



Structures, and far-infrared and Raman spectra of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-1.0$)

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ABSTRACT

We report the structural and optical properties of the perovskite $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-1.0$) compounds. Far-infrared (FIR) and Raman spectroscopy measurements were carried out at room temperature. The FIR spectra show four vibration modes at ~ 190 , ~ 250 , ~ 400 , and $\sim 600\text{ cm}^{-1}$ that correspond to external, torsional, bending, and stretching modes, respectively. It was found that the FIR active vibration energies exhibit splitting and shifting as the Co doping level increases. The Raman spectra reveal that the most intense spectral feature in the GdMnO_3 is at 612 cm^{-1} , which shifts to higher and lower energies, depending on the Co doping level.

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1. Introduction

The multiferroic materials which exhibit magnetism and the ferroelectric effect have drawn great attention due to their potential in emerging technological applications, as well as their exotic physical properties. The rare-earth compounds RMnO_3 (with R a rare earth element) have been numbered among these multiferroic materials since a very large magnetoelectric effect was discovered [1–3]. These RMnO_3 systems are interesting compounds for the study of the correlation between spin-phonon coupling and the magnetoelectric effect. This correlation can be examined by tuning the Mn^{3+} magnetic structure using different rare-earth and transition metal ions. The structures of the RMnO_3 compounds can be grouped into hexagonal structure for $R=\text{Ho-Lu}$ and distorted orthorhombic structure for $R=\text{La-Dy}$. The hexagonal RMnO_3 compounds show both ferroelectric and magnetic order, but the corresponding ordering temperatures differ by an order of magnitude. GdMnO_3 , TbMnO_3 , and DyMnO_3 have comparable transition temperatures. TbMnO_3 and DyMnO_3 exhibit an incommensurate antiferromagnetic order below 40 K [1–6]. Cobalt is one of the typical transition metals that can significantly affect the magnetic and optical properties of the RMnO_3 compounds [7]. Infrared active phonons have been observed and investigated for $\text{HoMn}_{1-x}\text{Co}_x\text{O}_3$ [8]. Co doping shows a great effect on the structures and on the spin glass and spin states in $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ for $x<0.5$ [7]. In this paper, we report the crystal structures and active phonon

modes of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ from $x=0$ to 1.0, with a step size of 0.1, using far-infrared (FIR) and Raman spectroscopy.

2. Experiments

Polycrystalline samples of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-1.0$) were synthesized by standard solid-state reaction. The appropriate amounts of Gd_2O_3 , Mn_2O_3 , and CoCO_3 were well mixed, pelletized, and sintered at $900\text{ }^\circ\text{C}$ for 24 h in air. The final sintering was carried out at $1200\text{ }^\circ\text{C}$ for 12 h. The structures of the $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.2-0.9$) compounds were characterized by using a Philips diffractometer with $\text{CuK}\alpha$ radiation. For FIR transmission experiments, the $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x=0-1.0$) powders were diluted in CsI , finely milled, and then pressed into pellets 1 mm in thickness and 10 mm in diameter. A pure CsI pellet was also prepared as a reference sample. The FIR transmission measurements were carried out employing a Bomen DA3.26 rapid scan interferometer with a detector that has a range of $10-700\text{ cm}^{-1}$. The resolution and scan speed were 4 cm^{-1} and 0.2 cm^{-1} per second, respectively. Raman spectroscopy measurements were carried out using a JOBIN YVON HR800 Confocal Raman system with 632.8 nm diode laser excitation on a 300 lines/mm grating in the range of $100-2000\text{ cm}^{-1}$. Both FIR and Raman spectra were obtained at room temperature.

3. Experimental results and discussion

The crystal structure of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ is schematically shown in Fig. 1. The calculated and observed X-ray diffraction patterns of the $\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ sample are shown in Fig. 2. The $(\text{Mn/Co})\text{O}_6$ octahedron distorts with the various Co doping levels. The Rietveld refinement results show that $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ is crystallized in the orthorhombic structure with space group $P1mn$. The lattice

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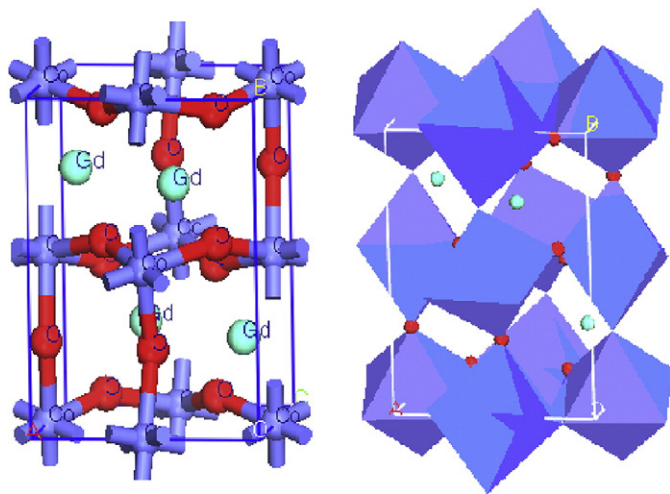


Fig. 1. The crystal structure of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$.

parameters of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ as a function of x are shown in Fig. 3. It can be seen that the lattice parameter b remains constant while the lattice parameters a and c increase with increasing Co content. This is an indication that the $(\text{Co}/\text{Mn})\text{O}_6$ octahedron becomes more elongated along the a -axis with larger amounts of cobalt doping.

