

## Infrared Spectroscopic Evidences for the Superconductivity of $\text{La}_2\text{CuO}_4$ -related Compounds: A Superconductivity Probe

Jung-Chul Park,<sup>\*</sup> Seon-Woog Cho, Jong-Hak Jeong,<sup>†</sup> and Gi-Ho Jeong<sup>\*</sup>

*Department of Chemistry of New Materials, Silla University, San 1-1, Kwaebop-Dong, Sasang-Cu, Pusan 617-736, Korea*

*<sup>†</sup>Department of Chemistry, Pusan National University, San-30, Jangjeon-Dong, Kunjeong-Gu, Pusan 609-735, Korea*

*Received December 17, 1999*

We present the effects of temperature (between 10 K and 298 K) and of hole concentration on the frequency and intensity of characteristic phonons in polycrystalline  $\text{La}_2\text{CuO}_4$ -related compounds using FT-IR spectroscopy. The influences of the concentration of carrier doped on the phonon modes are prominent in the IR spectra of  $\text{La}_2\text{CuO}_4$ -related compounds. For  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0.00, 0.03, 0.07, 0.10, \text{ and } 0.15$ ) and electrochemically (or chemically) oxidized  $\text{La}_2\text{CuO}_4$ , the intensities of the transverse oxygen mode around  $680\text{ cm}^{-1}$  which corresponds mainly to Cu-O(1) stretching vibration in the basal plane of  $\text{CuO}_6$  octahedron, are decreased and disappeared depending on the Sr-substitution rate and the amount of excess oxygen, while the longitudinal oxygen mode around  $510\text{ cm}^{-1}$  corresponding to the Cu-O(2) stretching in the basal plane of  $\text{CuO}_6$  octahedron are nearly invariable. In particular, after two cycles of cooling-heating between 10 K and 298 K for these sample, the phonons around  $680\text{ cm}^{-1}$  are blue shifted by about  $13\text{--}15\text{ cm}^{-1}$ , while the phonons around  $510\text{ cm}^{-1}$  are nearly constant. The introduction of the charge carrier by doping would give rise to the small contraction of  $\text{CuO}_6$  octahedron as  $\text{Cu}^{3+}$  requires a smaller site than  $\text{Cu}^{2+}$ , which results in the shortening of the Cu-O(1) bond length and Cu-O(2) bond length with the increased La-O(2) bond length. These results in the frequency shift of the characteristic phonons. The IR spectra of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  which exhibits an insulator behavior despite the  $\text{Cu}^{3+}$  of nearly 100%, corroborate our IR interpretations. The mode around  $710\text{ cm}^{-1}$  corresponding to Cu-O(1) stretching vibration is still strongly remained even at low temperature (10 K). Thus, we conclude that the conduction electrons formed within  $\text{CuO}_2$  planes of  $\text{La}_2\text{CuO}_4$ -related superconductors screen more effectively the transverse oxygen breathing mode around  $680\text{ cm}^{-1}$  depending on the concentration of the doped charge carrier in  $\text{La}_2\text{CuO}_4$ -related compounds, which might use as a superconductivity probe.

### Introduction

Despite the enormous works that have been performed for superconducting materials, the understanding of the mechanism of superconductivity has not been completed even on the simplest high- $T_c$  superconductors.  $\text{La}_2\text{CuO}_4$ -related compounds.

$\text{La}_2\text{CuO}_4$ -related compounds have been intensively focused on the elucidation of the origin of the superconductivity as it has the simple local structure. The structure of  $\text{La}_2\text{CuO}_4$ -related compounds can be depicted as charge accepting  $\text{CuO}_2$  planes and charge donating  $\text{La}_2\text{O}_7$  layers which is called the blocking layer.<sup>1</sup> So, the charge carrier concentrations in two different reactions can be transferred from  $\text{La}_2\text{O}_7$  layers to  $\text{CuO}_2$  layers as follows:

- i)  $\text{La}_2\text{CuO}_4$  after electrochemical oxidation<sup>2,3</sup>  
 $[\text{La}_2\text{O}_7]^{2-}[\text{CuO}_2]^{2-} \rightarrow [\text{La}_{2-x}\text{Sr}_x\text{O}_7]^{2-2x}[\text{CuO}_2]^{-2+2x}$
- ii)  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as prepared<sup>4,5</sup>  
 $[\text{La}_2\text{O}_7]^{2+}[\text{CuO}_2]^{2-} \rightarrow [\text{La}_{2-x}\text{Sr}_x\text{O}_7]^{+2-x}[\text{CuO}_2]^{-2-x}$

For electrochemical oxidation, the electronic structural evolution of  $\text{La}_2\text{CuO}_4$  may be due to the variation of the concentration of oxygen intercalated in the vicinity of the LaO rock salt planes. Assuming ionic model, the charge of  $\text{CuO}_2$  planes varies from 2 to  $2 + 2x$  depending on the amount of excess

oxygen intercalated into the  $\text{La}_2\text{CuO}_4$  lattice by electrochemical oxidation. In case of  $\text{Sr}^{2+}$ -substitution for  $\text{La}^{3+}$ , the charge of  $\text{CuO}_2$  planes changes from 2 to  $2 + x$  in proportion to the substitution ratio of  $\text{Sr}^{2+}$ .

