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Structural evolution of the double perovskites $Sr_2B'UO_6$ (B′ = Mn, Fe, Co, Ni, Zn) upon reduction: Magnetic behavior of the uranium cations

R.M. Pinacca [a,*], M.C. Viola [a], J.C. Pedregosa [a], R.E. Carbonio [b], M.J. Martínez Lope [c], J.A. Alonso [c]

[a] *Área de Química General e Inorgánica "Dr. Gabino F. Puelles", Departamento de Química, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, Chacabuco y Pedernera, 5700 San Luis, Argentina*

[b] *INFIQC (CONICET), Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, X5000HUA Córdoba, Argentina*

[c] *Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco, 28049 Madrid, Spain*

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ABSTRACT

We describe the preparation of five perovskite oxides obtained upon reduction of $Sr_2B'UO_6$ (B′ = Mn, Fe, Co, Ni, Zn) with H_2/N_2 (5%/95%) at 900 °C during 8 h, and their structural characterization by X-ray powder diffraction (XRPD). During the reduction process there is a partial segregation of the elemental metal when B′ = Co, Ni, Fe, and the corresponding B′O oxide when B′ = Mn, Zn. Whereas the parent, oxygen stoichiometric double perovskites $Sr_2B'UO_6$ are long-range ordered concerning B′ and U cations. The crystal structures of the reduced phases, $SrB'_{0.5-x}U_{0.5+x}O_3$ with $0.37 < x < 0.27$, correspond to simple, disordered perovskites; they are orthorhombic, space group Pnma (No. 62), with a full cationic disorder at the B site. Magnetic measurements performed on the phase with B′ = Zn, indicate uncompensated antiferromagnetic ordering of the U^{5+}/U^{4+} sublattice below 30 K.

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1. Introduction

The so-called double perovskite $A_2B'B''O_6$ oxides contain two suitable B′ and B″ cations at the octahedral positions. Double perovskites may present different kind of cationic ordering at the octahedral sites as it has been reviewed by Anderson et al. [1]. The most common ordering is a rock-salt arrangement of the $B'O_6$ and $B''O_6$ octahedra in a perfectly alternated disposition along the three directions of the crystal. Double-perovskite oxides have attracted great interest in recent years, mainly due to their important physical properties, such as superconductivity [2,3], dielectricity [4,5] or magnetoresistivity [6–8].

The reduction of stoichiometric phases into novel oxygen hypo-stoichiometric oxides is a powerful tool for the development of new materials with novel magnetic or transport properties. Moreover, the stabilization of transition-metal perovskites with an adequate concentration of oxygen vacancies under reducing atmosphere can also be applied in new mixed electronic-ionic conductors for energy-conversion devices such as solid oxide fuel cells, oxygen separation membranes or solid oxide electrolyzers. For instance, Viola et al. [9] showed that the topotactic reduction of the stoichiometric Sr_2CoMoO_6 double perovskite leads to an oxygen hypo-stoichiometric perovskite $Sr_2CoMoO_{6-\delta}$ with ferromagnetic order above room-temperature and induced magnetoresistance. Furthermore, this oxide has also recently been proposed as anode material for SOFC evidencing a high performance even with wet CH_4 as a fuel [10].

Whereas the chemical reduction of $A_2B'B''O_6$ double perovskites with B″ = Mo, W has been investigated, this process has not been explored for uranium-containing $A_2B'UO_6$ phases. We have recently prepared and studied the structural and magnetic properties of oxygen-stoichiometric double perovskites $Sr_2B'UO_6$ with B′ = Mn, Fe, Co, Ni, Zn. The crystal structure is monoclinic (space group $P2_1/n$), as shown from XRPD data and NPD for the phase with B′ = Co. The B′–O distances obtained in the structural study suggest the presence of a partial disproportionation of the type $B'^{2+} + U^{6+} \Leftrightarrow B'^{3+} + U^{5+}$ for Fe, Mn and Ni cations [11,12].

