Synthesis and characterization of iron-doped GdMnO$_3$ multiferroic ceramics

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Abstract

In this research work, monocristalline Fe-doped GdMnO$_3$ ceramics specimens were prepared through solid-state reaction technique, several characterization methods, for instance, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDX) and Vibrating Sample Magnetometer (VSM) were used to investigate the topographical, structural and magnetic behaviours of the produced samples. All the samples show a single phase which confirmed by XRD and SEM. Magnetic properties of all the prepared samples at the low temperature (10 K) showed antiferromagnetic behaviour with a small difference in magnetization. The slight change in magnetic characteristics could probably occur because of small lattice structural distortion. Fe-doped GdMnO$_3$ could be a material of choice for multiferroic application showing a superior antiferromagnetic property.

Keywords: multiferroic materials, doping, GdMnO$_3$ ceramics, solid-state reaction, magnetic properties
Kulcsszavak: multiferoikus anyagok, adalékolás, GdMnO$_3$ kerámia, szilárdfázisú reakció, mágneses tulajdonságok

1. Introduction

The research topics in ceramic materials generally [1-8] and advanced ceramic particularly [9-12] are becoming more popular. After Landau and Lifshitz revealed theoretically in the early 1960s, the thermodynamic potential energy contains coupled magnetic and electric components that can influence each other [13], a flurry of research about multiferroics has been triggered up to now [14-18]. Although these materials are interesting and worth studying, the first dilemma is that multiferroics are very rare [19-20]. Secondly, their coupling of multiferroic properties is often too small for the application or appears only at low temperatures [21]. To overcome these difficulties, large efforts have been made to find new single-phase multiferroics as well as to enhance multiferroic couplings with heterogeneous structures of a ferromagnetic and a ferroelectric components [22-23].

The rare-earth manganites perovskite materials have drawn huge attention recently due to the coupling of (anti) ferromagnetic and ferroelectric orders in the same phase [24-27]. This behaviour enables this material to be used in future information-technology devices in which data can be transfer through the applied electric fields to the magnetic memory elements [28-29]. REMnO$_3$ can be found either in hexagonal or orthorhombic perovskite structure; generally, the orthorhombic REMnO$_3$ shows multiferroic behaviour since its magnetic phase can be controlled by an applied electric field at low temperature [30-31].

In this study, we partially substitute Fe cations in GdMnO$_3$ (GMO) compound. Single-phase GdMn$_{1-x}$Fe$_x$O$_3$ compounds were prepared by solid-state reaction route. Since GMO compounds are multiferroic compounds, Fe-doped GMO materials could be fascinating ceramic materials because of the existence of ferromagnetism characteristic of Mn moments and distortion of the lattice, which can improve the dipole ordering.

2. Experimental methods

2.1 Synthesis of GdMn$_{1-x}$Fe$_x$O$_3$

A single-phase GdMn$_{1-x}$Fe$_x$O$_3$ (x = 0.2 and 0.8) ceramic in a powder form were prepared through conventional solid-state synthesis route (Fig. 1). GdO$_3$ (99.9%; Alfa Aesar), Mn$_2$O$_3$ (98%; Alfa Aesar) and Fe$_2$O$_3$ (99.9%; Alfa Aesar) were used as reactants. An appropriate amount of these powders were milled and mixed in ethanol in a plastic container using zirconium balls for 6 hours. Two different compositions were prepared; GdMn$_{1-x}$Fe$_x$O$_3$ where x= 0.2 and 0.8. The slurry was...
then dried by evaporating the ethanol at 100 °C for 24 h. The resultant powders were initially calcined at 600 °C for 10 h followed by cooling to room temperature. After grinding, the produced powders were heat-treated at different temperatures between 1000-1350 °C for 10 h with a heating and cooling rate of 300 °C/h to observe the phases development. Powders were also used to make pellets, which were used to produce dense ceramics. Pellets with 10 mm in diameter and 2 mm thickness were prepared by a compaction machine using a pressure of 10 MPa. Sintering was performed at 1350 °C for 20 h with a heating and cooling rate of 120 °C/h. Calcination and sintering studies were made using a high-temperature programmable furnace [32]. The fired specimens were characterized by different techniques like XRD and SEM. Besides, the magnetic characteristic of the Fe-doped GdMnO₃ samples (GdMn₁₋ₓFeₓO₃) were also investigated.

