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57Fe Mossbauer and electrical studies of Mn doped YFeO3 prepared via sol-gel technique

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Abstract

Polycrystalline YFe1−xMnxO3 (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples are prepared via sol-gel method. Structural characterization of these samples is done by x-ray diffraction (XRD) technique and Raman spectroscopic method. Intense peaks in XRD graphs show that the sample is crystalline in nature and Reitveld refined XRD data shows that the samples are formed in single phase. Raman spectroscopic study confirms the structure and phase purity of the samples. Room temperature 57Fe Mossbauer studies confirm that Fe ion exists in ferric state. The hyperfine field (Bhf) values are found to decrease with increase in manganese (Mn) concentration. This decrease in Bhf value indicates the increase in antiferromagnetic nature of the samples, which arises due to the weakening of magnetic interactions between the Fe ions. From room temperature leakage current density (J−E) measurements, it is observed that leakage current density increases with increase in Mn doping. Scanning electron micrographs explain the reason of increase in leakage current density based on the microstructure of the samples. The samples are found to exhibit Ohmic conduction mechanism in entire electric field range.

1. Introduction

Materials with perovskite structure have a chemical formula ABO3. Here ‘A’ is a cation with larger radius (rare earth or alkaline earth materials), ‘B’ is a cation of smaller radius (transition metal) and ‘O’ is Oxygen. In perovskite family, some of the materials show a unique property of exhibiting both ferroelectric and ferromagnetic nature simultaneously in same phase and these properties are tunable to the applied field. Such materials are called multiferroic materials [1]. These materials are having many applications in micro-technological devices like magneto-optical current sensors [2], fast latching optical switches [3], spintronic devices [4], ultra fast lasers in magnetic devices [5], etc.

ABO3 orthoferrite, in the form of AFeO3 usually crystallizes in distorted orthorhombic structure. This structure contains Fe3+ ion bonded to six oxygen ions in an octahedron configuration with Fe3+ ion at the center. The cation A is present at the interstitial area between the octahedron, coordinated by 12 oxygen anions [6]. In AFeO3 exchange interactions exists between Fe3+–Fe3+, A3+–Fe3+ and A3+–A3+ (A3+ is magnetic active ion) [7] ions. Below Neel temperature (TN), Fe3+–O–Fe3+ super exchange interactions are dominant which leads to ordering of Fe3+ magnetic moments and results in weak ferromagnetism [8, 9]. The origin of weak ferromagnetism is attributed to antisymmetric Dzyaloshinkii–Moriya (DM) exchange between neighboring spins [10–12]. Spin reorientation is observed due to A3+–Fe3+ exchange interactions. By applying external field or varying temperature, the direction of magnetization can be changed from one axis to another [8]. Weak interactions between A3+–A3+ ions gives rise to ordering of A3+ ions at low temperatures. In orthoferrites in which ‘A’ is a non magnetic cation such as ‘Y’, no spin reorientation is seen at room temperature. But spin
reorientation in these materials can be induced by applying strong magnetic field or by lowering temperatures [13].

Generally, ferroelectricity is not seen in Centro symmetric phase groups like Pnma/Pbnm. Tokunaga et al [14] studied the existence of low temperature ferroelectricity in Gd(Dy)FeO$_3$ and room temperature ferroelectricity in SmFeO$_3$. Shang et al [15] suggested that there is ferroelectric ordering in YFeO$_3$ even at room temperature. Hence, it is observed that every atom present in the periodic table can be accommodated in the ideal template of perovskite to obtain new class of materials with tailored properties, which can be tuned to desired applications through doping. Earlier works on orthoferrites and transition metal oxides have shown that the structural and physical properties can be modified by doping [16, 17]. Zaghrioui et al [18] and Cheng et al [19] has observed that doping of transition metals in YMnO$_3$ and BiFeO$_3$ has affected the magnetic properties of the compound. As YFeO$_3$ possesses same crystallite structure as of these compounds, the physical properties of YFeO$_3$ are also expected to be effectively modified. These modifications in their properties can be used to explore different applications in technical fields.

