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The Influence of Cr doping on the Structural and Magnetic Properties of HoMnO₃ Multiferroic Ceramics

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Abstract. In this research single-phase Cr-doped HoMnO₃ ceramics were synthesized via solid state reaction method. The structural and magnetic characteristics of the prepared samples were examined using various characterization techniques, including x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and vibrating sample magnetometer (VSM). All samples exhibit single phase that emphasized by SEM and XRD. Magnetic properties of the prepared samples at low temperature (10K) showed the presence of different magnetic characteristics. The change in magnetic behavior could probably occur due to slight decrease in the unit cell volume that leads to a structural distortion in the lattice. Cr-doped HoMnO₃ could be a good candidate with a better ferromagnetic property for practical multiferroic applications.

1. Introduction

Nowadays the research, development and applications of ceramic materials are the most fast growing field of material science [1-16]. Multiferroic materials which show coexistence of (anti) ferromagnetic and ferroelectric orders have achieved a great deal of interest for many years [17-19]. In principle, these materials could enable single device components to perform multiple functions [20]. Due to magnetoelectric effect in these materials many expected technical applications are recommended such as, future multiple-state memory technologies, traditional magnetic data storage tools and high-density low-power data storage devices [21]. Furthermore, they could be applied in various ways for sensors, transducers as well as fiber optical communications [22]. Although these materials are highly interesting, different challenges have emerged in dealing with multiferroicity, which hinder the practical applications of these materials, the first dilemma is that multiferroic materials are rare and normally show small coupling of multiferroic characteristics or exist only at low temperatures [23]. Also, synthesizing these kind of materials normally produces a mixture of the main phase along with other impurity phases [24]. To address these obstacles, intensive work has been done to discover new single phase multiferroic materials, as well as to improve the multiferroic properties through doping processes.

Single-phase rare-earth manganites are one of the well-known multiferroic materials, it is of huge interest in the context as different cations can be chosen in order to combine magnetic and polar properties. The multiferroic phenomenon normally occurs in perovskite-structure oxide [25]. In these materials multiferroic properties can be enhanced through A-site doping which is a partial replacement in the rare-earth site, or B-site doping which is a partial replacement in manganese site.



Multiferroic behavior has been reported in hexagonal and orthorhombic $REMnO_3$ [26, 27], $REMn_2O_5$ [28, 29] and some other compounds lately. Strong enhancement of magnetoelectric coupling has been reported in Dy^{3+} doped $HoMnO_3$, Fe-substituted Mn in $YMnO_3$ and $ErMnO_3$ respectively [30-32]. Moreover, substantial changes in the electric and magnetic properties have been observed in Yttrium doped $GdMnO_3$ [33]. Since $HoMnO_3$ (HMO) compounds in either the orthorhombic or hexagonal structure are multiferroic and exhibiting both antiferromagnetic and ferroelectric order below antiferromagnetic transition temperature, Cr-doped HMO samples may become interesting due to formation of ferromagnetism of Mn moments and structural distortion in the lattice, which can enhance the dipole ordering. Cr-doped HMO samples could be the promising candidate for multiferroic applications performing good ferroelectric and ferromagnetic properties. As far as is concerned, the effect of Cr doping in $HoMnO_3$ will be performed first time in the literature. This research work aims at substituting Cr into Mn site in the $HoMnO_3$ to produce single phase perovskite multiferroic ceramics.

2. Experimental methods

2.1. Synthesis of $HoMn_{1-x}Cr_xO_3$

Single-phase $HoMn_{1-x}Cr_xO_3$ ($x = 0.2$ and 0.8) bulk ceramic materials were prepared by conventional solid state synthesis technique. A high purity Ho_2O_3 (99.9%; Alfa Aesar), Mn_2O_3 (98%; Alfa Aesar) and Cr_2O_3 (99.9%; Alfa Aesar) powders were used as reactants. Stoichiometric proportions of these powders were milled to obtain a homogeneous mixture of green powder of fine particle size. The green powder was then mixed in ethanol in a plastic container using zirconium balls for 6 hours. Two different compositions were prepared; $HoMn_{1-x}Cr_xO_3$ where $x = 0.2$ and 0.8 . After drying the liquid mixture in an oven at $95^\circ C$ for 24 h, the powder mixture was calcined at $600^\circ C$ for 10 h, then ground in a mortar to refine particles and sintered at different temperatures between 1100 - $1350^\circ C$ for 10 h with a heating and cooling rate of $5^\circ C/min$ to obtain the phases development. Part from the powders were used to produce dense cylindrical pellets with radius about 5 mm and thickness 2 mm, using pressing device with pressure of 10 MPa. Heat treatment was carried out in a high temperature programmable furnace at $1400^\circ C$ for 24 h with a heating and cooling rate of $2^\circ C/min$.

