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Influence of Ba and Mo co-doping on the structural, electrical, magnetic and optical properties of BiFeO₃ ceramics

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Abstract:
In this work, Bi₀.₈Ba₀.₂Fe₁₋ₓMoₓO₃ (x = 0, 0.5, 0.10 and 0.15) ceramics were synthesized by conventional solid-state reaction to evaluate the influence of Ba²⁺ and Mo⁶⁺ co-doping on the structure, morphology, electrical, magnetic and optical properties of BiFeO₃ ceramic. Rietveld refinement of x-ray diffraction data was done to obtain the subtle structural information. A tetragonal structure of P4mm type was revealed for Bi₀.₈Ba₀.₂FeO₃ (x = 0) ceramic. Evolution of rhombohedral (R3c) phase was observed with Mo⁶⁺ doping and a complete transformation to R3c phase from P4mm was found for 15 wt% Mo⁶⁺ doping. This type of transformation causes distortion in the structure and results in changing bond angle. Magnetization was found to be improved with increasing the percentage of Mo⁶⁺ up to 10 wt%. Canting of spin due to the change in Fe-O-Fe bond angle is believed to be the main reason behind this improvement. One secondary phase BaMoO₄ was found and becomes prominent with Mo⁶⁺ doping. Possible formation of this impurity and its correlation with properties are explained. Microstructural analysis was done to observe the Ba²⁺ and Mo⁶⁺ co-doping effect on grain size and distribution. A correlation of grain size with electric and magnetic properties is drawn and elucidated. Dielectric constant shows an increasing trend with Mo⁶⁺ doping. Reduction in oxygen vacancy, due to charge compensation upon high charged Mo⁶⁺ addition, believed to be the staple reason behind the dielectric constant increment. Lastly, optical band gap energy found to be decreased with the addition of Mo⁶⁺ and possible reasons behind this are evaluated. Overall, co-doping of Ba²⁺ and Mo⁶⁺ found to have a positive influence over materials electrical, optical as well as magnetic property.

1. Introduction

Materials that show more than one ferroic-ordering (ferroelectric, ferromagnetic and ferro-elastic) simultaneously are called multiferroics [1]. Multiferroic magnetoelectric in which spontaneous magnetic and dielectric ordering occur have fascinated scientists for centuries [2]. They have a spontaneous magnetization that can be switched by an applied magnetic field, a spontaneous polarization that can be switched by an applied electric field. Furthermore, mutual coupling between these order parameters enhances degree of freedom of device applicability [3]. Such materials have all the potential to be used in spintronics, transducer, memory devices, sensors etc [1]. Among the very few multiferroic materials, bismuth ferrite (BiFeO₃) having distorted perovskite structure has been considered as the most promising single-phase candidate for practical applications due to its high ferroelectric Curie temperature (Tᶜ = 1103 K) and antiferromagnetic Neel temperature (Tₙ = 643 K) [2].

But the main difficulties for the implementation of BiFeO₃ (BFO) for device application is its structural instability along with associated fickleness of functional behavior [4]. It shows G-type anti-ferromagnetism.
That means, a spatially modulated spin structure prevents it from net magnetization and make it reluctant to show magnetoelastic effect [5]. Besides, high leakage current generated in BFO due to oxygen vacancies, results in poor ferroelectric and dielectric properties [6]. In addition, difficulty in the single-phase synthesis due to narrow temperature range makes its use in practical applications more difficult [3].

