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Synthesis, structural and magnetic characterisation of the double perovskite A_2MnMoO_6 (A = Ba, Sr)

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Abstract

A study of the crystallographic structure and magnetic properties of the double perovskites Ba₂MnMoO₆ and Sr₂MnMoO₆ in polycrystalline form has been carried out by means of neutron powder diffraction (NPD) and magnetization measurements. The Rietveld analysis of room temperature data shows that the Mn²⁺ and Mo⁶⁺ ions are B-site ordered, i.e. the structure is a NaCl-type ordered double perovskite. Ba₂MnMoO₆ crystallizes in the cubic space group $Fm\overline{3}m$ (a = 8.1680(1)) and Sr₂MnMoO₆ crystallizes in the space group $P4_2/n$ (a = 7.9575(5), c = 7.9583(9)). Bond valence sum (BVS) calculation revealed that these compounds have the valency pair of {Mn²⁺(3d⁵;t³_{2g}e²_g), Mo⁶⁺(4d⁰)}. The magnetic measurements suggest that these compounds transform to an antiferromagnetic state below 10 K. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

The double perovskites $A_2BB'O_6$ host two different B-site cations, which tend to order in a NaCl-type superlattice structure, doubling the elementary perovskite cell [1]. Compounds where A is an alkaline earth cation and B = Cr, Fe; B' = Mo, W, Re, are ferromagnetic [2–6]. Interest in this type of compound was revived in a recent report by Kobayashi et al. that Sr₂FeMoO₆ is a colossal magnetoresistance (CMR)-type half-metallic ferromagnet [2] with a Curie temperature of ~415 K, significantly higher than for any mixed-valence manganite. This interest has also been driven by the possible technological applications of these materials in magnetoelectronic devices, stimulating the search for new CMR compounds. Recently, similar CMR properties were described for other double perovskites which exhibit half-metallic ferromagnetism with a high spin polarization

* Corresponding author. Present address: The Studsvik Neutron Research Laboratory, Uppsala University, SE-611 82 Nyköping, Sweden. Tel.: +46-155-221-871; fax: +46-155-263-001. at the Fermi level, making them promising candidates for future spin electronics. These findings have stimulated research on other double perovskites. Antiferromagnetism at low temperature is also very common in these types of compounds depending on the cation composition [7,8]. The ideal double perovskite structures can be viewed as a regular arrangement of corner-sharing BO₆ and B'O₆ octahedra alternating along the three directions of the crystal, with the large A cations occupying the voids in between the octahedra. Depending on the relative size of the B and B' cations with respect to the A cations, the crystal structure can be defined as cubic ($Fm\bar{3}m$), tetragonal (I4/m) or monoclinic ($P2_1/n$) [8,9].

In the present work we have given our attention to the Mn analogues of Ba₂FeMoO₆ and Sr₂FeMoO₆. The double perovskite Sr₂MnMoO₆ was first studied in the 1960s and described as cubic with a = 7.98 Å [10]. Recently, the compound was reported as cubic, a = 7.9973(1)Å and antiferromagnetic, $T_N = 12$ K [11]; and monoclinic, a = 5.6671(1), b = 5.6537(1), c = 7.9969(2) Å, $\beta = 89.92(2)^{\circ}$ and antiferromagnetic, $T_N = 15$ K [12]. A solid solution of Mn and Mo at the B-site gives a ma-

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terial of the type BaMn_{0.5}Mo_{0.5}O₃ showing a hexagonal structure with a = 11.238 and c = 15.758 Å, and a diffuse ferroelectric behavior [13]. To our knowledge no structural characterization has previously been done for ordered Ba₂MnMoO₆.

In the present study we have described the synthesis of these materials, prepared by solid state reaction procedures, and the results of high-resolution neutron powder diffraction (NPD) studies on well-crystallized samples. We have reported complete structural data for these materials and described the magnetic properties from the magnetization measurements.

2. Experimental details

2.1. Sample preparation

The Ba₂MnMoO₆ and Sr₂MnMoO₆ compounds were prepared as polycrystalline powders by the solid state reaction technique. Stoichiometric amounts of analytical grade BaCO₃ or SrCO₃, MnO and MoO₃ were mixed together by ethanol. The finely mixed powders were pre-sintered in a furnace for 15 h at 950 °C. The powders were mixed in an agate mortar again and pressed into small discs and heated up to 1200 °C for 48 h. The sample was again reground and heated at 1350 °C for 48 h and finally at 1400 °C for 48 h. All heat treatments were conducted under nitrogen environment.