As a natural continuation of our previous work, we found it interesting to investigate the conditions for the possible formation of reduced $Sr_2B'UO_6$ phases, by reduction with H_2/N_2 (5%/95%). We obtained and characterized disordered perovskites $SrB'_{0.5-x}U_{0.5+x}O_3$ with $0.37 < x < 0.27$. In this paper we report on the results of a XRPD study for these phases; the impact of the temperature control on the reduction process is analyzed. The optimum conditions for the synthesis of a well crystallized phase with a maximum amount of $SrB'_{0.5-x}U_{0.5+x}O_3$ perovskite were established; the macroscopic magnetic measurements for the phase with B′ = Zn with U^{5+}/U^{4+}

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* Corresponding author. Fax: +54 2652430224.
E-mail address: rmp@unsl.edu.ar (R.M. Pinacca).

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as unique and responsible of the magnetic behavior are presented and discussed.

2. Experimental

The $Sr_2B'UO_6$ double perovskites with B′ = Mn, Fe, Co, Ni, Zn were obtained as well-crystallized powders by the standard ceramic method [11]. Stoichiometric amounts of analytical grade $SrCO_3$, $B'CO_3$ and $UO_2(CH_3COO)_2$ were mixed, ground, placed in a platinum crucible and treated at 600 °C in air for 12 h and the resulting powder was reground and calcined at 900 °C for 12 h. Finally the product was fired at 1150 °C in air in four periods totaling 24 h with intermediate milling of the reaction mixture. For the $Sr_2B'UO_6$ phases with B = Mn and Fe the citrate-precursor method was used. The corresponding carbonates/acetates were dissolved in citric acid with formation of a resin which was decomposed at 700 °C in air. The precursor powders underwent a subsequent heating at 800 °C in air. Finally, the products were fired at 950 °C during 6 h in reducing atmosphere (1% H_2/99% Ar) in order to stabilize the Fe^{2+} and Mn^{2+} cations.

The initial identification and characterization of the final products was carried out by X-ray powder diffraction (XRPD) recorded at room temperature in a Rigaku D-MAX-IIIC diffractometer with Cu Kα ($\lambda = 1.5406$ Å) radiation. For the structural refinements the data were collected in 2θ steps of 0.02° and 5 s counting time in the range $10° \leq 2\theta \leq 120°$. The refinement of the crystal structures was performed by the Rietveld method [13] with the program Fullprof [14]. The peak profiles were modeled by a pseudo-Voigt function. The following parameters were refined in the final run: scale factors, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, and isotropic thermal factors.

Thermal programmed reduction (TPR) curves were recorded in a Quanta Chrome Corp., model Chembet-3000 TPD/TPR device. The data were obtained between 25 and 1000 °C with a heating rate of 10 °C/min under a H_2/N_2 (5%/95%) flux of 20 mL/min.

The magnetic measurements were performed in a commercial superconducting quantum interference device magnetometer (SQUID) from Quantum Design. The magnetic susceptibility data were collected in the $4 < T < 400$ K range under an applied magnetic field of 0.1 T. Isothermal magnetization curves were obtained with magnetic fields up to 5 T at $T = 5$ K.

The FTIR spectra for Sr_2CoUO_6 and $SrCo_{0.5-x}U_{0.5+x}O_3$ with $x = 0.288(4)$ were recorded between 1000 and 350 cm^{-1} with a Nicolet-Magna 550 FTIR spectrometer, using the KBr pellet technique. In the investigated spectral range, the resolution was ±4 cm^{-1}.

3. Results and discussion

3.1. Sample preparation

These oxygen-stoichiometric $Sr_2B'UO_6$ perovskites (B′ = Fe, Mn, Co, Ni, Zn) were prepared as black (B′ = Fe, Mn, Co, Ni) or yellow (B′ = Zn) polycrystalline powders. In order to determine the optimum conditions for the preparation of well-crystallized reduced $Sr_2B'UO_6$ phases, a previous experiment was carried out with Sr_2CoUO_6. Fig. 1 shows the XRPD of the oxygen-stoichiometric phase at 25 °C and of the reduction products at different temperature. Fig. 2 displays the thermal programmed reduction (TPR) diagram of Sr_2CoUO_6. A wide band with center on 500–550 °C, a strong peak on 800–850 °C, and a weak peak at 400 °C that seems to be caused by impurities are observed. This indicates the existence of reduction processes above 500 °C for the main phase. Therefore, the oxygen-stoichiometric Sr_2CoUO_6 was treated by reduction in an H_2/N_2 (5%/95%) flow at 500, 550, 700, 800, 900 and 1000 °C for 10 h. Thermal treatments longer than 10 h did not produce changes in the obtained samples, suggesting that the reduction products reach equilibrium with the atmosphere after this treatment time.

