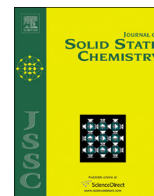




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High-pressure synthesis and characterization of $\text{BiCu}_3(\text{Mn}_{4-x}\text{Fe}_x)\text{O}_{12}$ ($x=0, 1.0, 2.0$) complex perovskites



P. Kayser^{a,*}, M.J. Martínez-Lope^a, J.A. Alonso^a, J. Sánchez-Benítez^b, M.T. Fernández^c

^a Instituto de Ciencia de Materiales de Madrid, C.S.I.C., Cantoblanco E-28049, Madrid 28049, Spain

^b Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

^c Institut Laue Langevin, BP 156X, Grenoble F-38042, France

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ABSTRACT

We have studied the series of nominal composition $\text{BiCu}_3(\text{Mn}_{4-x}\text{Fe}_x)\text{O}_{12}$ ($x=0, 1.0, 2.0$) where Mn is replaced by Fe cations in the ferrimagnetic perovskite $\text{BiCu}_3\text{Mn}_4\text{O}_{12}$. These compounds have been prepared from citrate precursors under moderate pressure conditions (3.5 GPa) and 1000 °C in the presence of KClO_4 as oxidizing agent. All the samples have been studied by x-ray and neutron powder diffraction (NPD) at room temperature and 4 K. The crystal structure has been defined in a cubic $Im\bar{3}$ (No. 204) space group with a $2a_0 \times 2a_0 \times 2a_0$ unit-cell. The doubling of the unit-cell occurs due to the ordering of Bi^{3+} and Cu^{2+} cations over A sites of the $\text{AA}'_3\text{B}_4\text{O}_{12}$ structure. The A-site accommodates 12-fold coordinated Bi^{3+} ions and, at the A'-site, Jahn–Teller Cu^{2+} ions form pseudo-square planar units aligned perpendicular to each other. $\text{Mn}^{4+}/\text{Fe}^{3+}$ cations randomly occupy the centre of slightly distorted octahedra. These materials have also been characterized by magnetic and magnetotransport measurements. We found that all the samples are ferrimagnetic and show a progressive decrease of T_C as the Fe content increases, since Fe ions disturb the ferromagnetic interactions within the B magnetic sublattice. In fact, the Curie temperature diminishes from $T_C=360$ K ($x=0$) to $T_C=219$ K ($x=2$). The magnetic structures, studied by low-temperature NPD data, correspond to an antiferromagnetic arrangement of spins at 8c and 6b sites; the ordered moments are in excellent agreement with those obtained from the saturation magnetization at 4 K. A significant magnetoresistant effect is determined for the $x=1.0$ oxide, with low-field values as high as 5% at 300 K and 1 T.

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1. Introduction

Complex perovskites with general formula $\text{AA}'_3\text{B}_4\text{O}_{12}$ have attracted the attention of the scientific community owing to their unusual structural characteristics, ordered arrangement of the A-site cations, and to their wide variety of intriguing properties, such as giant dielectric constant across a large temperature range, ferromagnetic order above room temperature and colossal magnetoresistance (CMR) in low magnetic field [1]. Particularly, CMR materials have been considered highly interesting in recent years, due to its potential technological applications [2], and substantial effort is still to be done to prepare materials with practical applications. The CMR response at low field and room temperature is still small in the best known systems such as rare-earth manganite perovskites [3], $\text{Tl}_2\text{Mn}_2\text{O}_7$ pyrochlores [4] or double perovskites [5]. During the last years, the complex perovskite $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ has attracted scientific and technological interest of the CMR community since it exhibits semimetallic and ferromagnetic properties ($T_C=345$ K), it shows a good low-field

magnetoresistance response and it does not display the strong temperature dependent decay characteristic of other perovskite-based oxides. This compound was first reported by *Chenavas* et al. in the 1970s [6] and it constitutes a paradigmatic example of the $\text{AA}'_3\text{B}_4\text{O}_{12}$ perovskite-like family: the A-site is generally occupied by a large monovalent, divalent or rare-earth cation and A' requires the presence of Jahn–Teller cations, such as Cu^{2+} or Mn^{3+} . This particular characteristic is essential to stabilize the structure and also plays an important role on the properties of these materials. At the B sites, located in axially distorted octahedral units, the tetravalent Mn^{4+} , Ti^{4+} , Ru^{4+} , Sn^{4+} cations have been described to participate in this structure [1]. The crystal symmetry is cubic (space group $Im\bar{3}$) with a doubling of the ideal perovskite cell. This superstructure is due to the 1:3 ordering of A and A' ions and the distortion of the oxygen sublattice, which leads to a tilted three-dimensional network of BO_6 octahedra sharing corners.

The Ca^{2+} cations at A-sites can be replaced by rare-earths in the $\text{RCu}_3\text{Mn}_4\text{O}_{12}$ [7] family or by other trivalent cations such Bi^{3+} in $\text{BiCu}_3\text{Mn}_4\text{O}_{12}$ [8]. In previous works we investigated the effect of Fe-doping the Mn sublattice, in $\text{CaCu}_3(\text{Mn}_3\text{Fe})\text{O}_{12}$ [9] and $\text{RCu}_3(\text{Mn}_3\text{Fe})\text{O}_{12}$ [10] oxides, which stimulated the present study of the $\text{BiCu}_3(\text{Mn}_{4-x}\text{Fe}_x)\text{O}_{12}$ ($x=0, 1.0, 2.0$) series. Although the parent compound, $\text{BiCu}_3\text{Mn}_4\text{O}_{12}$, was previously synthesized at pressures up

* Corresponding author.