2.2. X-ray diffraction, neutron diffraction and Rietveld analysis

X-ray powder diffraction measurements of the samples were carried out to check the quality and phase distribution of the samples using a Guinier Camera (Cu K α_1 radiation) at the KEMLAB of Studsvik Neutron Research Laboratory, Sweden. Silicon (NBS 640b) was used as an internal standard and a computerized line scanner for evaluation of the film. Indexing and refinement of the lattice parameters were made using TREOR90 [14] and Checkcell [15] software, respectively. Neutron diffraction data were collected at the NPD instrument at the R2 reactor, Sweden. The double monochromator system consists of two copper crystals aligned in (220) mode giving a wavelength of 1.470 Å. The neutron flux at the sample position was $\sim 10^6$ neutron $cm^{-2} s^{-1}$. The step scan covered the 2θ range 4° -139.92 ° with a step size 0.08° . NPD data sets were refined by the Rietveld method using FullProf software [16] including the coherent scattering length supplied by the software. Diffraction peak shapes were quantified by a pseudo-Voigt function, with a peak asymmetry correction applied at angles below 45° in 2θ . Background intensities were described by a Chebyshev polynomial with six coefficients. Each structural model was refined to convergence, with the best result selected on the basis of agreement factors, chemical sense and stability of the refinement.

2.3. Magnetisation measurement

Magnetization measurements were carried out using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer. Magnetization versus temperature curves were measured between 0 to 300 K in field-cooled (FC) and zero-field-cooled (ZFC) modes with applied fields (μ_0H) of 20 Oe.

3. Results and discussions

3.1. Crystal structure

The crystal structure determination was performed on the neutron powder diffraction data collected at room temperature with a wavelength $\lambda = 1.47$ Å. In case of Ba_2MnMoO_6 , the structure was cubic with the unit cell parameter a = 8.1680(1) Å at 295 K. The space group was Fm3m and the Rietveld refinement resulted in good *R*-factors ($R_p = 3.31\%$, $R_{wp} = 4.24\%$, $R_{Bragg} = 2.71\%$ and $\chi^2 = 1.85$). The x coordinate of oxygen was varied during the refinement and determined to be 0.2643(1). The possible presence of oxygen non-stoichiometry was not confirmed during the final Rietveld refinements. The cation occupancies were also found to be very close to their nominal values. From the Rietveld analysis we obtain an elemental ratio Ba:Mn:Mo:O = 0.332(3):0.167(1):0.165(1):1.000, which is in excellent agreement with the nominal composition of the sample, Ba₂MnMoO₆. The Mn and Mo ions were ordered at the B-sites and form together with oxygen a NaCl-type lattice where both the cations show perfect octahedral anion coordination. The MnO₆ octahedra are larger than the MoO₆ octahedra, an observation in accordance with the larger ionic size of Mn^{2+} ($r_{Mn}2+=0.83$ Å) compared to Mo^{6+} ($r_{Mo}6+=0.59$ Å). The volumes of the octahedra are calculated to be 13.41(1) $Å^3$ for MnO₆ and 9.51(1) $Å^3$ for MoO₆. Each barium ion is coordinated to 12 oxygen ions, being part of the ccp layers. The average Ba-O bond lengths at 295 K compare well with the expected values calculated as the sum of the ionic radii. The average observed Mn–O and Mo–O bond distances are 2.158(1) and 1.926(1) Å, respectively. Bond valence sum (BVS) [17] calculation from the average observed bond lengths ($d \le 3.5$ Å) between Mn or Mo and O shows that the charges of Mn and Mo cations are +2.214 and +5.706, respectively. The tolerance factor was calculated to be 1.05 using the Shannon ionic radii [18]. If we calculate the parameters considering completely ordered and pure oxidation state for Mn^{2+} and Mo⁶⁺ using SpuDS software [19], we get the lattice parameter a = 8.207 Å, bond lengths between Mn–O = 2.1965 Å and Mo–O = 1.907 Å, and a tolerance factor, t = 1.016, which are in good agreement with the experimental values. BVS calculation using Mn³⁺ and Mo⁵⁺ gives the value 2.046 and 5.718 Å, respectively, in which very different from the expected value. The small disagreements may be



Fig. 1. Observed (circles) and calculated (continuous line) NPD intensity profiles for (a) Ba_2MnMoO_6 and (b) Sr_2MnMoO_6 at room temperature (295 K). The short vertical lines indicate the angular position of the allowed Bragg reflections (second row for the second phase). At the bottom in each figure the difference plot, I_{obs} - I_{calc} , is shown.

