High-pressure synthesis and study of the crystal and magnetic structures of the distorted SeMO$_3$ (M= Mn, Co, Ni, Zn) perovskites

J.A. Alonso$^a$*, M.J. Martínez-Lope$^a$, Cristina de la Calle,$^a$ A. Muñoz$^b$, E. Morán,$^c$ G. Demazeau$^d$

$^a$ Instituto de Ciencia de los Materiales de Madrid, CSIC, E-28049, Cantoblanco-Madrid, Spain.

$^b$ Dpto. de Física Aplicada, EPS, Universidad Carlos III, Avda. Universidad 30, E-28911, Leganés-Madrid, Spain.

$^c$Depto. de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, E-28040 Madrid, Spain.

$^d$ ICMCB, CNRS, Université Bordeaux 1, site de l’ENSCPB, 87 Av. Dr. A. Schweizer, 33608 Pessac Cedex, France

ja.alonso@icmm.csic.es

Abstract. We describe the preparation of SeMO$_3$ (M= Mn, Co, Ni, Zn) under high pressure conditions (3.5-7 GPa), starting from reactive SeO$_3$H$_2$ and MO mixtures, contained in sealed platinum capsules under the reaction conditions (850-900º C for 30-60 min). The polycrystalline samples have been studied by x-ray diffraction (XRD) or neutron powder diffraction (NPD) data. SeMO$_3$ crystallize in an O-orthorhombically distorted perovskite structure (space group Pnma), where the strongly tilted MO$_6$ octahedra show average rotation angles in the 25-27º range. The coordination environments of selenium atoms are strongly distorted due to the presence of the electron lone pair of Se(IV), giving rise to effective (SeO$_3$)$_2^-$ polyhedra; the strongly covalent Se-O bonds contribute to the stability of the a+b-b' tilt system of the MO$_6$ octahedral network. The same antiferromagnetic structure is observed for SeMnO$_3$ and SeNiO$_3$, defined by the propagation vector $k$=0 and the basis vector (0,0,$A_z$). It is a collinear antiferromagnetic arrangement of Ni$^{2+}$ or Mn$^{2+}$ spins lying along the c-direction, defined as G-type (Pbnm setting). For SeCoO$_3$ the magnetic structure is given by the basis vectors (A,$A_x$,0). The different magnetic interactions at low temperature are discussed as a function of the bonding distances and angles.

1. Introduction

There are very few examples of ABO$_3$ perovskite oxides with valence combination A$^{4+}$B$^{2+}$O$_3$, i.e. containing divalent transition metals at the B positions; perovskites such as ThCuO$_3$ or CeZnO$_3$ have never been stabilized. The only 4-2 perovskite oxides described so far contain a
$p$ element at the A positions ($\text{Se}^{4+}$, $\text{Te}^{4+}$), in such a way that the considerably covalent A-O bonds and the fact that these cations present a “lone pair” of electrons able to fill the space in the A site contribute to the global stability of the crystal structure.

The $\text{SeMO}_3$ and $\text{TeMO}_3$ oxides, with M= Mg, Mn, Co, Ni, Cu and Zn, must be stabilized under high pressures and temperature conditions [1,2], given the relatively small size of $\text{Se}^{4+}$ and $\text{Te}^{4+}$ ions which require a framework of strongly tilted $\text{MO}_6$ octahedra, in orthorhombically distorted perovskite structures. This gives rise to rather bent M-O-M superexchange $\phi$ angles, which account for varied magnetic properties [2,3], spanning from the ferromagnetism observed for $\text{SeCuO}_3$, exhibiting $\phi$ angles of 121º, to the antiferromagnetism described for $\text{TeCuO}_3$, with $\phi = 131^\circ$.

The aim of this paper is to report on the synthesis and the crystal and magnetic structures of $\text{SeMO}_3$ (M= Mn, Co, Ni, Zn), studied from neutron diffraction data. $\text{SeNiO}_3$, $\text{SeCoO}_3$ and $\text{SeMnO}_3$ had been previously described as antiferromagnets with $T_N= 98(1)$ K, 49(1) K and 51(1) K, respectively [1].

