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Temperature dependent Raman spectroscopy of $La_{1-x}Ca_xMnO_3$ (x = 0.0, and 0.3)

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ABSTRACT

Temperature dependent Raman spectroscopy of polycrystalline bulk samples of $La_{1-x}Ca_xMnO_3$ (x = 0.0, and 0.3) synthesized by solid-state reaction method is presented. As the temperature is decreased, there is significant change in intensity and full width half maxima of all major Raman modes. This implies a structural rearrangement resulting in change of space group. This study brings out the variations in Raman spectra with temperature and also effect of Ca doping on A-site in the compound $LaMnO_3$. Possible effect of Laser heating on the samples has also been discussed. Copyright © 2014 VBRI press.

Keywords: Solid state reaction; Raman modes; orthorhombic.

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Introduction

The compositional perovskites A(B'B")O_3 are important materials for both scientific research and practical applications in ceramic dielectrics because modification in cation combinations of A, B' and B" sites of perovskite oxides results in tailoring their properties **[1–2]**. The mixed valent oxides of the type $R_{1-x}A_xMnO_3$ where R is a rare earth element and A the divalent cation Ca, Sr, or Ba have been a subject of scientific investigations for many decades **[3-4]**. The recent interest in these compounds emanates from the observation of a large negative magnetoresistance **[5-6]**, charge and spin ordering effects as a function of Mn^{3+}/Mn^{4+} ratio **[7-8]** and similarity of many issues with the high Tc superconductivity in the cuprates **[9]**. The most extensively studied derivatives of the above general class of oxides are the compounds with formula $La_{1-x}A_xMnO_3$.The electronic and magnetic properties of these compounds were found to be very sensitive to small changes of crystallographic structure. Generally, the perovskite distortions can be divided into two groups: distortions changing Mn-O-Mn bond angles governed by the tolerance factor $t = (r_R + r_O) /(r_{Mn} + r_O)\ 2^{1/2}$, and distortions changing the Mn-O distances governed by the magnitude and the spatial coherence of the Jahn-Teller distortions of the $Mn^{(3+)}O^{(2-)}{}_6$ octahedra. Almost all of the compounds exhibiting colossal magnetoresistance (CMR)

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have either orthorhombic (Pnma) or rhombohedral (R3c) static distortions as well as dynamical distortions of the MnO_6 octahedra. The Raman spectroscopy is a most suitable experimental tool for investigation of these distortions since there are no active Raman lattice vibrations in the ideal cubic Pm3m perovskite and, therefore, all phonon features in the spectra originate from either static or dynamical distortions. These distortions or the compositional disorder associated with the introduction of non-stoichiometric Ca may result in direct lattice vibrations observable by Raman spectroscopy and hence provides information on magnetic and charge –ordering effects indirectly.

The Raman spectra of the orthorhombic and the rhombohedral phases of the parent $LaMnO_3$ compound were studied previously **[10-11]**. It was established for the rhombohedral phase that the angle of the long-range coherent static tilt of MnO_6 octahedra is proportional to the frequency of the ``soft`` A_{1g} mode, whereas the strong broad lines in the 450 to 600 cm^{-1} range were assigned to vibrations activated by the dynamic Jahn-Teller distortions. In order to investigate the role of phonons in these transitions we have undertaken an extensive series of Raman spectroscopy measurements on the polycrystalline compound of $La_{1-x}Ca_xMnO_3$ for $x = 0.0$ and 0.3 as a function of temperature in the range 80–300 K. Irwin *et al* **[12]** have studied the temperature and oxygen-isotope-exchange dependence of the phonon lines seen for polycrystalline $La_{1-x}Ca_xMnO_3$ with $x = 0.2$, 0.35. Congeduti *et al* **[13]** have studied the pressure dependence of the Raman scattering in polycrystalline $La_{0.75}Ca_{0.25}MnO_3$ up to 14 GPa. Li *et al* [14] have studied the magnetostriction up to 20 kOe on same composition. Present report is on the temperature dependence of the Raman spectra of $LaMnO_3$ as well as doped $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) bulk samples. Possible explanation for the observed change in intensity of all major modes and subsequent softening and hardening behaviors at various temperature regimes are discussed.

