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Mixed valence transition metal 2D-oxides: Comparison between delafossite and crednerite compounds

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ABSTRACT

Transition metal oxides offer large opportunities to study relationships between structures and properties. Indeed these compounds crystallize in numerous frameworks corresponding to different dimensionalities and, accordingly, show a huge variety of properties (as high Tc superconductivity, colossal magnetoresistivity, multiferroicity..). The control of the oxidation state of the transition metal, *via* the monitoring of the oxygen content, is of prime importance to understand and optimize the properties, due to the strong coupling that exists between the lattice and the charges and spins of the transition metals. In this large playground for chemists, we reinvestigated several 2D-compounds derived from delafossite structure.

Considering this paper as a very short review, we report here the results obtained on $CuMO_2$ compounds (with M = Cr, Mn or Mn+Cu) by using a combination of techniques, as X-ray, neutrons and/or electrons diffraction on poly-crystals for structural characterisations that are correlated with electrical and/or magnetic properties. The complementarity of studies is also addressed by the synthesis and characterization of single crystals in addition to poly-crystals. Moreover the comparison of the structures of similar Cr and Mn based oxides highlights the crucial role of the Jahn-Teller effect of trivalent manganese to lift the degeneracy, which is responsible of the magnetic frustration in $CuCrO_2$.

1. Introduction

New developments were made in the field of multiferroic materials in the past years due to their possible applications in various fields, like spintronics or data storage. These materials present two or three ferroic orders: ferroelectricity, ferromagnetism and ferroelasticity and the coupling between them open new perspectives. In this area of research, intensive studies are dedicated to ferroelectric and antiferromagnetic metal transition oxides, in which the magnetic order induces symmetry breaking. A favourable criterion to obtain simultaneously both states is the stabilization of a complex antiferromagnetic structure (like helicoidal type), induced by magnetic frustration in a triangular lattice of magnetic cations, for example. In this context, the ABO_2 delafossite-type systems have attracted the interest of scientific community, since the transition metal (B) forms a triangular lattice and a 2D structure characterized by the stacking of compact layers of BO_6 octahedra sharing edges (CdI_2-type) in between which A cations (without oxygen) are inserted. Two members of this family will be described in the following: $CuCrO_2$ and $CuMnO_2$ (A=Cu and B=Cr or Mn). Despite a similar structure, they crystallize in two different space groups (related to the Jahn-Teller effect of trivalent manganese) and they present different electric and magnetic properties. This paper summarizes results (previously published for a part) in a form which has a two-fold purpose. Firstly, it deals to highlight how the study of compounds with similar structures allows relevant parameters to be extracted to understand the link between structures and physical properties. Secondly, attention is focused on the interest of single crystal characterization, in addition to powder and ceramic samples, as the only tool for accessing further crucial information (on anisotropy for instance).

2. Experimental techniques

2.1. Synthesis of polycrystalline samples

The compounds have been all obtained by solid state reaction in air at high temperature, starting from oxides.

2.1.1. Delafossite

The samples have been prepared starting from a 5 g mixture of

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Cu_2O and Cr_2O_3 weighted in the 1:1 stoichiometric ratio. The thermal treatment was performed in air in 3 steps (each plateau during 12 h) with intermediate grinding. The powder is kept at 900 °C then at 1000 °C (in alumina crucibles) before being pressed in shape of bars (2×2×10 mm) which are heated at 1200 °C in Pt crucibles.

2.1.2. Crednerite

In that case, the synthesis is done in one single step, starting from a 5 g stoichiometric mixture [1 CuO: 1 MnO] compressed in shape of bars (2×2×10 mm) which are introduced in an alumina crucible and then in a silica tube which is sealed under primary vacuum. The tube is then heated at 950 °C for 12 h.

2.2. Single crystals growing

In both cases, the flux method has been successfully applied [1].

2.2.1. Delafossite

$CuCrO_2$ single crystals have been obtained by heating in air a mixture of 80% $K_2Cr_2O_7$ and 20% CuO (wt%), in Pt crucible, at 900 °C for 24 h; cooling is then made with the rate of 30 °C/h, following Crottaz method [2]. The obtained platelet single crystals are shiny/black with rectangular or hexagonal shape and dimensions of 0.2×0.1×0.006 cm^3. The single crystals are extracted and washed with hot water (bath and Soxhlet).

2.2.2. Crednerite

For this compound, it is necessary to first synthesize $CuMnO_2$ which is mixed with $LiBO_2$ (1 g of crednerite for 3 g of flux). The mixture is then heated at 1000 °C for 6 h under argon flux, cooled to 840 °C at 2 °C/h and then by thermal inertia down to room temperature. The single crystals extraction is more difficult than for delafossite samples, the crucible is put for several days in diluted nitric acid, following Topfer report [3]. The obtained single crystals are as well black but much smaller (1.9×0.17×0.012 mm^3) and with needle like shape.