2.2. Characterization

The structural properties of the sintered ceramic materials were investigated using a Bruker D2 PHASER powder x-ray diffractometer, operated in the Bragg-Brentano geometry with $Cu K\alpha$ radiation at 1.54 \AA in the angular range of $10^\circ \leq 2\theta \leq 70^\circ$ with a scanning rate of $1^\circ/min$ and a step size of 0.01016° . FullProf/Rietveld software was used for computer based examination. Microstructures of the sintered samples were studied using scanning electron microscopy (SEM, JEOL5910 LV) with different magnification values using secondary and back-scattered electrons and surface analyses of samples were investigated by energy dispersive X-ray spectrometer (EDX). Furthermore, the magnetic measurements of Cr doped $HoMnO_3$ samples were made at low temperature (10 K) using the vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Structures

Figure 3.1 shows the XRD pattern of B-site doped $HoMn_{1-x}Cr_xO_3$ ($x = 0.2, 0.8$) ceramics carried out at ambient temperature. The unit cell parameters were obtained using FullProf/Rietveld software. The observed and standard diffraction peaks from Inorganic Crystal Structure Database showed good matching and no additional peaks were seen. Rietveld refinements on all the samples confirmed the synthesizing of pure single-phase perovskite structure crystallized in an orthorhombic structure (Figures. 1, 2 and 3).

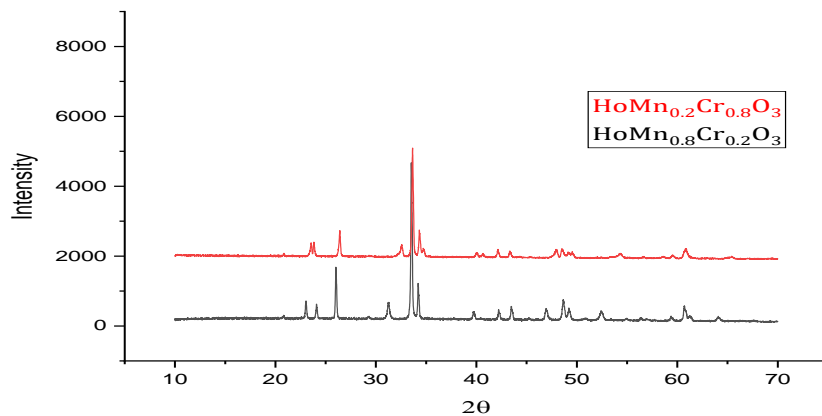


Figure 1. Room temperature XRD patterns of $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ ceramics compound ($x=0.2$ and 0.8) sintered at 1350°C .

