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The Effect of Europium Doping on the Structural and Magnetic Properties of $GdMnO_3$ Multiferroic Ceramics

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A B S T R A C T

Single phase Eu doped $GdMnO_3$ ceramics were prepared using solid state reaction route. Several different characterization techniques were used to investigate the structural and magnetic properties of the samples, including X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and Vibrating Sample Magnetometer (VSM). All samples indicated single phase which confirmed by XRD and SEM. Magnetic measurements of the doped samples at the low temperature (10 K) revealed the existence of the ferromagnetic order with the certain doping concentration which could be possibly due to slight structural distortion in the lattice.

1. INTRODUCTION

Multiferroic compounds are materials that show coexistence between the magnetic polarization and the ferroelectric ordering. They have drawn a tremendous interest due to the promising technological importance and the more fundamental research interests [1-3].Thus, an intensive work has been devoted to study them, lately. Based on the magnetoelectric effect in multiferroic materials, a large numbers of practical applications in the electronic and magnetic devices are expected, such as a memory block, transducer and magnetic sensor [4,5]. Among the rare single phase multiferroic materials, the archetype $BiFeO_3$ has been studied in details to understand the main principle and the mechanism toward the existence of the multiferroism [6-8].

The magnetoelectric effect has been also observed in rare-earth manganite, such as hexagonal $REMnO_3$ [9]. orthorhombic $REMnO_3$ [10,11], $REMn_2O_5$ (RE=Ho to Lu and Y) [12,13] and other compounds in the recent years.

Depending on the radius of the rare-earth ion (RE^{3+}) the rare-earth manganites, $REMnO_3$ can either exist in the hexagonal or orthorhombic crystal structure. The small ionic radius rare-earth ions (Ho-Lu, Y and Sc) show a hexagonal crystal structure. On the other hand, large ionic radius rare-earth ions (La, Gd and Dy) crystallize in an orthorhombic (distorted perovskite) structure.

Great enhancement of electric and magnetic behaviors of $REMnO_3$ can be achieved through doping process. Generally, two doping mechanisms are considered: A-site doping which is a partial substitution in the rare-earth site, or B-site doping which is a partial substitution in manganese site. Andreev, N. V., et al. demonstrated that, Yttrium substitution at Gadolinium site of $GdMnO_3$ modified the crystal structure and led to substantial changes in the magnetic and electric properties [14]. Moreover, an improvement in multiferroic properties with increasing doping concentration had been revealed in three different studies regarding substitution of Fe by Mn in $YMnO_3$ and $ErMnO_3$ respectively [15,16].

These multiferroic ceramic materials have new functionalities and attractive potential applications for applying in microelectronic, information technology and data storage devices. As far as is concerned, no previous work has been done concerning the effect of Eu doping in $GdMnO_3$. Eu doped $GdMnO_3$ could be the potential candidate for multiferroic application exhibiting better ferromagnetic property.This work aims at substituting Eu into Gd site in the $GdMnO_3$ to produce single phase ceramics.

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2. EXPERIMENTAL

2.1. Synthesis of $Gd_{1-x}Eu_x MnO_3$

The bulk ceramic powders of single phase $Gd_{1-x}Eu_xMnO_3$ (x= 0.2 and 0.8) were synthesized through the conventional solid state reaction route. A high purity powders of Gd_2O_3 (99.9%; Alfa Aesar), Mn_2O_3 (98%; Alfa Aesar) and Eu_2O_3 (99.9%; Alfa Aesar) were used as the starting materials. Appropriate proportion of these compounds were carefully weighted using $Gd_{1-x}Eu_xMnO_3$ composition, where x= 0.2 and 0.8, and then well milled and mixed in ethyl alcohol in a plastic container using zirconium balls. After drying the slurry in a drying oven at 95 ^oC for 24 h, the mixture was calcined at 600 ^oC for 10 h. The calcined powder was ground into a fine powder and heat-treated at different temperatures between 1000-1350 ^oC for 10 h, with a heating and cooling rate of 300 ^oC/h to observe the phases growth. Powders were also used to make pellets in order to produce dense ceramics. Cylindrical pellets with the diameter of approximately 10 mm and the thickness of 2 mm were prepared under a pressure of 10 MPa. Sintering was performed at 1350 ^oC for 20 h with a heating and cooling rate of 120 ^oC/h. Calcination and sintering studies were made using a high temperature programmable furnace.