The  $\text{La}_2\text{CuO}_4$  compound is charge-transfer (CT) insulator with an energy gap between occupied O 2p and the lowest Cu 3d (upper Hubbard) bands. The band structure calculations for  $\text{La}_2\text{CuO}_4$  reveal that a Fermi energy  $E_f$  lies between a broad  $\sigma^*$  band and the top of a  $\pi^*$  band.<sup>6-8</sup> The  $\sigma^*$  band that is primarily Cu-3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> in character, results from the covalent mixing of Cu-3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> and O-2p  $\sigma$  orbitals, while the  $\pi^*$  band that is primarily O-2p  $\pi$  in character is formed by the covalent mixing between Cu-3d<sub>xy</sub> and O-2p  $\pi$  orbitals.<sup>9,10</sup> Carrier doping into  $\text{CuO}_2$  planes by oxygenation reaction, such as high oxygen pressure and electrochemical oxidation,<sup>2,3,11</sup> would give rise to the correlation splitting of the  $\sigma^*$  band which is above the top of the  $\pi^*$  band, which results in the formation of the mobile holes.

It is generally accepted that there is a certain interaction between the conduction electrons and the transverse oxygen vibrations as the carrier doping occurs mainly in the  $\text{CuO}_2$  planes. In this point of view, it is of great importance to examine the phonon (lattice vibrations) in superconducting materials using Raman scattering, infrared absorption and reflection, and neutron scattering technique.

The space group of  $\text{La}_2\text{CuO}_4$ -related compounds crystallized in the tetragonal  $\text{K}_2\text{NiF}_4$  structure belongs to  $I4/mmm$  ( $D_{4h}^{17}$ ) with  $z = 2$ , and the primitive unit cell consists of one formula unit.<sup>12,13</sup> Therefore, group theory predicts 7 infrared and 4 Raman active modes for this structure, as follows:

$A_{2u} + E_u$	Acoustic
$3A_{2u} + 4E_u$	IR
$2A_{1g} + 2E_g$	Rama
$B_{2u}$	Silent

The vibrational spectra have been obtained by means of Raman spectroscopy on polycrystalline sintered and single crystal samples of  $\text{La}_2\text{CuO}_4$ -related compounds.<sup>14-17</sup> The infrared spectra of  $\text{La}_2\text{CuO}_4$ -related compounds have been also reported.<sup>18-22</sup> Despite several IR and Raman Studies on  $\text{La}_2\text{CuO}_4$ -related compounds, there still are many controversies concerning their intrinsic spectra and assignments.

In particular, there was no systematic IR and Raman study on  $\text{La}_2\text{CuO}_4$ -related compounds as a function of hole concentration (or the concentration of  $\text{Cu}^{3+}$ ) and temperature as far as we know.

Therefore, special attention will be paid to the effects of temperature and of hole concentration on the frequency and the intensity of characteristic phonons using FT-IR spectroscopy on polycrystalline  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

### Experimental Section

**Sample preparation.** For preparing the polycrystalline samples of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0, 0.03, 0.07, 0.10$ , and  $0.15$ ), stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and  $\text{CuO}$  were mixed in an agate mortar, then calcined at  $800^\circ\text{C}$  for 24 hours in air. This powder was finely ground, and pressed as pellets, then sintered in air at  $1050^\circ\text{C}$  for 16 hours, and finally sintered in the same condition for 16 hours. For  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ , stoichiometric  $\text{La}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Li}_2\text{CO}_3$  were heated at  $1000^\circ\text{C}$  for 20 hours with an intermittent grinding, and then pressed pellets were treated at  $1100^\circ\text{C}$  for 6 hours in air and allowed to cool in furnace.

