Structural and magnetic characterization of the new GdMn$_{1-x}$Fe$_x$O$_3$ perovskite material

J A Cardona Vasquez$^{1,2}$, D A Landínez Téllez$^1$, C A Collazos$^2$ and J Roa Rojas$^1$

$^1$ Universidad Nacional de Colombia, Bogotá, Colombia.
$^2$ Universidad Manuela Beltrán, Bogotá, Colombia.

E-mail: joacardonava@unal.edu.co

Abstract. In this paper we present the synthesis process of the GdMn$_{1-x}$Fe$_x$O$_3$ perovskite material by conventional solid state reaction method. Crystalline phase evolution during the synthesis was studied by X-ray Diffraction (XRD) in powder of the materials, observing that the chemical reaction of the precursor oxides was significant above 1000°C. Rietveld refinement of DRX patterns shows a perovskite structure with octahedral distortions (space group Pbnm, # 62) for studied values of $x$ (0, 0.1 and 0.2). The degree of substitution generates an increasing tendency on lattice parameters $a$ and $c$, while for $b$ is decreasing just as for the volume of the unit cell. The effect of the change in the lattice parameters directly affects the octahedral distortions, ie, with increasing degree of substitution (increased parameter $c$) octahedra tend to arrange one above the other aligned with the $c$ axis. Magnetization measurements as a function of temperature were performed above room temperature between 300K and 860K with an applied field of 20Oe and below room temperature in Field Cooling (FC) and Zero Field Cooling modes (ZFC) between 4.2K and 300K with an applied field of 200Oe. Magnetic behavior above room temperature is paramagnetic for used values of $x$, on the other hand at low temperatures ($T<30K$) magnetic phase transitions associated to the apparition of an antiferromagnetic phase are observed. In addition for $x=0.1$ the derivative of magnetization shows a peak around 31K, associated to the ferrimagnetic transition for this material. Curie-Weiss fit reveals the antiferromagnetic (ferrimagnetic) behavior of the materials, also shows that the configurations with $x=0$ and $x=0.2$ have an effective magnetic moment very similar to the reported value of undoped material, while for $x=0.1$ a higher value is observed confirming the ferrimagnetic behavior of this configuration.

1. Introduction

Perovskites are ceramic materials that combine metal with non-metallic elements. The perovskite structure is represented as ABX$_3$, there are variety of behaviours and properties associated with the materials with structure perovskite due to the relative ease of the election of the cations A and B, which may be occupied by different elements. Commonly the A position is occupied by alkali, alkaline earth or rare earth ions; and the B position usually is occupied by transition metals, giving a large number of possible combinations associated with different properties [1]. An example of the variety of properties are the rare earth manganites.

In recent years, rare earth manganites have been the subject of intense research due to its attractive properties [2-6], mainly associated with the interaction between the 4f orbitals of the rare earth ions with 3d orbitals of the manganese ions, these interactions generate interesting electrical and magnetic behaviours and transport properties [3]. Some of the best known properties in this type of material are
the antiferromagnetism, ferroelectricity (spontaneous and/or induced by magnetic fields), multiferroicity, colossal magnetoresistance and exchange interactions between the magnetic moments of manganese Mn$^{3+}$, as well as some of the ions rare earth R$^{3+}$ [5]. The properties mentioned above depend on the temperature range in which to study, and the ion R.

The aim of this paper is to report the synthesis process of the GdMn$_{1-x}$Fe$_x$O$_3$ system ($x=0; 0.1$ and $0.2$) and study the effect of Fe substitution in the structural and magnetic properties in order to determine if the multiferroic behavior can be improved by this substitution.

2. Experimental details

GdMn$_{1-x}$Fe$_x$O$_3$ system was synthesized by the conventional solid state reaction method, from high purity oxides commercially available. The mass required was obtained by stoichiometrically calculations. Precursor oxides were dried at 160°C for 1 hour and the calculated masses are weighted. Oxides were manually mixed in an agate mortar (around 2h), heat treatments at 700, 800 and 900°C were performed on the resultant powders. Subsequently, the materials were pressed at 10ton/cm$^2$, and subjected to heat treatment at 1000, 1100 and 1200°C. Between each heat treatment the powders were grinded and analysed by XRD.