2.2. Characterization

The sintered samples were characterized by a Bruker D2 PHASER X-ray diffractometer (XRD) operated in the Bragg-Brentano geometry and the samples were scanned between 2θ of 10-70° with a scanning rate of 1°/min and a step size of 0.01016° using CuKα radiation (λ= 1.54184 Å). For computer based examination, FullProf/Rietveld software was used. Surface morphology investigation of produced samples was carried out using scanning electron microscopy (SEM, JEOL5910 LV) and surface analyses of samples were carried out by energy dispersive X-ray spectrometer (EDX). Fractured surfaces of the samples were coated with gold by SC7680 Super Coater before SEM analysis. Gold coated fracture surfaces of produced samples were investigated with different magnification values using secondary and back-scattered electrons. In addition, the magnetic properties of the Eu doped $GdMnO_3$ samples ($Gd_{1-x}Eu_xMnO_3$) at low temperature (10 K) were also investigated using the vibrating sample magnetometer (VSM) and magnetization of the sample as a function of magnetic field (M–H) was obtained.

3. RESULTS AND DISCUSSION

3.1. Structures

Fig. 1 shows the XRD pattern of an undoped and A-site doped $Gd_{1-x}Eu_xMnO_3$ (x= 0, 0.2, 0.8) ceramics heat treated at 1350 ^oC for 24 h. Rietveld refinements on all the samples confirmed the samples purity, and all diffractogrmas were successfully analysed using a single phase perovskite structure. (Figs. 1, 2 and 3). This indicates that Eu doping even at the high amount (x= 0.8) doesn't result in a second phase formation and completely dissolves in the lattice giving a substitutional solid solution. Most importantly, a close examination of the patterns reveals slight shifts about 0.25758 of peak positions toward lower angles by increasing doping concentration. This feature agrees with Vegard's law [17], as the substitution of small radius Gd^{q+} ion (r_{Gd} = 2.54 Å) by larger Eu^{q+}(r_{Eu} = 2.65 Å) leads to an increase in the cell parameters that may cause a slight distortion in the lattice, and a modification of the crystal structure. This latter might be a significant parameter governing the magnetic properties of the material.

The experimental lattice parameters and volume of the unit cell (Table 1) were estimated using FullProf, when the concentration of Eu increased the lattice parameter also increased due to the larger ionic radius of Eu (2.56 Å) compared to Gd (2.54 Å). In addition, when Eu content was low (x= 0.2), the XRD pattern was matched with the XRD pattern of $GdMnO_3$ and the XRD pattern of sample with the higher concentration of Eu (x= 0.8) matched with $EuMnO_3$. This indicates that the compounds are converted to $EuMnO_3$ rather than $GdMnO_3$ by increasing the content of Eu.

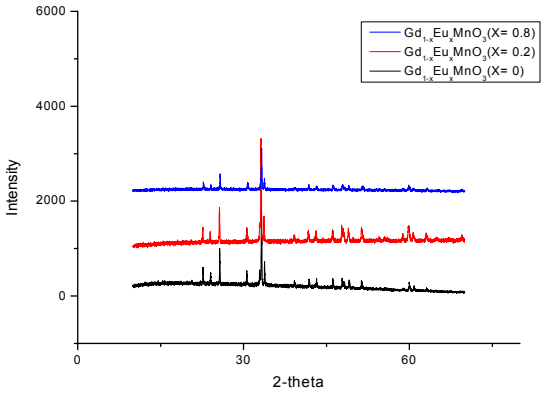


Figure 1. Room temperature XRD patterns of $Gd_{1-x}Eu_xMnO_3$ ceramics compounds (x= 0, 0.2 and 0.8) heat treated at 1350 ^oC for 24 h