Table 1			
Refined structural parame	ters of Sr ₂ MnMoO ₆	at RT (295 K	0

Atom	Positions	x	у	Z	B (Å) ²
(a) Main phase	e: space group $P4_2/n$, a	a = b = 7.9575(5) Å, $c =$	= 7.9583(9) Å; $R_{\rm p} = 3.15\%$, R	$_{\rm wp} = 4.08\%, R_{\rm Bragg} = 2.97\%,$	$\chi^2 = 2.12$
Sr(1)	2a	0.25	0.25	0.25	0.29(7)
Sr(2)	2b	0.25	0.25	0.75	0.66(8)
Sr(3)	4e	0.75	0.25	0.2638(7)	0.28(6)
Mn	4c	0.00	0.00	0.00	0.11(8)
Mo	4d	0.00	0.00	0.50	0.57(6)
O(1)	8g	0.2659(9)	-0.0361(2)	-0.0111(2)	0.34(9)
O(2)	8g	0.2386(6)	0.0296(2)	0.5153(7)	0.24(9)
O(3)	8 <i>g</i>	0.0104(1)	0.0237(5)	0.2592(4)	0.65(8)
(b) Impurity p	hase: space group $I4_1/a$	a, a = b = 5.3897(5) Å,	c = 12.0209(8) Å		
Sr	4b	0.00	0.25	0.625	0.067(6)
Мо	4a	0.00	0.25	0.125	0.11(4)
0	16f	0.2373(4)	0.1146(2)	0.0433(4)	0.62(7)

caused by the oxidation of a small amount of Mn^{2+} ions to Mn^{3+} to form a $Mn^{3+}Mo^{5+}$ pair due to a strong tendency of oxidation of divalent Mn^{+2} ions. An impurity phase in the form of BaMoO₄ was present. The weight fraction of the impurity phase was determined to be 2.7(3)% from the Rietveld refinement and was refined as a second phase using the tetragonal symmetry (space group $I4_1/a$, No. 88, choice 2). The Wyckoff positions of Ba, Mo and O were 4b, 4a and 16f, respectively. The unit cell parameters were a = b = 5.569(2) and c = 12.854(8) Å. Fig. 1(a) shows the observed, calculated, difference curve and Bragg reflection positions for both phases.

In Sr₂MnMoO₆ the Bragg reflections were indexed with a tetragonal unit cell and the structure was refined in the tetragonal space group $P4_2/n$. The good agreement between the observed and calculated patterns after the refinement is shown in Fig. 1(b). The lattice parameters and final atomic coordinates for original and impurity phases are given in Table 1.

In a recent study of the crystallographic structure of Sr_2MnMoO_6 [12], the monoclinic space group $P2_1/n$ has been proposed. In the monoclinic description, the Sr position can vary in all three x, y, z directions. Although in the tetragonal space group $P4_2/n$, we need to use three different positions for Sr, almost all positions are special, and only one position can vary in the z-direction. The number of variable atomic co-ordinates is less in this model than in the monoclinic model. Based on our experimental data we carried out a fitting of the crystallographic structure in space group $P2_1/n$. The resulting *R*-factors obtained were; $R_p = 3.17\%$, $R_{wp} = 4.00\%$, $R_{Bragg} = 3.34\%$ and $\chi^2 = 2.16$. The cell parameters were a = 5.6392(9) Å, b = 5.6223(6) Å, c = 7.946(1) Å and $\beta = 89.96(2)^{\circ}$. When refining a model in space group $P4_2/n$ (No. 86, choice 2) the agreement was even better ($R_p = 3.15\%$, $R_{wp} = 4.08\%$, $R_{\text{Bragg}} = 2.97\%$ and $\chi^2 = 2.12$). The cell parameters were refined to a = b = 7.9575(5) Å, c = 7.9583(9) Å. Since it is a well established convention to use symmetry as high

as possible, we preferred to use the tetragonal description for the compound. The number of variable parameters are also less and the unit cell parameters are very close to the cubic description of the structure in the tetragonal model.

