Structural and Magnetoelectric studies on new Sr$_2$TiMoO$_6$ material

C.E. Alarcón, D. A. Landínez Téllez, and J. Roa-Rojas

Grupo de Física de Nuevos Materiales, Departamento de Física,
Universidad Nacional de Colombia, Bogotá DC, Colombia,
e-mail: jroar@unal.edu.co

Recibido el 25 de junio de 2010; aceptado el 14 de octubre de 2010

A study of the crystallographic structure and magnetic properties of the double perovskite Sr$_2$TiMoO$_6$ in polycrystalline form has been carried out by means of X-Ray diffraction and magnetization measurements. The Rietveld analysis of room temperature data shows that the structure is ordered double perovskite with space group I-1 (n=5) the lattice parameters are $a=5.5236$ Å, $b=5.5224$ Å and $c=7.8058$ Å using GSAS code. DC susceptibility measurements show the occurrence of antiferromagnetic ordering for a Néel temperature $T_N=20.1$ K using the Curie-Weiss fitting and the value for effective magnetic moment was 1.3 $\mu_B$. Ferroelectric response of material was established from curves of polarization as a function of applied electric field and the results reveal that Sr$_2$TiMoO$_6$ double perovskite evidences a ferroelectric hysteretic behavior at ambient temperature.

Keywords: Complex perovskite; new material; magnetic properties.

1. Introduction

The ceramic materials represent a great percentage of systems which are actually investigated by the physics and chemistry of solids. Particularly, the perovskite family has concentrated important attention in last decades. From the point of view of chemical composition, perovskites are characterized by the ideal formula ABO$_3$, where A generally is an alkaline earth element, B represents a transition metal element and X, is usually oxygen. Modifications of atomic radii of A and B, introduces structural distortions and new crystalline phases. Inclusions of rare earth elements instead the alkaline earth in the A site, and magnetic elements in the B site, give the possibility to produce materials with exotic electric and magnetic properties [1,2]. When B cation is 50% substituted, the A$_2$BB’O$_6$ complex perovskite is created. It chemical configuration supplies multiple chances to combine different elements of periodic table, generating the possibility to synthesize new materials, which involve a more large gamma of physical properties. Sometimes, it is possible to combine diverse properties in a same material, as the case of multiferroic perovskites, which evidence the coexistence of ferromagnetic and ferroelectric ordering [3]. These combinations of properties have stimulated the research on ferromagnetic perovskite-like oxides. Recently interest in this type of compounds was revived because these exhibit interesting properties like intrinsic tunneling-type magnetoresistance (TMR) at room temperature [4], showing evidence of electronic and ionic conductivity, which are relevant for applications as anodes or cathodes in solid-oxide fuel cells [5], half-metallic systems [6] and making them promising candidates for future spintronics and magnetoelectronic devices. These properties are strongly dependent of the B and B’ cations in the A$_2$BB’O$_6$ structure. For example, depending on the cation composition the antiferromagnetism at low temperature can change [7].

In order to explore the magnetoelectric properties of the new system Sr$_2$TiMoO$_6$, in this paper we have described the synthesis of this material prepared by solid state reaction procedures, and the characterization by X-Ray diffraction (XRD), scanning electron microscopy and the magnetic response from magnetization measurements.

2. Experimental

The samples were produced by the solid state reaction method. The precursor powders SrCO$_3$, TiO$_2$ and MoO$_3$ (Aldrich 99.9%) were mixed in stoichiometric proportions according to the chemical formula Sr$_2$TiMoO$_6$. The structural characterization was performed through X-ray diffraction (XRD) experiments by using a PanAlytical X’Pert PRO-MPD equipment with $\lambda=1.5406$ Å radiation in the 2θ range from 5° up to 90°. XRD patterns reveal the presence of peaks, which are characteristics of the complex perovskite systems. A Rietveld refinement of diffraction pattern was made by the GSAS code [8].
The morphology was studied by scanning electron microscopy (SEM) and composition was analyzed using the energy dispersive X-ray (EDX) technique in a FEI Quanta 200 Model high vacuum mode equipment.

Electric polarization curves were measured by means of a radiant ferroelectric tester, which include a 10 kV source for experiments in bulk samples. Measurements of DC susceptibility as a function of temperature were carried out by using an MPMS Quantum Design SQUID.

### 3. Results and discussion

The analysis of XRD pattern showed in Fig. 1 reveals the presence of characteristic peaks of complex perovskite systems. In Fig. 1, crosses represent the experimental data and lines correspond to simulated pattern by means of GSAS code. Rietveld refinement permitted to establish that this material crystallizes in a tetragonal double perovskite with space group I-1 (#5) and lattice parameters $a=5.5236$ Å and $c=7.8058$ Å. The atomic positions in the structure are shown in Table I.