**Electrochemical and chemical oxidation.** In order to control the oxygen content of  $\text{La}_2\text{CuO}_4$ , the electrochemical oxidation was performed as previously reported.<sup>2,3</sup> In this experiment, sintered pellets ( $\phi = 8$  mm, 2 mm thickness) were embedded in epoxy resin to form rotating disk electrodes. Based on the cyclic voltammogram of  $\text{La}_2\text{CuO}_4$ , the electrochemical oxidation was carried out in 1 N KOH solution at 500 mV relative to Hg/HgO reference electrode. The chemical oxidation was also performed to oxidize  $\text{La}_2\text{CuO}_4$  in an aqueous solution of  $\text{KMnO}_4$ .<sup>23,24</sup>  $\text{La}_2\text{CuO}_4$  powder (1 g) was put into the saturated  $\text{KMnO}_4$  solution (20 cc), then was maintained at  $50^\circ\text{C}$  for 48 hours. After oxidation, the powder was filtered off, washed with distilled water and ethanol, and dried under vacuum at room temperature.

**Physicochemical characterization.** X-ray diffraction patterns were obtained with Shimadzu instrument using Ni filtered  $\text{Cu K}\alpha$  radiation. The oxygen contents of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  before and after oxidation were determined by iodometric

titration.<sup>25</sup> The thermal evolutions of the electrical resistivity were obtained using four probe method on sintered pellets.

**Infrared spectroscopy.** For infrared spectroscopic measurements, the pellets were thoroughly ground and mixed with dried KBr. The mixtures were pressed as thin pellets of about 0.3 mm thickness. Transmission spectra were measured with Mattson Polaris Fourier-transform infrared spectrometer (resolution :  $4\text{ cm}^{-1}$ ). The measuring temperatures were controlled between 298 K and 10 K using CTI cryogenics.

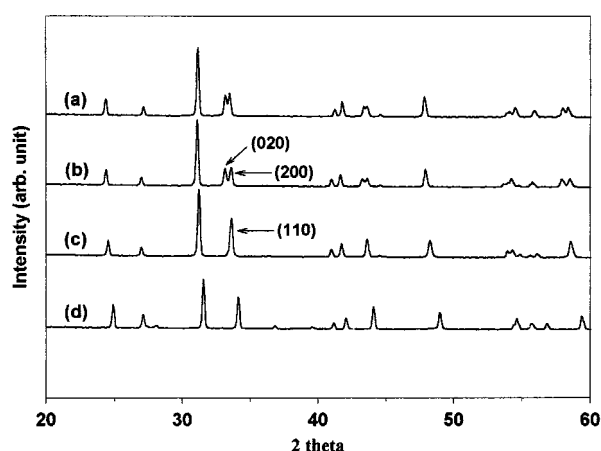
### Results and Discussion

**Sample characterization.** The X-ray diffraction patterns for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0.00$  and  $0.15$ ),  $\text{La}_2\text{CuO}_4$  after oxidation, and  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are displayed in Figure 1. For  $\text{La}_2\text{CuO}_4$  as prepared, the splitting of (200) and (020) peaks which can be considered as the degree of the orthorhombicity, is appeared. For  $\text{La}_2\text{CuO}_4$  after electrochemical oxidation, this splitting is more enhanced by oxygen intercalation in the vicinity of the LaO rock salt planes, which results in the more strongly distorted orthorhombic structure compared with  $\text{La}_2\text{CuO}_4$  as prepared.

For  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as prepared, it seems that the higher symmetric tetragonal structure is progressively stabilized at room temperature in proportion to Sr-substitution ratio. At  $x = 0.15$ , this splitting is disappeared, and (110) line of the tetragonal structure is observed.  $\text{La}_2\text{Li}_{0.5}\text{M}_{0.5}\text{O}_4$  ( $M = \text{Co}, \text{Ni}, \text{Cu}, \text{and Au}$ ) compounds have been reported.<sup>26-29</sup> Among them,  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  has been widely mentioned as  $\text{Cu}^{3+}$  in  $\text{CuO}_2$  planes is stabilized by the direct substitution of lithium for copper in  $\text{La}_2\text{CuO}_4$ . The structural strain reduces in proportion to lithium concentration until the tetragonal structure of space group  $I4/mmm$  is eventually stabilized at room temperature. Thus,  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  compound can be considered as an adequate reference material for  $\text{Cu}^{3+}$ .

The refined lattice parameters obtained from XRD data of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are listed in Table 1.