### 2. Experimental

About 0.6 g of a stoichiometric mixture of $\text{H}_2\text{SeO}_3$ and MO (M= Ni, Co, Mn) was thoroughly ground and put into a platinum capsule (6 mm dia.), sealed and placed in a cylindrical graphite heater. The reactions were carried out in a piston-cylinder press (Rockland Research Co.), at a pressure of 3.5 GPa at 850°C for 1 h. Then the materials were quenched to room temperature and the pressure was subsequently released. The preparation of $\text{SeZnO}_3$ failed under the mentioned conditions and was then achieved in a belt –type equipment at 7 GPa, at 900°C for 30 min.

The products were initially characterized by laboratory XRD (Cu K$\alpha$, $\lambda = 1.5406$ Å) for phase identification and to assess phase purity. The neutron powder diffraction (NPD) data were acquired at the Institut Laue-Langevin, Grenoble (France) for M= Mn, Co and Ni. The fitting of the crystallographic structure was carried out from NPD patterns collected at the high resolution D2B diffractometer with a 1.594 Å wave-length at room temperature. The magnetic structures were analysed from sets of NPD patterns collected at low temperature in the high-flux D20 diffractometer, with a 2.42 Å wave-length. The analysis of the NPD patterns was carried out by the Rietveld method using the Fullprof program [4]. For the simulation of the peak profile a pseudo-Voigt function was considered. The background was fitted with a fifth degree polynomial function.

### 3. Results and Discussion

#### 3.1. Synthesis

The use of $\text{H}_2\text{SeO}_3$ as starting reactant seems to be crucial for the crystallization of the perovskites; previous trials with $\text{SeO}_2$+MO mixtures as starting reactants were unsuccessful. Perhaps the reaction proceeds via a water-vapor transport-driven mechanism. The XRD patterns (Fig. 1 and 2) are characteristic of well crystallized perovskites and can be indexed in orthorhombic unit cells in the space group $\text{Pnma}$. 
3.2. Crystallographic refinement. The refinement of the crystallographic structure of SeMO₃ (M= Mn, Co, Ni) was performed from NPD patterns obtained at room temperature with a λ=1.594 Å wavelength. In spite of the relatively small amount of sample (0.5 g) available from the high-pressure synthesis procedure, reasonably good NPD patterns could be collected in the D2B diffractometer operating in the high-flux mode. Unhappily, the much smaller available sample for SeZnO₃ did not allow us the collection of exploitable NPD patterns, thus the structure was refined from XRD data. In all cases the structure was defined in the orthorhombic space group Pnma (No. 62), Z= 4, with unit-cell parameters related to \(a_0\) (ideal cubic perovskite, \(a_0\approx 3.8\) Å) as \(a=c=\sqrt{2}a_0\), \(b=2a_0\). Se atoms were located at 4c positions, M (Mn, Co, Ni, Zn) at 4b and oxygen atoms at 4c and 8d positions, respectively. The good agreement between the observed and calculated NPD patterns is illustrated in Fig. 3 for M= Mn, Co and Ni. The Rietveld plot obtained for SeZnO₃ from XRD data is displayed in Fig. 2.
The main crystallographic parameters and the reliability factors obtained after the structural fit for SeZnO₃ are included in Table 1. Details of the NPD Rietveld refinements for M= Co, Mn, and Ni are given elsewhere [5,6]. The main results for all SeMO₃ perovskites are included in Table 2.

Table 1. Structural parameters for SeZnO₃ refined in the orthorhombic Pnma space group at room temperature from XRD data.a

| Atom | Site | x     | y   | z         | B(Å²) |
|------|------|-------|-----|-----------|-------|
| Se   | 4c   | 0.0256(4) | 1/4 | -0.0146(6) | 0.23(9) |
| Zn   | 4b   | 0     | 0   | 1/2       | 1.4(1) |
| O1   | 4c   | 0.105(2) | 1/4 | 0.333(3)  | 1.6(2) |
| O2   | 8d   | 0.2102(16) | 0.0859(15) | 0.8752(18) | 1.6(2) |

aDiscrepancy factors: Rp= 9.49, Rwp= 12.08 and Rbragg= 8.96 %
Table 2. Main crystallographic parameters for SeMO₃ (M= Mn, Co, Ni, Zn) determined at RT from NPD (M= Mn, Co, Ni, taken from references [5,6]) or XRD (M= Zn).