The present work presents the systematic study of synthesis of Mn doped yttrium iron oxide via sol-gel technique. Generally, solid state reaction method is widely used to produce ceramic oxides. But, formation of secondary oxides is the common problem faced while producing the materials using this method. Furthermore, it is observed that the end product is non homogeneous in nature. In order to get a pure homogeneous product, sample is subjected to several thermal treatments and intermediate grindings. This problem has paved path to develop a new method called ‘sol-gel’ technique [20]. In this technique, the compounds are mixed at molecular levels and the samples are formed in pure single phase which are free from secondary phases. This method is opted for sample synthesis, as it is fast, effective and inexpensive process which yields pure homogeneous single phase compounds.

The main purpose of the present work is to probe the changes occurring in the structure and ferroelectric properties of YFe$_{1-x}$Mn$_x$O$_3$ samples. Mossbauer studies help us to understand the Fe–Mn interactions and the origin of antiferromagnetism in YFe$_{1-x}$Mn$_x$O$_3$ samples. The scope of this paper is to understand the effect of Mn doping on the electric and magnetic properties of the samples and an attempt is made to correlate them to the crystallographic changes occurring in the samples.

2. Experimental

Multiferroic YFe$_{1-x}$Mn$_x$O$_3$ samples ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) are prepared through sol-gel method. Yttrium oxide (Y$_2$O$_3$) is weighed in stochiometric ratio and dissolved in nitric acid to form nitrates. Iron (III) nitrate nano hydrate [Fe(NO$_3$)$_3$.9H$_2$O] and citric acid taken in 1:1 ratio with metallic ion are dissolved in water. Freshly prepared Manganese carbonate (MnCO$_3$) is dissolved in nitric acid and stirred thoroughly to get a clear solution. All the prepared solutions of Y$_2$O$_3$, Fe(NO$_3$)$_3$.9H$_2$O, citric acid and MnCO$_3$ were added together and stirred continuously for 30 min. By adding ammonium hydroxide solution, PH of the solution is adjusted to be neutral. This solution is heated and stirred continuously for 4 h. When the volume of the solution is reduced to one third of its original, ethylene glycol is added in the ratio of 1:1.2 to convert the solution into gel. This gel is
heated at 150 °C until it converts into black fluffy ash. This ash is carefully crushed to fine powder and calcinated at 600 °C for 4 h. These samples are pelletized and are sintered at 1200 °C for 4 h.

Structural characterization of the materials is done by x-ray Diffraction (XRD) studies. The XRD measurements are carried out by using a Bruker D8 Advance x-ray diffractometer with Cu-Kα radiation. Scanning Electron Microscope (Evo 18 eds Oxford model of Zeiss make) is used to record the corresponding Micrographs, which give information about size and morphology of the particles. Vibration spectrum of the samples is studied by Raman Spectra which is recorded in back scattering geometry with LABRAM Jobin-Yvon spectrometer. This spectrometer is equipped with microscopic objective of 20 X and having a laser source of 473 nm with power of 25 mW. Leakage current density (J-E) measurements were carried out using P-E loop tracer (M/s Radiant Premier). 57Fe Mossbauer measurements were carried out in transmission mode with 57Co (Rh) radioactive source in constant acceleration mode using a standard PC-based Mossbauer spectrometer equipped with a WissEl velocity drive. Velocity calibration of spectrometer is carried out by a natural iron absorber at room temperature.

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the XRD plots of Mn doped YFeO₃ samples with their Miller Indices. The peaks of the samples are sharp with high intensities indicating good crystallization of the samples. All the compounds possess distorted orthorhombic structure with space group Pbnm [21–23]. No extra peaks are found in the XRD plots confirming that the sample is in pure form without any impurities. Figure 2 shows the Rietveld refined XRD graphs and the enlarged portion of 2θ from 31° to 33°. It can be seen from the figure that with the increase in Mn
concentration the diffraction peak (2 0 0) is slightly shifted towards lower 2θ value indicating an increase in lattice parameter. This shift is a signature of substitution of dopant (Mn) in the YFeO$_3$ lattice. Reitveld refined parameters like Residual factor $R_p$, Weighted Residual factor $R_{wp}$ and $\chi^2$ are given in table 1. From the table it is

Table 1. Reliability factors of refinement, lattice parameters and cell volume of YFe$_{1-x}$Mn$_x$O$_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$). The error in the estimation of lattice parameter is typically about 0.01 Å$^2$.

