1	925	4	$Bi_{0.8}La_{0.2}FeO_3$	90.2
			$Bi_{0.8}La_{0.2}Fe_{0.99}Ta_{0.01}O_3$	74.6
			$Bi_{0.8}La_{0.2}Fe_{0.97}Ta_{0.03}O_3$	74.1
			$Bi_{0.8}La_{0.2}Fe_{0.95}Ta_{0.05}O_3$	72.9
2	950	4	$Bi_{0.8}La_{0.2}FeO_3$	93.4
			$Bi_{0.8}La_{0.2}Fe_{0.99}Ta_{0.01}O_3$	82.9
			$Bi_{0.8}La_{0.2}Fe_{0.97}Ta_{0.03}O_3$	82.2
			$Bi_{0.8}La_{0.2}Fe_{0.95}Ta_{0.05}O_3$	80.8
3	975	4	$Bi_{0.8}La_{0.2}FeO_3$	96.8
			$Bi_{0.8}La_{0.2}Fe_{0.99}Ta_{0.01}O_3$	93.1
			$Bi_{0.8}La_{0.2}Fe_{0.97}Ta_{0.03}O_3$	92.8
			$Bi_{0.8}La_{0.2}Fe_{0.95}Ta_{0.05}O_3$	92.4

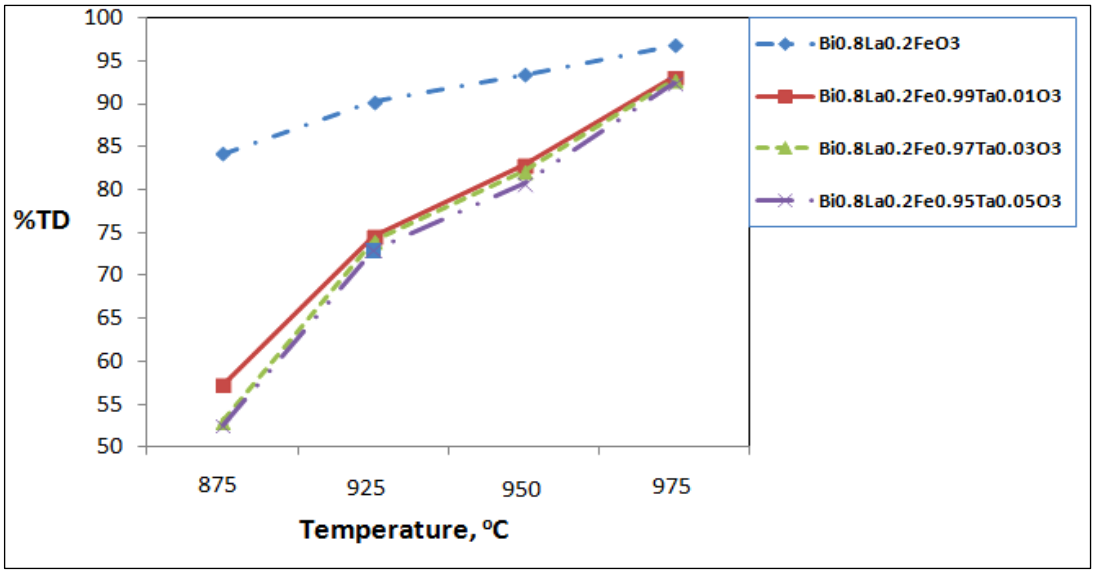


Figure 3: Variation of %TD with temperature for $Bi_{0.8}La_{0.2}Fe_{1-x}TaxO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics

The variation of %TD with sintering temperature for $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$(x = 0.00, 0.01, 0.03 and 0.05) ceramics are shown in Fig. 3.

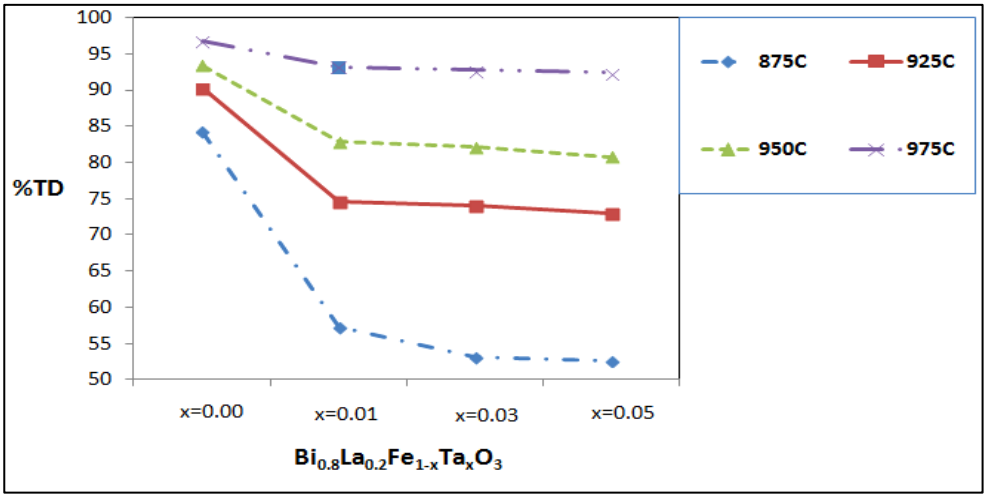
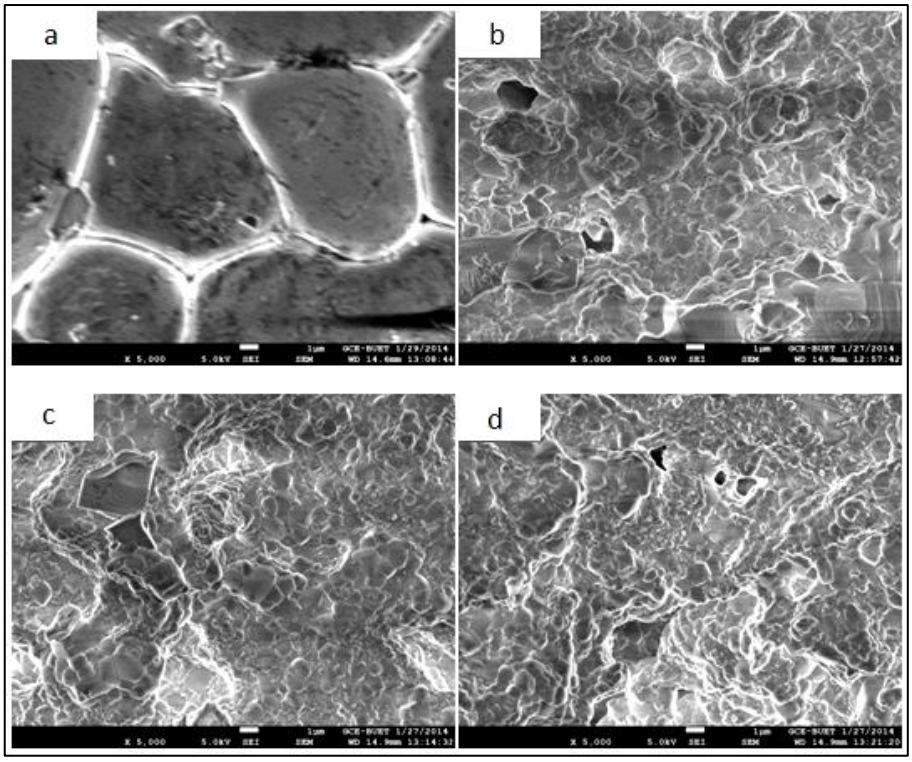