| M   | a(Å)   | Co   | Ni   | Zn   |
|-----|--------|------|------|------|
| Mn  | 6.0930(2) | 5.9300(2) | 5.87912(8) | 5.9239(2) |
| b (Å) | 7.8638(2) | 7.5961(2) | 7.52467(9) | 7.6684(3) |
| c (Å) | 5.1426(2) | 5.0287(2) | 4.93737(7) | 5.0421(2) |
| V (Å³) | 246.409(13) | 226.515(11) | 218.421(8) | 229.05(1) |
| <M-O> | 2.232(3) | 2.149(2) | 2.114(2) | 2.16(1) |
| <Se-O> | 1.712(3) | 1.715(3) | 1.724(3) | 1.78(1) |
| <M-O-M> | 125.48(9) | 126.17(8) | 128.86(6) | 127.0(1) |
| a(Å) | 6.0930(2) | 5.9300(2) | 5.87912(8) | 5.9239(2) |
| b (Å) | 7.8638(2) | 7.5961(2) | 7.52467(9) | 7.6684(3) |
| c (Å) | 5.1426(2) | 5.0287(2) | 4.93737(7) | 5.0421(2) |
| V (Å³) | 246.409(13) | 226.515(11) | 218.421(8) | 229.05(1) |
| <M-O> | 2.232(3) | 2.149(2) | 2.114(2) | 2.16(1) |
| <Se-O> | 1.712(3) | 1.715(3) | 1.724(3) | 1.78(1) |
| <M-O-M> | 125.48(9) | 126.17(8) | 128.86(6) | 127.0(1) |

A view of the crystallographic structure of SeMnO₃ is presented in Fig. 4, highlighting the significant tilting of the MO₆ octahedra. The ionic radius of the Se⁴⁺ cation, 0.64 Å [7], is very small to occupy the A-perovskite position (typical A³⁺ and A²⁺ cations sizes are around 1-1.4 Å), which gives rise to a huge tilting effect of the MO₆ octahedra in order to optimize the Se-O distances. In SeMO₃, average <M-O-M> angles (ϕ) are in the range 125.5-128.9º (Table 2), which are abnormally small in perovskite-related structures. The average tilting angles, estimated as ϕ = (180 - <ϕ>) / 2 are 25.6º and 27.3º for M= Ni, Mn, respectively. The Mn perovskite is the more distorted perovskite and the Ni compound is the less distorted one, as it corresponds to the ionic radii sequence (0.83 Å, 0.745 Å, 0.74 Å and 0.69 Å for Mn²⁺, Co²⁺, Zn²⁺ and Ni²⁺, respectively [7]) yielding increasing tolerance factors.

Fig. 4. View of the crystal structure of SeMO₃, highlighting the strong tilting of the MO₆ octahedra and the threefold coordination of Se⁴⁺ cations.

As a consequence of the strong tilting effect, the oxygen environment of Se⁴⁺ cations is very irregular, showing 3 short bond lengths (1.69-1.73 Å) and 5 long bonds in the 2.8-3.0 Å range [5,6].
Therefore, Se$^{4+}$ cations form strong covalent bonds with three out of the 8 surrounding oxygens, forming a (Se-O$_3$)$^{2-}$ polyhedron, in a trigonal pyramidal conformation with O-Se-O angles between 98º-104º [5,6]. The coordination of Se to 3 oxygens is also illustrated in Fig. 6. This irregular oxygen environment around Se is the result of the presence of the Se$^{4+}$ non-bonded lone 4s$^2$ electron pair, which is thought to be directed towards the apex of each trigonal pyramid. It is very plausible that the formation of the mentioned very covalent Se-O bonds are an important ingredient for the stability of this family of SeMO$_3$ perovskites.

Fig. 5. Thermal evolution of the NPD patterns for SeMO$_3$ (M= Mn, Co, Ni)

3.3. Magnetic structure resolution. The magnetic structure resolution was carried out from a set of low temperature NPD patterns acquired with $\lambda=2.42$ Å, for SeMO$_3$ M=Mn, Co, Ni. As shown in Fig. 5, on decreasing the temperature new peaks of magnetic origin appear for the three compounds at positions forbidden by the space group Pnma; in particular, the new peaks appear below 53.5 K, 104 K and 54 K for SeMnO$_3$, and SeCoO$_3$ and SeNiO$_3$, respectively, implying the appearance of a magnetic order below $T_N$, in good agreement with the magnetic measurements [5,6]. In all the three compounds the magnetic structure is defined by the propagation vector $\mathbf{k}=0$, indicating that the magnetic unit cells coincide with the chemical ones.
Fig. 6. Magnetic structures of SeMO₃ (M= Mn, Ni, Co)