| Sample         | $R_p$  | $R_{wp}$ | $\chi^2$ | a (Å$^2$) | b (Å$^2$) | c (Å$^2$) | Volume (Å$^3$) |
|----------------|--------|----------|----------|-----------|-----------|-----------|----------------|
| YFeO$_3$       | 6.98   | 8.97     | 1.26     | 5.283     | 5.588     | 7.605     | 224.54         |
| YFe$_{0.9}$Mn$_{0.1}$O$_3$ | 6.62   | 8.46     | 1.15     | 5.280     | 5.598     | 7.590     | 224.35         |
| YFe$_{0.8}$Mn$_{0.2}$O$_3$ | 7.30   | 9.58     | 1.34     | 5.279     | 5.608     | 7.577     | 224.32         |
| YFe$_{0.7}$Mn$_{0.3}$O$_3$ | 7.06   | 9.04     | 1.17     | 5.276     | 5.628     | 7.559     | 224.26         |
| YFe$_{0.6}$Mn$_{0.4}$O$_3$ | 7.86   | 10.00    | 1.36     | 5.272     | 5.641     | 7.535     | 224.10         |
| YFe$_{0.5}$Mn$_{0.5}$O$_3$ | 8.61   | 11.10    | 1.68     | 5.261     | 5.654     | 7.511     | 224.03         |

Figure 4. Variation of lattice parameters of YFe$_{1-x}$Mn$_x$O$_3$ obtained from the analysis of XRD.

Figure 5. Raman Spectra of YFe$_{1-x}$Mn$_x$O$_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) recorded at room temperature.
observed that, with increase in Mn doping the lattice parameter ‘b’ increases but ‘a’ and ‘c’ decreases. This can be explained as follows.

When large sized Mn$^{3+}$ (0.72 Å) is substituted in place of small Fe$^{3+}$ (0.69 Å), it results in change in crystal structure. The rotation around the orthorhombic b-axis results in tilted FeO$_6$ octahedra as shown in figure 3 (octahedral distortion in YFe$_{0.9}$Mn$_{0.1}$O$_3$ composition is shown here). With the increase in Mn content the magnitude of tilting of FeO$_6$ octahedral also increases [24, 25]. When more Mn is substituted the FeO$_6$ octahedra is more tilted around b-axis so that the lattice parameter along ‘b’ increases and along ‘a’ and ‘c’ decreases, which is shown in figure 4. This increase in ‘b’ with increase in Mn doping indicates the presence of Jahn-Teller distortion, which arises from an electronic instability inherent to Mn$^{3+}$ ions in an octahedral crystal field. The change in lattice parameters suggests that substitution of Mn induces a distortion in the crystal structure. Table 1 shows that there is decrease in cell volume with increase in doping concentration which is attributed to the difference in the radius of Mn$^{3+}$ and Fe$^{3+}$ ions. This change in unit cell parameters is expected to cause a change in Fe–O bond lengths and Fe–O–Fe bond angles [26] which will have significant effects on the electrical and magnetic properties of these materials.

3.2. Raman spectroscopy

Figure 5 shows the room temperature Raman spectra of YFe$_{1-x}$Mn$_x$O$_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) samples within the wave number range of 100–800 cm$^{-1}$. The Raman spectrum of pure YFeO$_3$ confirms that the sample possess orthorhombic structure with Pbnm space group which is in good agreement with literature [27]. The total irreducible representation of the crystal at the zone center can be written as

\[ \Gamma_{\text{Raman}} = 7A_{1g} + 8A_{1u} + 5B_{1g} + 8B_{1u} + 7B_{2g} + 10B_{2u} + 5B_{3g} + 10B_{3u} \]

Out of these 60 modes, 24 are Raman active modes, 25 are Infra red active modes, 3 are acoustics vibration modes and 8 are optically inactive modes.

