Synthesis and characterization of iron-doped $GdMnO_3$ multiferroic ceramics

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Abstract

In this research work, monocrystalline 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: multiferroikus anyagok, adalékolás, $GdMnO_3$ kerámiák, szilárdfázisú reakció, mágneses tulajdonságok

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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 $GdMn_{1-x}Fe_xO_3$ 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 $GdMn_{1-x}Fe_xO_3$

A single-phase $GdMn_{1-x}Fe_xO_3$ (x= 0.2 and 0.8) ceramic in a powder form were prepared through conventional solid-state synthesis route (*Fig. 1*). Gd_2O_3 (99.9%; Alfa Aesar), Mn_2O_3 (98%; Alfa Aesar) and Fe_2O_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; $GdMn_{1-x}Fe_xO_3$ 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 $GdMnO_3$ samples ($GdMn_{1-x}Fe_xO_3$) were also investigated.

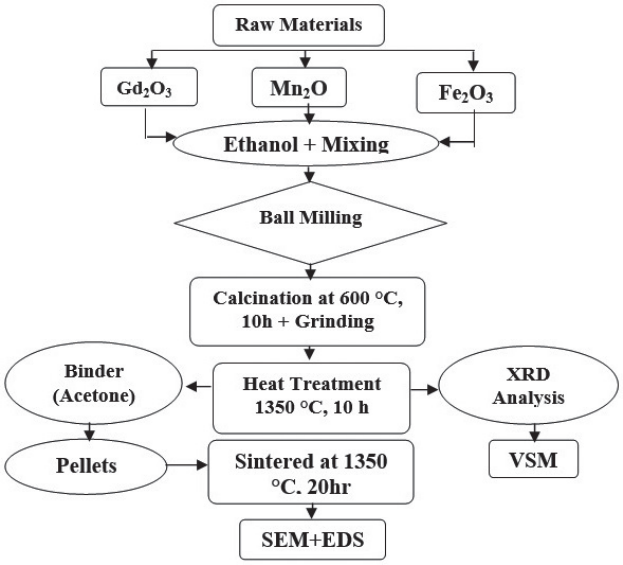


Fig. 1 Flow diagram for the preparation of $GdMn_{1-x}Fe_xO_3$ ceramics
1. ábra A GdMn1-xFexO3 kerámiák készítésének folyamata

2.2 Characterization

The prepared samples were characterized by a Bruker D2 PHASER X-ray diffractometer (XRD) operated in the Bragg-Brentano geometry and the tested samples were examined in 2θ range 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, DIFRACT measurement program was used. Surface morphology investigation of the produced samples was carried out using scanning electron microscopy (SEM, JEOL5910 LV) and surface analyses of the samples were carried out by energy-dispersive X-ray spectrometer (EDX). The fractured surface of the samples were coated with gold by SC7680 Super Coater before SEM analysis. Gold-coated fracture surfaces of the produced samples were investigated with different magnification values using secondary and back-scattered electrons. Also, the magnetic properties of the Fe-doped $GdMnO_3$ samples $GdMn_{1-x}Fe_xO_3$ at low temperature (10 K) were investigated using the vibrating sample magnetometer (VSM) and magnetization of the samples as a function of the magnetic field (M–H) was obtained.

3. Results and discussion

3.1 Structures

Fig. 2 shows the XRD patterns of undoped and B-site doped $GdMn_{1-x}Fe_xO_3$ (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. DIFRACT.measurement programme was used to calculate the unit cell's lattice parameters and volume (*Table 1*). Undoped $GdMnO_3$ 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 smaller ionic radius of Fe (1.17 Å) than Mn (1.79 Å).