Experimental

All chemicals used for the experiment were of GR grade. La_2O_3 (Sigma Aldrich >99.9% purity), Mn_2O_3 (Sigma Aldrich >99.9% purity) and $CaCO_3$ (Sigma Aldrich >99.9% purity) were used in the present investigation. Ceramic samples of $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ were prepared through solid state reaction method. La_2O_3, Mn_2O_3 and $CaCO_3$ were used as starting raw materials and were mixed together in an appropriate composition. The mixture thus obtained was thoroughly and repeatedly ground in acetone to a powder using agate mortar and pestle to ensure homogeneity. The resultant powdered samples were then precalcinated at 1000 °C for 12 hours. The precalcinated materials were again ground and calcinated at 1200 °C for 12 hours. Finally, the samples were ground to fine powder, pressed to the pellet form, and sintered at 1250 °C for 24 hours. The phase analysis of these sintered pellets was carried out by X-ray diffraction (XRD) using Bruker D-8 Advance diffract meter Cu-Kα radiation (1.54 A^0) at room temperature in the 2θ range of 20-80° at the scanning rate of 1^0 per minute. The operating voltage and current for an X-ray gun are 40 kV and 40 mA, respectively

Raman spectra were collected in the back scattering geometry using a He–Ne laser of wavelength 248 nm coupled with a Labram-HR800 micro-Raman spectrometer equipped with a 50× objective, an appropriate notch filter and a Peltier-cooled charge-coupled device detector. The laser power was kept at 10 mW for excitation. However, with this power no melting or phase transformation was found in the sample. For the low-temperature Raman measurements, the sample was mounted on a THMS600 stage from Linkam, UK. During the low-temperature measurements, a 1800 gmm^{-1} grating was used in the high-resolution dispersive geometry. In order to achieve very high positional accuracy, the grating was kept stationary during the entire temperature scan. A spectral window of 325 cm^{-1} was covered with a positional accuracy of 0.33 cm^{-1} in such a configuration.

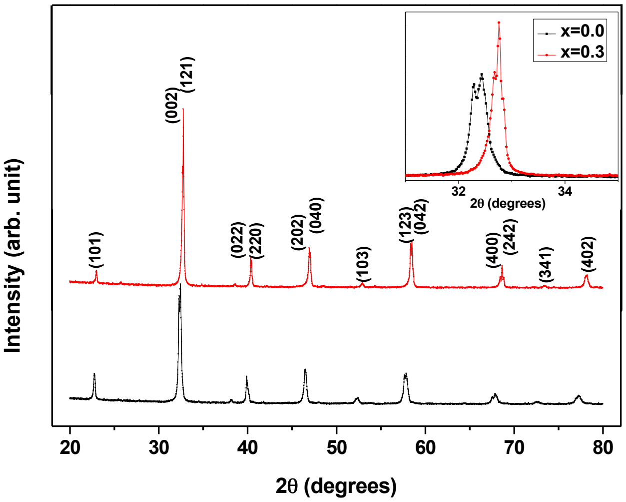

Fig. 1. XRD pattern of $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ with the inset showing shifting of (121) peak. Inset shows the enlarged view of region between 31 to 33 degrees.

Results and discussion

The XRD pattern of $La_{1-x}Ca_xMnO_3$ ($x = 0.0$, and 0.3) are shown in **Fig. 1**. The characteristic reflections correspond to (101), (002), (121), (022), (220), (202), (040), (103), (123), (042), (400), (242), (341) and (402) planes are indexed to an orthorhombic crystal structure using powder X software and reveal that the single phase of these samples. The inset of fig.1 shows the enlarged (121) peak and reveals that the peaks shift towards higher 2θ values with Ca content indicating the development of strain in the crystal structure and the change in lattice parameters. From the XRD pattern of the samples, lattice parameters, c/a ratio and the unit cell volume were calculated and are given in **Table 1**.

Table 1. The lattice parameters (a, b, c), c/a ratio and the unit cell volume of the compounds $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$.