The Raman data is de-convoluted into different modes using peak analyzer software considering Gaussian line shape. It is observed that there are 10 active vibration modes i.e. 7A$_g$ modes at 148, 152, 181, 276, 340, 362, 497 cm$^{-1}$, two B$_{2g}$ modes at 217 and 644 cm$^{-1}$, one B$_{1g}$ mode at 428 cm$^{-1}$. The perfect data fitting shows that...
there are no defects or impurities present in the samples and they are in single pure phase corroborating the XRD results as shown in figure 2. In spectra of polycrystalline samples, the strong wide feature of 644 cm\(^{-1}\) mode arises from two-phonon process. Mandal et al [28] deconvoluted this band at 644 cm\(^{-1}\) and found that at this energy there are two (second order) phonons with different symmetries. It is observed from figure 4 that the peak intensity of 644 cm\(^{-1}\) mode is also increasing with increase in Mn concentration. This mode corresponds to in phase stretching vibration mode of FeO\(_6\). As more Mn is substituted in place of Fe ions there is tilt in FeO\(_6\) which leads to crystal disorder. As Mn concentration increases, it is found that the intensity of the first two Raman peaks (Raman modes below 200 cm\(^{-1}\)) appear to decrease. But in fact, the width of the peaks is becoming broader and is merging with the back ground. Broadening of peaks indicate the distortion induced in the system due to Mn doping. On the whole, it is observed that the Raman modes above 300 cm\(^{-1}\) are more affected when Mn is doped at Fe site and lower wave-number modes below 200 cm\(^{-1}\) are less affected as compared to higher wave number modes, which is consistent with the fact that they are sensitive to doping at Y site [29].

### 3.3. 57Fe Mössbauer spectroscopy

Figure 6 shows 57Fe Mössbauer spectra of YFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples recorded at room temperature. For x = 0 to x = 0.3 concentrations a six line pattern (sextet) is observed confirming the magnetic ordering of Fe sub lattices [11]. The only one sharp magnetic sextet in the spectra indicates that there exists only one Fe site and rules out the existence of magnetic impurities. Zero-field Mossbauer spectral lines are constrained to fit in the ratio of 3:2:1:1:2:3 as determined by the radiation probabilities for a magnetically ordered system [30, 31]. However, when Fe is substituted with Mn, the lines become broader which indicates the presence of several sub spectra [31]. These sub spectra are attributed to various environments around octahedral Fe\(^{3+}\) ions due to random distribution of Mn\(^{3+}\) ions [31]. For x = 0.4, the spectrum possesses a broad sextet and for x = 0.5, it consists of a central paramagnetic doublet. Therefore, the data is fitted to a model, based on random distribution of Fe and Mn ions on the octahedral site. The paramagnetic doublet indicates the non magnetic behavior of the sample which is due to the decrease in Fe\(^{3+}\)-Fe\(^{3+}\) magnetic interactions. 57Fe Mossbauer parameters of YFe\(_{1-x}\)Mn\(_x\)O\(_3\) samples are given in table 2.

Table 2. 57Fe Mossbauer parameters of YFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples recorded at room temperature.

| Sample           | Isomer shift (IS) ± 0.02 (mm s\(^{-1}\)) | Quadrupole splitting (QS) ± 0.02 (mm s\(^{-1}\)) | Hyperfine field (\(B_0\)) ± 0.1 (Tesla) | Line width (\(\Gamma\)) ± 0.02 (mm s\(^{-1}\)) |
|------------------|---------------------------------------|-----------------------------------------------|------------------------------------------|---------------------------------------------|
| YFeO\(_3\)       | 0.37                                  | −0.01                                         | 49.8                                     | 0.47                                        |
| YFe\(_{0.5}\)Mn\(_{0.5}\)O\(_3\) | 0.37                                  | −0.02                                         | 48.5                                     | 0.61                                        |
| YFe\(_{0.4}\)Mn\(_{0.6}\)O\(_3\) | 0.37                                  | −0.04                                         | 46.5                                     | 0.77                                        |
| YFe\(_{0.3}\)Mn\(_{0.7}\)O\(_3\) | 0.37                                  | −0.06                                         | 43.3                                     | 0.97                                        |
| YFe\(_{0.2}\)Mn\(_{0.8}\)O\(_3\) | 0.32                                  | —                                             | (38.0)                                   | —                                           |
| YFe\(_{0.1}\)Mn\(_{0.9}\)O\(_3\) | 0.27                                  | —                                             | (28.00)                                  | —                                           |

Isomer shift value of 0.37 mm s\(^{-1}\) corresponds to high spin state of Fe\(^{3+}\) ion at Fe site [32]. It is observed that as Mn concentration increases the line width also increases showing that the larger Mn\(^{3+}\) ions are substituted in place of smaller Fe\(^{3+}\) ions. This substitution leads to distortion in the structure as discussed in the results of XRD. Figure 7 shows the variation of hyperfine field with Mn doping concentration in YFe\(_{1-x}\)Mn\(_x\)O\(_3\) (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5). With increase in Mn concentration, there is decrease in hyperfine field values.
indicating the weakening of magnetic interactions between the Fe\(^{3+}\) ions. This decrease in strength of interactions leads to increase in antiferromagnetic nature. The small change in quadrupole shift values suggests the possibility of coexistence of canted antiferromagnetic and antiferromagnetic phases \[33\]. The variation in Mossbauer parameters indicates that the structure of YFeO\(_3\) is affected by Mn doping.