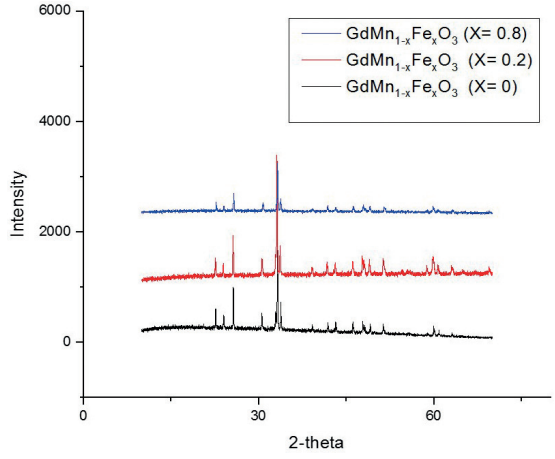


Fig. 2 Room temperature XRD patterns of $GdMn_{1-x}Fe_xO_3$ ceramics compounds (x= 0, 0.2 and 0.8) heat treated at 1350 °C for 24 h
2. ábra 1350°C-on 24 órán át hőkezelt $GdMn_{1-x}Fe_xO_3$ kerámiák XRD mintázata (x = 0; 0,2 és 0,8) szobahőmérsékleten

Composition	a (Å)	b (Å)	c (Å)	Volume (Å)³	Space group
$GdMnO_3$	5.31	5.84	7.43	230.41	Pnma
$GdMn_{0.8}Fe_{0.2}O_3$	5.316	5.679	7.611	229.77	Pnma
$GdMn_{0.2}Fe_{0.8}O_3$	5.3	5.6	7.62	226.16	Pnma

Table 1 Lattice parameters resulted from refinement procedure of powder XRD pattern of $GdMn_{1-x}Fe_xO_3$ ceramics compound (x=0.2, 0.8)
1. táblázat A rácsparaméterek a $GdMn_{1-x}Fe_xO_3$ kerámia alkotók XRD mintázatából adódtak (x = 0,2; 0,8)

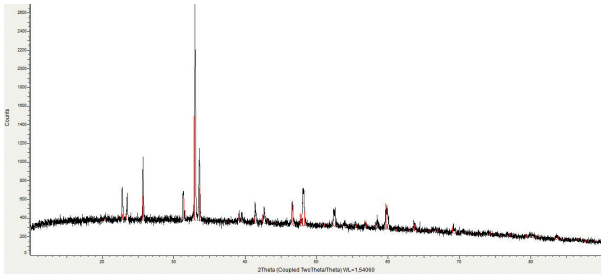


Fig. 3 XRD pattern for $GdMn_{1-x}Fe_xO_3$ ceramics sample at (x= 0.2)
3. ábra A $GdMn_{1-x}Fe_xO_3$ kerámia XRD mintája (x = 0,2)

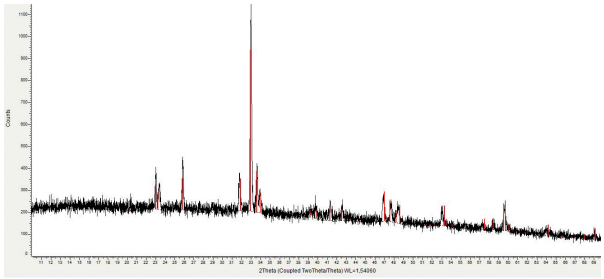


Fig. 4 XRD pattern for $GdMn_{1-x}Fe_xO_3$ ceramics sample at (x= 0.8)
4. ábra A $GdMn_{1-x}Fe_xO_3$ kerámia XRD mintája (x = 0,8)

