Raman scattering study of perovskite manganites

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Abstract. Raman spectroscopy is shown to be a useful tool for the study of phase transitions, oxygen disorder and local vibrational modes in lanthanum manganese compounds of the perovskite type. In this work, we present results of the Raman scattering and x-ray diffraction studies of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$M$_x$O$_3$ manganites (M=Fe, Co, Ni, Cr). A part of Mn atoms was substituted by M with x in the range of 0.0-0.60. Raman spectra of the La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$M$_x$O$_3$ exhibit a significant dependence on the amount and kind of the dopant M, and they are sensitive to the structure and transitions driven by both doping and temperature. X-ray diffraction (XRD) analysis of these samples indicates a change in the cell parameters vs. doping content. Our main focus is the Raman peak at high frequency (>630 cm$^{-1}$), that is somewhat controversial. The Raman spectra exhibit an additional high frequency mode attributed to the local breathing vibration of oxygen surrounding the substituent ion. The frequency and intensity of Raman spectra in these manganites is very sensitive to the type and content of substituent. From above results, a critical content of substituent at which the structural phase changed was shown.

Keywords: Raman spectroscopy, perovskite, doping.

1. Introduction

The magnetoresistance effect has been known for over 100 years. The discovery of “Giant Magneto Resistance” (GMR) in 1986 [1] started a new area of research in magnetic materials in view of their potential incorporation in efficient technological devices, particularly those used in magnetic recording heads [2]. More recently it was found that another class of materials exhibits much greater magnetoresistance properties, and the effect was accordingly dubbed “Colossal Magneto Resistance” (CMR) [3]. Most representative of the CMR materials are the manganite perovskites La$_{1-x}$R$_x$MnO$_3$ where the lanthanide cation is trivalent (La$^{3+}$) and R is a divalent alkaline earth cation (R = Ca, Sr, Ba). The end members of this series, with x = 0 (LaMnO$_3$) and x = 1 (e.g., CaMnO$_3$) are antiferromagnetic insulators in their ground states. The CMR effect is accompanied by a ferromagnetic to paramagnetic phase transition largest and is near the transition temperature T$_c$. The various aspects of CMR are described in a variety of publications and reviews [4, 5]. While much of works is driven by potential applications, there is also considerable intrinsic interest in the study of the basic physics and chemistry of the doped perovskite manganites. Many different experimental techniques are used alongside theoretical models in this undertaking. Among these, the technique of Raman spectroscopy has proven itself to be of considerable importance in the study of solid state materials in general. It is the purpose of this presentation to report on a series of Raman spectroscopic experiments on doped in the B site.
2. Experiment
The samples of La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)M\(_x\)O\(_3\) (x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) used in the present study were prepared by solid state reaction method [6]. The room temperature X-ray diffraction (XRD) patterns were collected using a Rigaku X-ray diffractometer. Raman measurements were performed in a back scattering geometry using Jobin Yvon T 64000 triple spectrometer equipped with a cryogenic charge-coupled device (CCD) array detector, using 514.5 nm and 647.1 nm line of Ar and Kr ion lasers, respectively.

3. Result and discussion
3.1. Manganite structure and selection rules for optical vibrational modes
The La\(_{1-x}\)R\(_x\)MnO\(_3\) system may exist in one of the several phases: paramagnetic and ferromagnetic insulators and metals, canted antiferromagnetic insulator and antiferromagnetic insulator phases, depending on the doping value x, and the temperature. Moreover, early structural studies of manganite and related systems have shown that this material may be have cubic [7], rhombohedral [8] or orthorhombic [9] symmetries depending on the temperature and value of doping x. The activities of vibrational modes in optical spectra are obtained by the methods of group theory. For the three commonly reported symmetries of La\(_{1-x}\)R\(_x\)MnO\(_3\) materials these are summarized below. The perfect perovskite structure belongs to the cubic space group \( \Gamma hO \) (m3m), and a unit cell contains one formula unit. The optical vibrations are classified as:

\[
\Gamma = 3F_{\text{u}}(\text{IR}) + F_{2u},
\]

where the three \( F_{\text{u}} \) species are allowed (active) in infrared (IR) absorption while the \( F_{2u} \) species are inactive (“forbidden”) in both IR and Raman scattering (RS). The IR active modes of La\(_{1-x}\)R\(_x\)MnO\(_3\) materials were analyzed within this assumed symmetry [7]. No Raman modes are allowed in the first order spectra. However, the crystal lattice of most real La\(_{1-x}\)R\(_x\)MnO\(_3\) materials is distorted, for example due to the Jahn-Teller (JT) and other effects. The existing lattice distortions therefore permit the appearance of a first order Raman spectrum. At moderate values of doping, e.g., \( x \approx 0.3 \), the rhombohedral symmetry \( D_{3d}^6(R\bar{3}c) \) is expected. For this structure the unit cell contains two formula units. Therefore the following activity of optical vibrational modes is expected:

