Synthesis, structural, magnetic and ferroelectric characterization of biferroic Bi$_3$R$_2$FeTi$_3$O$_{15}$

O.D. Gil Novoa, D.A. Landínez Téllez*, and J. Roa-Rojas
Grupo Física de Nuevos Materiales, Departamento de Física, Universidad Nacional de Colombia,
AA 14490, Bogotá D. C., Colombia.
*e-mail: dalandinezf@unal.edu.co

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In this work we report for the first time synthesis of polycrystalline samples of Bi$_3$FeTi$_3$O$_{15}$ (BFTO) and Bi$_3$R$_2$FeTi$_3$O$_{15}$ compounds with R= Gd, Dy. The materials were synthesized by the standard solid-state reaction recipe from high purity powders of Bi$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, Fe$_2$O$_3$ and TiO$_2$, submitted to thermal treatments of 650, 800 and 810°C by 10, 20 and 24 h, respectively. We analyzed the structural characteristics by XRD technique, obtaining pure phase in all compounds with orthorhombic crystal structure. Polarization (P-E) measurements were performed, showing hysteretic behavior, which indicates that the compounds can be used as ferroelectric materials. Magnetic susceptibility measurements as a function of temperature were obtained with a MPMS SQUID Magnetometer between 5 and 300 K, on the application of an applied magnetic field of 0.01 T. Results reveal that materials evidence paramagnetic behavior. Using the Curie-Weiss fitting, we obtain the characteristic parameters C and θo. From the Curie constant, we determine the effective magnetic moment, which is in agreement with the theoretical expected value for Gd$^{3+}$ and Dy$^{3+}$ cations, calculated by the Hund’s rule.

Keywords: New materials; rietveld refinement; electric hysteresis; magnetic susceptibility.

Se reporta por vez primera la síntesis de muestras policrystalinas de los compuestos Bi$_3$FeTi$_3$O$_{15}$ (BFTO) y Bi$_3$R$_2$FeTi$_3$O$_{15}$ para R= Gd y Dy, sinterizados a través de la técnica de reacción en estado sólido a partir de precursores óxidos de alta pureza (Aldrich 99.99%): Bi$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$; con tratamientos térmicos de 650°C, 800°C y 810°C durante 10 h, 20 h y 24 h respectivamente. Posteriormente se analizaron las características estructurales a través de la técnica DRX, obteniendo fase única en cada compuesto con estructura cristalina ortorrombica. Se realizaron medidas de polarización en función de campo eléctrico aplicado (P-E) para voltajes aplicados, observándose comportamiento histerético, el cual indica que los compuestos pueden ser usados como materiales ferroeléctricos. Las medidas de susceptibilidad magnéticas en función de la temperatura se obtuvieron con un magnetómetro SQUID, para rangos de temperatura de 5 K a 300 K, con un campo aplicado de 100 Oe; los compuestos muestran comportamiento paramagnético que se ajusta a la ley de Curie-Weiss. Los parámetros C y θo fueron encontrados realizando el ajuste de las curvas respectivas, así mismo se determinó que el momento magnético efectivo calculado a través de la regla de Hund para los iones Gd$^{3+}$ y Dy$^{3+}$ coincide relativamente bien con el momento magnético efectivo de los iones de tierras.

Descriptors: Nuevos materiales; refinamiento Rietveld; histéresis eléctrica; susceptibilidad magnética.

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1. Introduction

The layered bismuth oxides structures in special Aurivillius structure have attracted the attention from a number of researchers because to biferroic properties and the potential technologies in the storage devices non-volatile [1-5]. The Aurivillius oxides are structures whose growth is obtained [001] direction, thus generating a series of layers of perovskite blocks alternating with layers of (Bi$_2$O$_2$)$_{+2}$ oxides [6]. The stacking of octahedral blocks is given by [A$_{n-1}$B$_n$X$_{3n+1}$]$^{+2}$. Where A is a mono, di or trivalent cation (or mixture of them). B is a tri, tetra or hexavalent cation and X represents the position of oxygen ion [7-8].

In this work we report the synthesis process, structural, ferroelectric and magnetic characteristics of Bi$_3$FeTi$_3$O$_{15}$ and Bi$_3$R$_2$FeTi$_3$O$_{15}$ with R=Dy and Gd.

2. Experimental

The polycrystalline samples Bi$_3$FeTi$_3$O$_{15}$ (BFTO), Bi$_3$Gd$_2$FeTi$_3$O$_{15}$ (BGFTO) and Bi$_3$Dy$_2$FeTi$_3$O$_{15}$ (BDFTO), were prepared by the solid state reaction route, starting stoichiometric mixture of high purity precursor powders oxides: Bi$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$ (Aldrich 99.99%). The powders were ground in an agate mortar to get a homogeneous mixture, and then submitted to thermal treatments of 650°C, 800°C and 810°C for 10 h, 20 h and 24 h respectively with milling process intermediate. The powders were pressed by the action of load 8 ton. The structural analysis carried out with the X Ray Diffraction by means of a PW1710 diffractometer with λCu-Kα = 1.54064 Å. The structural refinement was performed by the Rietveld method by means of GSAS code [9], the input data were taken from the card Nº 74037 using the Data Base crystallographic ISCD [10].

The electric hysteresis loops were obtained with the Ferroelectric test system of Radiant Technologies, for different values of applied electric field. The remanent polarization (2P$_r$) and coercive field (2E$_c$), showed the ferroelectric behavior for all compounds.

