



Synthesis and structural and magnetic characterization of the frustrated magnetic system $\text{La}_2\text{Ni}_{4/3-x}\text{Co}_x\text{Sb}_{2/3}\text{O}_6$



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ARTICLE INFO

Article history:

Received 18 June 2013

Received in revised form

12 August 2013

Accepted 8 September 2013

Available online 21 September 2013

Keywords:

Double perovskites

Neutron diffraction

Rietveld refinement

Ferrimagnetism

Magnetic frustration

ABSTRACT

We report the synthesis of double perovskites $\text{La}_2\text{Ni}_{4/3-x}\text{Co}_x\text{Sb}_{2/3}\text{O}_6$ with $x=0, 1/3, 2/3$ and 1 by a solid state method. Rietveld refinements of X-ray and neutron powder diffraction data show that all samples crystallize in space group $P2_1/n$, with almost perfect occupation of the $2d$ octahedral site with the transition metals, while all Sb^{5+} are randomly distributed in a $2c$ octahedral site. The saturation magnetization in hysteresis loops indicates that the samples are ferrimagnetic throughout all the series. Virgin magnetization curves lie outside hysteresis loops at low temperatures and thermal evolution of H_m – defined as the inflection point of these curves – follows the de Almeida–Thouless dependence for $x \neq 0$. This spin glass like behavior below 30 K is also supported by thermal evolution of the coercivity, which follows an exponential law typical of magnetic clusters, not found in the pure Ni^{2+} perovskite, $x=0$ extreme.

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1. Introduction

Pioneer work in magnetic perovskites AMnO_3 near room temperature was done more than sixty years ago [1]. In the following decades rhenium [2] and molybdenum and tungsten [3] perovskites were studied. However, renewed interest emerged in the last few years as new properties were reported: high temperature superconductivity in Ba-LaCu-O [4], colossal magnetoresistance in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ thin films [5] and half-metal properties in $\text{Sr}_2\text{FeMoO}_6$ [6], with potential applications in *spintronics*, just to name three examples.

General formula for perovskite oxides is ABO_3 , where A is usually an alkali-earth ion and B a transition metal. The ideal cubic structure can be constructed as a three dimensional array of corner sharing $B\text{O}_6$ octahedra with A cations placed at cuboctahedral sites between eight $B\text{O}_6$ octahedra. The structure is highly versatile and can accommodate almost any element in A and/or B sites, and also more than one in each site. This explains the wide spectrum of physical phenomena found in perovskite systems and drives the search for new materials and properties.

Two different B ions placed in the structure can occupy two octahedral sites, usually in a rock salt pattern [7], and then the perovskite is double. The degree of order depends on several factors [8], but the order is mainly favored when the differences in size and charge between the involved cations are large. Besides, the different sizes of A and B cations can lead to important structural distortions. It has been shown in some systems that the degree of order and distortions strongly affect the physical properties [9–11].

Because many studied systems have equal amounts of two B ions it has become common use to write the formula of double perovskites as $\text{A}_2\text{BB}'\text{O}_6$. In this case, if only B has unpaired electrons and the order is maximum, this is all B cations placed at one octahedral site and the other site fully occupied by B' , interactions occur only through super-superexchange $B\text{-O-B}'\text{-O-B}$ paths, usually antiferromagnetic in nature. Because of the long distance between B ions, transition temperatures T_N are frequently low. In this picture disorder introduces superexchange $B\text{-O-B}$ interactions, antiferromagnetic or ferromagnetic according to the number of unpaired electrons and bond angle [12] – among other factors – and also intriguing magnetic phenomena, like spin glass behavior, formation of magnetic clusters, and frustration [13–16].

Another approach for the emergence of interesting magnetic properties is the design of new materials with different B/B' proportion. Few reports of $\text{A}_2\text{B}_{4/3}\text{B}'_{2/3}\text{O}_6$ double perovskites are found in bibliography. The particularity of this stoichiometry is that even the most ordered situation has superexchange