Ion doping of BFO has been widely explored to reduce the leakage current, improve the ferroelectric behavior, and strengthen the ME coupling in BFO [7]. It has been reported that heterovalent dopants like alkaline earth metal ions (Ba$^{2+}$, Ca$^{2+}$, Sr$^{2+}$) at A site of BFO enhance magnetic properties by suppressing spin cycloid structure [8]. But some reports the generation of oxygen vacancies due to charge compensation which contributes to increase leakage currents [9]. On the other hand, doping of higher valence ions (e.g. Ti$^{4+}$, Nb$^{5+}$, Mo$^{6+}$ etc) at B site has been found has decreased the leakage current [3]. That’s why, doping simultaneously at both sites have gained significant attention recently. Further, co-doping of rare earth or alkaline earth ions at Bi-site and transition metal ions at Fe-site has been realized as a versatile tool to enhance ferroelectric as well as magnetic properties of BFO [3]. Among the various transition elements used, Mo$^{6+}$ is the less explored dopants for BFO. Zhang et al reported increased polarization, reduced current density and improved magnetism for Mo doping in BFO [8]. Similar result is found by Hu et al who claimed a positive influence of Mo on filling oxygen vacancy [10]. But structural and morphological characteristics are not well explored in both cases. Therefore, it will be interesting, to observe the structure and morphology change due to Mo doping in BFO. In our study, we tried to analyze structural and morphological changes in details due to Ba$^{2+}$ and Mo$^{6+}$ co-doping in BFO. Previous studies show that Ba$^{2+}$ doping creates a weak ferromagnetism in BFO, though creates significant oxygen vacancies [11]. So, it can be expected that Mo$^{6+}$ doping in Ba-doped BFO could significantly suppress the oxygen vacancy and thus improve dielectric property. Moreover, magnetic and optical properties of material were evaluated. We tried to draw a correlation of structural and morphological change with this possible improvement in properties. Another challenge of this study, is the single-phase formation of doped BFO by solid state reaction. The source of Mo$^{6+}$ used in this study is MoO$_3$ powder which have a melting temperature of 795$^\circ$C only and leads to select low calcination/sintering temperature for this case. As several previous studies concluded that sintering below 800$^\circ$C results in impurity phases in BFO, it is therefore a tough task to zero out the possibility of impurity formation [11]. However, possible impurities and their effects on the properties of BFO is explained further in this study.

2. Experimental

Polycrystalline samples of Bi$_{0.8}$Ba$_{0.2}$Fe$_{1-x}$Mo$_x$O$_3$ ceramic, where x = (0%, 5%, 10% & 15%) were produced using conventional solid-state reaction method. Highly pure starting raw materials of ($>99.9\%$, Merck Specialties, India) Bi$_2$O$_3$, Fe$_2$O$_3$, BaCO$_3$ and MoO$_3$ powders were used with proper stoichiometric ratio and thoroughly mixed by ball milling in ethanol media (purity $>99.8\%$, Merck, Germany) for 20 h. After milling, the powder was dried in an oven (100$^\circ$C–24 h) and hand milled for 2 h followed by a calcination at 700 $^\circ$C for 2 h. The calcined powder was then ground and pressed into pellet (13 mm diameter and 2 mm thickness) using PVA as binder. Sintering was carried out at 800 $^\circ$C for 2 h in a muffle furnace at an ambient pressure. X-Ray diffraction analysis was done using a diffractometer (Bruker Advanced D8, Germany) for phase identification having a Cu x-ray source (Wavelength: K$_{\alpha 1}$ = 1.54060 Å and K$_{\alpha 2}$ = 1.54439 Å). FULLPROF software was used for structural refinement by Rietveld analysis. Surface morphology of sintered samples were analyzed by SEM (ZEISS-EVO 18, UK). Grain size was calculated using linear intercept method and distribution was measured using IMAGE J software. Room temperature dielectric constant was measured at 500 mV by varying frequency with Impedance analyzer (Wayne Kerr 6500B series, UK) and optical band gap was measured using UV–vis spectroscopy (SHIMADZU UV/Vis-1650 PC, JAPAN) in the range of 200–800 nm. Finally, the room temperature magnetic property was measured by vibrating sample magnetometer (VSM: EV-9 Micro sense).

