

## Magnetic property of $\text{BiMn}_2\text{O}_5$ single crystal

M.C. Silva-Santana<sup>a</sup>, N.O. Moreno<sup>a</sup>, D. Reyes Ardila<sup>b</sup>, and J.P. Andreeta<sup>c</sup>

<sup>a</sup>*Departamento de Física, Universidade Federal de Sergipe, São Cristóvão, SE, 49100-000, Brazil.*

*e-mail: marcoscleison@gmail.com*

<sup>b</sup>*Departamento de Física, Universidade Federal de Sergipe, Itabaiana, Se, Brazil.*

<sup>c</sup>*DDFCM, Instituto de Física de São Carlos, 13560-590 São Carlos, SP, Brazil.*

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We report magnetic measurements in the single crystal sample of  $\text{BiMn}_2\text{O}_5$  known as a multiferroic system. The magnetic susceptibility as a function of temperature ranging from 2 K to 400 K, was measured indicating a magnetic ordering below at Néel temperature  $T_N = 42$  K. At low temperature, both the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization curves diverge for the applied magnetic field parallel to  $c$  axis. The magnetization versus magnetic field shows hysteresis behavior with coercive field of  $\sim 2700$  Oe at 2 K, this suggests the presence of a weak ferromagnetic component. The effective paramagnetic moment for the two crystallographic orientations determined from the Curie-Weiss law, was  $4.39 \mu_B$  and  $4.57 \mu_B$ , respectively, indicating the presence of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{Bi}_2\text{MnO}_5$ .

**Keywords:** Multiferroic; manganese oxides; magnetic properties.

Presentamos mediciones magnéticas en el monocristal de  $\text{BiMn}_2\text{O}_5$  conocido como un sistema multiferroico. La susceptibilidad magnética en función de la temperatura que va desde 2 K a 400 K, se determinó indicando un ordenamiento magnético por debajo de la temperatura de Néel  $T_N = 42$  K. A baja temperatura, tanto las curvas de magnetización enfriadas sin campo (ZFC) y con campo (FC), divergen para el campo magnético aplicado paralelo al eje  $c$ . La magnetización versus el campo magnético muestra un comportamiento de histéresis con campo coercitivo de  $\sim 2700$  Oe a 2 K, esto sugiere la presencia de un componente ferromagnético débil. El momento paramagnético efectivo de las dos orientaciones cristalográficas determinado a partir de la ley de Curie-Weiss, fue de  $4.39 \mu_B$  y  $4.57 \mu_B$ , respectivamente, lo que indica la presencia de  $\text{Mn}^{3+}$  y  $\text{Mn}^{4+}$  en  $\text{Bi}_2\text{MnO}_5$ .

**Descriptores:** Multiferroicos; Óxidos de manganeso; las propiedades magnéticas.

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### 1. Introduction

Multiferroics are materials with more than one order of ferroicity, *i.e.* within them it can coexist many kinds of fundamental ferroicities like: (anti)ferromagnetic order, (anti)ferroelectric order, or ferrotoroid order [1]. Multiferroics with ferroelectric and some of ferromagnetic order are interesting because their magnetoelectric coupling. These compounds may lead to a new type of electrical devices such as sensors, improved magnetic random memory access (MRAM) with low writing energy, spintronics and so on [2-5]. Although the materials that are both ferromagnetic and ferroelectric are limited, several families of magnetic ferroelectrics have been reported in which the spontaneous electric polarization can be controlled largely by an external magnetic field.

$\text{RMn}_2\text{O}_5$  series oxides, [6-8] where R means rare-earth metals, or Y and Bi, are among the few oxides showing significant magneto electric or magneto dielectric effects.  $\text{BiMn}_2\text{O}_5$  is an important manganite with mixed-valence  $\text{Mn}^{3+}/\text{Mn}^{4+}$ , and was first studied early in 1960 due to the interesting structure [9]. It crystallizes at room temperature in the orthorhombic structure with the space group  $Pbam$ , which is composed of  $\text{Mn}^{4+}\text{O}_6$  octahedral and  $\text{Mn}^{3+}\text{O}_5$  pyramidal units. The octahedra form chains along the  $c$  axis while sharing their edges. Moreover, a pair of pyramids links these chains within the  $ab$  plane. It is believed that the appearance of ferroelectricity arises from the pyramidal  $\text{Mn}^{3+}$  sites.

