Experimental report

10/05/2017

Proposal: 5-31-2416 **Council:** 4/2015

Title: Understanding magnetic behavior of new Sr2Mn2-xSbxO6 (0.05≤х<1) solid solutions with mixed Mn3+/Mn4+ oxidation states

Research area: Materials

This proposal is a new proposal

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Samples:
Sr2Mn1.85Sb0.15O6
Sr2Mn1.6Sb0.4O6
Sr2Mn1.17Sb0.83O6

Instrument	Requested days	Allocated days	From	To
D2B	4	3	09/06/2016	12/06/2016

Abstract:

We propose to perform a detailed study of new solid solutions formed between SrMnO3 (Mn4+) and Sr2MnSbO6 (Mn3+). The introduction of a non-magnetic Sb5+ cation on the Mn4+ position of the perovskite structure induces different ordering at B-site cations (Mn3+/Mn4+/Sb5+) leading to interesting magnetic behavior. Our preliminary study revealed the formation of two solid solutions:
(1) Sr2Mn2-xSbxO6 (0.05<x<0.18) has a distorted 6H-SrMnO3 structure (sp.gr. C2/c) and an ordered distribution of cations on B-sites; magnetic susceptibility measurements showed a magnetic transition to an antiferromagnetic state at 180 K;
(2) Sr2Mn2-xSbxO6 (0.35<x<1) has a tetragonal double perovskite structure (sp. gr. I4/m) with partial ordering of the B-cations in octahedral positions. Magnetic susceptibility measurements showed two transitions: at T = 10-20 K and at 450 K.
The aim of the proposed experiment is to reveal details of the crystal structure, to describe the magnetic structures of the two solid solutions and to correlate structural data with magnetic behavior. Neutron diffraction experiments are planned to be carried out at the D2B line at 298 K, liquid helium temperature and at 460 K.

Understanding the magnetic behavior of new $Sr_2Mn_{2-x}Sb_xO_6$ ($0.05 \le x < 1$) solid solutions with mixed Mn^{3+}/Mn^{4+} oxidation states

Our preliminary study using X-ray powder diffraction and transmission electron microscopy revealed the formation of two solid solutions (Figure 1):

(1) $Sr_2Mn_{2-x}Sb_xO_6$ ($0.05 \le x < 0.18$) has a distorted 6H-$SrMnO_3$ structure (sp.gr. *C*2/*c*) and ordered distribution of cations on B-sites;

(2) $Sr_2Mn_{2-x}Sb_xO_6$ ($0.35 \le x \le 1$) has a tetragonal double perovskite structure (sp. gr. *I*4/*m*) with partial ordering of the B-cations in octahedral positions.

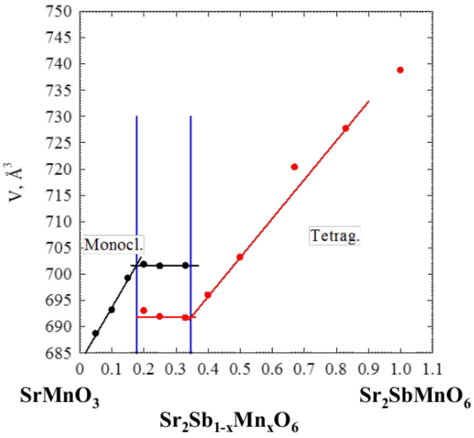

Figure 1. Dependence of unit cell volume on manganese content.

For a detailed study of the crystal and magnetic structures low and high temperature NPD data were collected at D2B for four single-phase and well-crystallized samples of $Sr_2Mn_{2-x}Sb_xO_6$ with x = 0.15, 0.40, 0.67 and 0.83.

The crystal structure refinement was carried out with the GSAS[1,2] program suite using the NPD data collected for low and high temperatures and a combination of XRPD and NPD data for room temperature. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = x*L(2\theta) + (1-x)*G(2\theta)$ (where *L* and *G* are the Lorentzian and Gaussian part, respectively). The angular dependence of the peak width was described by the relation $(FWHM)^2 = Utg^2\theta + Vtg\theta + W$, where *FWHM* is the full line width at half maximum. We fixed Mn/Sb ratios to 0.667/0.333 and set the values of the thermal motions to 0.025 for this site for all full-profile refinements of the $Sr_2Mn_{1.33}Sb_{0.67}O_6$ structure based on neutron data only, namely for temperatures 5 and 500 K. In the analysis of the low-temperature NPD data, a two-phase refinement for every temperature was performed. In each case, the crystal structure was refined taking as starting parameters those obtained at room temperature. The magnetic structure was refined as an independent phase with *P*1 space group for which only magnetic atoms were defined. The scale, atomic coordinates and displacement parameters were constrained for both the nuclear and magnetic structures.