TABLE 1. Calculated lattice parameters of Eu doped $GdMnO_3$ samples ($Gd_{1-x}Eu_xMnO_3$ ceramics where x= 0.2 and 0.8 heat treated at 1350 ^oC for 24 h) by using FullProf

Composition	a (Å)	b (Å)	c (Å)	Volume ($Å^3$)	Space group
$GdMnO_3$	5.826	7.445	5.312	230.4057	Pnma
$Gd_{0.8}Eu_{0.2}MnO_3$	5.8576	7.44808	5.33035	232.69468	Pnma
$Gd_{0.2}Eu_{0.8}MnO_3$	5.85019	7.45798	5.3393	232.9576	Pnma

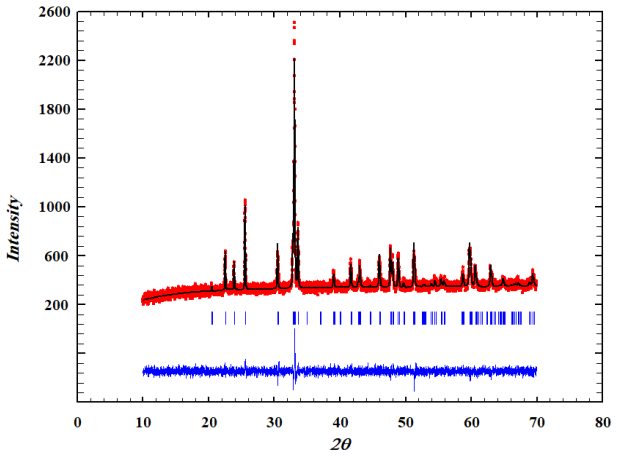


Figure 2. XRD pattern of $Gd_{1-x}Eu_xMnO_3$ ceramic sample at (x= 0.2) heat treated at 1350 °C for 24 h (Rietveld fit agreement factors are: Rp= 56.8, Rwp = 31.7 and Gof= 1.098.)

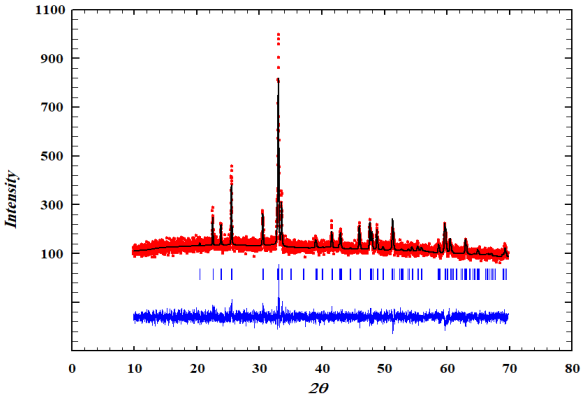


Figure 3. XRD pattern of $Gd_{1-x}Eu_xMnO_3$ ceramics sample at (x= 0.8) heat treated at 1350°C for 24h. Rietveld fit agreement factors are Rp= 88.4, Rwp = 48.2 Gof= 1.0919.

3.2. SEM and EDS investigation of $Gd_{1-x}Eu_xMnO_3$

Fig. 4 shows secondary and back-scattered electron micrographs of the $Gd_{0.8}Eu_{0.2}MnO_3$ and $Gd_{0.2}Eu_{0.8}MnO_3$ ($Gd_{1-x}Eu_xMnO_3$ compound where x= 0.2 and 0.8). In addition, Fig. 5 shows larger magnifications of the same materials. SEM micrographs confirm that there is not any second phase as observed in the XRD. Back-scattered electrons show none phase contrast indicating no other second phases. The typical grain size of x= 0.2 and 0.8 samples are in the range of 4-7 μm and 5-12 μm, respectively that shows a clear effect of Eu doping. EDS analyses of grains show that compositions are close to the theoretical values (Fig. 6). The slightly high content of Eu and low content of Gd are possibly explained by the coincidence of Eu-Mn and Eu-Gd peaks. No additional peaks revealing impurities are detected in the EDS. Au and Pd are caused by the coating of the samples for analysis.

