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Far Infrared Spectra of La$_{1-x}$Ca$_x$Mn$_{0.9}$Li$_{0.1}$O$_3$

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Abstract. This work is a study on phonon modes of polycrystalline La$_{1-x}$Ca$_x$Mn$_{1-y}$Li$_y$O$_3$ (x = 0.1 - 0.5) by far infrared (FIR) spectroscopy. Samples were prepared by a conventional solid state reaction method. Lithium is a volatile element which can cause changes in the FIR spectra of La$_{1-x}$Ca$_x$Mn$_{0.9}$Li$_{0.1}$O$_3$ compared to the spectra of La$_{1-x}$Ca$_x$MnO$_3$. The far infrared spectra show that the external mode [La(Ca)] - [Mn(Li)O$_3$], the O - Mn(Li) - O bending mode and Mn(Li) - O stretching mode behave similarly and increase in energy as the Ca concentration increases. The Li$^+$ ion is lighter than the Mn^{3+} ion and its ionic radius is slightly larger than that of the Mn^{3+} ion. Thus Li doping introduces unit cells that are even smaller due the Mn^{4+} ions radius being smaller than Mn^{3+}. This will lead to new lattice modes. Also the high ionicity of Mn^{4+} leads to a stronger inter-ion electrostatic interaction. As a result the frequencies of lattice vibrations increase. Some evidence of Li incorporation in the crystal lattice is useful, and Li ion doping has now been detected by our FIR spectroscopic technique. These phenomena are all observed in FIR transmission measurements.

1. Introduction

Far-infrared spectroscopy is sensitive to lattice modes and thus is an appropriate probe to study the optical properties of perovskite-structure materials. Systematic studies of ABO(LaMnO) perovskites on the effects of La-site doping by Ca at different doping levels have been widely reported since the electronic and magnetic properties dramatically change depending on the doping level. On the introduction of secondary ions to replace Mn, the magnetic and resistive transitions shift continuously to lower temperature, until the resistive one finally disappears [1, 2]. Phonons and the electron-phonon interaction play an important role in the phenomenon of colossal magneto resistance (CMR) observed in lanthanum perovskites. The lattice plays an important role [3] in the understanding of optical properties of CMR as demonstrated in isotopic-doping experiments [4] and in electron-phonon coupling calculations [5, 6]. FIR reflectivity measurements have been carried out to examine whether the energies of the principal phonons provide a signature of the paramagnetic insulator/ferromagnetic metal (PMI/FMM) transition [7]. The phonon energies fall in the range 20-100 meV and so are ideally suited to investigation by infrared spectroscopy. Lewis et al. [8] reported on the reflectivity spectra of

$La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.8}Li_{0.2}MnO_3$ samples, and noted a shift between the samples in the "external" phonon mode (~ 200 cm^{-1}) arising from the (La, Ca/Li) vibration against the MnO$_3$ octahedra which is explained on the basis of composition. In the infrared spectrum of $La_{0.8}Li_{0.2}MnO_3$, the "bending" and the "stretching" modes, both attributed to motion of the (Mn, Li) ions relative to the O atoms, occur at a higher frequency than in $La_{0.7}Ca_{0.3}MnO_3$. This is explained by the average mass on the Ca site being reduced by the introduction of Li ions.

In this work, we investigate the phonon modes of simultaneous systematically doping of Ca for $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ (x = 0.1 - 0.5) by FIR optical spectroscopy and compare with the FIR spectra without Li ion doping.

2. Experimental

Samples of $La_{1-x}Ca_xMn_{1-y}Li_yO_3$ were prepared by a conventional solid-state reaction method. High-purity stoichiometric mixtures of La_2O_3, $CaCO_3$, $MnCO_3$ and Li_2CO_3 were weighed out according to nominal composition. The mixtures were first sintered at a temperature of 1100 °C for 24 hours. After grinding them well, the powders were pressed into pellets and re-sintered at 1150 °C for over 24 hours. At 500 °C the samples were quenched. The phase and crystal structure of the synthesized samples were examined by X ray diffraction (XRD) using a Philips diffractometer with CuKα radiation and scanning electron microscopy (SEM). In view of the volatile character of Li, some evidence of its incorporation in the crystal lattice is useful. Unfortunately, Li is too light to be detected by energy disperse spectroscopy (EDS). The magnetic properties were studied over the temperature range 77 - 300 K.