In the temperature interval from 1.5 K to 500 K all diffraction patterns of $Sr_2Mn_{2-x}Sb_xO_6$ with x = 0.15 have been indexed with a monoclinic unit cell and sp. g. *C*2/*c* (15); the degree of monoclinic distortion decreases when heated.

NPD patterns of $Sr_2Mn_{2-x}Sb_xO_6$ with x = 0.40, 0.67 and 0.83 collected at room, low and high temperatures have been indexed with a tetragonal body-centered unit cell (sp. g. *I*4/*mcm*). The degree of tetragonal distortion is minimized when heated and that results in a polymorphic transition at 500 K to a cubic perovskite structure type for $Sr_2Mn_{1.60}Sb_{0.40}O_6$ (sp. g. $Pm\bar{3}m$, a = 3.87998(2) Å). The crystal structure of $Sr_2Mn_{2-x}Sb_xO_6$ with x = 0.40, 0.67 and 0.83 is described as double perovskite with lattice parameters related to cubic perovskite as following: $a_t \sim a_c\sqrt{2}$ and $c_t \sim 2a_c$, and results from tilting of the octahedra.

The magnetic structure for $Sr_2Mn_{1.85}Sb_{0.15}O_6$ investigated from NPD data collected at 1.5 K and 80 K was defined by propagation vector k = (0, 0, 0). The magnetic symmetry analysis was performed with the program BasIreps in the FullProf suite[3]. Beside the irreducible representations (IRREPs) of the magnetic structure for space group *C*2/*c* and k = (0, 0, 0) the program also calculates the general expressions of the Fourier coefficients Sk(j) of the atoms not related by lattice translations for different sites, in our case the 4*a* and 8*f* sites occupied by magnetic manganese ions with fractions 0.775 and 1.0, respectively. There are two IRREPs, Γ_1 and $\Gamma_{3,}$ corresponding to the long-range magnetic ordering of these two magnetic subsystems and the former only perfectly describes NPD data. Both magnetic subsystems might have antiferromagnetic (AFM) spin canting in the direction of the *a* axis and ferromagnetic in the direction of the *b* axis, which means that spins are slightly tilted rather than being parallel, and a nonzero net moment is possible. In first approximation the magnetic structure was well described as A-type AFM, where spins are parallel to the *c* axis. Within the plane, coupling is ferromagnetic while inter-plane coupling is antiferromagnetic. The magnitude of the saturated moments at 1.5 K, 1.85(9) μ_B for 4*a* and 1.13(6) μ_B for 8*f* sites, respectively, is much lower than the predicted value for Mn^{4+} with a degree of covalency[4], 2.6 μ_B. The combined population on both sites of 92.5 % of *S*=3/2 Mn^{4+} and 7.5 % of *S*=2 Mn^{3+} ions mainly leads to antiferromagnetic interactions, although local orbital ordering of Mn^{3+} could create some ferromagnetic coupling causing frustration.

The magnetic structure of $Sr_2Mn_{2-x}Sb_xO_6$ (x = 0.40, 0.63) was determined from NPD data collected at 5 K. An analysis of the profiles fit after refinement of the nuclear structure showed extra intensities in the (100) plane at $d \approx 5.403$ Å, (012) at $d \approx 3.188$ Å, (120) at $d \approx 2.416$ Å and (122) at $d \approx 2.061$ Å. The magnetic symmetry analysis was performed similar to the one described above. For space group *I*4/*mcm*, k = (1, 0, 0) and the 4*c* site occupied by magnetic manganese ions with fractions 0.8 and 0.667 for x = 0.40, 0.63, respectively, there are three IRREPs, Γ_1, Γ_7 and Γ_{10}, corresponding to magnetic ordering. Three models were constructed with starting magnetic moment equal to 3 μ_B and directions constrained according to the Γ_1, Γ_7 and Γ_{10} IRREPs. The refinement showed that the Γ_7 model perfectly describes the extra peaks. The magnetic structure is described as C-type AFM, where spins are parallel to the *c* axis with AF intraplanar and F interplanar coupling. The refined saturated magnetic moments at 5 K, 2.79(2) μ_B and 2.00(4) μ_B for $Sr_2Mn_{2-x}Sb_xO_6$ (x = 0.40 and 0.63), respectively, fit well to the predicted value for Mn^{4+}, but are lower than those for Mn^{3+}. A comprehensive manuscript based on the obtained data is in preparation.

[1] Toby, B.H. J. Appl. Crystallogr. 2001, 34, 210–213.

[2] A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2004).

[3] FullProf, http://www.ill.eu/sites/fullprof/.

[4] B.C. Tofield and B.E.F. Fender /Covalency parameters for Cr^{3+}, Fe^{3+} and Mn^{4+} in an oxide environment// .I.P hys. Chem. Solids 1970. Vol. 3 1, pp. 2741-2749.