The unit cell parameters are related to that of ideal cubic perovskite as $a \approx 2a_{\rm p}$, $b \approx 2a_{\rm p}$, $c \approx 2a_{\rm p}$ ($a_{\rm p} \approx 3.89$ Å). To illustrate the combined effect of cation ordering and octahedral tilting, consider the tetragonally distorted $(a^+a^+c^-)$ [20] tilt system. The Wyckoff positions were Mn on 4c, W on 4d, Sr on 2a, 2b, 4e and O on 8g (three positions), which gives an ordered perovskite structure of so-called elpasolite type. Mn and Mo are found to occupy alternate B-sites. A schematic representation of the MnO₆ and MoO₆ octahedral distortion is shown in Fig. 2. The distances between Mn and O in the a-b plane and parallel to c-axis are about 2.14(1), 2.07(1) and 2.08(4) Å, respectively. The distances between Mo and O in the a-b plane and parallel to c-axis are about 1.88(1), 1.94(2) and 1.94(4) Å, respectively. BVS calculation from the average observed bond lengths ($d \le 3.5$ Å) between Mn^{2+} or Mo^{6+} and O^{2-} shows that the charge distributions of Mn and Mo cations are +2.59 and +5.93, respectively. Again, using Mn3+ and Mo5+ we get the BVS values +2.394 and +5.94, which is a larger discrepancy than expected indicating that a mixed valence state is probable, and the difference from ideal charge distribution Mn^{+2} and Mo^{+6} may be caused by the oxidation of a small amount of Mn^{2+} ions to Mn^{3+} to form a $Mn^{3+}Mo^{5+}$ pair due to a strong tendency of oxidation of divalent Mn⁺² ions.

The MnO₆ octahedra (volume = 12.20(2) Å³) are significantly larger than the MoO₆ octahedra (volume = 9.40(3) Å³). The MnO₆ and MoO₆ octahedra are ordered and alternate along the three directions in the crystal structure in such a way that each MnO₆ octahedra is linked to six MoO₆ octahedra and vice versa. Based on the ionic radii of Sr²⁺ (r = 1.44 Å), Mn²⁺ (r = 0.67 Å), Mo⁶⁺ (r = 0.59 Å) and O²⁻ (r = 1.40 Å) [17] in appropriate coordination number, the tolerance factor was calculated to be t = 0.989.



Fig. 2. A schematic representation of the MnO_6 and MoO_6 octahedral distortion, volume and alternate arrangement. The O atoms are not shown for simplicity, but are located at the corners of each octahedra.

A second phase, SrMoO₄, was observed as an impurity and refined in the tetragonal space group $I4_1/a$ using multi-pattern Rietveld analysis of FullProf software. The amount of the impurity phase was calculated to be 3.4(2)%. The refinement of the impurity phase gave the following reliability factors: $R_{\text{Bragg}} = 4.73\%$ and $R_F = 2.83\%$. The unit cell parameters were a = b = 5.3897(5) and c = 12.0209(6) Å. The fractional atomic coordinates, Wyckoff positions and isotropic thermal parameters are given in Table 1(b).



Fig. 3. Inverse DC mass susceptibility versus temperature at 20-Oe field. Dashed lines represent a linear Curie–Weiss fitting.

3.2. Magnetic properties

The temperature dependence of the mass magnetic susceptibilities for Ba2MnMoO6 and Sr2MnMoO6 are shown in Fig. 3. Both the Mn^{2+} and Mo^{6+} ions contribute to the paramagnetic behavior and the effective magnetic moment of the compounds (μ_{eff}) are given by the following equation: $\mu_{eff}^{2} = \mu_{eff} (Mn^{2+})^{2} + \mu_{eff} (Mo^{6+})^{2}$. By fitting the Curie-Weiss equation to the experimental data in the temperature range 0-300 K, the effective magnetic moment (μ_{eff}) and the Weiss constant (θ) are determined to be 5.80 $\mu_{\rm B}$ and -94 K for Ba₂MnMoO₆ and 4.5 $\mu_{\rm B}$ and -108 K for Sr₂MnMoO₆. This negative Weiss constant is indicative of the presence of predominant antiferromagnetic interaction. No divergence between the ZFC and FC magnetic susceptibilities or no magnetic hysteresis in the magnetization-magnetic field curve indicates that at low temperature (below 10 K) these compounds transform to an antiferromagnetic state without weak ferromagnetic properties.

4. Conclusions

Rietveld analysis of NPD data shows that the doubleperovskites Ba₂MnMoO₆ and Sr₂MnMoO₆ are B-site ordered. Ba₂MnMoO₆ crystallizes in the space group $Fm\overline{3}m$ with the doubling of unit cell axes of the ideal perovskite. Sr₂MnMoO₆ crystallises in the space group $P4_2/n$ which is related to the ideal cubic perovskite as $a \approx 2a_p$, $b \approx 2a_p$, $a \approx 2a_p$ ($a_p \approx 3.89$ Å). Valency pair of these materials was considered to be (Mn²⁺, Mo⁶⁺) from the bond valence sum calculation and compared with the calculated values. The magnetic measurements suggest that these compounds transform to an antiferromagnetic state below 10 K. The study of magnetic structure below 10 K is in progress.

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