\[
\Gamma = 4A_g(\text{IR}) + 2E_g(\text{IR}) + 3A_g(\text{RS}) + 3A_{2g}(\text{IR}) + 3E_{2g}(\text{IR}) + 3E_u(\text{IR}) + 2A_{2u}(\text{IR}) + 2E_u(\text{IR}).
\]

So far Raman spectra for the rhombohedral structure of La\(_{1-x}\)R\(_x\)MnO\(_3\) single crystals were considered. However, no significant difference with the spectra from the orthorhombic phase was detected. The symmetry of the parent LaMnO\(_3\) material, as well as those lightly doped (x < 0.125) is usually described by the space group \( D_{2h}^9(\text{mmm}) \). In this case the unit cell has four formula units and the optical vibrations are classified as:

\[
\Gamma = 9A_g(\text{IR}) + 9B_{1g}(\text{IR}) + 7B_{2g}(\text{RS}) + 5B_{3g}(\text{RS}) + 5B_{1u}(\text{IR}) + 7B_{2u}(\text{IR}) + 9B_{3u}(\text{IR})
\]

Accordingly, the Raman spectrum is expected to be composed of seven \( A_g \), five \( B_{1g} \), seven \( B_{2g} \), and five \( B_{3g} \) modes. Since the early study by Geller [10], LaMnO\(_3\) is known to possess a distorted perovskite orthorhombic structure with both \( \sqrt{2} \times \sqrt{2} \) doubling of the unit cell in the \( a-c \) plan and additional doubling along the \( b \) axis. This structure was studied by Raman spectroscopy in [7, 11].

3.2. X-ray data
XRD patterns showed that all of the samples are single phase when x < 0.3, and multiphase in case x > 0.3. All of the reflection lines are successfully indexed with a rhombohedral ABO\(_3\)-type perovskite structure. The cell parameters decrease as increasing substituted content in all cases (see figure 1).
However, it monotonously decreases in the range of $x < 0.3$. At higher content, the tendency seems more complex. The reason might be related to the existence of some secondary phases in the samples. An insight into the differences among the substituents can be obtained by analyzing the X-ray data [4]. A particularly important information is provided by the B–O distance, i.e., the mean distance between the central ion in the perovskite ABO$_3$ structure and neighbouring oxygens. Since the average valence of the Mn ions is kept constant and their radius is thus fixed, the B–O distance should depend on the radii of the M ions.

![Graph showing cell parameters vs. M content.](image)

**Figure 1.** Cell parameters vs. M content.

### 3.3. Raman scattering

Our samples crystallize in rhombohedral structure, space group D$_{3d}^5$, $Z = 2$. This structure can be obtained from the simple cubic perovskite by the rotation of the adjacent MnO$_6$ octahedra in the opposite directions around the [111] cubic direction. Of the total of 20 -point modes ($A_{1g} + 3A_{2g} + 2A_{1u} + 4A_{2u} + 4E_g + 6E_u$), five ($A_{1g} + 4E_g$) are Raman active, eight ($3A_{2u} + 5E_u$) are infrared active, and five ($2A_{1u} + 3A_{2g}$) are silent. We assign the 427 cm$^{-1}$ line to the $E_g$ mode with the predicted frequency of 468 cm$^{-1}$. The frequencies of the two modes are close to the results obtained on a single crystal (199 and 426 cm$^{-1}$, respectively). Podobedov *et al.* [11] did not assign the weak band at 663 cm$^{-1}$ to the manganite because its intensity varies substantially from measurement to measurement. They also assumed that it was due to a small proportion of manganese oxide; e.g. Mn$_3$O$_4$ has a strong Raman line at about this frequency.