Figure 4: Variation of %TD with Ta addition (x) for $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics

Table 2 reveals that with an increase in sintering temperature the % TD increases significantly for all compositions. Moreover, as expected, the highest % TD is achieved in $Bi_{0.8}La_{0.2}FeO_3$ at 975°C, and due to the absence of Ta the % TD of this ceramic is only slightly affected by the increase in temperature as shown in Fig.3. However, Fig. 3 also shows that for a particular composition of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.01, 0.03 and 0.05) a sharp increase in %TD is observed during the transition of sintering temperature from 875 to 925°C, after which the %TD increases gradually up to a sintering temperature of 975°C. This implies that at sintering temperatures above 925°C the pinning effect of Ta becomes less significant. At 975°C all compositions have % TD above 90%. Fig.4 confirms that with increasing additions of Ta the %TD decreases at all sintering temperatures and for all compositions. Ta suppresses the grain growth during sintering by pinning of grain boundaries thus resulting in poorer densification. In Fig. 5, the FESEM images of the $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics sintered at 975°C verify



(a) x=0; Avg. Grain Size = 6 µm; % TD = 95.2 (b) x=0.01; Avg. Grain Size = 1.3 µm; % TD = 86.8 (c) x=0.03; Avg. Grain Size=1.1 µm, %TD= 85.9 (d) x=0.05; Avg. Grain Size= 0.8 µm; %TD= 85

Fig 5: FESEM Micrograph of $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics sintered at 975°C for 4 hours

the grain growth suppression action of Ta. It is obvious that for a particular sintering temperature grain size decreased with increasing Ta addition from 6 µm in $Bi_{0.8}La_{0.2}FeO_3$ to 0.8 µm in $Bi_{0.8}La_{0.2}Fe0_{.95}Ta0_{.05}O_3$. Density measurement also indicates that with increase in grain size the density of the ceramics increased which is in accordance to previous researchers [2]. However, even though high densification of $Bi_{0.8}La_{0.2}FeO_3$ was achieved when sintered at 975°C for 4 hours, the excessive grain growth may have detrimental effect on its multiferroic properties.

This significant decrease in grain size with increasing Ta^{5+} is supported by previous studies [22, 32, 33]. The Ta^{5+} ion plays the role of a donor in BLFTO because it possesses a higher valence than Fe^{3+}. The addition of Ta^{5+} to BLFO requires charge compensation by filling of oxygen vacancies; the Ta^{5+} substitution can suppress the formation of oxygen vacancies. The decrease in grain size of Ta codoped samples might be interpreted in terms of the suppression of the oxygen vacancy concentration, which slows oxygen ion motion, consequently reducing the grain growth and resulting in smaller grain size of BLFTO in comparison to that of BLFO.

IV. CONCLUSION

In summary, this work reports the effect of sintering temperature and dopants, La^{3+} and Ta^{5+}, on the densification, phase purity and microstructure development of pure BFO. The importance and consequences of doping BFO for its applications in spintronic devices has been discussed in detail in the paper. Single phase BLFO and BLFTO ceramics with distorted rhombohedral structure of space group R3c were successfully synthesized using the solid state reaction method. Percent theoretical density as high as 96.8% was achieved for $Bi_{0.8}La_{0.2}FeO_3$ ceramics although this was associated with excessive grain growth. The best % TD values for $Bi_{0.8}La_{0.2}Fe_{1-x}Ta_xO_3$ (x = 0.0, 0.01, 0.03 and 0.05) ceramics were attained at a sintering temperature of 975°C for 4 hours. Moreover, the grain size of BLFTO was found to decrease with increasing additions of Ta^{5+}. Since this research was successful in attaining % TD above 90%, future work in this field may involve studying the ferroelectric and ferromagnetic properties of the BLFO and BLFTO ceramics and investigating their structure-property relationship.

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