$\text{BiMn}_2\text{O}_5$  has been described as a noncollinear commensurate antiferromagnet at low temperatures with propagation vector  $k = (1/2, 0, 1/2)$ , and the spins pointing nearly along the  $a$  direction, as inferred from neutron powder diffraction measurements [10]. This compound, at low temperatures, is antiferromagnetic with Néel temperatures  $T_N \approx 39\text{--}42$  K. On the other hand,  $\text{BiMn}_2\text{O}_5$  shows the dielectric, pyroelectric, and ferroelectric orders below 290 K, which was due to the presence of highly polarizable  $\text{Bi}^{3+}$  ions with an unshared electron pair [11].

Here, we present magnetic measurements in high quality single crystal of  $\text{BiMn}_2\text{O}_5$  synthesized by floating zone in a modified laser-heated pedestal growth (LHPG) apparatus.

### 2. Experimental details

The crystal growth is controlled by a process of solidification in direction of a floating zone seed. Mixed polyvinyl alcohol (PVA) and powders of  $\text{Bi}_2\text{O}_3$  (99.99%),  $\text{Mn}_3\text{O}_4$  (98%) and  $\text{MnO}_2$  (99.9%), from Alfa Aesar, were used as starting materials. A mixture of reducing gas ( $\text{N}_2/\text{H}_2$ , 95/5 vol./vol.) forming an isostatic atmosphere was used as the growth ambient. The crystals were obtained by the laser-heated pedestal growth technique using the extruded minirods as source and feed rods displaced vertically, upwards, without rotation. The more stable crystal growth was evidenced when the molar ratios of starting reagents were 2:1:1, the pressure of the reduc-

ing atmosphere was between 0.25 atm and 0.50 atm, and the seed and source rods speeds were between 0.2-0.3 mm/min and 0.1-0.2 mm/min, respectively.

X-ray diffraction studies were carried out by using Rigaku D-Max 2200 diffractometer equipped with  $\text{CuK}\alpha$  radiation. The magnetic properties of  $\text{BiMn}_2\text{O}_5$  compound were studied by means of a SQUID magnetometer (Quantum Design) in the temperature range 2–400 K in magnetic fields up to 7 Tesla.

### 3. Results and discussion

The XRD pattern of the  $\text{BiMn}_2\text{O}_5$  at room temperature is shown in Fig. 1. The  $\text{BiMn}_2\text{O}_5$  single crystalline sample is orthorhombic (space group  $Pbam$ ). No impurity phases such as Bi or Mn binary oxides were detected. The lattice parameters for  $\text{BiMn}_2\text{O}_5$  obtained by least squared analysis are  $a=7.555 \text{ \AA}$ ,  $b=8.525 \text{ \AA}$ , and  $c=5.755 \text{ \AA}$ , which are in good agreement with the previous reported data [8,10].

Figure 2a presents the temperature dependence of the dc magnetic susceptibility performed in a  $H = 3.5 \text{ kOe}$  magnetic field along  $c$ -axis,  $\chi_{\parallel}$  and perpendicular (filled circles)  $c$ -axis,  $\chi_{\perp}$  for the  $\text{BiMn}_2\text{O}_5$ . These data were taken under zero-field-cooling ZFC and field-cooling FC conditions, but in Fig. 2 we show only the FC data. At low temperature, dc susceptibility curves are characteristic of an antiferromagnetic (AF) behavior with maxima around 40 K.

The Néel temperature was estimated as the minimum value in the  $d\chi/dT$  vs.  $T$  curve given  $T_N = 43.5(4) \text{ K}$ , consistent to that reported in literature [10,11]. As shown in Fig. 2b, at high temperatures ( $T > 50 \text{ K}$ ), the susceptibility follows Curie-Weiss behavior and from the slope we obtained an effective magnetic moment of  $4.39\mu_B$  and  $4.57 \mu_B$  for both orientations. These values are, between  $\mu_{eff} = 4.89 \mu_B/\text{Mn}$  expected for  $\text{Mn}^{3+}$  ( $3d^4$ ,  $S = 2$ ) and  $\mu_{eff} = 3.87\mu_B/\text{Mn}$  expected for  $\text{Mn}^{4+}$  ( $3d^3$ ,  $S = 3/2$ ). This experimental  $\mu_{eff}$  value corroborates the coexistence of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{BiMn}_2\text{O}_5$ . The paramagnetic Curie temperature ( $\theta$ ) was