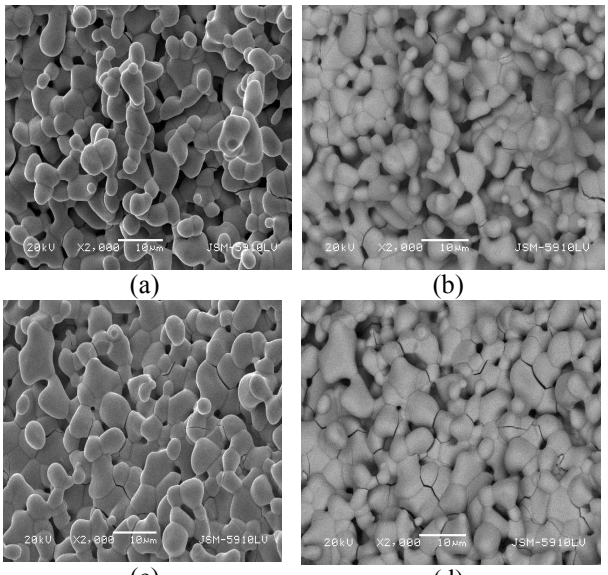


Figure 4. SEM micrographs of Eu doped $GdMnO_3$ sample ($Gd_{1-x}Eu_xMnO_3$ ceramic where x= 0.2 and 0.8 heat treated at 1350 °C for 24 h) at X2.000 a) Secondary Electron Imaging (SEI) of $Gd_{0.8}Eu_{0.2}MnO_3$, b) Back-scattered Electron Imaging (BEI) of $Gd_{0.8}Eu_{0.2}MnO_3$, c) SEI of $Gd_{0.2}Eu_{0.8}MnO_3$ and d) BEI of $Gd_{0.2}Eu_{0.8}MnO_3$

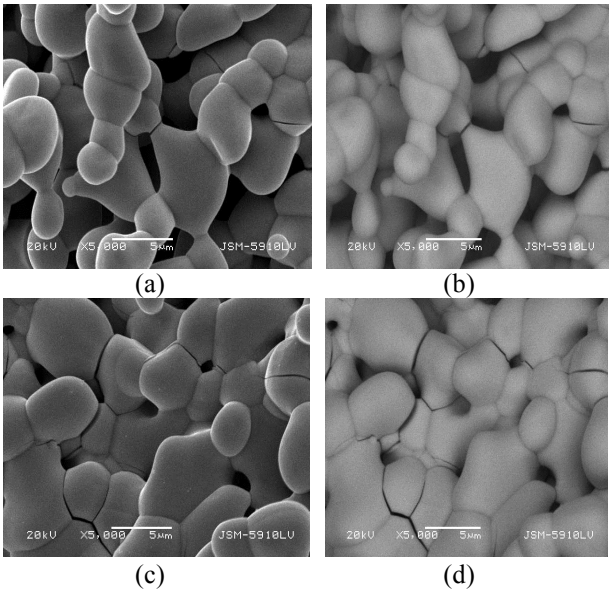
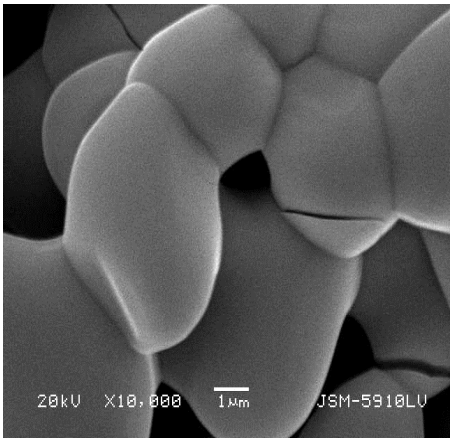