E-mail address: paula.kayser@icmm.csic.es (P. Kayser).

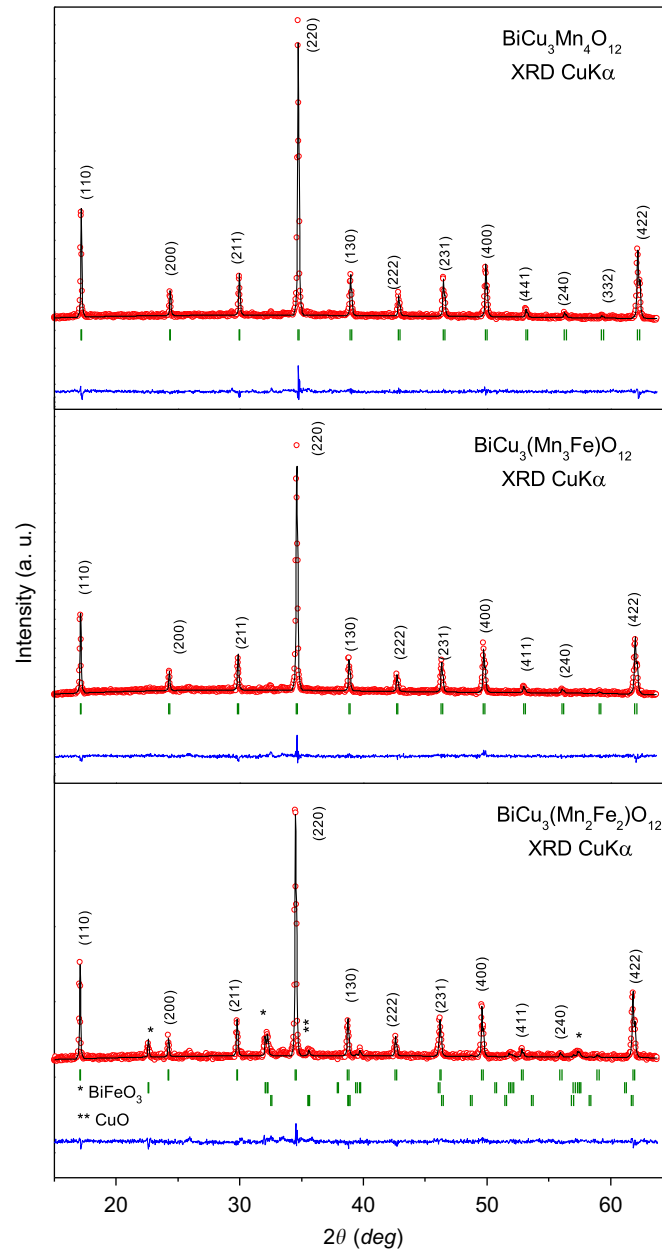


Fig. 1. XRD patterns (CuK α , $\lambda=1.5406$ Å) of BiCu $_3$ (Mn $_{4-x}$ Fe $_x$)O $_{12}$ ($x=0, 1.0, 2.0$) oxides.

to 6 GPa, we have been able to synthesize polycrystalline samples of this material at moderate pressure conditions (3.5 GPa), starting from very reactive precursors obtained by wet-chemistry procedures, in the presence of KClO $_4$ as *in-situ* oxidizing agent. The same conditions are used to synthesize an Fe-doped series in BiCu $_3$ (Mn $_{4-x}$ Fe $_x$)O $_{12}$, where a dramatic variation of the magnetic and transport properties is observed. The crystal and magnetic structures are studied by NPD, in complement with the mentioned properties of interest.

2. Experimental section

The synthesis of BiCu $_3$ (Mn $_{4-x}$ Fe $_x$)O $_{12}$ series requires the previous preparation of very reactive precursors, via citrate–nitrate method. Stoichiometric amounts of Bi $_2$ O $_3$, Cu(NO $_3$) $_2 \cdot 3$ H $_2$ O, MnCO $_3$ and FeC $_2$ O $_4 \cdot 2$ H $_2$ O were dissolved in a citric acid aqueous solution with some droplets of HNO $_3$. This solution was then slowly evaporated leading to organic resins that contain a homogeneous distribution

of the involved cations. After evaporation, the resulting resins were dried at 140 °C and then heated at 600 °C for 12 h in order to decompose the organic materials and eliminate the nitrates. KClO $_4$ (30% in weight), which is an oxidizing agent, was ground with the precursor powder. The mixture was put into a gold capsule, sealed and introduced in a cylindrical-graphite heater. The synthesis was carried out in a piston-cylinder press (Rockland & Co) at 3.5 GPa and 1000 °C for 1 h. Then the materials were quenched to room temperature and the pressure was slowly released. Finally, the polycrystalline samples were washed in a dilute HNO $_3$ aqueous solution to eliminate the KCl, originated from the decomposition of KClO $_4$, and the small amount of unreacted CuO.

Phase identification was initially determined by x-ray diffraction (XRD) using a Bruker-AXS D8 diffractometer (40 kV, 30 mA), controlled by DRIFFACT^{PLUS} software, in Bragg–Brentano reflection geometry with CuK α radiation ($\lambda=1.5418$ Å) and a PSD (Position Sensitive Detector). For the structural refinements, NPD data were collected at room temperature (RT) and at 4 K at the high resolution

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