### 3.4. Electrical properties

Figure 8 shows the room temperature leakage current densities \((J-E)\) plots of YFe\(_1-x\)Mn\(_x\)O\(_3\) \((x = 0, 0.1, 0.2, 0.3, 0.4\) and 0.5) samples, measured for different dopant (Mn) concentrations as a function of applied electric field.

![Figure 8. Leakage current density (J-E) plots of YFe\(_1-x\)Mn\(_x\)O\(_3\) (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5).](image)

Figure 9. SEM images of YFe\(_1-x\)Mn\(_x\)O\(_3\). Scale bar (200 nm) is same for all images.
Increasing doping levels, a gradual increase in leakage current density is observed, showing that the samples are becoming lossy. Three main factors affecting the leakage current in ceramics are: presence of multiple oxidation states of cation, presence of oxygen vacancies and microstructure [34]. From $^{57}$Fe Mossbauer parameters (Table 2), the isomer shift value 0.37 mm s$^{-1}$ corresponds to the ferric state at the Fe site ruling out the presence of multiple oxidation states.

Figure 9 shows the scanning electron micrographs (SEM) of the YFe$_{1-x}$Mn$_x$O$_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and $0.5$) samples. SEM images demonstrate the effects of Mn concentration in YFeO$_3$ on the grain size and porosity of the sample. The average grain size of these samples is around 200 nm to 300 nm. The grain boundaries for samples with $x = 0$ and 0.1 are sharp. Samples with compositions $x = 0.2, 0.3, 0.4$ and 0.5 possess diffused grain boundaries resulting in porous material. It can be seen from the images that the porosity increases as doping increases. The increase in porosity is attributed to the increase in leakage current. The grains with regular arrangement of ions offer less opposition to the flow of charge carriers and show conductive behavior with minute capacitance. For compositions, $x = 0.2$ to $x = 0.5$, the grains are found to be coalescing with each other resulting in the porous structure. The non-uniform grain structure leads to increase in the leakage current as contact between grains of very different sizes gives rise to charge exchange between the grains, which is known as hetero size charging [35]. This confirms the role of microstructure on the electrical properties of samples. The observed variation in grain structure is expected to modify the electrical conduction of the samples as discussed in the above section.

Conduction mechanism obeys the power law relationship, $J \propto E^{m}$, where the value of $m$ estimates the possible conduction mechanism involved in the transport properties. The value of $m$ is the slope of ln(J) versus ln(E) plot which is normally less than one for grain boundary limited conduction, equal or more than one for Ohmic conduction and equal or more than 2 for space charge limited conduction [36, 37]. Figure 10 shows ln(J) versus ln(E) plots for the samples. For $x = 0, 0.1, 0.2, 0.3$ and $0.4$ compositions, the slopes (m) are $1.25 \pm 0.00, 1.06 \pm 0.01, 1.15 \pm 0.01, 1.24 \pm 0.01$ and $1.12 \pm 0.02$, respectively. As the value of $m$ is more than one, it indicates that Ohmic conduction is dominant in entire electric field range. In the doped samples there is continuous increase in slope with increase in doping level which may be attributed to increase in the density of charge carriers.

**Figure 10.** ln J–ln E plots for YFe$_{1-x}$Mn$_x$O$_3$ and the obtained slope (m) values are also shown.
4. Conclusions

YFe$_{1-x}$MnxO$_3$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) samples are synthesized via sol-gel method. Structural analysis done by XRD reveals that the samples are crystalline and Rietveld refinement of XRD data confirm that the samples possess distorted orthorhombic structure. Raman spectroscopic studies confirm the structure and phase purity of the prepared samples. The isomer shift values indicate the high spin (Fe$^{3+}$) state of Fe ion. Doping of Mn at Fe site reduces the strength of magnetic interaction between Fe$^{3+}$-Fe$^{3+}$ leading to increase in antiferromagnetic nature of the samples. Leakage current density is found to increase with increase of Mn concentration indicating that higher doping of Mn is not suitable for high electrical field applications. Ohmic conduction mechanism is found to be dominant in Mn doped YFeO$_3$. The variations in parameters indicate that the structural, magnetic and electric properties of YFeO$_3$ are affected by Mn doping.