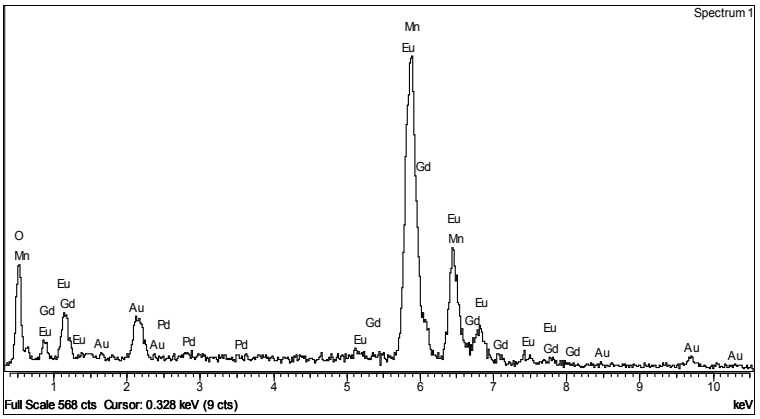
Figure 5. SEM micrographs of Eu doped $GdMnO_3$ sample ($Gd_{1-x}Eu_xMnO_3$ ceramic where x= 0.2 and 0.8 heat treated at 1350 °C for 24 h) at X5.000 a) SEI of $Gd_{0.8}Eu_{0.2}MnO_3$, b) BEI of $Gd_{0.8}Eu_{0.2}MnO_3$, c) SEI of $Gd_{0.2}Eu_{0.8}MnO_3$ and d) BEI of $Gd_{0.2}Eu_{0.8}MnO_3$

3.3. Magnetic properties

Magnetic measurements of doped samples were performed at low temperature (10 K) in order to explore the effect of dopants on the magnetic properties. Magnetization of $Gd_{1-x}Eu_xMnO_3$ ceramics (x= 0.2 and

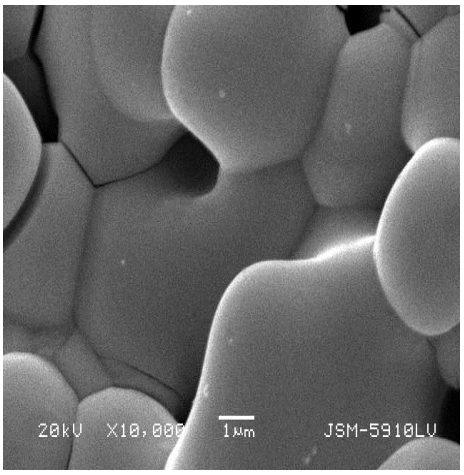
0.8) at low temperature (10 K) as a function of magnetic field (M–H) is given in Fig. 7. A remarkable ferromagnetic behavior is obtained for the x= 0.2 sample which have a saturation magnetization (M_s) of about 35 emu/g. The crystal volume changed from 232.694687 to 232.957673 ($Å^3$) by increasing the concentration of the dopant element from x= 0.2 to x= 0.8and as a result, the magnetic behavior is dramatically changed from ferromagnetic to paramagnetic by a decrease in M_s to almost 14 emu/g.

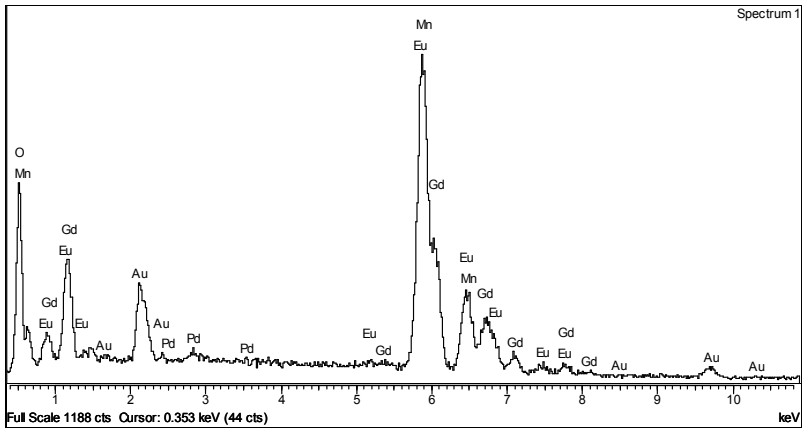




Elements	O	Mn	Eu	Gd	Total
Weight percentage	18.76	22.32	27.72	31.20	100.00
Calculated weight percentage	18.52	21.20	11.73	48.55	100.00