3. Results and discussions

3.1. Structural analysis

X-ray diffraction analysis (XRD) was done to attain the structural information. Room temperature XRD curve is shown in figure 1 and the curve matched well with the peaks of BFO. 0%, 5%, 10% and 15% Mo doped BBFO (Ba doped BFO) are denoted by BBFMO-0, BBFMO-5, BBFMO-10 and BBFMO-15 respectively. The magnified portion of the XRD curve in the range of 2$\theta$ = 30$^\circ$–35$^\circ$ shows that there is complete merging of the (104) and (110) neighboring peaks for BBFMO-0 and BBFMO-5. But those two peaks started splitting for BBFMO-10 and completely reverted back to split state for BBFMO-15. Pure BFO has rhombohedral R$3c$ type structure and (104) and (110) peaks usually remained split. As merging of the major neighboring peaks depicts a structural transformation, in our case transformation from the usual rhombohedral R$3c$ type structure is a possibility [12].
To further analyze the structure, Reitveld refinement was done for all the XRD pattern using FULLPROF package. Reitveld refinement was carried out for all possible structures and curve fitting is shown in figure 2. Tetragonal P4mm type structure found to be best fitted for BBFMO-0 and rhombohedral R3c type structure for BBFMO-15. Merging of (104) and (110) peaks supports the transformation from R3c to P4mm type for BBFMO-0. Peak splitting of BBFMO-15 supports the reversion back to the rhombohedral R3c structure. And this result is consistent with the previous studies [9]. For 5% BBFMO and 10% BBFMO a mixture of both types found to be fitted well. Gradual peak splitting from 0% BBFMO to 15% BBFMO and weak peaks at the foot of each major peak justify this structural transformation from tetragonal P4mm type to rhombohedral R3c type. Moreover, the Goodness of Fit (GoF) when fitted along with impurity phase BaMoO₄ was found to be within the range of 1.2–1.8 which indicates the reliability of our refinement.

Formation of this impurity phase BaMoO₄ can be explained with the help of enthalpy using the equation [13]; $\Delta H_f = P_{AB} \times (\varepsilon_{AB} - 0.5 \varepsilon_{AA} - 0.5 \varepsilon_{BB})$; where, $P_{AB}$ is the number of A–B bonds (Fe–O or Mo–O bonds) and $\varepsilon$ is the bond energy which is proportional to the negative of the bond strength, $I$. Bond strength, $I$ can be calculated using the Pauling’s equation [14]: $I = 1 - e^{-\frac{\Delta E}{k_BT}}$; where, $(X_A)$ and $(X_B)$ denote the average electronegativity of cation and anion. Now, putting the electronegativity values of Fe³⁺ (1.83), Mo⁶⁺ (2.16), O²⁻ (3.44), Bi³⁺ (1.9) and Ba²⁺ (0.89) in Pauling’s equation separately, it was found that Fe–O bond strength (0.477) is higher than Mo–O bond strength (0.336). Thus, from the enthalpy equation it can be found that enthalpy of formation for undoped BBFO is more negative than Mo doped BBFO. According to the free energy of formation equation [13], $\Delta G_f = \Delta H_f - T \Delta S_f Z$, more negative enthalpy means more negative free energy of formation (considering negligible entropy change) and more negative free energy means more stable. That’s why, Mo–doped BBFO is less stable than its pure counterpart and thus some Mo reacts with Ba to form most stable impurity phase BaMoO₄ among the other possible impurity phases. The percentage of impurity phase (0%, 3.9%, 10.71% and 14.95%) for BBFMO-0, BBFMO-5, BBFMO-10 and BBFMO-15 respectively obtained from the Reitveld refinement is coherent with this explanation as impurity phase percentage increases gradually with Mo doping. Low calcination temperature (700 °C) might be another reason of these impurities formation as reported in other cases [11].