X	a(Å)	b (Å)	c (Å)	c/a	V (Å^3)
0.0	5.615	7.693	5.630	1.002	243.19
0.3	5.543	7.721	5.641	1.017	241.43

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It was observed that the lattice parameters monotonically increase with Ca doping. A similar trend was observed for cell volume and c/a ratio. This is attributed to change in A-site ionic radius **[15]**. The cations La and Ca have almost similar size (see **Table 2** [taken from Ref. **16**]) and are randomly substituted on A site. The size of the ions determines the extent of distortion in the perovskite compounds. If the size of A site cation $r_A < a/\sqrt{2} - r_o$ (here 'a' is the cubic lattice parameter and r_o is the radius of oxygen ion), the distortion is probably due to rigid tilts of oxygen octahedron. Whereas on contrarily if $r_B < a/2 - r_o$ (r_B is the radius of B site cation) the distortion is most likely due to movement of B site cation within the oxygen octahedron. With these parameters and ionic sizes (from **Table 1, 2** and **Table 3**) into consideration it is found that the system in present study follows the former ($r_A < a/\sqrt{2} - r_o$) relation between its contributing ions. This is suggestive of the distortion due to rotation of oxygen octahedral at room temperature.

Table 2. Ionic radii of the constituent elements of $La_{1-x}Ca_xMnO_3$ (taken from [16]).

Symmetry	$NdFeO_3$ [**21**]	Present study Mode (cm^{-1})	Main assignment
$B_{2g}(1)$	643	624	Mn-O, stretching, breathing
$A_g(2)$	464	499	O-Mn-O, rotation, bending
$B_2g(3)$	432	427	MnO_6, stretching, rotation
$A_g(4)$	345	355	MnO_6, stretching, bending
$B_{2g}(5)$	295	230	MnO_6, bending, breathing

Table 3. The observed Raman modes with corresponding atomic motion.

Symmetry	$NdFeO_3$ [**21**]	Present study Mode (cm^{-1})	Main assignment
$B_{2g}(1)$	643	624	Mn-O, stretching, breathing
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The Raman effects in crystals is due to the scattering of light by the lattice vibrations, leading to annihilation or creation of crystal phonons. The energy lost or gained by the lattice is compensated by the increase (anti-Stokes part of the Raman spectrum) or the decrease (Stokes part of the Raman spectrum) of the energy of the scattered light. Moreover, as optical photons have very small wave vectors (approx. 105 cm^{-1}) if compared with lattice vibrations (up to 108 cm^{-1}), due to the conservation of the crystal momentum in the scattering process only phonons at the centre of the Brillouin zone (namely, having q=0 wave vector) can be involved in the scattering process **[17]**. Raman signature of perovskite structure can be attributed to be made of the two interpenetrated lattices: the covalent entities constituting the structure (MnO_6 octahedron sharing common oxygen ions) and the second one, made of highly Columbic ions that contribute to the translation oscillation modes which couple themselves with other vibrational modes of the neighboring entities: translations and rotations/Vibrations of iono-covalent MnO_6 entity leading to the wave. Raman peaks were observed at their finger point positions and following irreducible representations at the Brillouin zone center are presented by the group theory and are consistent with the literature **[18]**.

$$7A_g + 2B_{1g} + 7B_{2g} + 5B_{3g}.$$

Taking MnO_6 into consideration, the above stated Raman modes can be classified in the following way. Primarily the Raman modes are classified into twelve internal and nine external modes. Out of twelve internal modes five are of stretching type [$A_g(1)$, $A_g(2)$, $B_{3g}(2)$, $B_{2g}(1)$, and 6 $B_{2g}(2)$] while the remaining seven internal modes are of bending type ($A_g(3)$, $A_g(4)$, $A_g(7)$, $B_{1g}(2)$, $B_{3g}(1)$, $B_{2g}(3)$, and $B_{2g}(7)$]. From the external modes six are of translational type [$A_g(5)$, $A_g(6)$, $B_{3g}(4)$, $B_{3g}(5)$, $B_{2g}(5)$, and $B_{2g}(6)$] and three are of rotational type [$B1g(1)$, $B3g(3)$, and $B2g(4)$]. On account of their high frequency, the Raman lines between 450 and 650 cm^{-1} correspond to internal modes **[18-20]**. Table II shows the observed modes with corresponding atomic motion, the assignments were done based ref **[21]**.