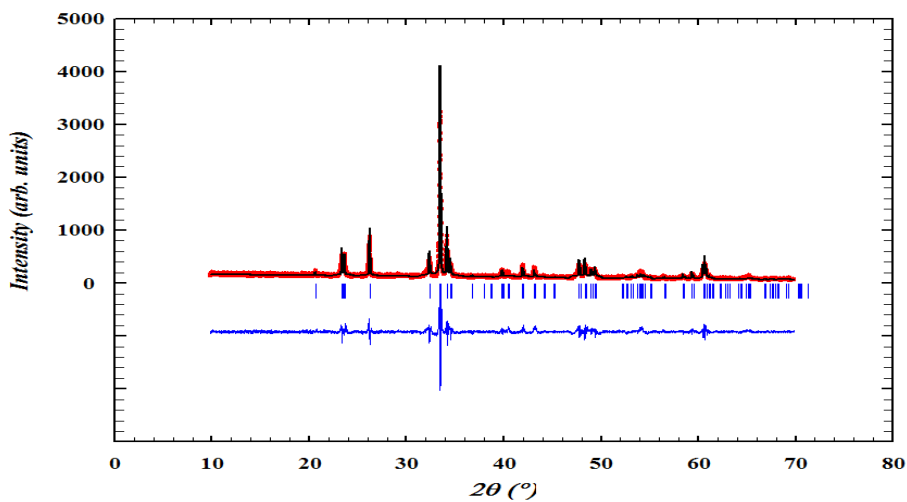


Figure 2. XRD pattern for $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ ceramics sample at ($x=0.2$) Rietveld fit agreement factors are $R_p=56.8$, $R_{wp}=37.0$, $\chi^2=3.48$.

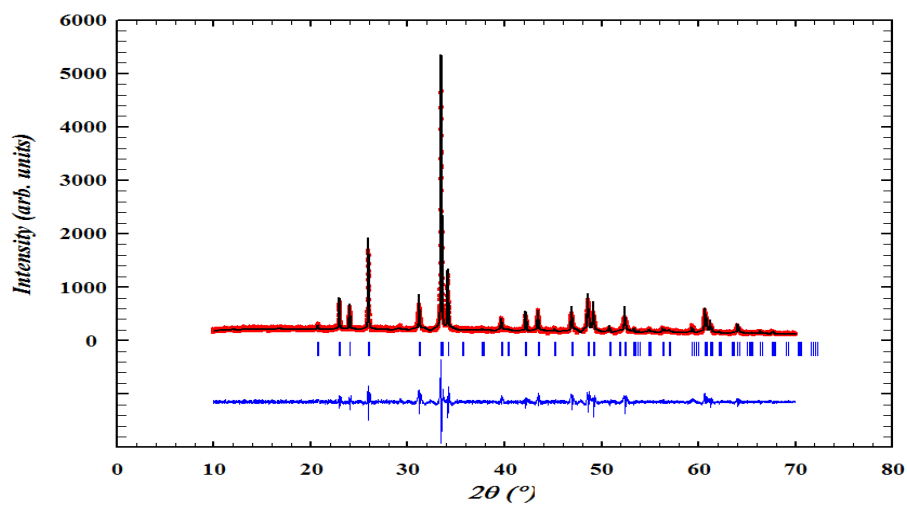


Figure 3. XRD pattern for $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ ceramics sample at ($x=0.8$) Rietveld fit agreement factors are $R_p=73.4$, $R_{wp}=48.0$, $\chi^2=4.32$.

The most important notice to be made here is that a close investigation of the peaks shows a presence of a shift in the peak positions to the higher angles with increasing the amount of doping elements. This feature agrees with Vegard's law [34], as the replacement of large radius Mn_{q+} ion ($r_{Mn} = 1.79 \text{ \AA}$) by smaller Cr_{q+} ($r_{Cr} = 1.18 \text{ \AA}$) result on decrease in the unit cell volume that may cause a slight distortion in the lattice and a modification of the crystal structure. This latter might be a crucial factor controlling the magnetic behavior of the material. FullProf/Rietveld software was used to evaluate the unit cell parameters (Table 1). With increasing the amount of Cr the units cell volume is decreasing due to the smaller ionic radius of Cr (1.18 \AA) compared to Mn (1.79 \AA).

Table 1. Lattice parameters resulted from refinement procedure of powder XRD pattern of $HoMn_{1-x}Cr_xO_3$ ceramics compound ($x=0.2, 0.8$).