We performed FIR measurements on $La_{1-x}Ca_xMn_{1-y}Li_yO_3$ samples at room temperature using a Bomem DA3.26 rapid scan interferometer with DTGS detector between 10 - 700 cm^{-1}. The experimental resolution and scan speed were 4 cm^{-1} and 0.2 cm^{-1}/s respectively. The samples for FIR experiment were made of $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ polycrystalline powder diluted in CsI, finely mixed and pressed into pellets. The absorption spectra were analyzed by taking the ratio of $I(\omega)/I_0(\omega)$, where $I(\omega)$ is transmitted intensity through the pellet containing lanthanum manganese oxide and $I_0(\omega)$ is the transmitted intensity through a pure CsI pellet. The energy range is limited to 150 - 680 cm^{-1} as CsI is opaque at low frequencies [9].

3. Results and discussion

For samples $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ (x = 0.1 - 0.5), XRD data show that all compounds are orthorhombic structures. The unit volume decreases as Ca doping increases. The Curie temperature increased from 190 to 270 K for x = 0.1 - 0.3 and decreased to 180 K for x = 0.5. The details of structures and magnetic properties have been discussed elsewhere [10].

In Fig. 1, the FIR transmission spectra were measured at room temperature are shown. In manganite perovskites, the order external, bending, stretching has been given for the phonon features [7]. Three main phonon bands for $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ (x = 0.1 - 0.5) are as signed to: the external mode [La(Ca)] - [Mn(Li)O$_3$] at $\omega_1 \sim 190$ cm^{-1}, the bending mode O - Mn(Li) - O at $\omega_2 \sim 390$ cm^{-1}, and the stretching mode Mn(Li) - O at $\omega_3 \sim 600$ cm^{-1}. They all decrease in absorption and increase in energy as the Ca concentration increases. The energies of three principal modes are listed in Table 1. Compared to $La_{1-x}Ca_xMnO_3$ (x = 0.1 – 0.5) compounds, in which the external mode increases in energy as x increases, the bending mode behaves similarly and the stretching mode moves to lower energy as the Ca content increases [11]. The energies of all three modes of $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ (x = 0.1 - 0.5) shift to high frequencies, especially the stretching mode. Note that the stretching mode vibration frequencies are all above 600 cm^{-1} in Fig. 1, compared below 600 cm^{-1} to without Li ion doping [11], thus Li ion doping into the Mn site can be indirectly measured by FIR spectroscopy. This shift is observed in our transmission measurements as shown in Fig. 2. For x = 0.3, with Li ion doping,

we found that energies moved higher, the bending mode shifts by 20 cm^{-1} and the stretching mode shifts by about 30 cm^{-1}. The shift in the external mode is the smallest, about 5 cm^{-1}.
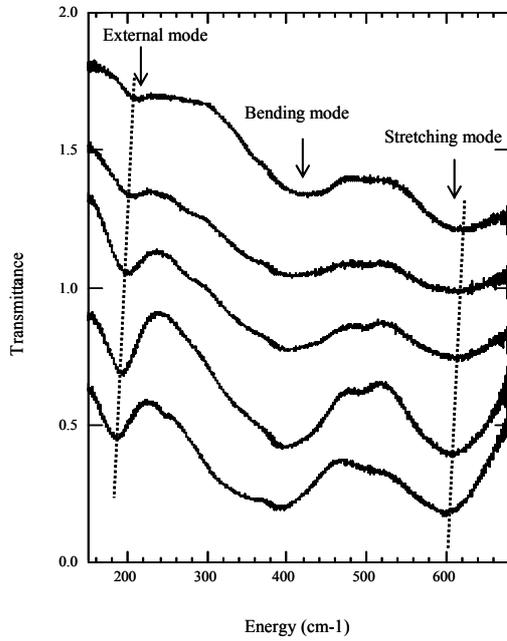