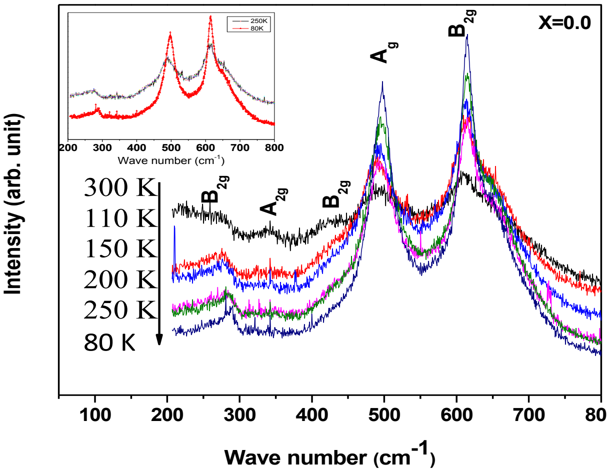

Fig. 2 Raman Spectra of $LaMnO_3$ at various temperatures from 80 K to 300K.

One of the interesting characteristic of Raman scattering is its sensitivity to strain in the sample. When the material is under strain, its Raman wave will deform/shift from the original status and in that case this mechanical quantity is possible to be directly measured. It has been established that compressive stress results in the shift of the position of the Raman peak towards higher wave number region (commonly called "Blue shift"), while tensile stress

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results in a shift towards lower wave no. ("Red shift") **[22]**. **Fig. 2** and **Fig. 3** shows the temperature dependent Raman spectra of $LaMnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$ in the temperature range of 80 to 300 K respectively.

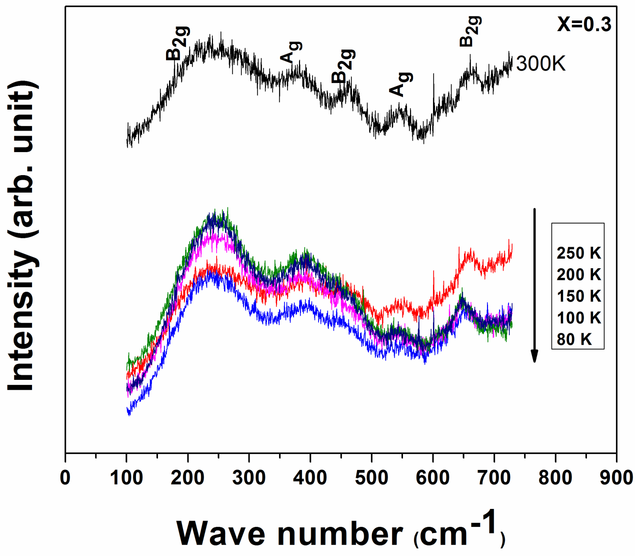

Fig.3. Raman Spectra of $La_{0.7}Ca_{0.3}MnO_3$ at various temperatures from 80 K to 300K.

