Abstract. Phase pure BiFeO$_3$ (BFO) and Bi$_{0.5}$Sr$_{0.5}$FeO$_3$ (BSFO) ceramics were synthesized by solid state reaction method at different sintering conditions. Structural characterization with XRD revealed that the rhombohedral phase changed to cubic due to substitution of Sr in the A-site of BFO. SEM micrographs of BSFO samples indicated improved microstructure with higher density particularly the samples sintered for longer durations. The XPS data suggested the change in oxidation state of Fe from Fe$^{3+}$ to Fe$^{2+}$ as a result of aliovalent substitution of Sr at Bi site. As a consequence, oxygen vacancies were created to neutralize charge disorder. The BSFO samples exhibited ferromagnetism with enhanced remnant magnetization and coercive field as compared to the linear magnetization in BFO. These improved results obtained by Sr doping were majorly due to the structural change and creation of oxygen vacancies.

1. Introduction
BiFeO$_3$ (BFO) is one of the most interesting prototype multiferroic material that exhibits both magnetic and ferroelectric properties at room temperature. It is a ferroelectric below Curie temperature $T_C \approx 830^\circ$C and antiferromagnetic below Neel temperature $T_N \approx 370^\circ$C [1]. BFO shows G-type antiferromagnetism with a long range cycloidal spin arrangement of 62 nm. Despite its high value of $T_C$ and $T_N$, the problems such as; appearance of secondary phases during synthesis, high leakage current, weak magnetic properties, small remnant polarization are the major limitations which hindered the utilization of BFO ceramics into practical applications as sensors, actuators, multistage memory devices etc [2]. To address the above issues new synthesis techniques as well as suitable modifications in existing processes, were pursued [3-7]. However, the preparation of single-phase BFO ceramics having enhanced magnetoelectric properties remains a major challenge. The issues of coarse grain formation, porous microstructure and evolution of abnormal grain growth during sintering are considered to be the possible causes for the deterioration of the ferroelectric and ferromagnetic collective properties. Particularly, the formation of coarse powder during calcination and the very rapid grain growth during sintering creates ample difficulties in controlling the microstructure of the bulk ceramics [2, 8-9].

Substitution of various dopants at A-site or/and B-site of BFO, has emerged as a fertile approach to suppress the formation of secondary phase and sinterability, which helps reducing leakage current and enhancing ferroelectric properties. It also induces ferromagnetism by destroying the spatially modulated cycloid spin structures [10-15]. In this regard, rare-earth doped BFO systems have been widely studied and many of the researchers are partially successful in improvising the multiferroic properties of BFO [15,16]. Nevertheless, in recent years, the substitution of divalent non-magnetic alkaline earth metals at Bi$^{3+}$ site have been employed to improve the multiferroic properties.
of BFO [17,18]. In this regard, Sr$^{2+}$ (ionic radius = 1.18Å) has been understood as an appropriate alternative for Bi$^{3+}$ (ionic radius = 1.03Å) substitution owing to their ionic radii compatibility. The difference in ionic charge and electro-negativity between Sr$^{2+}$ and Bi$^{3+}$ may lead to mixed oxidation state of Fe, formation of oxygen vacancies, change in nature of bonding and subsequently the modification of structural and multiferroic properties of BFO. However, the reports on Sr doped BFO bulk ceramic system were very much rare in literature and some of the results reported were contradictory. Balamurugan et. al. [19] reported no structural change in BFO with 50% Sr substitution at A-site whereas Hussain et. al. observed a structural change from rhombohedral to pseudo-cubic with 45% Sr substitution in BFO [20]. Hence, further studies on BSFO bulk ceramics are much needed. In this paper, we synthesized single phase BiFeO$_3$ and Bi$_{0.5}$Sr$_{0.5}$FeO$_3$ ceramics by conventional solid state reaction at different sintering time and studied their structure, microstructure and magnetic properties. The results were analyzed in view of the effect of Sr on various properties of BFO.

2. Experimental

Bulk polycrystalline BFO and BSFO ceramics were prepared by taking high purity Bi$_2$O$_3$, Fe$_2$O$_3$ and SrCO$_3$ in stoichiometric ratio and ball-milled for 24h in ethanol using ZrO$_2$ balls and polypropylene bottles. Before weighing, the powders were pre-heated at 200°C for 24h. The dried slurry was crushed using agate mortar-pestle and sieved to 150 μm. Then the powder was calcinated at 800°C, 2h for BFO and 900°C, 4h for BSFO with a heating/cooling rate of 4°C/min. The calcined powder was again milled, dried, crushed and sieved to 150 μm. Finally, the powder was compacted to pellet of 8mm-diameter and 3mm thickness, then isostatically pressed under 200MPa. The green pellets were sintered at 850°C, 4h for BFO and at 950°C for 4h, 12h and 24h for BSFO samples abbreviated as BSFO04, BSFO12 and BSFO24, respectively in this article. The x-ray diffraction patterns were recorded for the powder samples obtained before and after sintering by x-ray diffractometer (D/MAX-IIIC(3kW), RIGAKU) with scan speed of 2º/min and step size of 1º. The sintered pellets were sectioned vertically and the sectioned surfaces were grinded and polished to 1μm finish with diamond paste suspension followed by thermal etching. The microstructure of etched surfaces was observed using scanning electron microscopy (Phillips XL 30 SEM, Phillips). XPS measurement was carried out using a VG Microtech ESCA 2000 and the M-H loop was measured by Superconducting Quantum Interference Device (SQUID) magnetometer (MPMS7, Quantum Design).