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References

[1] Spaldin N A 2017 Multiferroics: past, present and future MRS Bull. 42 385–90
[2] Didosyan Y S, Hauser H and Nicolic J 2000 Magnetooptical current sensors of high bandwidth Sensors and Actuators A: Physical 81 263–7
[3] Didosyan Y S, Hauser H, Raider G A and Toriser W 2004 Fast latching type optical switch J. Appl. Phys. 95 7339–41
[4] Giri S, Patra M and Majumdar S 2011 Exchange bias effect in alloys and compounds J. Phys.: Condensed Matter 23 073201
[5] Kimel A V, Kiriyuk A, Usachev P A, Pisarev R V, Balbashov A M and Rasing T 2003 Ultrafast non-thermal control of magnetization by instantaneous photomagnetic pulses Nature 435 655–7
[6] Ahmed M A, Selim M S and Arman M M 2011 Novel multiferroic La$_{0.95}$Sb$_{0.05}$FeO$_3$ orthoferrite Mater. Chem. Phys. 129 705–12
[7] Sivakumar M, Gedanken A, Battacharya D, Brukental J, Teshrayan Y, Zhong W, Du Y W, Feltner I and Nowik J 2004 Sonochemical synthesis of nanocrystalline rare earth orthoferrites using Fe(CO)$_5$ precursor Chem. Mater. 16 3623–12
[8] Yamaguchi T 1974 Theory of spin reorientation in rare-earth orthochromites and orthoferrites J. Phys. Chem. Solids 35 479–500
[9] Bhargava S C 1985 Mossbauer studies of spin reorientations in oxides Hyperfine Interact. 25 415–60
[10] Moriya T 1960 New mechanism of anisotropic super exchange interaction Phys. Rev. Lett. 4 228–30
[11] Eibschutz M, Shtrikman S and Treves D 1967 Mossbauer studies of Fe$^{57}$ in orthoferrites Phys. Rev. 156 562–77
[12] Dzyaloshinsky I 1958 A thermodynamic theory of weak ferromagnetism J. Phys. Chem. of Solids 4 241–55
[13] Durbin G W, Bonson C E and Thomas M F 1975 Direct observation of field-induced spin reorientation in YFeO$_3$ by the Mossbauer effect J. Phys. C: Solid State Phys. 8 3051–7
[14] Tokunaga Y, Furukawa N, Sakai H, Taguchi Y, Arima T H and Tokura Y 2009 Composite domain walls in a multiferroic perovskite ferrite Nat. Mater. 8 558–62
[15] Shang M, Zhang C, Zhang T, Yuan L, Ge L, Yuanhaa U and Feng S 2013 The multiferroic perovskite YFeO$_3$, Appl. Phys. Lett. 102 026203
[16] Shravan Kumar Reddy S, Raju N, Gopal Reddy Ch, Yadagiri Reddy P, Rama Reddy K, Gupta S M and Raghavendra Reddy V 2017 Study of Mn doped DyFeO$_3$ ceramics Ceram. Int. 43 6148–55
[17] Hemberger J, Lobina S, Krug von Nidda H A, Tristan N, Ivanov V Y, Mukhin A A, Balbashov A M and Loidi A 2004 Complex interplay of 3d and 4f magnetism in La$_{1−x}$GdxMnO$_3$ Phys. Rev. B 70 024414
[18] Zaghibou M, Grechene M, Aulet-Lambert C and Grevias M 2011 Effect of Fe substitution on multiferroic hexagonal YMnO$_3$. J. Magn. Magn. Mater. 323 509–14
[19] Cheng Z, Wang X L, Du Y and Dou S X 2010 A way to enhance the magnetic moment of multiferroic bismuth ferrite J. Phys.: D Appl. Phys. 43 242001
[20] Mathur S, Veith M, Rapaliviciute R, Shen H, Goya G F, Martins Filho W L and Berquo T S 2004 Sonochemical synthesis of nanocrystalline rare earth orthoferrites using Fe(CO)$_5$ precursor Chem. Mater. 16 3623–12
[21] Saha R, Sundaresan A and Rao C N R 2014 Novel features of multiferroic and magnetoelectric ferrites and chromites exhibiting magnetically driven ferroelectricity Mater. Horiz. 1 20–31
[22] Geller S and Wood E A 1936 Crystallographic studies of perovskite-like compounds: I. Rare earth orthoferrites and YFeO$_3$, YCrO$_3$, YAlO$_3$, Acta Crystallogr. 9 563–8
[23] Shen H, Xu J, Jin M and Jiang G 2012 Influence of oxygen vacancies on the temperature and magnetic properties of YFeO$_3$ nanocrystal Ceram. Int. 38 1473–7
[24] Alkathy M S, Zabotto F L, Lente M H and Eiras J A 2020 Octahedral distortion and oxygen vacancies induced band-gap narrowing and enhanced visible light absorption of Co/Fe co-doped Bi$_{2}$Sr$_2$Nd$_{0.25}$Ti$_{1.33}$O$_7$ ferroelectrics for photovoltaic applications J. Phys. D: Appl. Phys. 53 465106
[25] Alkathy M S, Zabotto F L, Lente M H and Eiras J A 2021 Bandgap narrowing of Ba$_{0.92}$Na$_{0.04}$Bi$_{0.04}$TiO$_3$ ferroelectric ceramics by transition metals doping for photovoltaic applications Mater. Chem. Phys. 257 123791