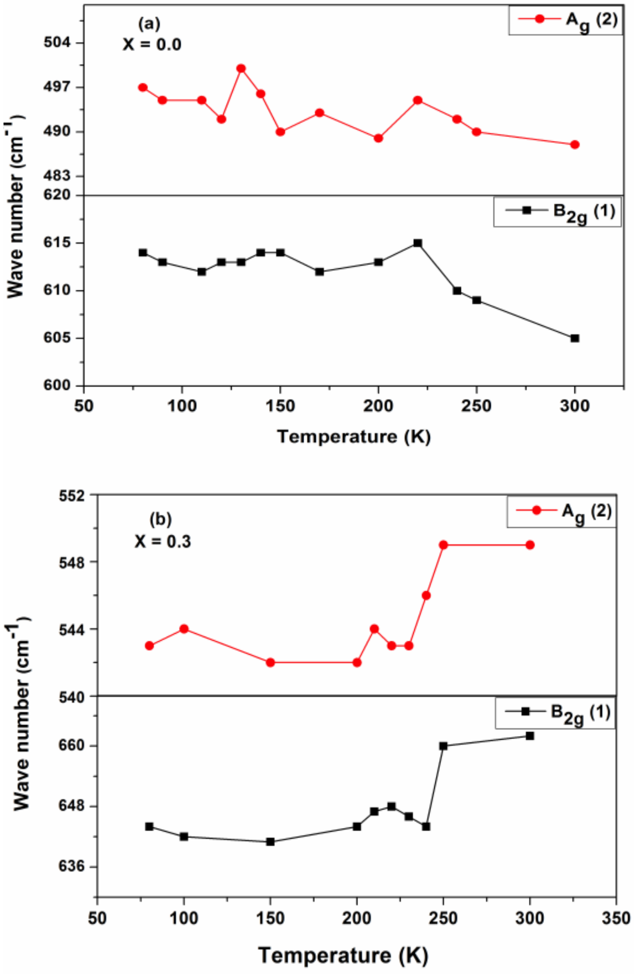

Fig. 4. Variation of the intensities of some observed modes of (a) $LaMnO_3$ and (b) $La_{0.7}Ca_{0.3}MnO_3$ with temperature.

From these figures, it is evident that there is reduction in intensity of all major peaks, most of the signal peaks shift towards lower wave number at lower temperature and the high wave number peaks severely broaden and merge into a broad peak. Unlike in other perovskite ceramics, the above observations can be explained by thermal broadening and thermal disorder; the so-called anharmonic effects of the lattice. Apart from these anharmonic effects, the change in bond length between oxygen and cations may also account for the shifting of the peak position with increasing temperature. It is also evident from the **Fig. 2** and **Fig. 3** that from room temperature to transition temperature the peak positions shifts towards higher wave number region and below transition temperature the peak positions shifts towards lower wave number region. In this study it is also clear that the modes exhibit a blue shift (hardening behavior) in the doped samples which may arise due to compressive stress. The observed shift in wave no. with doping clearly indicates change in bond lengths. As seen from the Fig.2 and 3, the broadening of the bands with increase in temperature is most probably due to the loss of degeneracy upon lowering of symmetry of the octahedron and increase of the unit cell to include more than one ABO_3 unit **[23-24]**. The rise in temperature induces disorder due to change in lattice parameters and therefore broadening of bands too. However, further reduction in orthorhombic distortion may reduce the intensity or number of bands **[25]**.

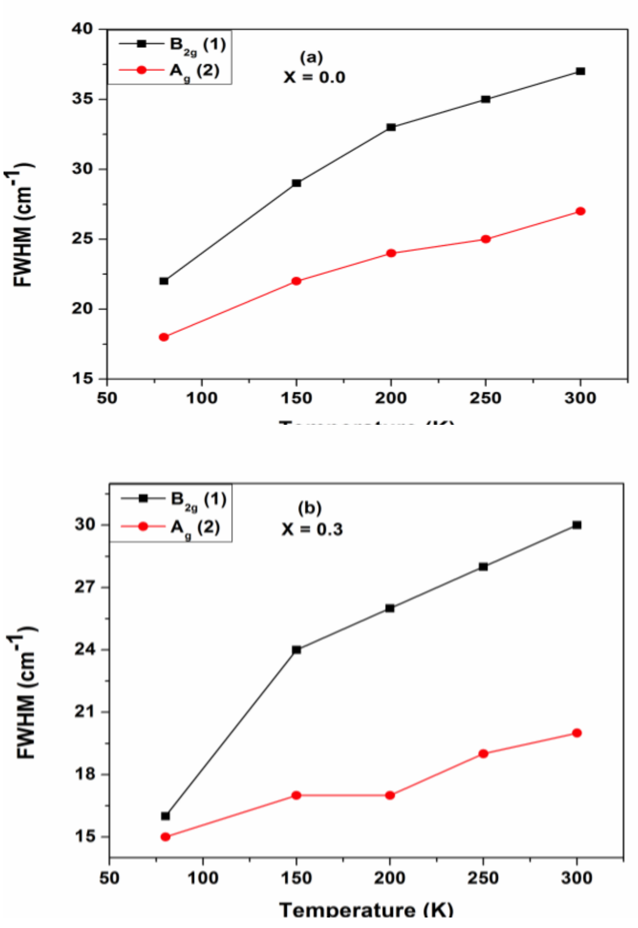

Fig. 5. Variation of FWHM with temperature of B_{2g} (1) and A_g (2) mode (a) $LaMnO_3$ and (b) $La_{0.7}Ca_{0.3}MnO_3$.

