Magnetic and ferroelectric response of Ca$_2$TiMnO$_6$ manganite-like perovskite

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The synthesis and characterization of the new manganite-like material Ca$_2$TiMnO$_6$ are reported. The samples were produced by the solid-state reaction recipe. X-ray diffraction experiments and Rietveld refinement reveal that material crystallizes in a tetragonal complex perovskite (space group 14/m, number 87) with lattice parameters $a=5.5858$ Å and $c=7.7518$ Å. The magnetic properties were studied by a Quantum Design MPMS SQUID. From measurements of magnetization as a function of temperature, we determine the occurrence of a paramagnetic-antiferromagnetic transition with Néel temperature $T_N=15.5$ K. A Curie-Weiss fitting permitted to obtain the magnetic characteristic parameters. Curves of magnetization as a function of applied field show the magnetic hysteresis which is characteristic of magnetically ordered systems. Curves of electric polarization, including the application of voltages up to 560 V, evidence the ferroelectric character of material at room temperature.

Keywords: New materials; complex perovskite; multiferroic.

Se reporta la síntesis y caracterización del nuevo material tipo manganita Ca$_2$TiMnO$_6$. Las muestras fueron producidas siguiendo los procedimientos usualmente utilizados para reacciones en estado sólido. Los análisis por difracción de rayos X y refinamiento Rietveld revelan una cristalización tetragonal de perovskita compleja del material (grupo espacial 14/m, número 87), con parámetros de red $a=5.5858$ Å y $c=7.7518$ Å. Las propiedades magnéticas se estudiaron mediante un MPMS SQUID Quantum Design. A partir de las medidas de magnetización en función de la temperatura, se determinó la presencia una transición paramagnética-antiferromagnética con temperatura de Néel $T_N=15.5$ K. A partir de la aproximación de Curie-Weiss se obtuvieron los parámetros magnéticos característicos del material. Las curvas de magnetización en función del campo aplicado muestran la histéresis magnética característica de los sistemas magnéticamente ordenados. De las curvas de polarización eléctrica, con voltajes de hasta 560 V, se evidencia el carácter ferroeléctrico del material a temperatura ambiente.

Descriptores: Nuevo material; perovskita compleja; multiferróico.

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1. Introduction

Perovskites usually behave as good electrical and thermal insulators at room temperature due to the absence of conduction electrons, have high melting temperatures and show different electrical and magnetic properties. These properties are due to structural distortions and substitutions with magnetic transition elements [1].

The physical properties of perovskite oxides, particularly the magnetic and magneto-resistive [2], have been used for a variety of technological applications since they can retain information in its crystalline structure without being connected to a power source. The information is stored by the electric polarization that can possess these materials [3].

In this work we report the synthesis and characterization of one new perovskite-like material Ca$_2$TiMnO$_6$, made by the standard method of solid-state reaction from the reaction of precursor oxides. The precursor oxides were mixed in stoichiometric ratios in accordance with the nominal composition Ca$_2$TiMnO$_6$. The material was structurally analyzed, and its magnetic behavior was evaluated by measurements of magnetization as a function of applied magnetic field and the electrical response measured through polarization curves.

2. Experimental

The production of Ca$_2$TiMnO$_6$ double-perovskite samples was performed by standard solid state reaction of precursor oxides CaCO$_3$, TiO$_2$, MnO$_2$. The precursor oxides were weighed in stoichiometric amounts. Before weighing, the precursor materials were subjected to a pre-drying process to eliminate the presence of moisture. Once weighed, the precursor materials were mixed and ground in an agate mortar, then are compacted into an double effect matrix with 382.2 GPa of pressure. Thus was obtained cylindrical samples 7 mm in diameter and 5 mm high. The samples were subjected to the process of calcination and sintering at 1200°C for 24 hours. The diffractograms were obtained using a PANalytical’s X’Pert diffractometer with $\lambda=1.54064$ Å of Cu, cooper line and subsequent analysis by Rietveld refinement code GSAS [4]. Magnetic measurements were made
with a model 2000 Magnetic Properties Measurement System (MPMS) manufactured by Quantum Design with Superconducting Quantum Interference Device (SQUID) technology. Were performed Zero field cooling (ZFC) and field cooling (FC) measurements of AC susceptibility for frequencies of 1 and 5 kHz and temperatures between 8 and 126 K. Were also carried out measurements of magnetic hysteresis.