Fig. 4 shows the doping dependent far-infrared transmission spectra of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ in the range of $130\text{--}700\text{ cm}^{-1}$. For the $Pbnm$ space group of orthorhombic RMnO_3 , a factor group analysis predicts $9B1u + 7B2u + 9B3u$ infrared-active modes and $7Ag + 7B1g + 5B2g + 5B3g$ Raman-active modes. These modes are associated with three phonon bands that correspond to the normal modes of the ideal cubic perovskite: the external mode is due to R and MnO_6 , while the bending and stretching modes are mainly due to the oxygen vibration [6,9]. In FIR

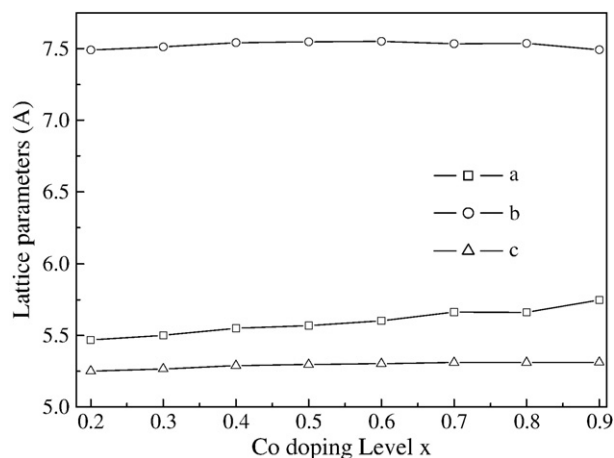


Fig. 3. Lattice parameters of $\text{GdMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.2\text{--}0.9$).

transmission spectra of GdMnCoO_3 samples, the most active phonon modes at $\sim 190\text{ cm}^{-1}$, $\sim 250\text{ cm}^{-1}$, $\sim 400\text{ cm}^{-1}$ and $\sim 600\text{ cm}^{-1}$ are assigned to the external (E), torsional (T), bending (B), and stretching (S) modes, respectively. In Table 1, we list the value these four modes at various doping obtained from far-infrared measurement. There are some splits between the vibration bands. These results are similar to the FIR reflectivity spectrum observed from a GdMnO_3 sample [6,10]. The features of the phonon modes of $\text{GdMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ are observed to be very similar to what has been observed for $\text{RMn}_{0.5}\text{Co}_{0.5}\text{O}_3$ ($R = \text{La, Nd, Dy, Ho, and Yb}$) [11]. The external band is at $\sim 190\text{ cm}^{-1}$, and weak bands are seen on both sides ($\sim 172\text{ cm}^{-1}$, 210 cm^{-1}). The torsional band is at 290 cm^{-1} , and a weak band starts to develop at 272 cm^{-1} when $x = 0.5$. Both the bending and the stretching bands broaden at $\sim 400\text{ cm}^{-1}$ and $\sim 600\text{ cm}^{-1}$.

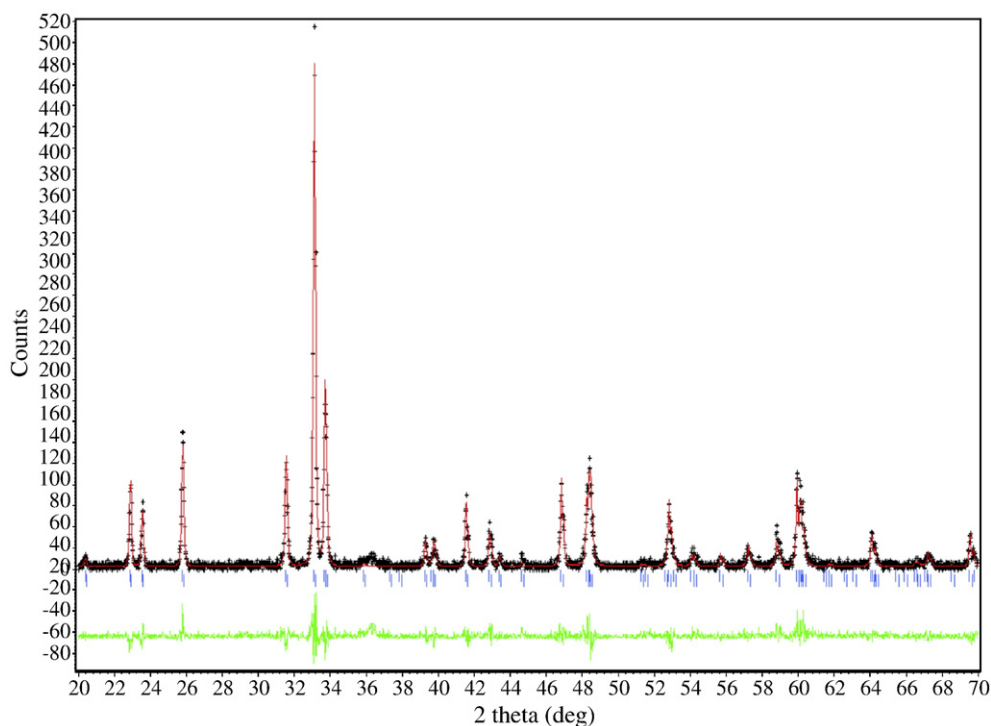


Fig. 2. The calculated (solid line) and observed (symbols) XRD patterns for the $\text{GdMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ sample. The bottom solid line shows the difference between them, and the short blue lines indicate the line positions of the standard.

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