Lattice parameters and other refined data are shown in table 1. The table depicts that with the increase of Mo doping, cell volume decreases gradually (374.4711 Å to 371.9237 Å). This volume data is consistent with the XRD pattern shown in figure 1 where major peak shifted towards right with the increase of Mo from 5% to 15%. This can be explained with the help of effective ionic radii of Mo⁶⁺ (0.62 Å) which is lower than the ionic radii of Fe³⁺ (0.64 Å). That’s why according to Vegard’s law doping with Mo⁶⁺ causes a shrinkage in structure and as a result volume get lowered and peak shifted towards right [15]. But what is inconsistent with this theoretical explanation is the left side shifting of major peak for BBFMO-5 than BBFMO-0. If Mo⁶⁺ doping in BBFO shrink the structure, major peak for BBFMO-5 should have been shifted towards right than BBFMO-0. A possible explanation for this anomaly is that doping with high charged cation (V⁵⁺, Nb⁵⁺, Ti⁴⁺ etc) causes charge neutralization through the reduction of oxygen vacancy [16]. Perhaps a great extent of oxygen vacancy reduction.

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![Figure 1.](image-url)

(a) Room temperature XRD pattern of BBFMO-(0, 5, 10 and 15) ceramics and (b) magnified pattern in the range of ~30–35.
occurs in the case of BBFMO-5 which has an expanding effect on the structure. If this effect is greater than the lower size ionic radii effect than it will leads to an increase of overall volume [17]. And this is justified by the volume of BBFMO-5 in table 1.

Tolerance factors (t) are calculated to observe the structural stability [18]. The following equation along with Shannon ionic radii is used to calculate t [19]:

\[ t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}} \]

where \( r_A, r_B, \) and \( r_O \) are the radii of A site, B-site cation and the O ion respectively. From the equation it is clear that substitution with larger size cation in A-site and smaller size cation in B-site increases t. In our case, A-site dopant Ba\(^{2+}\) (1.42 Å) has larger ionic radii than Bi\(^{3+}\) (1.17 Å) and B-site dopant Mo\(^{6+}\) (0.62 Å) has smaller ionic radii than Fe\(^{3+}\) (0.64 Å). That’s why tolerance factor gradually increases with Mo doping. However, increase in tolerance factors depicts a distortion in structure [18]. Thus, bond length and bond angle of Bi–O and Fe–O will be changed in BBFMO. This change is shown in table 1.

### 3.2. Morphological analysis

Surface morphology of BBFMO ceramics are observed by SEM and the micrographs are shown in figure 3. Microstructures of BBFMO clearly shows that grains are round in shape with irregular type. Careful observation depicts the roughness of surface and the presence of significant amount of porosity. It is clear from the SEM
images that porosity content as well as surface roughness decreases with Mo doping. To further ensure that percentage of porosity was calculated using the following formula:

\[ \text{Percentage of Porosity, } P\% = \left(1 - \frac{\rho_{\text{exp}}}{\rho_{\text{cr}}}ight) \times 100\% \]

Where, \( \rho_{\text{exp}} \) and \( \rho_{\text{cr}} \) are apparent density and crystal density respectively. All the relevant data are shown in table 2. Higher amount of porosity in BBFMO-0 might arise from the creation of oxygen vacancies due to the

Table 1. Structural parameters of BBFMO-\( (0, 5, 10 \text{ and } 15) \) ceramics obtained by Reitveld refinement.

