Magnetic properties of Aurivillius lanthanide-bismuth
\((\text{LnFeO}_3)_n \text{Bi}_4 \text{Ti}_3 \text{O}_{12} (n = 1, 2)\) layered titanates

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Bismuth titanates of Aurivillius layer-structure \((\text{BiFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) are of great technological interest because of their applications as non-volatile ferroelectric memories and high-temperature piezoelectric materials. The synthesis and crystallographic characterization of a new family of compounds \((\text{LnFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) was recently reported, in which the layers consist of \(\text{LnFeO}_3\) perovskites with a lanthanide \(\text{Ln}^3+\) substituting diamagnetic \(\text{Bi}^{3+}\). We report herein the magnetic properties of bulk samples, with \(\text{Ln} = \text{Nd}, \text{Eu}, \text{Gd} \text{and Tb}\), and \(n = 1 \text{ and 2}\). Single-layer materials are paramagnetic, similar to non-substituted bismuth titanate \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\) and show crystal field effects due to the crystallographic environment of \(\text{Eu}^{3+}\) and \(\text{Tb}^{3+}\). Several anomalies are detected in the magnetization \(M(T)\) of double-layer \((\text{LnFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) compounds, related to the strong magnetism of \(\text{Tb}\) and \(\text{Gd}\), since they weakly appear for \(\text{Nd}\) and they are absent in the VanVleck \(\text{Eu}^{3+}\) ion and in the parent \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\) compound.

Keywords: multiferroic materials, superexchange interactions, lanthanide perovskites, Aurivillius structure

**Propiedades magnéticas de titanatos laminares de lantánido-bismuto, con estructura tipo Aurivillius, \((\text{LnFeO}_3)_n \text{Bi}_4 \text{Ti}_3 \text{O}_{12} (n = 1, 2)\)**

Los titanatos de hierro y bismuto con estructura laminar tipo Aurivillius, \((\text{BiFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) tienen un gran interés tecnológico debido a sus aplicaciones como memorias ferroeléctricas no volátiles y como piezoeléctrico cerámico de alta temperatura. La síntesis y la caracterización cristalina de una nueva familia de compuestos \((\text{LnFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) han sido recientemente reportadas, en la que el catión diamagnético \(\text{Bi}^{3+}\) ha sido sustituido por los paramagnéticos \(\text{Ln}^{3+}\) en los bloques de perovskita.

Se estudian las propiedades magnéticas de muestras cerámicas en volumen con \(\text{Ln} = \text{Nd}, \text{Eu}, \text{Gd} \text{y Tb}\), y \(n = 1 \text{ y 2}\). Los materiales con \(n = 1\) son paramagnéticos y similares al no sustituido \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\) y muestran efectos de campo cristalino debido al entorno cristalino de \(\text{Eu}^{3+}\) y \(\text{Tb}^{3+}\). Se han detectado algunas anomalías en la magnetización \(M(T)\) de los compuestos \(n = 2\) \((\text{LnFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) que están relacionadas con el fuerte magnetismo de \(\text{Tb}\) y \(\text{Gd}\), que aparecen débilmente para \(\text{Nd}\) y que no aparecen para el ión VanVleck \(\text{Eu}^{3+}\) ni en el compuesto pariente \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\).

Palabras clave: materiales multiferroicos, interacciones de supercancje, perovskitas con lantánidos, estructura Aurivillius.

**1. INTRODUCTION**

Bismuth layered titanates \((\text{BiFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) of the well-known Aurivillius structure are interesting materials for technological applications such as non-volatile ferroelectric memories and high-temperature piezoelectricity (1,2). Because of the presence of ferroelectric and magnetoelectrical transitions they may be considered as potential multiferroic materials in which magnetic and ferroelectric order may coexist (3-6). The magnetic and magnetoelectric properties are governed by superexchange interactions between \(\text{Fe}^{3+}\) cations and as such, it becomes interesting to modulate the number of layers, the interlayer distance and to insert other magnetic ions in order to promote intra and interlayer magnetic interactions. One way to modulate such properties is to substitute diamagnetic \(\text{Bi}^{3+}\) by a magnetic lanthanide \(\text{Ln}^{3+}\) as, for instance, heavy lanthanides of large magnetic moment or lighter elements in which crystal field effects are predominant. We have recently reported the synthesis and crystallographic characterization of such new family of compounds \((\text{LnFeO}_3)\text{Bi}_n \text{Ti}_3 \text{O}_{12}\) in which the layers consist of \(\text{LnFeO}_3\) perovskites, the number of layers being kept to \(n = 1\) and \(2\) (7). In this work, we complete their characterization, by reporting the magnetic properties for \(\text{Ln} = \text{ Tb}, \text{Eu}, \text{Gd}\) and \(\text{Nd}\).

