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Synthesis, structural characterization and magnetic properties of the monoclinic ordered double perovskites $BaLaMSbO_6$, with M = Mn, Co and Ni

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ABSTRACT

Double perovskites $BaLaMnSbO_6$, $BaLaCoSbO_6$ and $BaLaNiSbO_6$, were synthesized by conventional ceramic method in air, as polycrystalline powders. The Mn and Ni compounds belong to the I 2/m monoclinic space group, while the Co perovskite belongs to the I 4/m tetragonal space group. Effective presence of Mn^{2+} has been well established by X-ray emission spectroscopy for $BaLaMnSbO_6$, and there is no evidence of Mn^{3+}. $BaLaCoSbO_6$ and $BaLaNiSbO_6$ only show the expected 3D-antiferromagnetic behavior typical of super-superexchange interactions, while $BaLaMnSbO_6$ displays signs of superparamagnetism in the 40–160 K range, which arises from unbalanced antiferromagnetism inside nanoclusters formed by regions which are rich in Mn^{2+}–O^{2-}–Mn^{2+} paths. Neutron powder diffraction data for $BaLaMnSbO_6$ reveals that at 3 K, only long range order antiferromagnetic arrangement of Mn^{2+} spins on *2d* octahedral sites is obtained.

1. Introduction

The study of double perovskites $A_2BB'O_6$, with a rock salt arrangement of B and B′ ion has increasing interest because of their wide range of properties. For instance, they can be metallic, half-metallic, ferromagnetic or magnetoresistive, etc. [1–8]. Particularly, in the last years, interest has been renewed due to the appearance of room temperature Colossal Magnetoresistance (CMR) in A_2FeMoO_6 [1–3] and A_2FeReO_6 (A = Ca, Sr, Ba) [5–8].

If B and B′ are selected in such a way that only B is paramagnetic, then magnetic properties originate on this ion, either from superexchange or super-superexchange magnetic interactions between the B ions with the rock salt arrangement. The presence of superexchange and super-superexchange paths depends of the B and B′ cationic disorder on octahedral sites [9].

A wide number of $AA'BB'O_6$ double perovskites with A = Ca, Sr and Ba; A′ = La, B = magnetic 3d transition metal ions and B′ = 4th and 5th rows closed shell transition metal ions or Sb^{5+}, among others, have already been studied by different authors [10–14]. Most of them are highly ordered double perovskites, with predominant antiferromagnetic interactions showed by their negative Curie Weiss temperatures (θ) (normally with very low values of Neel temperatures T_N) and/or magnetic frustration as a consequence of competing interactions between ferromagnetic and antiferromagnetic order. This magnetic behavior is sensitive to the order-disorder between B and B′ ions on octahedral sites.

The synthesis of new double perovskites containing M^{2+} and Sb^{5+} as B and B′ ions using the series Mn^{2+}, Co^{2+} and Ni^{2+} (with $S = 5/2$; 3/2 and 1) are interesting since they offer the possibility to observe the effect on the magnetic behavior of the decreasing magnetic moment at the B site. Here we report, for the first time, the synthesis of these double perovskites, their structural characterization using powder X-ray diffraction (PXRD) and powder neutron diffraction (PND), their magnetic characterization using Magnetization (M) vs. Temperature and M vs. Magnetic field (H) measurements, and Mn ion oxidation state determination from X-ray emission spectroscopy (XES).

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