(a)





Elements	O	Mn	Eu	Gd	Total
Weight percentage	13.54	23.35	49.92	13.19	100.00
Calculated weight percentage	18.75	21.46	47.49	12.30	100.00

(b)

Figure 6. EDS analyses of Eu doped $GdMnO_3$ samples heat treated at 1350 ^oC for 24 h a) EDS of $Gd_{0.8}Eu_{0.2}MnO_3$ and b) EDS of $Gd_{0.2}Eu_{0.8}MnO_3$ sample (Tables show the weight fractions of the elements found by calculation and EDS results)

The best ferromagnetic behavior of the sample with **x**= 0.2 might be ascribed to the substitution-induced suppression of the spiral spin modulation due to the suitable substitution of Eu. On the other hand, when **x** is larger than 0.2, the structural distortion may destroy the spin arrangement which deteriorates the ferromagnetic behavior and leads to a clear reduction in M_s [18].

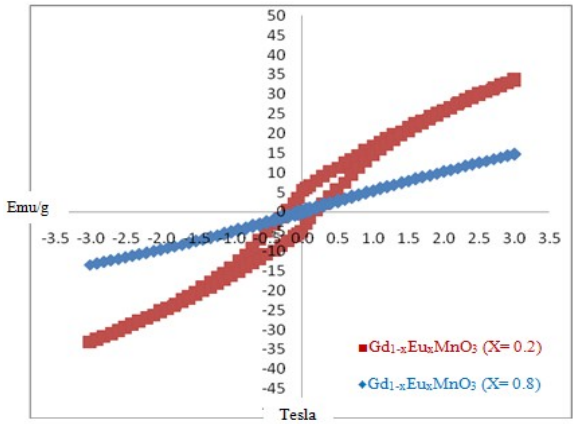


Figure 7. Magnetic hysteresis loops of $Gd_{1-x}Eu_xMnO_3$ ceramics compound (x= 0.2 and 0.8) heat treated at 1350 ^oC for 24 h

4. CONCLUSION

In conclusion, there are several features in the perovskite-based doping systems in this work. Firstly, the A-sites doping for some extend can influence the crystal structures, basically, through the atomic size of the dopant elements. Secondly, the produced doped systems show substantial change of the magnetic properties possibly due to the change of the structure. Moreover, the compounds show the slight change that indicates the small effect of the doping process in the structure. Therefore, the structural and magnetic characteristic is only partially enhanced through A-site doping. So, further kind of various doping and codoping may be necessary to improve the multiferroic properties in the orthorhombic $Gd_{1-x}Eu_xMnO_3$.