The calculated profiles gave reasonably good fits as can be seen from Fig. 1. The R values as well as the goodness of fit ($\chi^2 = 0.9927$) are quite satisfactory. The Fig. 2 shows SEM images of sample. The analysis shows a high yield of a unique mesostructure like rectangular parallelepiped and this tends to form an octagonal geometry. Grains sizes are between 4.0 $\mu$m and 10 $\mu$m. From EDX analyses we determine that the sample only contain chemical elements of $\text{Sr}_2\text{TiMoO}_6$, moreover the semi-quantitative analyses of the spectrum intensities show a 92% of agreement between nominal and experimental values. From the experimental values the stoichiometry calculated is $\text{Sr}_2.1\text{TiMo}_{1.3}\text{O}_{6.3}$ and can be approximated to the standard $\text{Sr}_2\text{TiMoO}_6$ formula.

![Figure 1. Rietveld refinement pattern for $\text{Sr}_2\text{TiMoO}_6$. Continuous line represents the theoretical diffractogram obtained from Rietveld refinement, crosses correspond to the experimental data and the bottom curve represents the difference between experimental and theoretical patterns.](image1)

![Figure 2. SEM Micrography for $\text{Sr}_2\text{TiMoO}_6$.](image2)

![Figure 3. Energy dispersive X-ray spectrum obtained for $\text{Sr}_2\text{TiMoO}_6$ perovskite-like material.](image3)

![Figure 4. Ferroelectric response in a curve of polarization as a function of the electric field. Hysteresis loops of the material in a capacitor configuration, under several applied voltages, which reveal the characteristic ferroelectric](image4)
Figure 4. Hysteretic ferroelectric feature of polarization as a function of applied electric fields for the Sr$_2$TiMoO$_6$ perovskite material.

Figure 5. Magnetic behavior obtained from measurements of magnetization as a function of temperature for Sr$_2$TiMoO$_6$. In the inset the inverse of susceptibility reveal the antiferromagnetic character of material.

response of Sr$_2$TiMoO$_6$. In this case for a maximum voltage applied of 2000 V, ferroelectric saturation is observed for an electric field of 15.359 kV/cm, which corresponds to a polarization of 0.073 µC/cm$^2$, in a curve with 0.026 µC/cm$^2$ remnant polarization and 4.523 kV/cm coercive field.

Figure 4 shows the temperature dependence of the DC magnetization as a function of temperature for STMO when measured by using the field cooling recipe. In the picture the fitting from the Curie-Weiss law $\chi = \chi_0 + C/(T + T_N)$ for temperature in the range of 25 K<T<150 K is shown.

The inset of Fig. 5 exemplifies the methodology used to determine the Néel temperature which characterizes the antiferromagnetic behavior of material. The results obtained reveal that Sr$_2$TiMoO$_6$ behaves as an antiferromagnetic material below a Néel temperature $T_N = 20.1K$. From the Curie-Weiss adjust we determine the temperature independent susceptibility $\chi_0$=0.0038 emu/mol and the effective magnetic moment $\mu = P_{eff} \mu_B$=1.3$\mu_B$. This value is in agreement with experimental studies in pyrochlore systems which reveal that the isolated ion Mo$^{4+}$ contributes to the effective magnetic moment of material with 1.33$\mu_B$ [9].

4. Conclusions

The synthesis and structural characterization of new Sr$_2$TiMoO$_6$ manganite-like material is reported. Rietveld analyses reveal that this material crystallizes in a tetragonal complex perovskite which corresponds to I-1 (#5) space group. Measurements of magnetic susceptibility showed an antiferromagnetic ordering transition for a $T_N = 20.1K$, which was fitted by Curie-Weiss equation. From the fitting we obtained the cell magnetic moment $\mu$=1.3 $\mu_B$, which is in agreement with the expected value for the isolated cation Mo$^{4+}$. The ferroelectric behavior of system was examined from polarization hysteretic curves. Our results permit to infer that is possible produce multiferroic complex perovskites from the mixture of the ferroelectric SrTiO$_3$ and ferromagnetic SrMoO$_3$ simple perovskites.

Acknowledgements

This work was partially supported by DIB (Universidad Nacional de Colombia, Sede Bogotá) and CENM, contract 043-2005. Authors wish to thank Prof. Luis Ghivelder from IF-UFRJ for the susceptibility measurements.