2.3. Structural characterisations

The polycrystalline samples have been systematically characterized by powder X-ray diffraction at room temperature (RT). X-ray diffraction experiments have been also performed at Soleil Synchrotron (Cristal beamline) or at ESRF-Grenoble (ID31) between 4 and 300 K. The neutron powder diffraction (NPD) studies have been done at LLB-Saclay, ILL Grenoble and at ISIS-Didcot (UK) also in function of temperature. All these data have allowed to refine the structures (crystal and magnetic) and to follow the structural and magnetic transitions (*vs.* T). When needed, other investigations have been performed, by electronic microscopy (scanning, transmission or atomic force) and by single crystal X-ray diffraction (Laue method or pole figures).

2.4. Physical properties characterisations

2.4.1. Magnetic properties

The macroscopic properties (magnetisation and susceptibility) have been done with a Squid (Superconducting Quantum Interference Device) Quantum Design from 4 to 300 K, with a maximal magnetic field of 5 T (measurements in alternative or continue).

2.4.2. Electrical properties

Depending on sample behaviours, resistivity, dielectric constant or polarisation measurements have been performed (by using a PPMS-Physical Properties Measurement System) in function of temperature and/or applied electric/magnetic field.

3. Results

3.1. Structural description

The description of both structures in term of stacking of A and BO_6 layers is the same; nevertheless the chromium and manganese lattices are different: both of them are triangular but regular for $Cr^{3+}(d^3)$ and isosceles for $Mn^{3+}(d^4)$ because of Jahn-Teller effect. This different topology of the planar triangular lattice is characterized by one type of Cr-Cr distance and two types of Mn-Mn distances, which have a direct impact on the exchange interactions between the magnetic cations. The two structures are represented in Fig. 1 with their principal crystallographic characteristics, according to Crottaz [2] and Kondrachev [4]. The structural evolution as a function of temperature (down to 4 K) presents also a different behavior. The delafossite retains the same space group, the cell volume decreases with decreasing temperature, the *a* parameter follows the same dependence, but the *c* parameter presents an unusual evolution *i.e.* the so-called negative thermal expansion [5] (Fig. 2-a). This corresponds to a relaxation of the compression of the CrO_6 octahedra (along the *c*-axis). The evolution of the cell parameters occurs progressively even though an accident is observed at the temperature corresponding to the magnetic transition ($T_N \cong 24$ K). This is in strong contrast with the transition observed for the crednerite at T_N (≅65 K): the structural transition from *C*2/m to *P*−1 (*a*=3.142 Å, *b*=3.134 Å, *c*=5.892 Å; *α*=102.3°, *β*=102.4° and *γ*=54.6° at 2 K) is correlated with a strong magneto-elastic coupling. It is illustrated in Fig. 2-b by the (*a* and *b*) cell parameters *vs.* temperature evolution, with a clear split at T_N[6].

3.2. Properties and magnetic structures

The neutron powder diffraction allowed us to determine the magnetic structures, starting from the low temperature patterns plotted in Fig. 3. In all cases one single antiferromagnetic transition is observed but the spin ordering is totally different, non collinear incommensurable for delafossite and collinear for crednerite –type samples (Fig. 4).

The magnetic ordering is established at higher temperature for $CuMnO_2$ (65 K *vs.* 24 K for $CuCrO_2$) in agreement with the macroscopic characterisations. Indeed, the lift of degeneracy of the frustrated triangular lattice of Mn cations in crednerite leads to an increase of T_N and to intense and narrow magnetic Bragg peaks associated with a small diffuse signal at low angles in the NPD patterns. On the other hand, for delafossite samples the magnetic peaks are broader and overlapped and their intensity is much lower compared with the nuclear peaks (as shown in Fig. 3). For $CuCrO_2$, the refinement of the magnetic structure by using the symmetry analysis led to two models -helicoidal or cycloidal- impossible to differentiate with neutron powder diffraction data. The solution has been obtained by measuring the electrical polarisation (already measured on the polycrystalline sample) on single crystals: the polarisation should be induced in the (*a*,*b*) plane for the helicoidal structure and along the *c*-axis for the cycloidal one [7].

3.3. Study of the electrical properties of delafossite on single crystal

$CuCrO_2$ single crystals have a classic shape for 2D compounds (as presented in Fig. 5): plate-like with *c*-axis perpendicular to the surface,