Composition	a (\AA)	b (\AA)	c (\AA)	Volume (\AA^3)	Space group
$HoMnO_3$	5.2700	5.8400	7.360	226.52	Pnma
$HoMn_{0.8}Cr_{0.2}O_3$	5.2720	5.7950	7.380	225.45	Pnma
$HoMn_{0.2}Cr_{0.8}O_3$	5.2277	5.5080	7.508	215.92	Pnma

3.2. Scanning electron microscopy (SEM) and EDS investigation of $HoMn_{1-x}Cr_xO_3$

Microstructure investigations of Cr-doped $HoMnO_3$ are carried out by SEM and shown in Fig. 4(a), (b), (c) and (d). From the secondary and backscattered SEM photographs of the two samples ($HoMn_{0.8}Cr_{0.2}O_3$ and $HoMn_{0.2}Cr_{0.8}O_3$), it is clearly visible that there is no any phase contrast, which is a good indication for the formation of the single phase. The grain sizes of the prepared samples were between 2-4 μm and 1-3 μm respectively, showing that the grains sizes were decreasing when the doping concentration were increased.

The results of EDS analysis taken from grains of $HoMn_{0.8}Cr_{0.2}O_3$ and $HoMn_{0.2}Cr_{0.8}O_3$ showed that the theoretical weight percentages were near to the calculated values. Au and Pd were due to coating made on the samples.

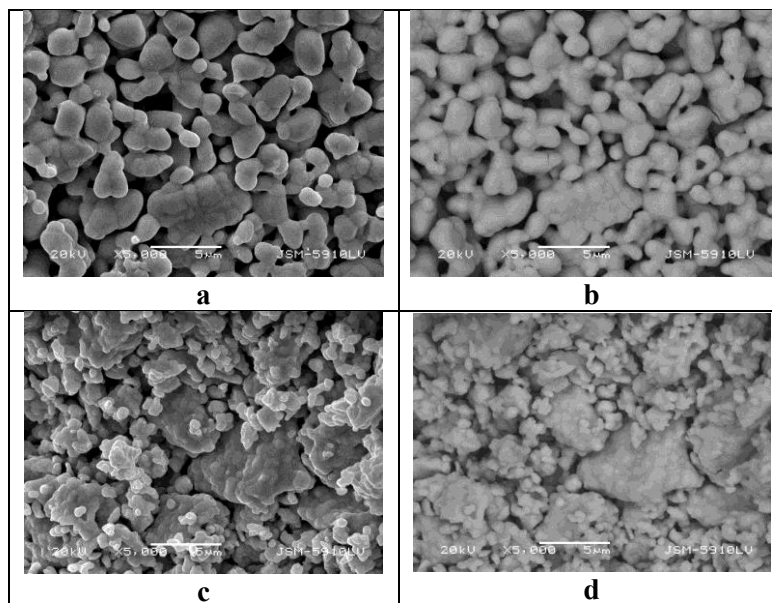


Figure 4. SEM micrographs of Cr doped $HoMnO_3$ sample at $\times 5.000$
a) SEI of $HoMn_{0.8}Cr_{0.2}O_3$, **b)** BEI of $HoMn_{0.8}Cr_{0.2}O_3$,
c) SEI of $HoMn_{0.2}Cr_{0.8}O_3$ and **d)** BEI of $HoMn_{0.2}Cr_{0.8}O_3$
 samples ($HoMn_{1-x}Cr_xO_3$ ceramic where $x=0.2$ and $x=0.8$).