Fig. 4 shows the shifting of B_{2g} (1) and A_g (2) modes with temperature for (a) $LaMnO_3$ and (b) $La_{0.7}Ca_{0.3}MnO_3$. It is seen that in case of $LaMnO_3$ both modes B_{2g}(610 cm^{-1}) and A_g(490 cm^{-1}) shows softening behavior above transition temperature (180 K), but the case is not same with $La_{0.7}Ca_{0.3}MnO_3$ where the modes B_{2g}(660 cm^{-1}) and A_g (548 cm^{-1}) shows hardening behavior above transition temperature(250 K).

The above spectral changes suggest a structural rearrangement in local structure and there may be a change in space group at this temperature range. Further the sharpening of the bands on cooling corresponds to either to a slowing down of the dynamics or to a gradual disorder-order transition. **Fig. 5** gives the variation of full width at half maximum (FWHM) of (B_{2g}(1) and A_g(2) for both the compositions (a) $LaMnO_3$ and (b)$La_{0.7}Ca_{0.3}MnO_3$.

It is seen that the line widths or FWHM increases with temperature. This behavior is outcome of lattice expansion and increase in phonon population as a result of increase in temperature. As mentioned earlier, present study used laser energy of around 10mW. Before doing so, different laser powers were employed and there was no pronounced change in Raman modes while using a lower power (1mWwith 50× objective). However, with increasing laser power, the intensities of the observed modes increased but there was no shift in the observed wave numbers.

Conclusion

Polycrystalline bulk compounds of Mn doped $La_{1-x}Ca_xMnO_3$ (x = 0.0, and 0.3) were synthesized by solid state reaction technique. XRD confirmed the orthorhombic structure with P*nma* space group. Lattice parameters (a, b and c), c/a ratio and the unit cell volume monotonically increase with Ca doping which was attributed to change in A-site ionic radius. It was observed that with Ca doping the peaks shift towards higher 2θ values indicating the development of strain in the crystal structure and the change in lattice parameters. Raman measurements were carried out from room temperature to 80 K and it was concluded that there is significant change in intensity and FWHM of all major Raman modes. It was seen that from room temperature to transition temperature, the peak positions shifts towards higher wavenumber region and below transition temperature the peak positions shifts towards lower wavenumber region. Different Raman band wave numbers were observed and tentative assignments with orthorhombic (*Pnma*) structure were made based on literature. With increasing laser power, the intensities of the observed modes increased but there was no shift in the observed wave numbers.