**2. EXPERIMENTAL PROCEDURE**

The compounds were prepared by solid-state reaction from submicronic powders of the corresponding oxides. The synthesis was carried out at 1000 - 1050 °C. X-ray powder diffraction analysis of the synthesized compounds showed a crystalline structure isomorphic with that of the \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\) and \(\text{Bi}_4 \text{FeTi}_3 \text{O}_{12}\). The sintering behaviour was characterized by...
dilatometric measurements. The microstructure was observed by Scanning Electron Microscopy. All crystallochemical, structural and microstructural results are published elsewhere (7).

Magnetic properties were measured on a MPMS XL5 Quantum Design SQUID magnetometer on the range [5 K - 400 K] and, when necessary, using the furnace option up to 800 K. An applied field of 1 kOe was used to measure the magnetic susceptibility below 400 K, while 10 kOe was preferred for the high temperature measurements. Magnetization as a function of field was also performed at $T = 5$ K.

Lanthanide-free Aurivillius phases, i.e., (BiFeO$_3$)(Bi$_n$Ti$_{3n}$O$_{12n}$), $n = 1$ and 2, were also studied as “blank” samples and they allowed to isolate the effect of the magnetic rare-earths inserted in between the Bi$_n$Ti$_{3n}$O$_{12n}$ layers. Supplementary data were also obtained for ceramic samples of BiFeO$_3$.

3. RESULTS

The lanthanide-free compounds Bi$_2$FeTi$_4$O$_{15}$ and Bi$_2$Fe$_4$Ti$_3$O$_{15}$ show paramagnetic properties, in contrast with reports about an antiferromagnetic state with Néel temperatures of 80 K and 160 K, for $n = 1$ and $n = 2$, respectively (8); their high-temperature behaviour was analyzed in terms of a Pauli-type temperature-independent paramagnetic susceptibility ($\chi$) of the order of $4.5 \times 10^{-5}$ and $11 \times 10^{-5}$ emu/mol, respectively (7). Data on the starting compounds were then subtracted from the total signal of the isostructural lanthanide-containing series, thus leaving solely the effect of the lanthanide ion. This procedure was done for the single-layer (LnFeO$_3$)(Bi$_n$Ti$_{3n}$O$_{12n}$) ($Ln = Eu$ and Tb) and double-layer (LnFeO$_3$)$_2$(Bi$_n$Ti$_{3n}$O$_{12n}$)$_2$, ($Ln = Nd$, Eu, Gd and Tb).

3.1. Single layer series

The lanthanide-free compounds Bi$_2$FeTi$_4$O$_{15}$ and Bi$_2$Fe$_4$Ti$_3$O$_{15}$ show paramagnetic properties, in contrast with reports about an antiferromagnetic state with Néel temperatures of 80 K and 160 K, for $n = 1$ and $n = 2$, respectively (8); their high-temperature behaviour was analyzed in terms of a Pauli-type temperature-independent paramagnetic susceptibility ($\chi$) of the order of $4.5 \times 10^{-5}$ and $11 \times 10^{-5}$ emu/mol, respectively (7). Data on the starting compounds were then subtracted from the total signal of the isostructural lanthanide-containing series, thus leaving solely the effect of the lanthanide ion. This procedure was done for the single-layer (LnFeO$_3$)(Bi$_n$Ti$_{3n}$O$_{12n}$) ($Ln = Eu$ and Tb) and double-layer (LnFeO$_3$)$_2$(Bi$_n$Ti$_{3n}$O$_{12n}$)$_2$, ($Ln = Nd$, Eu, Gd and Tb).

$3.2. \text{Double layer series (LnFeO}_3\text{)}_2(Bi_n\text{Ti}_{3n}\text{O}_{12n}) = Ln_2Fe_2Bi_4Ti_3O_{15}$

Similar procedure was used for analysis of the double-layer compounds. Figure 3 shows the case of Ln = Nd, for which the contribution of the lanthanide-free component Bi$_2$FeTi$_4$O$_{15}$ amounts to about 50 % of the total signal. The thermal dependence of the calculated difference is zoomed in the insert, for temperatures going from 50 K up to 350 K. A weak maximum is observed, centered at approximately 250 K. This anomaly gets larger and moves toward higher temperatures for the gadolinium and terbium-based compounds and, for this reason, measurements were performed up to 800 K, as shown in figure 4 for the case of the terbium compound Tb$_2$Fe$_2$Bi$_4$Ti$_3$O$_{15}$. The magnetic character of this anomaly is quite evident, since it is much stronger for highly magnetic ions (g(Gd$^{3+}$) = 7 $\mu_B$, g(Tb$^{3+}$) = 9 $\mu_B$), it weakens for Nd (g(Nd$^{3+}$) = 3.27 $\mu_B$) and disappears for the VanVleck Eu$^{3+}$ ion (not shown). We exclude the possibility of a phenomenon related to the magnetic behaviour of the Eu ion, is also plotted at the bottom of figure 1. The reciprocal value $1/\chi_{diff}$ of their difference (insert) yields an effective moment of about 5.35 $\mu_B$, which we attribute to the admixture between the $T_2^+$ and the $T_2$ multiplets of the VanVleck Eu$^{3+}$ ion.