3. Results and discussion

3.1 Structures

Fig. 2 shows the XRD patterns of undoped and B-site doped GdMn₁₋ₓFeₓO₃ (x = 0.2, 0.8) ceramics carried out at ambient temperature. All the samples show single-phase perovskite structure without any traces of impurities since there is a complete matching and no additional peaks were observed (Fig. 3 and 4). This indicates that Fe 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. The most significant notice to be mentioned here is that a close investigation of the peaks reveals a shift in the peak positions to the right side with increased doping concentration. This effect can be obtained due to the decrees in the lattice parameters. Thus the substitution of Mn by Fe causes a decrease in the volume of the unit cell since the atomic size of Fe with a radius (1.17 Å) is smaller than that of Mn with a radius (1.79 Å). The decrease in the unit cell volume with increasing the doping concentration leads to a unit cell distortion that may change the crystal structure. This change might be a significant factor for the materials’ magnetic properties. DIFFRACT measurement program was used to calculate the unit cell’s lattice parameters and volume (Table 1). Undoped GdMnO₃ sample has an approximate lattice parameter with the theoretical value obtained from the PDF file (PDF No: 74-1477). However, when Fe’s concentration increased, the lattice parameter decreased due to the smallerionic radius of Fe (1.17 Å) than Mn (1.79 Å).

| Composition | a (Å) | b (Å) | c (Å) | Volume (Å³) | Space group |
|------------|------|------|------|------------|-------------|
| GdMnO₃     | 5.31 | 5.84 | 7.43 | 230.41     | Pnma        |
| GdMnₐ₋ₓFeₓO₃ (x=0.2) | 5.316 | 5.679 | 7.611 | 229.77 | Pnma |
| GdMnₐ₋ₓFeₓO₃ (x=0.8) | 5.3 | 5.6 | 7.62 | 226.16 | Pnma |

Table 1 Lattice parameters resulted from refinement procedure of powder XRD patterns of GdMn₁₋ₓFeₓO₃ ceramics compounds (x = 0.2 and 0.8) heat treated at 1350 °C for 24 h.

Fig. 3 Flow diagram for the preparation of GdMn₁₋ₓFeₓO₃ ceramics

Fig. 4 Room temperature XRD patterns of GdMn₁₋ₓFeₓO₃ ceramics compounds (x = 0, 0.2 and 0.8) heat treated at 1350 °C for 24 h.
3.2 Scanning electron microscopy (SEM) and EDS investigation of GdMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3}

Fig. 5 shows secondary and backscattered electron micrographs of the GdMn\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3} and GdMn\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3}. In addition, Fig. 6 shows larger magnifications of the same materials. SEM micrographs reveal that there is no second phase or impurity in the microstructure, as observed in the XRD. Backscattered electrons do not show any phase-contrast indicating no other second phases. The grain sizes in x = 0.2 and x = 0.8 samples were in the range of 0.7-5 μm and 0.8-4.6 μm respectively, showing that the grains sizes do not change significantly with Fe-doping.

EDS analysis taken from grains shows that they were near to the theoretical values (Fig. 7). While Fig. 7-a gives the EDS analysis of Gd\textsubscript{0.2}Eu\textsubscript{0.8}MnO\textsubscript{3}, Fig. 7-b gives the EDS of Gd\textsubscript{0.2}Eu\textsubscript{0.8}MnO\textsubscript{3}. The weight percentages obtained from EDS results were near to the calculated values. No other peaks or impurities were detected in the EDS. Au and Pd were due to coating made on the samples.