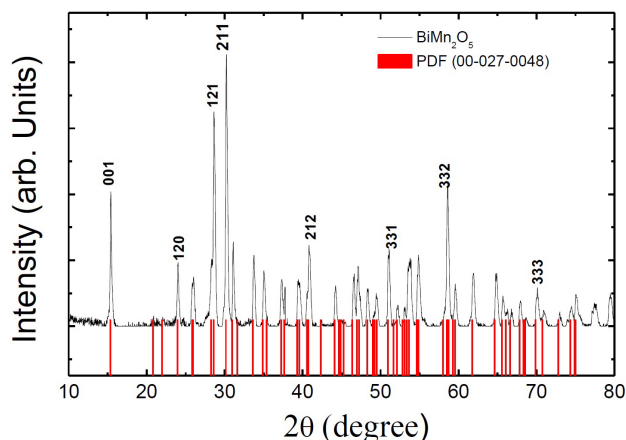


FIGURE 1. X-ray diffraction pattern for  $\text{BiMn}_2\text{O}_5$  at room temperature.

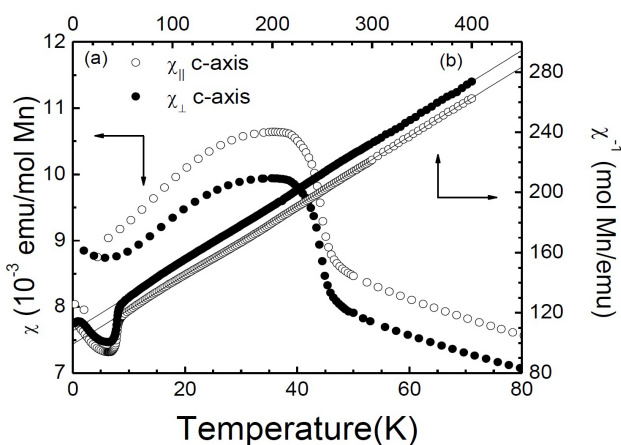


FIGURE 2. (a) Magnetic susceptibility,  $\chi$ , as a function of temperature for  $\text{BiMn}_2\text{O}_5$  measured in a field of 3.5 kOe (FC) parallel and perpendicular to  $c$ -axis. (b)  $\chi^{-1}$  vs.  $T$ . The straight lines show a fit with a Curie-Weiss law.

found to be -263 K and -274 K for  $H$  parallel and perpendicular  $c$  axis, respectively. Such a large negative values of the Curie temperature indicate strong magnetic frustration of the antiferromagnetic interactions on  $\text{BiMn}_2\text{O}_5$ .

The low temperature magnetic susceptibility curves under ZFC and FC procedures obtained with  $H = 3.5 \text{ kOe}$  are shown in Fig. 3. We identified a small anisotropy in the susceptibility to the applied field direction parallel to the  $c$  axis.  $\chi_{\parallel C}$  have a small anisotropy below  $T_N$  different from the behavior of  $\chi_{\perp C}(T)$ .

Magnetic isotherms were measured up to 70 kOe on both the parallel and perpendicular to  $c$ -axis sample. These isothermal curves are shown in Fig. 3 for the sample with both orientations at 2 K (AF regime) and 50 K (paramagnetic regime). The magnetization is linear with the applied field for  $H$  perpendicular to the  $c$  axis at all temperatures. Below

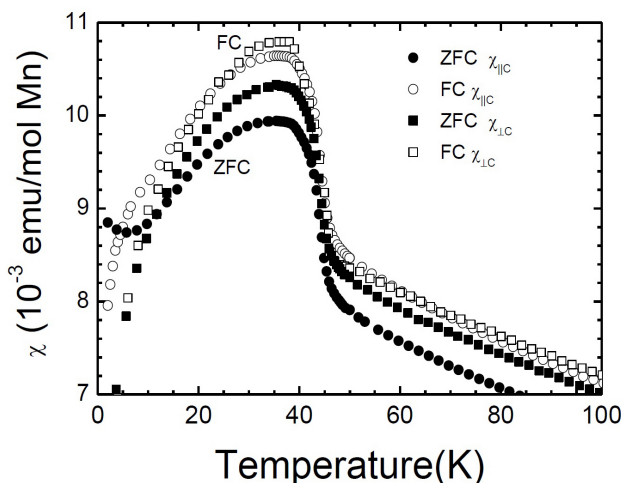


FIGURE 3.  $\chi$  vs.  $T$  of the zero-field-cooled (solid) and field-cooled (open) taken in 3.5 kOe for  $\text{BiMn}_2\text{O}_5$ . Solid circles  $\chi_{\parallel}$ ; squares  $\chi_{\perp}$ .