| Content     | BBFMO-0  | BBFMO-5  | BBFMO-10 | BBFMO-15 |
|-------------|----------|----------|----------|----------|
| Lattice parameter | P4 mm    | a = 3.9806 Å | a = 3.9842 Å | a = 3.9657 Å | — |
|              | P4 mm    | b = 3.9806 Å | b = 3.9842 Å | b = 3.9657 Å | |
|              | R3c      | c = 4.0027 Å | c = 4.0007 Å | c = 3.9829 Å | |
| Volume      | P4 mm    | 63.420 Å³  | 63.5061 Å³ | 62.638 Å³  | — |
|              | R3c      | —         | 374.4711 Å³ | 373.915 Å³ | 371.9237 Å³ |
| Phase percentage | P4 mm | 100%   | 81.56%   | 51.43%   | — |
|              | R3c      | —         | 14.54%   | 37.86%   | 85.05% |
| BaMoO₄       | —        | 3.90%    | 10.71%   | 14.95%   | |
| G. α. f      | 1.2      | 1.8      | 1.4      | 1.6      | |
| C/a²         | 1.27     | 2.64     | 2.37     | 2.75     | |
| Rexp         | 22.6     | 20.3     | 13.8     | 18       | |
| O–Fe–O bond angle | 175.3912° | 171.7°   | 97.909°  | 89.9°    | |
| Bond length  | Bi–O     | 2.322 Å  | 2.68 Å   | 2.39 Å   | 2.325 Å |
|              | Fe–O     | 1.9916 Å | 1.997 Å  | 2.005 Å  | 1.758 Å |
| Tolerance factor | 0.8927023 | 0.8931216 | 0.893559 | 0.8939985 |
partial substitution of Ba$^{2+}$ for Bi$^{3+}$ into BFO [20]. Addition of Mo$^{6+}$ causes the charge compensation by filling some vacant sites and this might be attributed for the reduction of porosity upon further doping [8].

Another lucid visualization from the SEM micrographs is the gradual increment of grain sizes with doping percentage. Grain sizes are calculated using linear intercept method [21]. The average grain size of BBFMO-0, BBFMO-5, BBFMO-10, and BBFMO-15 are found to be 0.361 μm, 0.363 μm, 0.392 μm, 0.61 μm respectively. Smallest size in BBFMO-0 is perhaps due to the inhibited grain growth by Ba$^{2+}$ ions resulting from divalent substitution for trivalent ions [22]. Further increment in grain size suggests that Mo$^{6+}$ might stimulates grain growth. This result is in good agreement with the recent study on Mo doped BFO [23]. Due to this grain growth, average grain size goes higher and distribution of grains becomes wide. Distribution of grains for all BBFMO ceramics are shown in figure 4. Presence of polygonal and some big grains are detected in BBFMO-10 and BBFMO-15 which might be due to the generation of secondary phase BaMoO$_3$.

### 3.3. Dielectric property

Room temperature frequency response of the real part of dielectric constant ($k$) and dissipation factor (tanδ) are shown in figures 5(a) and (b) respectively. All samples show high dielectric constant and dielectric loss at low frequency which implies the presence of dc conductivity in BBFMO ceramic. The dielectric constant values ($k$) of BBFMO-(0, 5, 10, 15) ceramics are 140, 175, 570, 1220 at 0.1 kHz respectively. Dielectric constant gradually decreases for all samples and at more higher frequencies it becomes stable. This phenomenon can be explained by two ways. First, among the four types of polarization, dipolar and interfacial polarizations only contribute at lower frequencies. Thus, there is less polarization contributors at high frequencies and results in low dielectric

| Grains size | Apparent density (g cm$^{-3}$) | Crystal density (g cm$^{-3}$) | Porosity (%) |
|-------------|-------------------------------|------------------------------|--------------|
| BBFMO-0     | 0.361 μm                      | 3.53                         | 8.237        | 55.5          |
| BBFMO-5     | 0.363 μm                      | 5.31                         | 8.44         | 37.08         |
| BBFMO-10    | 0.392 μm                      | 5.31                         | 8.336        | 36.3          |
| BBFMO-15    | 0.61 μm                       | 5.31                         | 8.380        | 36.6          |

![Figure 4](image-url)
constant \[9\]. Second, according to Maxwell-Wagner theory space charges move and pile up at grain boundaries if significant resistance is present. But, at high frequencies, space charges don’t get sufficient time to accumulate at grain boundaries and thus, deteriorate the dielectric properties \[24\].