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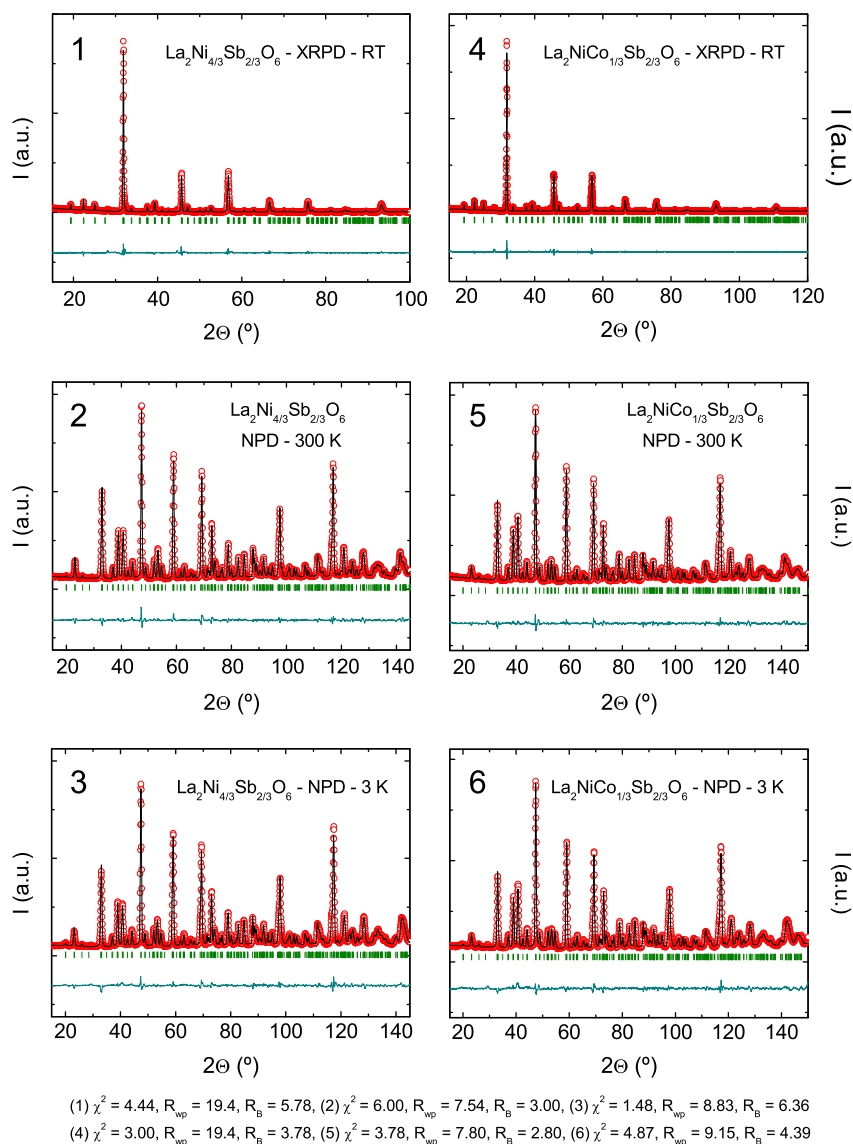


Fig. 1. Rietveld refinement in monoclinic space group $P2_1/n$ for $\text{La}_2\text{Ni}_{4/3}\text{Sb}_{2/3}\text{O}_6$ (left) and $\text{La}_2\text{NiCo}_{1/3}\text{Sb}_{2/3}\text{O}_6$ (right) of X-ray powder diffraction at room temperature (top, XRPD – RT) and neutron powder diffraction at 300 K (middle, NPD – 300 K) and 3 K (bottom, NPD – 3 K) data. Observed (circles), calculated (black line), difference (bottom line) and Bragg reflections (vertical bars).

interactions, originated by an octahedral site fully occupied by B and the other site with $1/3$ of B and $2/3$ of B' . Therefore a coexistence of different magnetic interactions occurs and competition between them may lead to a complex magnetic behavior.

Previously, a frustrated magnetic state at low temperatures was informed for $\text{La}_2\text{Ni}_{4/3}\text{Sb}_{2/3}\text{O}_6$ [17,18]. Also the synthesis, structure and magnetic properties of the double perovskite $\text{La}_2\text{Co}_{4/3}\text{Sb}_{2/3}\text{O}_6$ were reported [19]. Here we present the crystal structure of $\text{La}_2\text{Ni}_{4/3}\text{Sb}_{2/3}\text{O}_6$, which was not detailed before, and also the synthesis and crystal structure of three solid solutions between the perovskite with only Ni^{2+} or Co^{2+} : $\text{La}_2\text{Ni}_{4/3-x}\text{Co}_x\text{Sb}_{2/3}\text{O}_6$, where $x=1/3$, $2/3$ and 1. The magnetic properties of the double perovskites with nickel and cobalt are also studied and compared with the end members of the family.

2. Materials and methods

Polycrystalline samples of $\text{La}_2\text{Ni}_{4/3-x}\text{Co}_x\text{Sb}_{2/3}\text{O}_6$ with $x=0$, $1/3$, $2/3$, 1 and $4/3$ were synthesized by the solid state method from La_2O_3 , NiO , Co_3O_4 and Sb_2O_3 in stoichiometric amounts. The

powder mixture was ground and fired first at 950°C for 12 h in an air atmosphere to avoid antimony losses, given the low melting point of Sb_2O_3 (625°C). A second treatment at 1400°C , also for 12 h in the air atmosphere, was performed to obtain the single and crystalline desired phases.

The crystal structure was analyzed from X-ray (XRPD) and neutron (NPD) powder diffraction patterns. XRPD patterns were measured at room temperature on a PANalytical X'Pert PRO diffractometer in Bragg–Brentano geometry with 40 kV, 40 mA and $\text{Cu } K\alpha$ radiation of wavelength $\lambda=1.5418\text{\AA}$. The scanned angular range was $5^\circ < 2\theta < 120^\circ$ with a step size of 0.02° . NPD patterns were collected at 300 and 3 K in vanadium cans in high resolution diffractometer D2B at Institute Laue-Langevin, Grenoble, France. The wavelength used was $\lambda=1.5940\text{\AA}$, $0^\circ < 2\theta < 160^\circ$ and the step size was 0.05° in all the experiments.

Structure refinement of the diffraction data was performed using the Rietveld method [20] with Fullprof program [21]. In all cases a pseudo-Voigt function leads to good fits of the observed peaks. Background levels were estimated by interpolation between regions of the diffraction pattern where there were no peaks. The refined parameters were zero-point error, scale factor,

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