Figure 1. FIR spectra of La$_{1-x}$Ca$_x$Mn$_{0.9}$Li$_{0.1}$O$_3$ with Ca doping x = 0.1 - 0.5 (from bottom to top spectrum) at room temperature. The spectra shown were normalized by the spectrum of CsI.
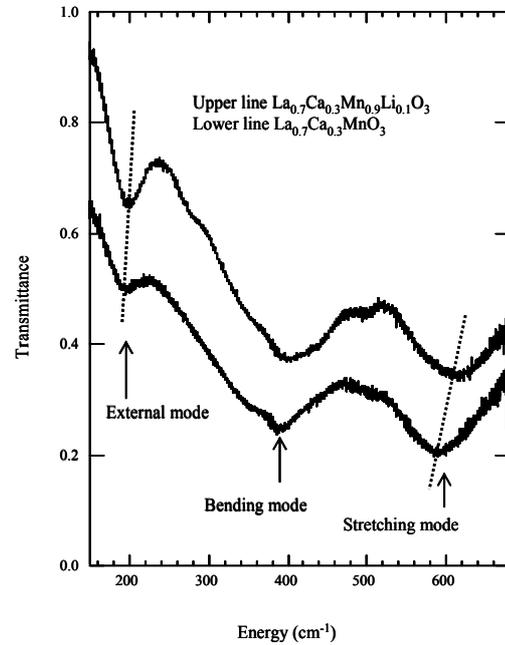
Figure 2. The spectrum of sample with Li ion doping. Compared to La$_{0.7}$Ca$_{0.3}$MnO$_3$, the energies of "external", "bending" and "stretching" modes move to higher frequencies.

Table 1. The energies of three principal phonon modes against the Ca ion doping levels in polycrystalline La$_{1-x}$Ca$_x$Mn$_{0.9}$Li$_{0.1}$O$_3$ samples.

Modes (cm^{-1})	x = 0.1	0.2	0.3	0.4	0.5
External	186	192	198	204	210
Bending	394	400	408	414	422
Stretching	602	606	612	616	620

The Li ion is lighter than the Mn ion and its ionic radius is slightly larger. Thus Li doping introduces unit cells that are smaller. This will lead to new lattice modes. As the Li fraction is increased to y = 0.3 in the absence of Ca substitution for La, a new phonon mode at ω_{Li} ~ 547 cm^{-1} and some small splitting between external and bending modes, related to Li$^+$ doping, is observed [12]. For all modes, Li substitution results in a higher frequency. Let us consider the stretching mode, for example: Li - O has a higher frequency than Mn - O. This is explained by the average mass on the Mn site being reduced by the introduction of Li ions. However, due to the small fraction of Li, the

oscillation strengths of Li-related modes are much smaller in our experiments. As the crystal symmetry is reduced, more optical modes are expected. In particular, the forbidden torsional mode F_{2u} (O_h^1) is now allowed and has been observed lying between the bending and stretching modes [13 - 15].

In Fig. 2 upper spectrum line, the shoulder at 280 cm^{-1} and the shallow minimum at 495 cm^{-1} may originate in a Li-related lattice vibration or torsional modes due to lattice symmetry distortion. Moreover, a certain percentage of Li makes the Ca doping more effective for a given value of x. The fractions of Mn^{4+} are higher for $La_{1-x}Ca_xMn_{0.9}Li_{0.1}O_3$ (x = 0.1 - 0.5) than $La_{1-x}Ca_xMnO_3$ (x = 0.1 - 0.5). The high value of Mn^{4+} leads to a stronger inter-ion electrostatic interaction. As a result the frequencies of lattice vibrations increase, especially the stretching mode.

4. Conclusion

The effects of doping Li into the Mn site together with Ca into the La site, on the energies of phonon modes have been determined by FIR spectroscopy. Li doping leads to more Mn^{4+} ions, which in turn cause a stronger inter-ion electrostatic interaction. As a result, the frequencies of lattice vibrations increase. Li is too light to be detected by EDS, but the FIR spectra indicate the Li ions occupy the Mn sites. CsI as a carrier was successfully used at room temperature and high magnetic field [16] for FIR transmission measurements and using CsI as a carrier under various magnetic fields and at lower temperatures will be further investigated to obtain more detailed knowledge of dielectric functions and lattice vibration modes in a variety of different samples with perovskite-structure.

Acknowledgments

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