Dielectric constant and loss tangent values for all BBFMO ceramics are tabulated in table 3. The increasing trend of dielectric constant can be unraveled by the grain size effect on dielectric properties. For larger grains, domain wall movement is much easier and this leads to an improved dielectric property \[25\]. SEM images in figure 3 lucidly show that partial substitution of Mo\(^{6+}\) for Fe\(^{3+}\) has an impact on increasing grain size. Calculated grain sizes tabulated in table 2 also show that highest grain size is achieved for BBFMO-15 and this contributed to its highest dielectric constant. Another way to elucidate this increment is by the relation of oxygen vacancy with domain switching. Low concentration and randomly distributed oxygen vacancy make the domain wall movement easier whereas high concentration and allied oxygen vacancy act as domain wall pinning centers \[26\].

Oxygen vacancy is expected to appear in our BBFMO-0 ceramic due to the substitution of low charge Ba\(^{2+}\) for Bi\(^{3+}\) as reported in other cases \[11\]. This can be shown by the following Kroger-Vink notations:

\[
2\text{BaO} = 2\text{Ba}_{\text{Bi}} + V_O
\]

It is well known that oxygen vacancy significantly reduced with high charged transition elements doping as evidenced in numerous cases \[3\]. That’s why we can expect that a charge compensation might occur by Mo\(^{6+}\) by filling oxygen vacancy. This trend is in good agreement as the observation of Zhang et al \[8\]. Probable defect reaction is shown below.

\[
2\text{MoO}_3 + 3V_O = 2\text{Mo}_{\text{Fe}} + 6\text{O}_5
\]

Perhaps with the increase of Mo doping, oxygen vacancy reduction becomes more prominent and that’s how it contributes to the increment of dielectric constant.

On the other hand, dielectric loss (\(\tan\delta\)) values of BBFMO-(0, 5, 10, 15) ceramics are in the range of 0.8–1.5 at low frequency (0.1 kHz) which is within the tolerance limit. The \(\tan\delta\) values of BBFMO-(0, 5, 10, 15) ceramics suggest that the defect chemistry of Ba doped BiFeO\(_3\) and Ba-Mo doped BiFeO\(_3\) was different. Only exception is that a huge dispersion is observed for BBFMO-15 in the range of 100–1000 kHz which indicated that at this frequency significant amount of space charges failed to follow the direction of electric field \[27\]. Mild humps are observed for other samples in this region. In this range of frequency, the phase difference between applied

![Figure 5. Frequency responded (a) dielectric constant and (b) dielectric loss of BBFMO-(0, 5, 10 and 15) ceramics.](image-url)
electric field and polarization of all ceramics might have become the maximum. Dielectric loss rises up with Mo doping. Perhaps the impurity phase BaMoO₄ has an effect in this regard [28]. High amount of porosity as shown in table 2 might have a contribution for high loss. Other parameters like domain density, internal stress etc need to be considered for the further clarification of this loss tangent (\(\tan\delta\)) behavior [25].

3.4. Magnetic property
Room temperature M–H hysteresis loops are shown in figure 6 for all BBFMO ceramics. Nonzero remnant magnetization and coercive field are observed for all samples. Magnetic parameters extracted from figure 6 are summarized in table 3. Pure BFO is antiferromagnetic in nature with spiral modulated spin structure and thus shows very low magnetization [29]. But doping BFO with Ba²⁺ shows substantial saturation magnetization as observed in figure 6. This is because of the fact that larger size Ba²⁺ (1.42 Å) substitution at A-site (Bi³⁺: 1.17 Å) distort the usual structure of BFO as evidenced in table 1. As a result, Fe–O–Fe bond angle got changed which in effect induces canting of the spins. This type of canted spins due to structural distortion enhance magnetism as observed in various doped BFO [29]. Besides this, local distortion induced ferromagnetic pinning could contribute to the magnetization [11].