For SeMO₃ (M= Mn, Ni) the magnetic structure that shows a better agreement with the experimental data corresponds to the magnetic mode (0,0,Aₚ). This mode defines that the magnetic moments are oriented along the z-direction. In SeNiO₃ the ordered magnetic moment for the Ni²⁺ ions at T=2.3 K is 2.11(3) µ_B, whereas in SeMnO₃ at T=2.6 K for Mn²⁺, |m|=4.64(2) µ_B. A view of the magnetic structures is shown in Fig. 6. The magnetic structure can be described as antiferromagnetic (010) layers of magnetic moments lying along the b-direction, which are antiferromagnetically coupled along the b-direction. For SeCoO₃ the magnetic structure is given by the basis vectors (Aₓ,Gᵧ,0), defining a non-colinear but non-canted structure (Fig. 6). In the (a,c) planes the coupling of the magnetic moments for each Co atom with its four closer neighbours is purely antiferromagnetic. For the x-component of the magnetic moment the coupling between the (010) layers along b is antiferromagnetic, whereas for the y-component the coupling is ferromagnetic. At T=2.2 K, the ordered magnetic moment for Co²⁺ ions is |m|=3.37(3) µ_B, suggesting a high-spin electronic configuration for Co²⁺ cations, t²g²e²g⁰, with some component of unquenched orbital moment.

Finally, it is surprising that the ordering temperatures are considerably different for SeNiO₃ vs SeCoO₃ and SeMnO₃ perovskites, with Tₓ=104 K vs Tₓ=54 K and Tₓ=53.5 K, respectively, suggesting that the superexchange interactions are stronger in SeNiO₃, despite the significantly larger magnetic moment of Mn²⁺ and Co²⁺. This fact can be interpreted by taking into account that the superexchange process is improved by the more open angles and shorter bond lengths observed in the Ni-O-Ni pathways (average Ni-O-Ni angle of 129°; average Ni-O distance of 2.114 Å) with respect to Mn-O-Mn and Co-O-Co superexchange paths (Table 2), favoring the overlap between oxygen and metal orbitals and thus enhancing the magnetic interactions.

4. Conclusions

We have prepared SeMO₃ (M= Mn, Co, Ni, Zn) under hydrostatic pressures in sealed Pt capsules; it seems that the choice of the starting reactants is of paramount importance for obtaining pure
perovskite phases. A neutron study for the Mn, Co and Ni compounds demonstrate that they are very distorted superstructures of perovskite. A sequential NPD study shows that the magnetic ordering temperatures are considerably different for SeNiO$_3$ vs SeCoO$_3$ and SeMnO$_3$ perovskites, with $T_N \approx 104$ K vs $T_N \approx 54$ K and $T_N \approx 53.5$ K. This fact can be related with the geometrical parameters (superexchange angles and bond lengths), favoring the overlap between oxygen and metal orbitals and thus enhancing the magnetic interactions for SeNiO$_3$.

Acknowledgments: We are grateful to Spanish Ministry of Education and Science for funding the project MAT2007-60536. This study was developed in the framework of the COST D30 program Working Group D30/03 (Development of Materials Chemistry under High Pressures).

References
[1] Kohn, K.; Inoue, K.; Horie O.; Akimoto, S. J. Solid State Chem. 1976, 18, 27.
[2] Subramanian, M.A.; Ramírez, A.P.; Marshall, W.J. Phys. Rev. Lett. 1999, 82, 1558.
[3] Lawes, G.; Ramírez, A.P.; Varma C.M.; Subramanian, M.A. Phys. Rev. Lett. 2003, 91, 257208.
[4] Rodríguez-Carvajal, J. Physica B 1993, 192, 55.
[5] Muñoz, A.; Alonso, J.A.; Martínez-Lope, M.J.; Morán, E.; Escamilla, R., Phys. Rev. B, 2006, 73, 104442.
[6] Muñoz, A.; Alonso, J.A.; Martínez-Lope, M.J.; Falcón, H; García-Hernández, M.; Morán, E; Dalton Trans. 2006, 4936.
[7] Shannon R.D. Acta Cryst. A 1976, 32, 751.