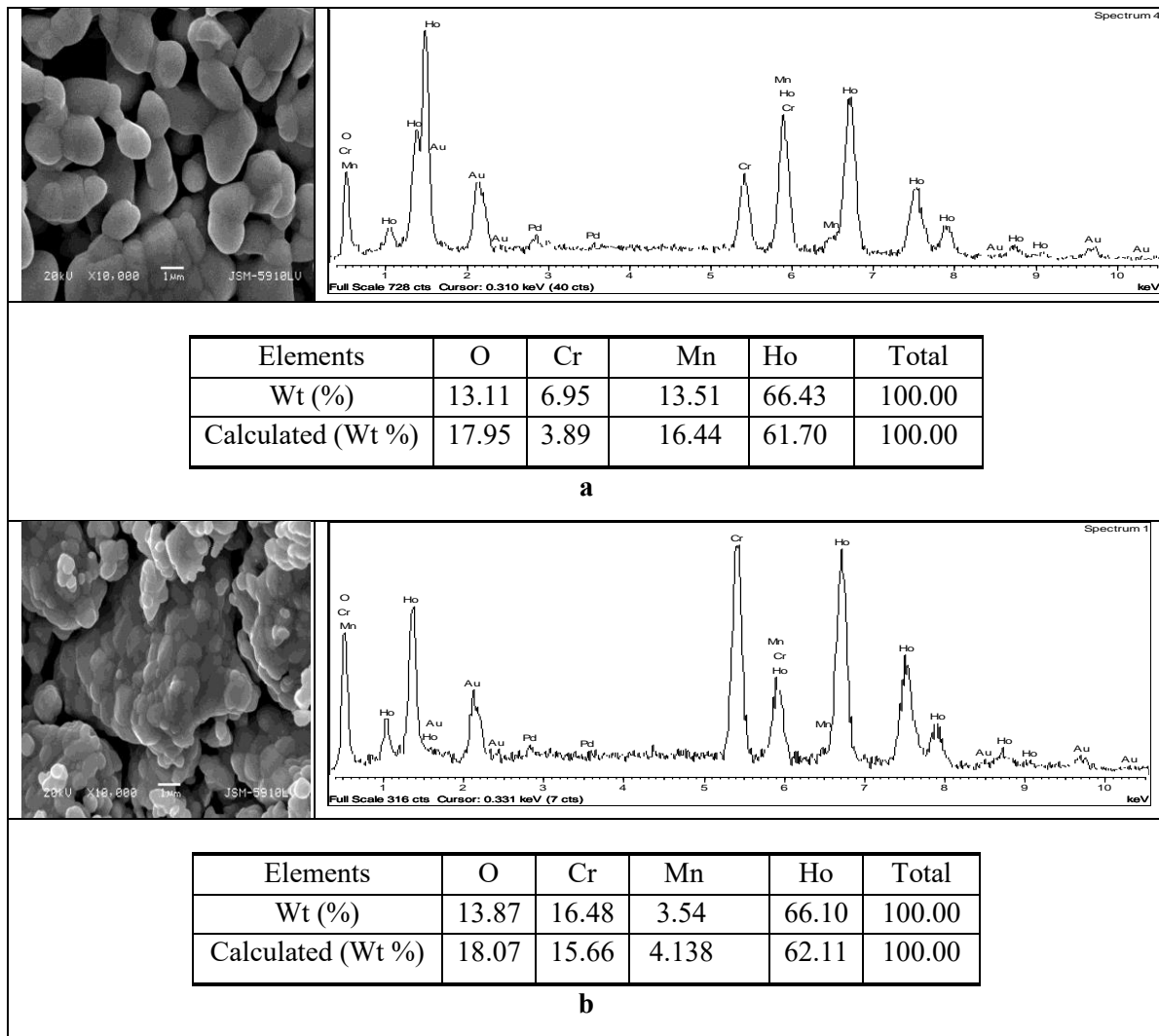


Figure 5. EDS analysis Cr doped HoMnO_3 samples a) EDS analysis of $\text{HoMn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ and b) EDS analysis of $\text{HoMn}_{0.2}\text{Cr}_{0.8}\text{O}_3$ sample (Tables show the theoretical weight fractions of the elements and practical values from EDS results).

3.3. Magnetic properties

The magnetic characteristics of $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ ($x = 0.2, 0.8$) multiferroic ceramics were studied at low temperature (10 K) to reveal the influence of Cr doping in the magnetic behaviors. Magnetization of $\text{HoMn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ and $\text{HoMn}_{0.2}\text{Cr}_{0.8}\text{O}_3$ at 10 K as a function of magnetic field ($M-H$) is shown in Fig. 5. The enhancement in the magnetization of $\text{HoMn}_{0.2}\text{Cr}_{0.8}\text{O}_3$ multiferroic ceramic might be attributed to the change in canting angle [35] or suppression of the complicated spiral spin structure [36] along with coupling interaction between the Mn^{3+} and Cr^{3+} ions in the sample [37].