- Fig. 3 XRD pattern for GdMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} ceramics sample at (x = 0.2)
- Fig. 4 XRD pattern for GdMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} ceramics sample at (x = 0.8)
- Fig. 5 SEM micrographs of Fe-doped GdMnO\textsubscript{3} samples at ×2.000 a) SEI of GdMn\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3}, b) BEI of GdMn\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3}, c) SEI of GdMn\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} and d) BEI of GdMn\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} (GdMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} ceramics where x = 0.2 and x = 0.8)
- Fig. 6 SEM micrographs of Fe-doped GdMnO\textsubscript{3} samples at ×5.000 a) SEI of GdMn\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3}, b) BEI of GdMn\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3}, c) SEI of GdMn\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} and d) BEI of GdMn\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3} (GdMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} ceramics where x = 0.2 and x = 0.8)

| Elements | O | Mn | Fe | Gd | Total |
|----------|---|----|----|----|-------|
| Wt (%)   | 26.19 | 1.52 | 8.20 | 64.08 | 100.00 |
| Calculated (W %) | 18.43 | 16.88 | 4.289 | 60.395 | 100.00 |

| Elements | O | Mn | Fe | Gd | Total |
|----------|---|----|----|----|-------|
| Wt (%)   | 14.14 | 8.90 | 11.31 | 65.65 | 100.00 |
| Calculated Wt (%) | 18.39 | 4.21 | 17.12 | 60.27 | 100.00 |
3.3 Magnetic properties

Fig. 8 shows magnetic field-dependent magnetization at low temperature (10K) for GdMn$_{1-x}$Fe$_x$O$_3$ (x=0.2, 0.8) ceramics. Both samples show antiferromagnetic behaviour at 10K with Fe—Fe, which leads to improvement in exchange interaction between Fe—Fe caused by the doping of Fe element. With increasing Fe concentration, the interatomic distance of Fe—O decreases, which leads to improvement in exchange interaction between Fe—RE, therefore enhance the magnetization [33].

Fig. 8 The magnetic hysteresis loops of GdMn$_{1-x}$Fe$_x$O$_3$ ceramics compound (0.2 and 0.8) sintered at 1350 °C.

4. Conclusion

GdMn$_{1-x}$Fe$_x$O$_3$ (x= 0, 0.2, 0.8) samples show single-phase orthorhombic crystal structure with space group Pnma as confirmed by XRD investigation. Increasing the doping concentration leads to decreased lattice parameters (basically, b and c while a remains almost constant). Due to the Fe dopant element’s small atomic radius, a decrease of the overall lattice volume has been observed. SEM examination reveals the synthesis of pure phase with no other impurities since the backscattered electrons micrograph does not show any phase contrast. EDS results of the produced samples show a close value between the experimental weight percentages and the calculated one, also no other peaks were detected in the EDS results, which is a strong indication for the formation of single-phase. The magnetic hysteresis loops of GdMn$_{1-x}$Fe$_x$O$_3$ (x= 0, 0.2, 0.8) carried out at low-temperature (10K) exhibit the antiferromagnetic characteristic in both samples, with only slight differences in the Ms.

