Infrared-active phonons of HoMn$_{1-x}$/Co$_x$/O$_3$ ($x = 0-0.8$)

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INFRARED-ACTIVE PHONONS OF HoMn$_{1-x}$Co$_x$O$_3$ (x= 0-0.8)

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We report an experiment study of infrared active phonons and present a comparative analysis of infrared spectra of polycrystalline HoMn$_{1-x}$Co$_x$O$_3$ (x= 0-0.8).

Perovskite containing rare earth and transitional metal cation on A and B sites (with general formula ABO$_3$) is a class of material which exhibits interesting and useful electronic and magnetic properties. The cobaltite/manganite perovskites A(Mn$_{1-x}$Co$_x$)$_2$O$_4$, where A is a lanthanide, exhibit ferromagnetism. The ferromagnetism arises from the superexchange interaction between Co$^{3+}$ and Mn$^{4+}$ ions mediated by oxygen [1]. The Curie temperature, $T_C$, is relatively high and decreases systematically with decreasing radius of the ion on the A site [2]. The magnetic behavior of rare-earth cobaltite/manganite perovskite compounds is therefore seen to be intimately related to their structure. The magnetic behavior of A(Mn$_{1-x}$Co$_x$)$_2$O$_4$ compounds having larger ions (La, Pr, Nd, Sm, Eu) and those having smaller ions (Gd, Tb, Dy, Y, Ho) on the A site has been investigated. Also phonon modes and phonon energies in cobaltite/manganites, have been determined by far-infrared spectroscopy. The phonon energies systematically shift and split, and new modes appear as the mass of the lanthanide is increased through the series A = La, Nd, Dy, Ho, Yb. This behavior of the phonon modes correlates with the magnetic properties of this series of compounds, in particular with the appearance of metamagnetism for the compounds with smaller ions on the A site [3].

Polycrystalline samples HoMn$_{1-x}$Co$_x$O$_3$ were synthesized by the standard solid-state reaction method. For the samples with x = 0-0.8 doping level, x-ray diffraction show that structures are orthorhombic and HoMnO$_3$ is hexagonal. The lattice parameter increases as Co doping level decreases. The ferromagnetism is gradual suppressed when doping level greater and less than x=0.5. The polycrystalline samples diluted in Csl have been finely milled and pressed into pellets for infrared transmission measurement. We performed infrared spectroscopy on the HoMn$_{1-x}$Co$_x$O$_3$ samples. For each sample we measured the ratio $I(\omega)/I_{0}(\omega)$, where $I(\omega)$ is the transmitted intensity through the pellet containing the holmium manganese oxide and that $I_{0}(\omega)$ is the transmitted intensity through pure Csl pellet. The infrared transmission spectra of polycrystalline HoMn$_{1-x}$Co$_x$O$_3$ at room temperature are shown in Figure 1. The normalized spectra of optical density is proportional to the optical conductivity $\sigma(\omega)$ [4,5].

$$\sigma(\omega) = \ln[I(\omega)/I_{0}(\omega)] \propto \sigma(\omega). \quad (1)$$

The energies of phonons HoMn$_{1-x}$Co$_x$O$_3$ samples can be obtained from spectra of optical density. The spectra exhibit numerous peaks associated with the infrared active phonons modes. To extract information on phonons we fit the spectra of optical density using a sum of noninteracting harmonic oscillators (lorentz model)[6,7]. The minimum number of oscillators obtaining a reliable fit for samples HoMn$_{1-x}$Co$_x$O$_3$ will be reported.

Fig. 1. Transmission spectra of polycrystalline HoMn$_{1-x}$Co$_x$O$_3$ (X= 0-0.8) at room temperature.

The optical modes of the ideal cubic structure have the irreducible representation $\Gamma = 3P_{1u}$ (infrared active) + $F_{g}$ (infrared inactive). Last [8] identifies the bands in order of increasing energy as external A-(BO$_2$) vibration, O-B-O bending, and B-O stretching. As the crystal symmetry is reduced, more optical modes are expected. There are 25 infrared active modes for orthorhombic (D$_{2h}$; Pnma) symmetry [9]. Consequently, the four broad bands for HoMn$_{1-x}$Co$_x$O$_3$ (x=0.2-0.8) at $\omega_1$~190 cm$^{-1}$, $\omega_2$~270 cm$^{-1}$, $\omega_3$~420 cm$^{-1}$, $\omega_4$~600 cm$^{-1}$, are assigned to the external, torsional, bending and stretching modes, respectively. The behavior of four main bands of HoMn$_{1-x}$Co$_x$O$_3$ with different Co element doping level will be analysed in detail.

References