Figure 2 shows the Raman spectra of the M (M=Fe, Co, Ni, Ti) substituted series. With increasing M concentration, the spectra exhibit the following main features: a fairly strong mode appears at about 670 cm$^{-1}$, the mode at 427 cm$^{-1}$ gradually disappears while two broad bands appear at around 500 cm$^{-1}$ and 620 cm$^{-1}$. For Fe and Co doped samples, when increasing doping content, the peak at higher than 600 cm$^{-1}$ up-shifts, whereas the peak downshifts in case of Ti and Ni doped.
Let us discuss the peak observed at the highest frequencies of 630-760 cm\(^{-1}\). Its common characteristics are, (a) its intensity increases with the concentration of substituents, (b) its frequency depends rather strongly on the type of the substituent. We assign the peak to a local breathing (in-phase stretching) mode of oxygens in a close vicinity of the substituent ion. This interpretation is further supported by the symmetry of the mode: the suggested eigenvector corresponds to a nondegenerate vibration, i.e., it has the A\(_g\)-like symmetry. Moreover, these modes are not infrared active which implies that the eigenvector should have a center of symmetry. Filho et al. [12] observed a similar peak at about 707 cm\(^{-1}\) in La\(_{0.70}\)Sr\(_{0.30}\)Mn\(_{1-x}\)Fe\(_x\)O\(_3\) and interpreted it as the silent A\(_{2g}\) mode activated by a symmetry breaking or as the phonon density of state feature.

Evidently, the frequency does not exhibit a simple mass effect. This is not surprising, because the substitutional ions do not take part in the vibration. An important role could be again played by the radius of the substituent ions. The oxygens vibrate along the Mn–O–M bonds. If the ion M is large, it creates an additional pressure on the oxygen, increasing the frequency of the vibration. Some other factor must play an important role. It could be, e.g., the degree of covalency of the M–O bond, which would imply a dependence of the frequency on the position of M atom in the periodic table. The peak of Fe-substituted compound observed in the data of Filho et al. [12] has also a very large intensity as compared with the other phonons. Another factor affecting this frequency can be the valence of the substituent that influence electrostatically the stiffness of the M–O\(^{-}\) bond. This effect would lower the frequencies corresponding to the substituents with valencies 2+ with respect to their hypothetical 3+ state. However, a clear understanding of the frequency and intensity variations remains a challenge for future studies. The properties of the high-frequency mode are even more complex.

Figure 2. Raman spectra of La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)M\(_x\)O\(_3\) (a): Fe, (b): Co; (c): Ti; (d): Ni.

3.4. The additional \(A_g\)-like high frequency mode

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4. Summary and conclusion
We have used Raman spectroscopy measurements and X-ray analysis to study the influence of Mn-site substitutions in optimally doped manganites. Our results support the idea that the main factor influencing the oxygen disorder and electric and magnetic properties of these compounds is the radius of the substituents and that their electronic and magnetic structure plays only a minor role. The substitution made local stress and produced by the substitutional ion modifies the Mn–O distances around the substitutional ion. This leads to changes of the energies of the eg orbitals, and to a localization of the itinerant electrons which competes with the double-exchange interaction. Consequently, the Jahn-Teller disorder is enhanced, d.c. resistivity increases, and Tc decreases. The Raman spectra exhibit an additional A_g-like mode that we attribute to the local breathing mode of oxygen in a close vicinity of the substituent ion. Its frequency and intensity is very sensitive to the type of substituent. They seem to depend on the position of the substituent ion in the periodic table suggesting that the electronic characteristics of the M–O bond are important. However, the origin of these effects remains an open question for future studies.

References
[1] Grunberg P, Schreiber R, Pang Y, Brodsky M B, Sowers H 1986 Phys. Rev. Lett. 57 2442
[2] Parkin S S P 1995 Annu. Rev. Mater. Sci., 25 357
[3] Jin S, Tiefel T H, McCormack M, Fastnacht R A, Ramesh R, Chen LH 1994 Science 264 413
[4] Salamon M B, Jaime M 2001 Reviews of Modern Physics, 73 583
[5] Haghiri-Gosnet A M, and Renard J P 2003 Journal of Physics D: Applied Physics 36 R127
[6] Minh N V, Kim S J and Yang I S 2003 Physica B 327 208
[7] Kim K H, Gu J Y, Choi H S, Park G W, Noh T W 1996 Phys. Rev. Lett. 77 1877
[8] Kawano H, Kajimoto R, Kubota M, Yoshizawa Y, 1996 Phys. Rev. B 53 R14709.
[9] Elemans J B A A, van Laar B, van der Veen K R, Loopstra B O 1971 J. Solid State Chem. 3 238
[10] Geller S. 1956 J. Chem. Phys. 24 1236
[11] Podobedov V B, Weber A, Romero D B, Rice J P, Drew HD 1998 Phys. Rev. B 58 43
[12] Souza Filho A G 2003 Phys. Rev. B 67 052405

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