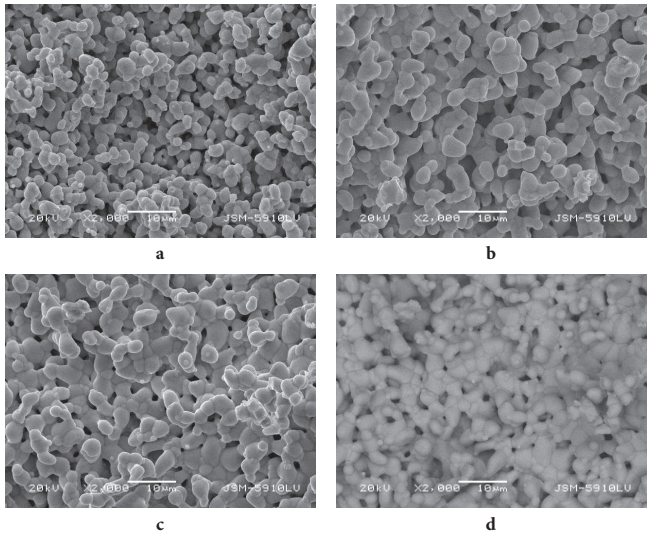


Fig. 5 SEM micrographs of Fe-doped $GdMnO_3$ samples at ×2.000 a) SEI of $GdMn_{0.8}Fe_{0.2}O_3$, b) BEI of $GdMn_{0.8}Fe_{0.2}O_3$, c) SEI of $GdMn_{0.2}Fe_{0.8}O_3$ and d) BEI of $GdMn_{0.2}Fe_{0.8}O_3$ samples ($GdMn_{1-x}Fe_xO_3$ ceramics where x= 0.2 and x= 0.8)
5. ábra Fe adalékolt $GdMnO_3$ minták SEM felvételei 2000x nagyítással a) $GdMn_{0.8}Fe_{0.2}O_3$ SEI, b) $GdMn_{0.8}Fe_{0.2}O_3$ BEI, c) $GdMn_{0.2}Fe_{0.8}O_3$ SEI és d) $GdMn_{0.2}Fe_{0.8}O_3$ BEI ($GdMn_{1-x}Fe_xO_3$ kerámiák, ahol x = 0,2 és x = 0,8)

3.2 Scanning electron microscopy (SEM) and EDS investigation of $GdMn_{1-x}Fe_xO_3$

Fig. 5 shows secondary and backscattered electron micrographs of the $GdMn_{0.8}Fe_{0.2}O_3$ and $GdMn_{0.2}Fe_{0.8}O_3$. 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 $Gd_{0.8}Eu_{0.2}MnO_3$, *Fig. 7-b* gives the EDS of $Gd_{0.2}Eu_{0.8}MnO_3$. 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.

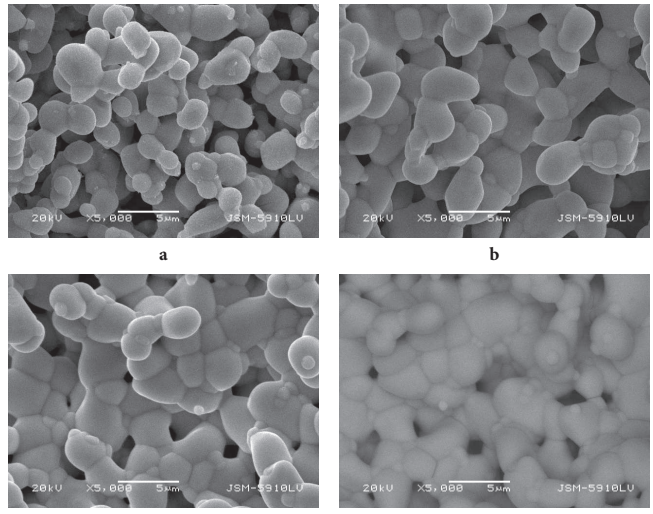
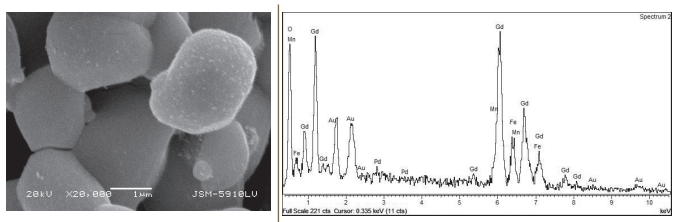
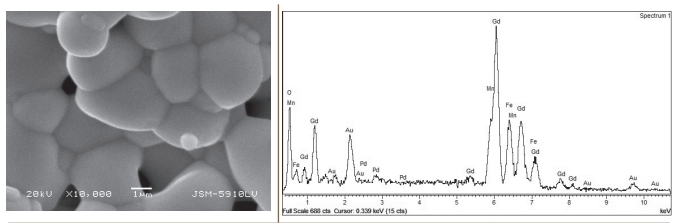


