Raman Study of Phonons in Sr$_3$Mn$_2$O$_{6.54}$ and Sr$_3$Mn$_2$O$_7$ Layered Manganites

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Polycrystalline $\text{Sr}_3\text{Mn}_2\text{O}_{6.54}$ and $\text{Sr}_3\text{Mn}_2\text{O}_7$ layered manganites were studied at room temperature using Raman spectroscopy. While the phonon spectrum of the stoichiometric $\text{Sr}_3\text{Mn}_2\text{O}_7$ sample is consistent with the group theoretical analysis for the $14/mmm$ structure, three additional modes are observed in the phonon spectrum of the oxygen deficient $\text{Sr}_3\text{Mn}_2\text{O}_{6.54}$ sample. Based on an analysis of the temperature dependence of the Raman spectrum of $\text{Sr}_3\text{Mn}_2\text{O}_{6.54}$ and a comparison with the Raman spectrum of $\text{LaSr}_2\text{Mn}_2\text{O}_7$, we conclude that the ‘extra’ modes should be viewed as disorder induced Raman scattering.

Keywords: Raman scattering; oxygen stoichiometry; Magnetoresistance; Manganite.

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Many manganese-based compounds, crystallizing in the three-dimensional perovskite structure, and exhibiting colossal magnetoresistance (CMR) have been extensively investigated over the past few years [1]. More recently the so-called "layered materials" which crystallize in the tetragonal structure and are exemplified by $\text{La}_{2-x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7$ [2], have also started to receive attention due to their CMR properties. In all these materials the role of phonons, doping, vacancies, etc., and their influence on the CMR effect, are still being investigated. In an effort to improve our overall understanding of these materials we investigate here the effect of oxygen vacancies on the phonon spectrum of the $n = 2$ Ruddlesden-Popper phase $\text{Sr}_3\text{Mn}_2\text{O}_{7-\delta}$ with $\delta = 0.0$ and 0.46).

The samples were synthesized by firing a stoichiometric mixture of $\text{SrCO}_3$ and $\text{MnO}_2$ at 1650 °C for 12 h and then quenching directly from synthesis temperature into dry ice. Measurements of oxygen stoichiometry were performed using two different techniques (TGA and iodometric titration). Raman spectra were obtained with a Jobin – Yvon triple spectrometer (T64000) with a liquid $\text{N}_2$ – cooled CCD detector, using the 476 nm line from a $\text{Kr}^+$ laser (spectra Physics – Model 171). A cylindrical focusing lens ($f = 10$ cm) and laser intensities of the order of 50 mw were used to avoid possible structural modifications due to overheating. All spectra were obtained in a quasi-backscattering geometry.

X-ray and time-of-flight neutron powder diffraction measurements revealed that the polycrystalline samples are single-phase materials and that at 300 K they
crystallize in a tetragonal structure belonging to the space group \( \text{I}4/\text{mmm} \) with one formula unit per primitive unit cell. From neutron diffraction experiments, it is observed that for the \( \delta = 0.46 \) compound there is an unusual defect structure. The oxygen vacancies are located in the \( \text{MnO}_2 \) planes and as a consequence, the Mn sites have two distinct coordination polyhedra, namely: octahedral and square pyramidal, where the octahedral sites are associated with \( \text{Mn}^{4+} \), whereas the square pyramidal sites with \( \text{Mn}^{3+} \) [3].

The Raman active modes predicted for the \( \text{I}4/\text{mmm} \) structure are: \( 4 \text{A}_{1g} + \text{B}_{1g} + 5 \text{E}_g \); where the \( \text{A}_{1g} \) modes are related to symmetric vibrations of \( \text{Sr}, \text{Mn}, \text{equatorial O}_{xy} \) and apical \( \text{O}_2 \) atoms, the \( \text{B}_{1g} \) mode is related to c-axis out-of-phase vibration of \( \text{O}_{xy} \) atoms, and the \( \text{E}_g \) modes are related to other vibrations involving \( \text{Sr}, \text{Mn} \) and \( \text{O}_{xy} \) atoms. In Fig. 1a we show our Raman spectrum of the fully stoichiometric sample (\( \delta = 0 \)) which shows peaks at \( \approx 320, 450 \) and \( 570 \text{ cm}^{-1} \). Following Ref.[4], these vibrations are assigned to: (i) the \( \text{B}_{1g} \) mode, (ii) an \( \text{A}_{1g} \) mode due to in-phase \( \text{O}_{xy} \) bending; and (iii) an \( \text{A}_{1g} \) mode related to the \( \text{O}_2 \) stretching vibration, respectively. The other two \( \text{A}_{1g} \) modes are at 170 and 243 cm\(^{-1}\), and the \( \text{E}_g \) modes are weak and have not yet been observed. In Fig. 1b we display the room temperature Raman spectrum of \( \text{Sr}_3\text{Mn}_2\text{O}_6.54 \). Apart from the modes in common with Fig. 1a, three extra modes are observed at \( \approx 510, 670 \) and \( 710 \text{ cm}^{-1} \). These modes disappear after annealing the sample in an oxygen atmosphere at 425 °C for 10 h. Because the features identified as zone center optical modes do not change on introducing vacancies, it is quite certain that no major structural change has occurred (consistent with the x-ray and neutron
experiments) and hence it is unreasonable to attribute the additional features to new zone center modes.

The origin of the extra modes, although clearly related to oxygen deficiency, is not clear. They can be explained as phonon modes which become Raman active due to local symmetry reduction (or due to the loss of translational symmetry) or it can be speculated that they could be due to electronic excitations of Mn ions in the 3+ state. The latter speculation can be tested by comparing the spectrum of Sr3Mn2O7 in Fig 1a with that of LaSr2Mn2O7 shown in Fig. 2. The substitution of Sr by La, which is known to change the ratio of Mn 3+ and 4+ but which does not change the space group of the crystal, does not give rise to the 'extra' Raman lines. We interpret this as a clear indication that the additional lines are not due to Mn3+.

Further insight into the nature of the extra peaks can be extracted from the temperature dependence of the Raman spectra. While the spectra from the Sr3Mn2O7 sample show a clear narrowing of the peaks as the temperature is lowered, the peaks in the Sr3Mn2O6.54 spectra remain broad at all temperatures. This behavior is indicative, albeit not conclusive, that the features in the non-stoichiometric sample are due to the loss of translational symmetry and not due to a local symmetry which activates the Raman process. If the peaks were due to an activated IR mode one might expect that they also would narrow as temperature is lowered. If, on the other hand, loss of translational symmetry activates modes throughout the Brillouin zone, no narrowing would be expected.
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References

FIGURE CAPTIONS

Fig. 1 – Room temperature Raman spectra at of: (a) Sr$_3$Mn$_2$O$_7$ and (b) Sr$_3$Mn$_2$O$_{6.54}$ polycrystalline samples.

Fig. 2 – Raman spectrum of LaSr$_2$Mn$_2$O$_7$ recorded at 300 K.
Sr$_3$Mn$_2$O$_7$  (b)

Sr$_3$Mn$_2$O$_{6.54}$  (a)

Raman shift (cm$^{-1}$)

Fig. 1 - I. Smith et al.
LaSr$_2$Mn$_2$O$_7$

Raman shift (cm$^{-1}$)