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Reference

1. Ahn, B.Y.; Kim, N.K. J. Mater. Sci. **2002, 37**, 4697.
   DOI: 10.1023/A:1020629222680.
2. Khalid Sultan , Ikram , M.; Asokan , K. J.Vaccum 2013.
   DOI: 10.1016/j.vacuum.2013.06.014.
3. Jonker, G.H.; van Santen, J.H. Physica ~Amsterdam **1950, 16**, 337.
   DOI: 10.1016/0031-8914(50)90033-4.
4. Wollan, E.O.; Koehler, W.C. Phys. Rev.**1951, 100**, 545.
   DOI: 10.1103/PhysRev.100.545.
5. Von Helmolt, R.; Wecker, J.; Holzapfel, B.; Schultz, L.; Samwer, K. Phys. Rev. Lett. **1993,71,** 2331.
   DOI: 10.1103/PhysRevLett.71.2331.
6. Jin, S.; Mc Cormack, M.; Tiefel, T.H.; Ramesh, R. J. Appl. Phys.**1994, 76,** 6929.
   DOI: 10.1063/1.358119.
7. Yoshizawa, H.; Kawano, H.; Tomioka, T.; Tokura, Y. Phys. Rev. B **1995, 52,** 13145.
   DOI: 10.1103/PhysRevB.52.R13145.
8. Goodenough, J.B. Phys. Rev. **1967, 164**, 785.
   DOI: 10.1103/PhysRev.164.785.
9. Khomskii, D.I.; Sawatzky, G.A. Solid State Commun. **1997, 102**, 87.
   DOI: 10.1016/S0038-1098(96)00717-X.
10. Iliev, M.N.; Abrashev, M.V.; Lee, H.G.; Popov, V.N.; Sun, Y.Y.; Thomsen, C.; Meng, R.L.; Chu, C.W. Phys. Rev. B **1998, 57**, 2872.
    DOI: 10.1103/PhysRevB.57.2872.
11. Abrashev, M.V.; Litvinchuk, A.P.; Iliev, M.N.; Meng, R.L.; Popov, V.N.; Ivanov, V.G.; Chakalov, R.A.; Thomsen, C. Phys. Rev. B **1999, 59**, 4146.
    DOI: 10.1103/PhysRevB.59.4146.
12. Irwin, J.C.; Chrzanowski, J.; Franck, J.P. *Phys. Rev.* B **1999**, **59** 9362.
    DOI: 10.1103/PhysRevB.59.9362.
13. Congeduti, A.; Postorino, P.; Caramagno, E.; Nardone, M.; Kumar, A.; Sarma, D.D. Phys. Rev. Lett. **2001, 86,** 1251.
    DOI: 10.1103/PhysRevLett.86.1251.
14. Li, J.H.; Huan, C.H.A.; Du, Y.W.; D. Feng, D.; Shen, Z.X. *Phys. Rev.* B **2000**, **63,** 024416
    DOI: 10.1103/PhysRevB.63.024416.
15. Samancloglu, Y.; Coskun, A. J. Alloys Compd. **2010, 507**, 385.
    DOI: 10.1016/j.jallcom.2010.07.212.
16. R.D Shannon *Acta. Cryst.* 32, **1976**, A 751–767.
    DOI: 10.1107/S0567739476001551
17. Anastassakis, E.; Canterero, A.; Cardona, M. Phys. Rev. B **1990, 41**, 7529-7535.
    DOI: 10.1103/PhysRevB.41.7529.
18. Yoon, S.; Ru¨bhausen, M.; Cooper, S.L.; Kim, K.H.; Cheong, S.W. Phys. Rev. Lett. **2000**, **85**, 3297.
    DOI: 10.1103/PhysRevLett.85.3297.
19. Yamamoto, K.; Kimura, T.; Ishikawa, T.; Katsufuji, T.; Tokura, Y. Phys. Rev. B.**2000**, **61**, 14706.
    DOI: 10.1103/PhysRevB.61.14706.
20. Argiriou, D.N.; Bordallo, H.N.; Campbell, B.J.; Cheetham, A.K.; Cox, D.E.; Gardner, J.S.; Hanif, K.; Dos Santos, A.; Strouse, G.F. Phys. Rev. B.**2000**, **61**, 15269.
    DOI: 10.1103/PhysRevB.61.15269.
21. K. Manoj Singh, K.; M. Hyun Jang, M.; H.C. Gupta, H.C.; S. Ram Katiyar, S. J. Raman Spectrosc. 2008, 39, 842–848.
    DOI: 10.1002/jrs.1923.
22. Campbell, I.H.; Fauchet, P.M. Solid State Communica-tions **1986, *58***, 739-741.
    DOI: 10.1016/0038-1098(86)90513-2.
23. Daturi, M.; Busca, G.; Willy, R.J. *Chem. Mater.* **1995, *7*,** 2115.
    DOI: 10.1021/cm00059a020.
24. Martin Corron, L.; de Adres, A.; Martinez Lope, M.J. *Phys. Rev. B* **2002, *66*,** 174303.
    DOI: 10.1103/PhysRevB.66.174303.
25. Mayr, F.; Hartinger, Ch.; Loidl, A. *Phys. Rev. B* **2005**, ***72*,** 024425.
    DOI: 10.1103/PhysRevB.72.024425.

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