3. Results and discussion

3.1. X-ray diffraction. Figure 1 shows the x-ray diffraction patterns of calcined and sintered BFO and BSFO04 ceramics respectively. No impurity phases were observed in the diffraction patterns suggesting single phase formation for BFO and BSFO samples. The splitting in the characteristic peaks (012) and (110) is prominent which confirms BFO has rhombohedrally distorted perovskite structure. The diffraction peaks are indexed using the JCPDS data (card number # 20-0169) for rhombohedral BFO with R3c symmetry. With 50% Sr substitution at Bi-site of BFO, the splitting in peaks (012) and (110) completely disappeared, suggesting cubic symmetry. The patterns of BSFO are indexed using JCPDS data (card number # 54-0683) for cubic structure. From the above observation, it is confirmed that the structure of BFO changed from rhombohedral to cubic with Sr doping at A-site. Figure 2 shows the XRD pattern of BSFO samples sintered at different durations. The patterns clearly indicate 100% perovskite phase however no meaningful change observed in the patterns recorded for the BSFO samples sintered for longer durations. This confirmed that all BSFO samples had a stable cubic structure, not altered even after 24h long sintering.

3.2 Microstructure Analysis. Figure 3 shows the morphology of the powder particles of BFO and BSFO. Majority of BFO particles seemed round in shape with particle size variation from 2-5μm.
These particles were mostly the agglomerates. Some of the BFO particles appeared almost equiaxed with sharp corners (see inset of Fig. 3a) and the particle size varies from 1-2µm, which may be due to recrystallization process [21]. For BSFO, the agglomerates still existed, nevertheless, the particle size reduced to less than 1µm.

![Figure 1. XRD patterns of (a) pristine BFO and (b) BSFO04 polycrystalline samples.](image1)

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![Figure 2. XRD patterns of BSFO samples sintered at 950°C for 4, 12 and 24 h.](image2)

The shape of the BSFO particles appeared to be almost cube shaped as shown in the insert of Fig 3b. This change in shape after Sr substitution indicates that there may be change in step free energy, which subsequently affects the grain coarsening behavior [22]. Figure 4a shows the SEM pictures of BFO samples. The micrographs display coarse and porous microstructure with grain size ranging from ~50 to 100µm. A large number of pores were observed inside the grains as well as at the grain boundary. Most of the pores seemed to be dry spherical pores. Figure 4 shows SEM pictures of BSFO04,
BSFO12 and BSFO24 samples respectively. The micrographs indicated an abrupt reduction of grain size to 3-4µm in comparison to the BFO samples. The grains were also distributed uniformly in BSFO samples. The BSFO samples sintered for 4h and 12h show large pores and most of them may contain Bi-liquid packets. The liquids are getting dried up when the sample is sintered at a longer duration due to volatilization of Bi.

**Figure 4.** SEM micrograph of (a) pure BFO (b) BSFO sintered at 950°C for 4h (c) BSFO sintered at 950°C for 12h and (d) BSFO sintered at 950°C for 24h.

3.3 X-ray Photoelectron Spectroscopy. Figure 5 shows narrow scan spectra of Fe-2p and O-1s peaks for both BFO and BSFO04 samples. BSFO04 was used for XPS analysis because of its better magnetization property compared to BSFO12 and BSFO24, which would be discussed later in this article. All core level binding energies were marked with respect to C-1s peak (284.6eV). Figure 5a shows the XPS spectra of the Fe-2p region of BFO and BSFO samples. The binding energy (B.E.) of Fe-2p3/2 is expected at 710.4eV for Fe³⁺ and 709.0eV for Fe²⁺ [23, 24]. The XPS peak of Fe-2p3/2 at 710.4eV with energy gap between spin-orbit component, Δ = 13.7eV, signified that the studied BFO sample was enriched with Fe³⁺. Substitution of Sr²⁺ in place of Bi³⁺ may result in the conversion of Fe³⁺ into Fe⁴⁺ to maintain the charge neutrality condition as per the following equation

\[ Fe^{3+} + Bi^{3+} \leftrightarrow Fe^{4+} + Sr^{2+} \]