The magnetic properties were obtained with the MPMS SQUID magnetometer (Quantum Design) in the range be-
The compound (BFTO) was synthesized, taking it as a target for determining of magnetic contribution on earth rare (Gd$^{3+}$ or Dy$^{3+}$).

### 3. Results

The data obtained of X-ray diffraction were refined using the Rietveld method. Figure 1 shows the powder x-ray diffraction patterns for all compounds. Rietveld Refinement of these experimental data is shown too. The continuous curve corresponds to the pattern calculated and the symbols represent the experimental diffractogram. In the same graph, locations of Bragg peaks are shown as vertical lines. Curve in bottom of figure represents the difference between experimental pattern and the calculated one. From Rietveld refinement we determined that this diffraction pattern is characteristic of orthorhombic structure, space group Fmmm. The cell parameters of compounds are $a=5.434520$, $b=41.234894$, $c=5.458526$ for the BFTO compound. For the compound with the gadolinium substitution BDFTO, the cell parameters are: $a=5.377405$, $b=41.557407$ and $c=5.393126$. For the dysprosium substitution compound (BDFTO), the cell parameters are: $a=5.401689$, $b=41.445927$, $c=5.404562$. All the cell parameters obtained are consistent with the data obtained of ICSD Card N° 74037.

The discrepancy factors obtained from Rietveld analysis are presented in the Table I; can see the small differences between observed and calculated data, inferring from it so that the structure obtained for all compounds, correspond to Aurivillius phase as reported for BFTO compound [2,4,5].

Measurements of polarization as a function of applied voltage were performed in order to establish the biferroic behavior of the materials. Figure 4 show hysteresis loops for all compounds in a capacitor configuration, under several applied voltages, which reveals a characteristic ferroelectric response.

All compounds showed a weak ferroelectric behavior. It is observed in the values $2P_r$ and $2E_c$ for all applied voltages (350, 1100 and 2000 V). With this data, was not possible to determine the saturation polarization ($P_s$).

It may be noted that the maximum remanent polarization is present in the substitution for Gd compound, the other hand the largest coercive field is obtained in the substitution of Dy compound; i.e. it has been improved the values $2P_r$ and $2E_c$ for Bi substitutions by rare earth ion as the Gd and Dy respectively.

| Table I. Discrepancy factors obtained from Rietveld refinement. |
|---------------------------------|---------------|---------------|
| Compound | $\chi^2$ (%) | $R_F^2$ (%) | $R_W^2$ (%) |
|--------|---------------|---------------|
| BFTO   | 2.214         | 5.13          | 4.48         |
| BGFTO  | 3.901         | 12.25         | 5.53         |
| BDFTO  | 1.974         | 4.86          | 3.79         |
SYNTHESIS, STRUCTURAL, MAGNETIC AND FERROELECTRIC CHARACTERIZATION OF BIFERROIC Bi$_3$R$_2$FeTi$_3$O$_{15}$

**Figure 2.** Hysteresis loops for (a) BFTO, (b) BGFTO and (c) BDFTO compound; the $2P_r$ and $2E_c$ data are shown in the insert tables.

Figure 3 shows the magnetic susceptibility dependence of temperature for the BFTO, BGFTO and BDFTO compounds. Figure 3(a) shows the magnetic susceptibility as a function of temperature for BFTO compound, in the first insert is shown the inverse susceptibility (open squares) and the linear regression (red line). Figure 3(b) shows the susceptibility loops of BFTO (open triangles) and BGFTO (open circles), in the first inset is shown the difference between the magnetic susceptibility of pure compound (after subtraction of the BFTO contribution) and the second internal graph show the inverse susceptibility of the calculated difference.

**Figure 3.** Magnetic susceptibility for (a) BFTO, (b) BGFTO and (c) BDFTO compound; the external graph show the magnetic susceptibility, the difference between magnetic susceptibility and pure compound (after subtraction of the BFTO contribution) and the second internal graph show the inverse susceptibility of the calculated difference.

I.e. after subtraction of
TABLE II. Constants obtained from fitting of Curie-Weiss theory

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_0$ (emu/mol)</th>
<th>C (emu/θc cm$^3$/K)</th>
<th>$\theta_c$ (K)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFTO</td>
<td>0.0033</td>
<td>1.1751</td>
<td>-3.322</td>
<td>3.062</td>
</tr>
<tr>
<td>BGFTO</td>
<td>0.0040</td>
<td>13.543</td>
<td>-2.025</td>
<td>5.198</td>
</tr>
<tr>
<td>BDFTO</td>
<td>0.0439</td>
<td>36.126</td>
<td>-1.136</td>
<td>8.490</td>
</tr>
</tbody>
</table>

The corresponding data of susceptibility independent of temperature $\chi_0$, the Curie constant $C$, the magnetic transition temperature $\theta_0$ and the effective magnetic moment are shown in the Table II.

The effective magnetic moment was determined by BFTO unit formula; the data for the BGFTO and BDFTO compounds correspond by ion of earth rare; this data are consistent with the literature report for Gd$^{3+}$ and Dy$^{3+}$ ions.

4. Conclusions

The synthesis of Bi$_3$R$_2$FeTiO$_{15}$ with R = Gd and Dy, were carried out, the Rietveld refinement reveals that experimental data correspond to orthorhombic structure belonging to $Pmm2$ (#42) space group. The polarization as a function of electric field has shown ferroelectric behavior in all compounds. The effective magnetic contribution of earth rare Gd and Dy ions was determined subtracting the magnetic contribution of pure compound BFTO. The magnetic moment obtained for BGFTO and BDFTO are consistent with the effective magnetic moment of earth rare substituent.