XRD measurements were carried out at room temperature using X’pert PRO PANalytical powder X-ray diffractometer with copper anode ($\lambda=1.54056\text{Å}$) in the $2\theta$ range between 20° and 70° with a step of 0.02° and 2 seconds of time step. Magnetic characterization was performed through curves of magnetization as a function of temperature, measured in a Quantum Design MPMS in a temperature range from 4K to 300K, and 200 Oe applied field.

3. Results and discussion

According to the literature the GdMnO$_3$ has an orthorhombic perovskite structure with octahedral distortion [4,6]. Evolution of the crystal structure during the heat treatments was studied by XRD. Figure 1 shows the study of structural evolution by XRD to different heat treatment temperatures of the GdMn$_{1-x}$Fe$_x$O$_3$ compound, the other two materials show the same behaviour. In Figure 1 can be seen that below 1000°C the formation of the orthorhombic phase of GdMn$_{1-x}$Fe$_x$O$_3$ is minimal, ie, until this temperature XRD patterns mostly agree with those of precursors. Above this temperature the formation of the orthorhombic phase associated with the material without substitution is observed. At 1200°C the XRD patterns did not show significant changes compared with the results obtained at 1100°C. Comparison of the diffraction peaks for different $x$ values show small shifts in the 20 positions as well as changes in the intensity ratio as a result of the inclusion of Fe in the crystal structure of the materials. Identification of the symmetry and space group was performed using the PANalitical X’Pert HighScore Plus software. The Rietveld refinement of crystal structures was performed using the GSAS + EXPGUI software [8,9]. The Rietveld refinement of the GdMn$_{1-x}$Fe$_x$O$_3$ confirms that as expected, Fe$^{3+}$ ions take the same atomic positions that Mn$^{3+}$ ions.

![Figure 1: Study of structural evolution by XRD to different heat treatment temperatures of the GdMn$_{0.9}$Fe$_{0.1}$O$_3$ compound. At the bottom are shown the 20 positions of reported peaks for precursors (Gd$_2$O$_3$, MnO$_2$ and Fe$_2$O$_3$) and on top of the peak positions of GdMnO$_3$.](image-url)
Where is more visible the influence of the percentage of substitution is on the lattice parameters of material which can be seen with increasing of substitution degree the parameters $a$ and $c$ grow, while the parameter $b$ and the unit cell volume decrease as shown in Table 1. More significant changes are observed in the parameters $b$ and $c$ (0.5% and 0.3% for 0.1 of substitution respectively). Figure 2 shows the distorted perovskite structure GdMn$_{1-x}$Fe$_x$O$_3$ where distortions MnO$_6$ octahedra are observed, besides in Figure 2 can be seen the results of Rietveld refinement for three configurations. One effect of changes in the lattice parameters directly affects the distortion of the structure, ie with increasing degree of substitution (increase of parameter $c$), octahedra tend to arrange one above the other aligned with the $c$ axis.

### Table 1: Refined lattice parameter and cell volume of GdMn$_{1-x}$Fe$_x$O$_3$ compounds.

| Compound          | $a$ [Å±0.0001] | $b$ [Å±0.0001] | $c$ [Å±0.0001] | Volume [Å$^3$±0.01] |
|-------------------|----------------|----------------|----------------|---------------------|
| GdMnO$_3$         | 5.3179         | 5.8345         | 7.4440         | 230.97              |
| GdMn$_{0.9}$Fe$_{0.1}$O$_3$ | 5.3191         | 5.8082         | 7.4694         | 230.76              |
| GdMn$_{0.8}$Fe$_{0.2}$O$_3$ | 5.3203         | 5.7765         | 7.4945         | 230.33              |

Figure 2: Rietveld refinement of the GdMn$_{1-x}$Fe$_x$O$_3$ compounds.