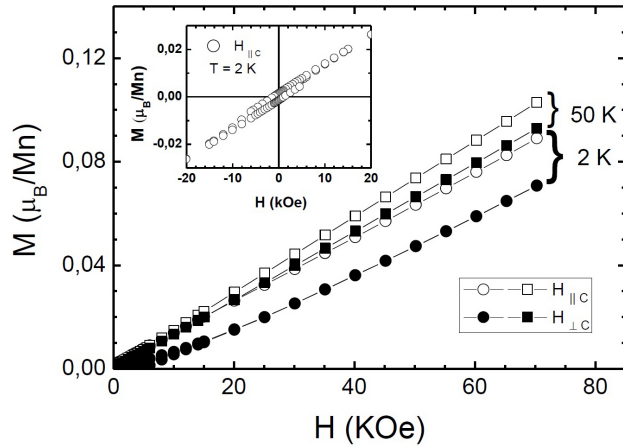


FIGURE 4. Magnetization isotherms of BiMn<sub>2</sub>O<sub>5</sub>, at 2 K and 50 K for  $H$  parallel and perpendicular to the  $c$  axis. The inset shows the hysteresis curve at 2 K for  $H$  parallel to the  $c$  axis.

$T_N$  for the sample with the  $c$  axis aligned parallel to the magnetic field exhibited a hysteresis. This result is consistent with the hysteresis observed in Fig. 3 for the applied magnetic field parallel to  $c$  axis. At 2 K the coercivity field is 1120 Oe and the remanent magnetization is  $1.5 \times 10^{-3} \mu_B/\text{Mn}$ . Saturated moment of the sample is  $0.02 \mu_B/\text{Mn}$ , which is much smaller than the full  $\text{Mn}^{3+}/\text{Mn}^{4+}$  moment ( $\sim 1.75 \mu_B$ ).

Therefore, we believe that the Mn moments are primarily antiferromagnetically ordered in the  $ab$  plane, but are canted along the  $c$  axis. Since the longitudinal component of the saturated effective magnetic moment, is only 1/175 of the ex-

pected value  $g_J \langle S \rangle = 3.5 \mu_B$ , where  $\langle S \rangle$  is a spin average of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions.

We explain the weak ferromagnetism below 43 K due to misalignment of  $\text{Mn}^{4+}\text{O}_6$  octahedra and  $\text{Mn}^{3+}\text{O}_5$  pyramids exactly below  $T_N$ , where a relatively large contraction of the  $a$  lattice parameter occurs [11].

#### 4. Conclusions

A single crystal sample of multiferroic BiMn<sub>2</sub>O<sub>5</sub> was synthesized by a floating zone technique in a modified laser-heated pedestal growth (LHPG) apparatus. Magnetic measurement shows that the Néel temperature of BiMn<sub>2</sub>O<sub>5</sub> is 43.5 K and the effective paramagnetic moment is  $4.39 \mu_B/\text{Mn}$  and  $4.57 \mu_B/\text{Mn}$  for  $H_{\parallel c}$  and  $H_{\perp c}$ , respectively. The high values of the paramagnetic temperature indicate a strong geometrical frustration associated with the effect of stacking AF zig zag chains leads to a five member frustrated Mn spin loop in the  $ab$ -plane:  $\text{Mn}^{4+}-\text{Mn}^{3+}-\text{Mn}^{3+}-\text{Mn}^{4+}-\text{Mn}^{3+}$  [12]. When  $H_{\parallel c}$  the ZFC and the FC susceptibility curves are slightly different below  $T_N$ , and magnetic hysteresis is observed at 2 K. The above results seem to elucidate the presence of weak ferromagnetism effects.

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