[26] Cao X Q, Kim C S and Yoo H I 2001 Effect of substitution of manganese for iron on the structure and electrical properties of yttrium ferrite J. Am. Ceram. Soc. 84 1265–72

[27] Coppens P and Eibschutz M 1965 Determination of the crystal structure of yttrium orthoferrite and refinement of Gadolinium orthoferrite Acta Crystallogr. 19 524–31

[28] Mandal P, Srinu Bhadram V, Sundarayya Y, Narayana C, Sundaresan A and Rao C N R 2011 Spin-reorientation, ferroelectricity, and magnetodielectric effect in YFe$_{1-x}$Mn$_x$O$_3$ (0.1 $\leq x \leq$ 0.40) Phys. Rev. Letters 107 137202

[29] Anjali P, Reddy V R, Gupta A and Sathe V G 2017 Study of spin-phonon coupling and magnetic field induced spin reorientation in polycrystalline multiferroic GdFeO$_3$ Mater. Chem. Phys. 196 205–12

[30] Raghavendra Reddy V, Kothari D, Gupta A and Gupta S M 2009 Study of weak ferromagnetism in polycrystalline multiferroic Eu doped bismuth ferrite Appl. Phys. Lett. 94 082505

[31] Sundarayya Y, Mandal P, Sundaresan A and Rao C N R 2011 Mössbauer spectroscopic study of spin reorientation in Mn-substituted yttrium orthoferrite J. Phys. Condens. Matter 23 436001

[32] Gutlich P, Bill E and Trautwein A X 2011 Mössbauer Spectroscopy and Transition Metal Chemistry: Fundamentals and Applications (Berlin: Springer)

[33] Gee S H, Hong Y K, Sur J C, Erickson D W, Park M H and Jefeers F 2004 Spin orientation of hematite ($\alpha$-Fe$_2$O$_3$) nanoparticles during the Morin transition IEEE Trans. Magn. 40 2691–3

[34] Neusel C, Jelitto H and Schneider G A 2015 Electrical conduction mechanism in bulk ceramic insulators at high voltages until dielectric breakdown J. Appl. Phys. 117 154902

[35] Lubomirsky I, Fleig J and Maier J 2002 Modeling of space charge effects in nanocrystalline ceramics: the influence of geometry J. Appl. Phys. 92 6819–27

[36] Shravan Kumar Reddy S, Raju N, Gopal Reddy Ch, Yadagiri Reddy P, Rama Reddy K and Raghavendra Reddy V 2015 Structural, electrical, magnetic and $^{57}$Fe Mössbauer study of polycrystalline multiferroic DyFeO$_3$ J. Magn. Magn. Mater. 396 214–8

[37] Makhdoom A R, Akhtar M J, Rafiq M A, Siddique M, Iqbal M and Hasan M M 2014 Enhancement in the multiferroic properties of BiFeO$_3$ by charge compensated aliovalent substitution of Ba and Nb AIP Adv. 4 037113