Fig. 6 SEM micrographs of Fe-doped $GdMnO_3$ samples at ×5.000 a) SEI of $GdMn_{0.8}Fe_{0.2}O_3$, b) BEI of $GdMn_{0.8}Fe_{0.2}O_3$, c) SEI of $GdMn_{0.2}Fe_{0.8}O_3$ and d) BEI of $GdMn_{0.2}Fe_{0.8}O_3$ samples ($GdMn_{1-x}Fe_xO_3$ ceramics where x= 0.2 and x= 0.8)
6. ábra Fe adalékolt $GdMnO_3$ minta SEM felvételei 5000x nagyítással a) $GdMn_{0.8}Fe_{0.2}O_3$ SEI, b) $GdMn_{0.8}Fe_{0.2}O_3$ BEI, c) $GdMn_{0.2}Fe_{0.8}O_3$ SEI és d) $GdMn_{0.2}Fe_{0.8}O_3$ BEI ($GdMn_{1-x}Fe_xO_3$ kerámiák, ahol x = 0,2 és 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

a



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

b

Fig. 7 EDS analysis Fe-doped $GdMnO_3$ samples a) EDS analysis of $GdMn_{0.8}Fe_{0.2}O_3$ and b) EDS analysis of $GdMn_{0.2}Fe_{0.8}O_3$ sample (Tables show the weight fractions of the elements found by calculation from EDS results)
7. ábra Fe-adalékolt $GdMnO_3$ minták EDS-elemzése a) $GdMn_{0.8}Fe_{0.2}O_3$ és b) $GdMn_{0.2}Fe_{0.8}O_3$ (A táblázat a számítással és az EDS-eredmények alapján meghatározott elemek tömegarányát mutatja)

3.3 Magnetic properties

Fig. 8 shows magnetic field-dependent magnetization at low temperature (10K) for $GdMn_{1-x}Fe_xO_3$ (x=0.2, 0.8) ceramics. Both samples show antiferromagnetic behaviour at 10K with small differences. The saturation magnetization (M_s) for the sample at x= 0.8 appears higher with a value of about 60 emu/g, while the sample at x=0.2 shows slightly lower M_s with a value of about 58 emu/g. The slight enhancement in magnetization might be attributed to the distorted spiral magnetic ordering 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].

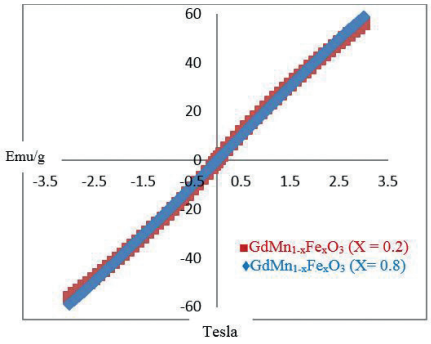


Fig. 8 The magnetic hysteresis loops of $GdMn_{1-x}Fe_xO_3$ ceramics compound (0.2 and 0.8) sintered at 1350 °C
8. ábra 1350°C-on szinterelt $GdMn_{1-x}Fe_xO_3$ kerámia alkotók (0,2 és 0,8) mágneses hiszterézis hurkjai

4. Conclusion

$GdMn_{1-x}Fe_xO_3$ (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 $GdMn_{1-x}Fe_xO_3$ (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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