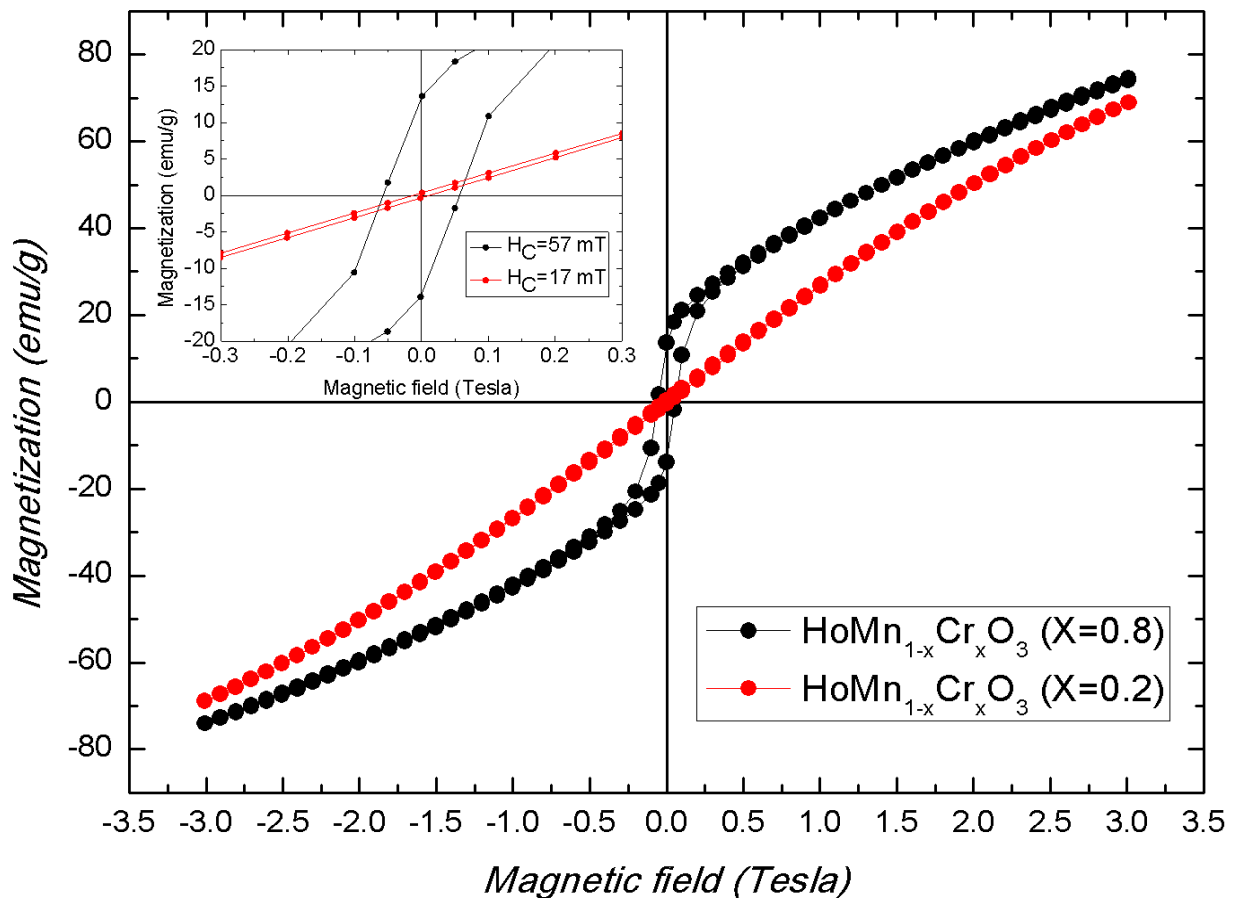


Figure 6. The magnetic hysteresis loops of $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ ceramics compound (0.2 and 0.8) sintered at 1350°C

4. Conclusion

The work in this research verifies the influence of B-site doping on the structural and magnetic properties of bulk HMO multiferroic ceramics. Through tuning the reaction conditions such as, sintering temperature and the chemical synthesis procedure, a variety of single phase orthorhombic $\text{HoMn}_{1-x}\text{Cr}_x\text{O}_3$ bulk samples with different morphologies, structure and compositions were successfully prepared via conventional solid state reaction route at ambient conditions, all samples showed distorted orthorhombic perovskite structures with space group Pnma. The produced doped samples exhibit significant change of the magnetic characteristics probably due to the structural distortion.

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