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References

[1] L. A. Gömze – L. N. Gömze (2009): Építőanyag–JSBCM 70 (1) 8. https://doi.org/10.14382/epitoanyag-jsbcm.2009.7
[2] L. A. Gömze – L. N. Gömze – S. N. Kulkov – L. I. Shabalin – L. Gotman – E. Pedraza – G. L. Lecomte – T. Mayorova – E. Kurovics – A. Hamza (2015): Építőanyag–JSBCM 70 (1) 38 http://dx.doi.org/10.14382/epitoanyag-jsbcm.2015.24
[3] Gömze, L. A., et al. 2018 Építőanyag–JSBCM 70 (1) 8. https://doi.org/10.14382/epitoanyag-jsbcm.2018.2
[4] Kurovics, E. – S. N. Kulkov – L. A. Gömze: Építőanyag–JSBCM 70 (1) 3 https://doi.org/10.14382/epitoanyag-jsbcm.2018.1
[5] S. Kulkov et al 2014 Építőanyag–JSBCM 66 (1) 1. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.1
[6] N. L. Savchenko, et al. Építőanyag–JSBCM 66 (2) 44. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.9
[7] O. B. Kotova, et al 2019 Építőanyag–JSBCM 71 (4) 125. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2019.22
[8] A. Apkaryan – S. N. Kulkov – L. A. Gömze 2014 Építőanyag–JSBCM 66 (2) 38. http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.8
[9] M. Títhil et al 2019 Építőanyag–JSBCM 71 (6) 190. https://doi.org/10.14382/epitoanyag-jsbcm.2019.35
[10] A. Y. Buzimov et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 175 012033 https://doi.org/10.1088/1757-899X/175/1/012033
[11] A. Y. Buzimov et al 2017 J. Phys.: Conf. Ser. 790 012004 https://doi.org/10.1088/1742-6596/790/1/012004
[12] P. David, Jr Penalozia 2019 Építőanyag–JSBCM 71 (3) 74. https://doi.org/10.14382/epitoanyag-jsbcm.2019.13
[13] L. D. Landau – E. M. Lifshitz: Statistical Physics.” Course of Theoretical Physics 5 (1980): 396–400.
[14] Eerenstein et al, 2006 nature 442(7104) 759. https://doi.org/10.1038/nature05023
[15] V. Popov, M. Melvin, 2015 “Fundamentals of multiferroic materials and their possible applications.” Critical Reviews in Solid State and Materials Sciences 40 (4) 223.
[16] L. W. Martin – R. Ramesh 2012 Acta Materialia 60 (6-7) 2470. https://doi.org/10.1016/j.actamat.2011.12.024
[17] T. Zhao et al 2006 Nature materials 5(10) 829. https://doi.org/10.1038/nmat1731
[18] Kim et al 2005 Materials Letters 59 (29-30) 4006. https://doi.org/10.1016/j.matlet.2005.07.050
[19] Lone et al. 2019 Nanoscale research letters 14 (1) 1 https://doi.org/10.1186/s11671-019-2961-7
[20] Nan et al 2019 National Science Review 6 (4) 620. https://doi.org/10.1093/nsr/nzw093
[21] J. F. Scott 2013 NPG Asia Materials 5(11) 72. https://doi.org/10.1038/am.2013.58
[22] W Prellier et al 2005 Journal of Physics: Condensed Matter 17(30) R803. https://doi.org/10.1088/0953-8984/17/30/R01
[23] L. W. Martin – D. G. Schlom 2012 Current Opinion in Solid State and Materials Science. 16(5).199. https://doi.org/10.1016/j.cossms.2012.03.001
[24] M. Mochizuki – N. Furukawa 2009 Physical Review B. 80(13):134416 https://doi.org/10.1103/PhysRevB.80.134416
[25] C. Dubourdieu et al 2007 Philosophical magazine letters 87(3-4) 203. https://doi.org/10.1080/09500830601137173
[26] G. Lalića – P. V. Reddy 2008: Journal of magnetism and magnetic materials. 320 (5) 754 https://doi.org/10.1016/j.jmmm.2007.08.014
[27] P. P. Rout et al 2012: Physica B: Condensed Matter 407(12) 2072. https://doi.org/10.1016/j.physb.2012.02.007
[28] M. Barbičesnay – A. Bibes 2008: Nat. Mater. (7) 425 https://doi.org/10.1038/nmat2189.
[29] Z. Surowiak et al Archives of acoustics. 33 (2) 243
[30] Y. W. Windsor et al 2014: Physical review letters. 113 (16) 167202. https://doi.org/10.1103/PhysRevLett.113.167202
[31] K. H. Wu et al 2010: Thin Solid Films 518 (8) 2275. https://doi.org/10.1016/j.tsf.2009.09.089
[32] J. F. M. Ibrahim et al 2017: Advanced Ceramics Progress 3 (4) 1. 10.30501/ACP.2017.90758
[33] Y. J. Zhang et al 2010: Journal of Magnetism and Magnetic Materials. 322 (15) 2251. https://doi.org/10.1016/j.jmmm.2010.02.020

Ref.: Ibrahim, Jamal Eldin F. M. – Mergen, Ayhan – Parlaқ, Umut – Kuvorics, Emese – Títhil, Mohammed – Gömze, László A.: Synthesis and characterization of iron-doped GdMnO$_3$ multiferroic ceramics Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 73, No. 1 (2021), 24–27. p. https://doi.org/10.14382/epitoanyag-jsbcm.2021.5