But the spectra of Fe-2p of studied BSFO sample exhibited a shift towards lower binding energy having Fe-2p3/2 peak at 709.2eV. This could be because of conversion of Fe⁴⁺ into Fe²⁺ which is far away from our initial expectation. This conversion generally leads to oxygen vacancies to neutralize the net charge inside the system. Figure 5b shows the XPS spectra of O-1s region for both the samples. The O-1s peak at 530eV in BFO sample is a clear indication of dominant Fe³⁺–O²⁻ bond [3]. The broadening of O-1s peak towards higher binding energy may be due to Bi–O, Bi–O–Fe bonds. However, a shift in O-1s peak towards lower energy was observed in studied BSFO sample. This shift might be the commutative effect of following individual effects: 1) conversion of Fe³⁺ into Fe²⁺ leads to formation of Fe²⁺–O²⁻ bond having lower energy, 2) conversion of Fe³⁺ into Fe²⁺ leads to
formation of oxygen vacancies for charge compensation and 3) the electro-negativity of Sr (0.95) is much less compared to O (3.44), Bi (2.02) and Fe (1.83) which could result in increased electron cloud near oxygen atoms. Furthermore, the very low electro-negativity of Sr compared to Fe and O, makes Sr–O bond more dominant and ionic, which is reflected as a peak at 530.5 eV. The Sr-3d wide peak (see inset) consists of a doublet ascribed to Sr–O bonds which confirmed the dominant Sr–O bonding in BSFO [25].

Figure 5. XPS narrow scan spectra of (a) Fe-2p and (b) O-1s for pure BFO sample and BSFO04 samples. Inset 5(b) shows the XPS narrow scan spectra of Sr-3d in BSFO04.

3.4 Magnetic Properties. Figure 6 shows the magnetisation vs. applied magnetic field (M-H) curves of BFO, BSFO04, BSFO12 and BSFO24 samples recorded at room temperature. The pure BFO sample is showing a linear magnetization curve evidencing the antiferromagnetic behaviour arises due to well known G-type anti-ferromagnetism with a long range cycloidal spin arrangement of 62nm.

Figure 6. M-H curves for pure BFO and BSFO sintered for 4 h, 12 h and 24 h.
However, 50% Sr substitution in BFO at A-site induced weak ferromagnetic behavior, which further becomes weaker with increasing sintering time duration. The variation in the value of residual magnetization ($M_R$), coercive field ($H_c$) and magnetization at 10KOe, in BSFO samples with different sintering duration (4h, 12h and 24h), is presented in table 1. The origin of ferromagnetic behavior in BSFO may be attributed to following facts: i) breaking of long range cycloidal spin arrangement that may be due to rhombohedral to cubic structural change (discussed in Section 3.1) and ii) creation of oxygen vacancies that resulted because of change in oxidation state of Fe [17,18,26].

**Table 1:** Variation in coercive field, residual magnetization and magnetization at 10KOe of three different BSFO samples sintered at 950 °C for 4, 12 and 24h.

| Sample   | BSFO04 | BSFO12 | BSFO24 |
|----------|--------|--------|--------|
| $H_c$ (KOe) | 3      | 2.9    | 3.1    |
| $M_R$ (emu/g) | 0.192  | 0.125  | 0.082  |
| $M$ (emu/g) at 10 KOe | 0.376  | 0.262  | 0.179  |

However, sintering in ambient atmosphere for longer time may reduce the oxygen vacancies. Additionally, the decrease in porosity and micro-structural defects are also seen in SEM analysis of BSFO samples with increase in sintering duration. Reduction of oxygen vacancies and defects may be the probable cause for the decrease in magnetization of BSFO samples sintered for longer duration. The coercivity ($H_c$) of BSFO samples does not show any significant change with variation of sintering duration. However, very little variation in the above parameters is noticed as given in table 1. Shape anisotropy, magnetoelastic anisotropy and magnetocrystalline anisotropy are the main source of $H_c$ for magnetic materials [27]. For the present study, no meaningful change in XRD of BSFO samples is observed with variation of sintering duration, thus the contribution of shape anisotropy in $H_c$ can be neglected. So, the minute change in $H_c$ in samples may be due to the magneto-crystalline anisotropy in addition to the magneto-elastic anisotropy.

4. Conclusion

In summary, we have synthesized phase pure BFO sample and Bi$_{0.5}$Sr$_{0.5}$FeO$_3$ samples by solid state reaction at optimized calcination temperature varying from 800-900°C for 2-4h. The Sintering temperature variation was done from 850-950°C for 4-24h. XRD results confirmed a structural change from rhombohedral to cubic phase after Sr substitution at Bi-site. The cubic symmetry remained stable for the BSFO samples even after sintering at longer durations. XPS studies exhibited conversion of Fe$^{3+}$ into Fe$^{2+}$ which led to the creation of oxygen vacancies for charge compensation. Large electronegativity difference in Sr and O (compared to Bi and O) changed the nature of bond in BSFO. Sr–O bond became more ionic than that of Bi–O bond. Not only the difference in oxidation state of Sr and Bi but also the difference in ionic radii and electronegativity of Bi and Sr played a major role in structural and electronic change in BSFO unit cell. Change in structure as well as creation of oxygen vacancies were found as the key reasons for appearance of weak ferromagnetism in Sr substituted BFO samples.

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