The magnetization ZFC/FC cycle (at 50 Oe) for TbFeBi$_4$Ti$_3$O$_{15}$ is shown in figure 2, together with the inverse susceptibility (at 1 kOe) before and after subtraction of the Bi$_2$FeTi$_4$O$_{15}$ contribution (insert). The effective moment (9.79 ± 0.05 $\mu_B$) is very close to the expected value for non-interacting Tb$^{3+}$ ions (9.72 $\mu_B$). No magnetic interactions Fe-Fe, Fe-Tb or Tb-Tb were then observed, as confirmed by the low Curie-Weiss temperature $\Theta = -6 \pm 0.5$ K. On the other hand, the “saturation” moment for Tb (5.5 $\mu_B$ at 50 kOe and 5 K; not shown), much lower than the expected value g(Tb$^{3+}$) = 9 $\mu_B$, indicates that crystal field effects are quite important at low temperatures.
related to the presence of iron oxide impurities (anomaly at about 750 K) or unreacted BiFeO$_3$ ($T_N = 640$ K).

The rapid increase of the magnetization below the anomaly was analyzed for Ln = Gd and Tb in terms of a Curie-Weiss law $\chi = C / (T-\Theta)$ in the range (100 K $\leq T \leq$ 180 K). In both cases, the curves can be fitted by independent paramagnetic Ln$^{3+}$ ions with large ferromagnetic exchange interactions, (i.e., $\Theta > 0$). For (GdFeO$_3$)$_{18}$, the Curie-Weiss equation was $\chi = 15.62 / (T-77.6)$, which corresponds to 2 Gd ions per formula unit, of 7.90 $\mu_B$. For the case of (TbFeO$_3$)$_{18}$, the corresponding results were $\chi = 24.32 / (T-80.6)$, due to 2 Tb ions of 9.86 $\mu_B$/Tb-at, compared to an expected moment of 9.72 $\mu_B$. These quite reasonable fits prompted us to subtract their contribution from the total magnetization. Figure 5 shows the experimental results before and after the subtraction of the contribution by independent Ln$^{3+}$ ions. The broad anomaly centred at about 350 K could be reminiscent of the antiferromagnetic behaviour of the ferroic BiFeO$_3$ compound, which is a typical example of a spatially modulated antiferromagnetic spin structure with zero remanent magnetization (10-12). This means in our case that Fe$^{3+}$-Fe$^{3+}$ interactions within the perovskite layers are extremely important but, at low temperatures, iron ions are coupled into a frustrated state of low remanent magnetization, just leaving the contribution of the lanthanide moment. In the absence of other examples of this series we must, however, be extremely cautious about these conclusions, especially if no such behaviour was observed in the single-layer family. More experiments (e.g., neutron diffraction) are necessary to confirm these asserts.

The frustrated state of the iron ions is confirmed by the magnetization curves as a function of field, measured at 5 K for all double-layer compounds (fig. 6). With the exception of Ln = Tb, for which a very slight irreversibility was observed at low field, all other samples showed fully reversible magnetization cycles, excluding long-range ferromagnetic order at these temperatures. If present, the effect of magnetic impurities is negligible in front of the large intrinsic moments of the lanthanide sublattice, and can be discarded in the present analysis.
4. CONCLUSIONS

Magnetic properties of the lanthanide-bismuth \((\text{LnFeO}_3)_2\text{Bi}_4\text{Ti}_3\text{O}_{12}\) materials strongly depend on the number \(n\) of the perovskite layers inserted in the \(\text{Bi}_4\text{Ti}_3\text{O}_{12}\) structure. For single-layer compounds, a paramagnetic behaviour is observed, similar to the lanthanide-free iron-bismuth Aurivillius phase. The effective moment obtained in the case of \(\text{LnFeBi}_4\text{Ti}_3\text{O}_{15}\), once the contribution of the matrix has been subtracted, corresponds to the expected value for independent non-interacting \(\text{Tb}^{3+}\) and VanVleck \(\text{Eu}^{3+}\) ions. For double-layer materials, a broad anomaly appears at high temperature, which depends on the magnetic nature of the \(\text{Ln}\) element (quite large for strongly magnetic \(\text{Gd}\) and \(\text{Tb}\) ions; weak anomaly for \(\text{Nd}^{3+}\) and negligible for \(\text{Eu}^{3+}\) moments). The origin of such anomaly, which seems related to a frustrated state of the iron ions with low remanent magnetization at low temperature, should be confirmed by other techniques, e.g. neutron diffraction, single crystals experiments, etc.

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