Literature indicates that the undoped material GdMnO$_3$ has A type antiferromagnetism [6]. Similarly three phase transitions are reported for this material [9], the first associated with the transition to the A type antiferromagnetic is reported close to 23K, the second associated with the orientation of the spins of Mn$^{3+}$ ions around 14K and finally the transition due to the orientation of the spins of Gd$^{3+}$ at 5K [9]. Figure 3 (right) shows the ZFC magnetization curves as a function of temperature of the three materials at the same scale, the inset shows the derivative of these curves, where are observed phase transitions around the reported temperatures for the ordering of Mn$^{3+}$ and Gd$^{3+}$; besides is indicated other temperature (30.7K) corresponding to an anomaly only noted in the material with $x=0.1$. This anomaly may be associated with ferrimagnetic character related with the imbalance created by the inclusion of Fe$^{3+}$ in the structure. In Figure 3 (left) are shown the graphs of derivative of the inverse of magnetic susceptibility versus temperature, in these graphs can be seen the transitions Para-Antiferromagnetic states (~21.8K - 25.2K) and the transition observed at 30.7K again.

Table 2 shows the results of Curie-Weiss fit of magnetic susceptibility, where the magnetic parameters of the materials were calculated. Effective magnetic moment ($\mu_{eff}$) obtained for GdMnO$_3$...
(9.18\(\mu_B\)) agrees with reported value for this material (9.2\(\mu_B\)) [9]. Figure 3 shows strong similarity between the materials with \(x=0\) and \(x=0.2\), in Table 2 is observed the same similarity in \(\mu_{\text{eff}}\). For \(x=0.1\) a higher value is observed in \(\mu_{\text{eff}}\), which reinforces the hypothesis of an imbalance in the antiferromagnetic arrangement generated by the distribution of iron in the crystal structure of GdMn_{0.9}Fe_{0.1}O_{3}.

**Figure 3:** Magnetic behaviour and phase transitions of GdMn_{1-x}Fe_{x}O_{3} compounds.

| Material               | \(C\) [KJm/Tk g] | \(\theta_p\) [K] | \(\mu_{\text{eff}}\) [\(\mu_B\)] |
|------------------------|------------------|------------------|--------------------------|
| GdMnO_{3}              | 0.000494         | -34.4            | 9.18                     |
| GdMn_{0.9}Fe_{0.1}O_{3}| 0.000897         | -22.1            | 12.34                    |
| GdMn_{0.8}Fe_{0.2}O_{3}| 0.000491         | -27.4            | 9.14                     |

### 4. Conclusions

We have synthesized the system GdMn_{1-x}Fe_{x}O_{3} by the solid state reaction method. Rietveld refinement shows an orthorhombic phase (Pbnm #62) for all values of \(x\). We observed that the chemical reaction of the precursor oxides occurs for temperatures above 1000°C, obtaining phases with high purity and crystallinity at 1200°C. Study of the magnetization as a function of temperature showed a paramagnetic behavior at room temperature with phase transitions to the antiferromagnetic below 25K for all configurations. We assume that the inclusion of Fe in the crystal structure induces a ferrimagnetic state for \(x=0.1\) which can be seen to 30.7K.

### Acknowledgements

Authors acknowledge to direction of research from Bogota (DIB) at the National University of Colombia and direction of laboratories, University Manuela Beltran.

### References

[1] J A Cardona-Vasquez, D A Landínez-Téllez, J Roa-Rojas 2014 *Physica B* **455** 39
[2] Xiang Li, Chengliang Lu, Jiyan Dai, et al 2015 *Scient Rep* (DOI: 10.1038/srep07019)
[3] Shuai Dong and Jun-Ming Liu 2012 *Modern Physics Letters B* **26-9** 1230004
[4] T Kimura, T Goto, H Shintani, K Ishizaka, T Arima & Y Tokura 2003 *Nature* **426** 55
[5] P P Rout, S K Pradhan, S K Das, B K Roul 2012 *Physica B* **407** 2072
[6] T Goto, T Kimura, G Lawes, A P Ramirez and Y Tokura 2004 *Phys Rev Let* **92-25** 257201
[7] A C Larson and R B Von Dreele 2004 *General structure analysis system (GSAS)* (USA: Los Alamos National Laboratory Report - LAUR) p 86
[8] B H Toby 2001 *J Appl Cryst* **34** 210
[9] W S Ferreira, J Agostinho Moreira, A Almeida, et al 2009 *Phys Rev B* **79** 054303