5% Mo addition (BBFMO-5) further increases the Ms. This can be explained by the fact that smaller size Mo⁶⁺ addition causes tilting of FeO₆ octahedron. As a result, Fe–O–Fe bond angle got decreased (table 1). Now, according to Goodenough–Kanamori rule, increase of Fe–O–Fe bond angle increases the antiferromagnetic (AFM) super-exchange interaction and is strongest at the angle of 180° [11]. So, in this case decreased bond angle weakens the AFM super-exchange interaction and in effect causes the spin canting away from the perfect AFM structure and thus induce ferromagnetism. Besides this, uncompensated spins originated from Fe³⁺ due to oxygen vacancy, improve magnetism [30]. However, improved ferromagnetism is observed up to 10% Mo doping and in fact highest Ms is observed for BBFMO-10. On the contrary, significant reduction of Ms is observed for BBFMO-15. Comparatively larger fraction replacement of magnetic Fe³⁺ with non-magnetic Mo⁶⁺ might be attributed for drastic reduction of Ms. Moreover, signification amount (14.95%) of impurity phase (BaMoO₄) is present in BBFMO-15 which is generally paramagnetic in nature and results in the deterioration of magnetic properties [31].

From table 3 it is clear that, highest coercivity is observed for BBFMO-5 and got reduced for further Mo doping. It is well known that coercivity decreases due to the nonuniformity of grains [32]. So, in our case, grains become nonuniform with Mo doping due to the broad distribution as observed in SEM micrographs.

3.5. Optical property
UV–vis spectroscopy was done to find out the reflectance value of BBFMO ceramics. Figure 7 represents the absorbance curve of BBFMO ceramics derived from Kubelka-Munk (K–M) function [33] given by

\[
F(R) = \frac{(1 - R)^2}{2R}, \quad \text{Where, } R \text{ is the reflectance value.}
\]

Absorbance edge shifting towards higher wavelength is defined as red shift which indicates doping concentration decreases the band gap [34]. For further clarification, \([F(R)h\nu]^2\) versus \(h\nu\) was plotted (figure 8) to measure the band gap energy, \(E_g\). The intersecting point of tangent...
line at x-axis [when \( [F(R)]^2h\theta = 0 \)] gives the band gap value. This band gap value represents the difference between top of the valence band (O 2p) and bottom of the conduction band (Fe 3d) of BFO [35].

The calculated band gap values are tabulated in Table 3 and clearly shows a decreasing trend with Mo\(^{6+}\) doping. Band gap energy is reduced from 2.35 eV to 2.26 eV for 15 wt% Mo doping in BBFMO-0 ceramic which is the lowest for BFO to the best of our knowledge [35]. Several studies report that, distortion in FeO\(_6\) octahedron causes different hybridization between O\(^{2-}\) and Fe\(^{3+}\) which leads to the formation of a unique energy level in between Fe 3d and O 2p states [36]. Distortion in structure and thus a reduction in Fe–O–Fe bond angle due to lower sized Mo\(^{6+}\) doping is evidenced in our structural refinement data and this probably account for the red shift in this case. In addition, there might also be an influence of oxygen vacancy and crystallite size on the optical band gap energy as reported earlier [25]. Due to the narrower bandgap, BBFMO ceramics might be useful for degradation of pollutants or photocatalytic hydrogen generation from water splitting under visible light [37].

4. Conclusion

In essence, BBFMO-(0, 5, 10 and 15) ceramics were prepared by standard solid-state reaction route. Structural analysis revealed that a gradual transition from tetragonal (P4mm) to rhombohedral (R3c) structure occur with the increase of Mo\(^{6+}\) doping from 0 to 15 wt%. Microstructural analysis suggests that Mo\(^{6+}\) might act as grain growth promoter. Thus, enlarged grains and broad distribution are observed. Structural distortion and grain
size are evidenced to have huge positive influence on magnetic properties. However, highest saturation magnetization was found for BBFMO-10 and further doping deteriorate the magnetic property. With Mo$^{6+}$ addition, a rising trend is observed in dielectric constant and loss. A significant reduction in oxygen vacancy thought to be occurred with high charged Mo$^{6+}$ doping and is attributed for high dielectric values. Optical band gap energy showed a decreasing trend. The overall finding suggests that BBFMO ceramics have sufficient potential to be applied in electromagnetic and electrooptic devices.

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Conflict of interest

The authors declare no conflict of interest.

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