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REFERENCES

1. Cheong, S.W., Mostovoy, M., "Multiferroics: a magnetic twist for ferroelectricity", ***Journal of Nature materials,*** Vol. 6, (2007), 13-20.
2. Wang, K.F., Liu, J.M., Ren, Z.F., "Multiferroicity: the coupling between magnetic and polarization orders", ***Journal of Advances in Physics,*** Vol. 58, (2009), 321-448.
3. Goto, T., Kimura, T., Lawes, G., Ramirez, A.P., Tokura, Y., "Ferroelectricity and giant magnetocapacitance in perovskite rare-earth manganites", ***Journal of Physical Review Letters,*** Vol. 92, No. 25, (2004), 257201.
4. Guo, Z., Yang, L., Qiu, H., Zhan, X., Yin, J., Cao, L., "Structural, magnetic and dielectric properties of Fe-doped $BaTiO_3$ solids", ***Journal of Modern Physics Letters B,*** Vol. 26, No. 9, (2012), 1250056-1250069.
5. Fujimura, N., Ishida, T., Yoshimura, T., Ito, T., "Epitaxially grown $YMnO_3$ film: New candidate for nonvolatile memory devices", ***Journal of Applied physics letters,*** Vol. 69, No. 7, (1996), 1011-1013.
6. RayanáSerrao, C., "New routes to multiferroics", ***Journal of Materials Chemistry,*** Vol. 17, No. 47, (2007), 4931-4938.
7. Mukherjee, A., Basu, S., Manna, P.K., Yusuf, S.M., Pal, M., "Enhancement of multiferroic properties of nanocrystalline $BiFeO_3$ powder by Gd-doping", ***Journal of Alloys and Compounds,*** Vol. 598, (2014), 142-150.
8. Sangian, H., Mirzaee, O., Tajally, M., "Reverse chemical co-precipitation: an effective method for synthesis of BiFeO3 nanoparticles", ***Journal of Advanced Ceramics Progress,*** Vol. 3, No. 1, (2017), 31-36.
9. Huang, Z.J., Cao, Y., Sun, Y.Y., Xue, Y.Y., Chu, C.W., "Coupling between the ferroelectric and antiferromagnetic orders in $YMnO_3$", ***Journal of Physical Review B,*** Vol. 56, No. 5, (1997), 2623-2626.
10. Kimura, T., Goto, T., Shintani, H., Ishizaka, K., Arima, T.H., Tokura, Y., "Magnetic control of ferroelectric polarization", ***Journal of Nature,*** Vol. 426, No. 6962, (2003), 55-58.
11. Lorenz, B., Wang, Y.Q., Sun, Y.Y., Chu, C.W., "Large magnetodielectric effects in orthorhombic HoMnO3 and $YMnO_3$", ***Journal of Physical Review B,*** Vol. 70, No. 21, (2004), 212412-212416.
12. Higashiyama, D., Miyasaka, S., Kida, N., Arima, T., Tokura, Y., "Control of the ferroelectric properties of DyMn2O5 by magnetic fields", ***Journal of Physical Review B,*** Vol. 70, No. 17, (2004), 174405.
13. Kobayashi, S., Osawa, T., Kimura, H., Noda, Y., Kagomiya, I., Kohn, K., "Reinvestigation of simultaneous magnetic and ferroelectric phase transitions in YMn_2O_5", ***Journal of the Physical Society of Japan,*** Vol. 73, No. 6, (2004), 1593-1596.
14. Andreev, N.V., Sviridova, T.A., Tabachkova, N.Y., Chichkov, V.I., Mukovskii, Y.M., "The growth, structure, and magnetic properties of thin epitaxial films of $GdMnO_3$ multiferroics", ***Journal of Russian Microelectronics,*** Vol. 41, No. 8, (2012), 511-515.
15. Van Aken, B.B., Palstra, T.T., Filippetti, A., Spaldin, N.A., "The origin of ferroelectricity in magnetoelectric $YMnO_3$", ***Journal of Nature materials,*** Vol. 3, No. 3, (2004), 164-170
16. Liu, P., Cheng, Z.X., Wang, X.L., Du, Y., Yu, Z.W., Dou, S.X., Kimura, H., "Iron doped hexagonal $ErMnO_3$: Structural, magnetic, and dielectric properties", ***Journal of Nanoscience and Nanotechnology,*** Vol. 12, No. 2, (2012), 1238-1241.
17. Vegard, L., "Die konstitution der mischkristalle und die raumfüllung der atome", ***Journal of Zeitschrift für Physik,*** Vol. 5, No. 1, (1921), 17-26.
18. Uniyal, P., Yadav, K.L. "Room temperature multiferroic properties of Eu doped $BiFeO_3$", ***Journal of Applied Physics,*** Vol. 105, No. 7, (2009), 07D914-07D917.