The electrical characterization was performed by polarization curves as a function of applied voltage at room temperature. The curves were taken with a precision equipment tester with at voltages between 100 to 560 V at frequencies of 1 and 2 Hz.

3. Results and discussion

Structural analysis of the sample was made through the technique of Rietveld refinement using the GSAS program. Then by comparing the theoretical and experimental patterns was observed that the diffractograms were slightly out of date with each other, because of that the parameters were adjusted manually until the best correlation through the program PCW23 (Fig. 1), which is essential to start a refinement by the Rietveld method.

The refining process allowed to identify the Ca$_2$TiMnO$_6$ sample as a perovskite that crystallizes with a tetragonal structure in the space group I/4m, number 87, and lattice parameters $a=5.29934$ Å and $c=7.71512$ Å.

The magnetic properties studied from measurements of magnetization as a function of temperature, allowed to infer the occurrence of a paramagnetic-antiferromagnetic transition with a Néel temperature of 15.5 K, as shown in Fig. 2. The behavior obtained for the frequency of 5 kHz is similar what it is shown in Fig. 2.

In the temperature regime below the Néel temperature are a separation between the ZFC and FC measurements, which are is attributed to the cationic disorder of Ti$^{4+}$ and Mn$^{4+}$ ions along the temperature, and Curie-Weiss fit for $T>40$ K.

The curve of magnetization as a function of applied field at temperature $T<T_N$ in Fig. 4, shows the characteristic of magnetic hysteresis of Ca$_2$TiMnO$_6$.

\[
\begin{align*}
\chi'_{\infty} &= 1.83 \times 10^{5}\text{Ti}(\text{Amplitude}) \\
\nu &= 1\text{ KHz} \\
\chi_0 &= 6.7 \times 10^{-4}\text{emu/mol} \\
\mu &= 3.2\mu_B \\
T_N &= 15.3\text{K}
\end{align*}
\]

Figure 2. AC molar susceptibility measurements at 1 kHz depending on the temperature, and Curie-Weiss fit for $T>40$ K.

Figure 3. Inverse of the susceptibility as a function of temperature that evidences an antiferromagnetic behavior with Néel temperature close to 15.3 K.

Figure 1. Diffractogram of Ca$_2$TiMnO$_6$ and results of the Rietveld-like refinement.

Figure 4. Magnetization measurements as a function of applied field at T= 4 K.

Figure 5. Electric polarization measurements for the Ca$_2$TiMnO$_6$ manganite-like material at room temperature and 1 Hz of frequency as a voltage function.

This curve confirms the existence of magnetization saturation of $3.3 \times 10^{-2}$ emu/cm$^3$, a remnant magnetization of about $1.7 \times 10^{-2}$ emu/cm$^3$ and a coercive field of 2 kG. However, it is expected that close to $T=0$, the existence of antiferromagnetic ordering decreases the hysteretic magnetization response.

Measurements of polarization curves as a function of applied voltage at a frequency of 1 Hz (Fig. 5), in a capacitive configuration for the material, show an electrical hysteresis loop. The same behavior was observed for the frequency of 2 Hz. The hysteresis loop obtained in the polarization curves reveals the existence of a ferroelectric behavior at temperatures above 300 K. This result, together with the behavior of the material at temperatures below the Néel temperature, in Fig. 2, and those showed by the magnetic hysteresis loop (Fig. 4), confirm the multiferroic behavior of the system Ca$_2$TiMnO$_6$ at temperatures below $T_N= 15.3$ K. This behavior is similar to that reported for the manganite Sr$_2$TiMnO$_6$ [6].

4. Conclusions

The new perovskite-like Ca$_2$TiMnO$_6$ was synthesized through the solid state reaction technique. This material presents a perovskite-like structure which corresponds to space group I4/m, number 87. Magnetization measurements allowed determining a Néel temperature of 15.5 K at which the paramagnetic-antiferromagnetic transition is presented. Measurements of electric polarization, as a function of applied electric field, reveal the relaxor ferroelectric characteristic of this new complex perovskite. The behavior of the material in the presence of magnetic and electric fields allowed classifying it as a material with multiferroic properties.

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