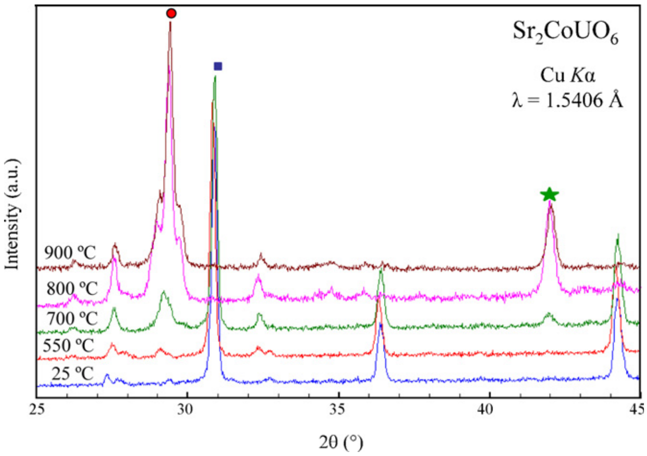

Fig. 1. XRPD for reduced Sr_2CoUO_6 taken at different temperatures of reduction with H_2/N_2 (5%/95%). The square represents the main reflection of ordered double perovskite $Sr_2B'UO_6$. The circle represents the main reflection of disordered simple perovskite $SrCo_{0.5+x}U_{0.5-x}O_3$. The star represents the main reflection of cobalt metal.

At 500 °C the reduction process did not occurs, but when the temperature is higher than 550 °C a new orthorhombic phase isostructural to $GdFeO_3$ [15] starts to appear (Fig. 1), with a chemical formula $SrCo_{0.5-x}U_{0.5+x}O_3$, as it will be described in the structural refinement Section 3.2. Upon the reduction process a Co^0 impurity appears (indicated with a star in the XRPD pattern); this fact is in agreement with the decrease of the Co content in the perovskite formula. There is a progressive decrease of the oxygen-stoichiometric Sr_2CoUO_6 double perovskite phase and an increment of the new disordered phase $SrB_{0.5-x}U_{0.5+x}O_3$, together with increasing amounts of elemental cobalt, as temperature rises. At 900 °C the quantity of the new perovskite phase is the biggest. The evolution of the initial stoichiometry Sr_2CoUO_6 along the solid solution $SrB_{0.5-x}U_{0.5+x}O_3$ with segregation of Co^0 implies the reduction of U^{6+} to U^{5+}/U^{4+}, since Co cannot adopt an oxidation state lower than 2+ within the perovskite structure.

The reduction of U^{6+} to U^{5+}/U^{4+} is also supported from infrared spectroscopy data: Fig. 3 shows the FTIR spectrum of the parent double perovskite and the reduced simple perovskite; the band assigned to the U–O antisymmetric stretching (ν_3) of the UO_6 octahedra of the reduced phase appears shifted to lower frequency

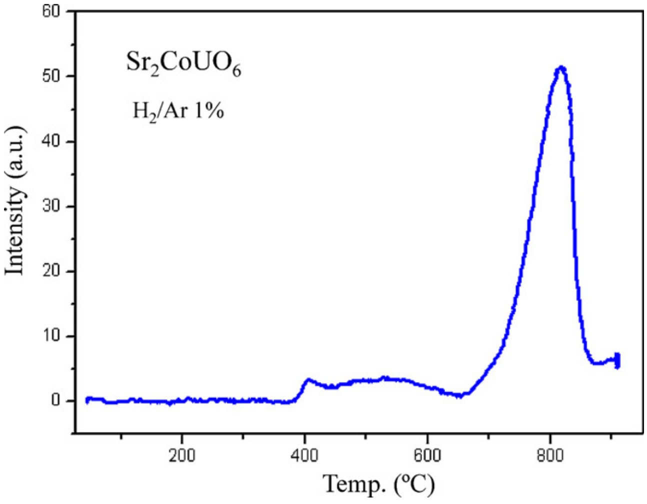

Fig. 2. TPR for double perovskite Sr_2CoUO_6.

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