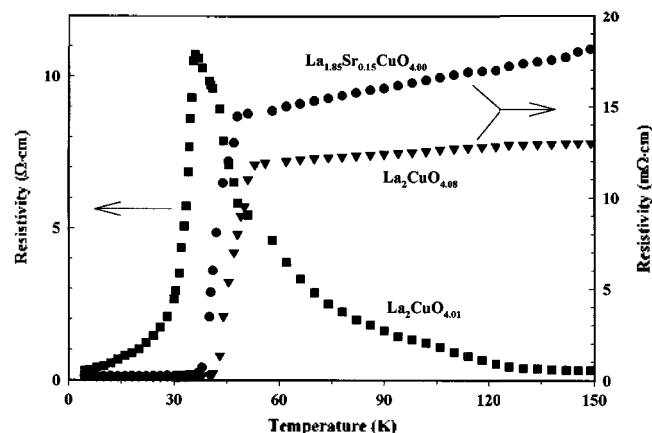
The temperature dependence of the electrical resistivity is shown in Figure 2 for  $\text{La}_2\text{CuO}_4$  before and after electro-



**Figure 1.** X-ray diffraction patterns of  $\text{La}_2\text{CuO}_4$  before electrochemical oxidation (a),  $\text{La}_2\text{CuO}_4$  after electrochemical oxidation (b),  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (c), and  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (d).

**Table 1.** Refined lattice parameters and orthorhombicity for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compounds

Compound	a (Å)	b (Å)	c (Å)	$2(a-b)/(a+b)$
$\text{La}_2\text{CuO}_4$	5.372	5.420	13.188	0.89%
$\text{La}_2\text{CuO}_4$ after oxidation	5.332	5.402	13.204	1.30%
$\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$	5.364	5.403	13.196	0.71%
$\text{La}_{1.95}\text{Sr}_{0.07}\text{CuO}_4$	5.362	5.374	13.218	0.23%
$\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_4$	3.792	3.792	13.263	—
$\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$	3.785	3.785	13.282	—
$\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{0.5}\text{O}_4$	3.717	3.717	13.156	—

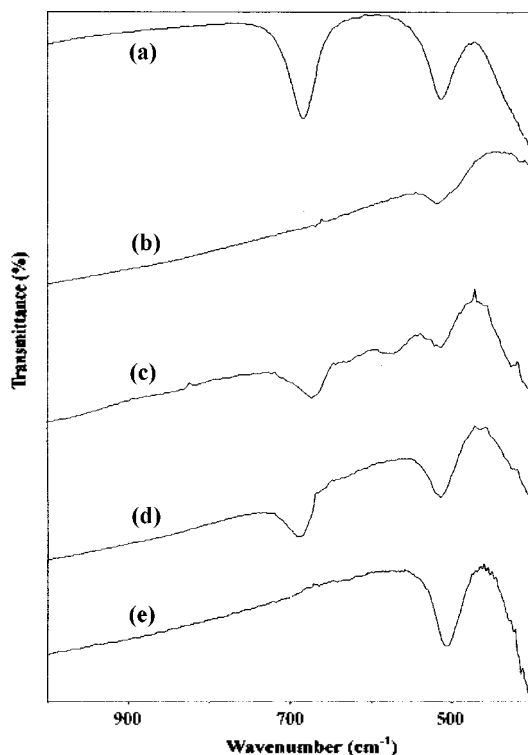
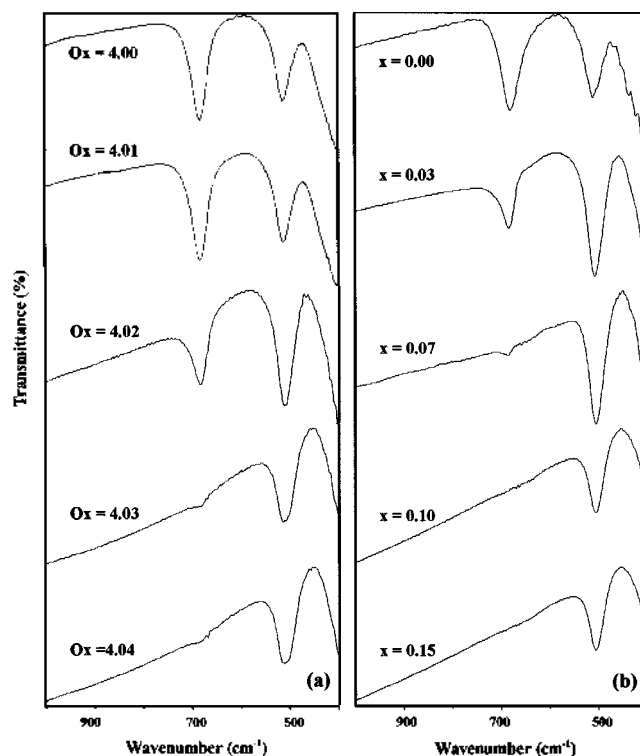
**Figure 2.** Thermal evolution of the electrical resistivity of  $\text{La}_2\text{CuO}_4$  before and after oxidation, and of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4.00}$ .

chemical oxidation, and the electrical resistivity of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  as prepared is also displayed. The material prepared by electrochemical oxidation,  $\text{La}_2\text{CuO}_{4.08}$  reveals zero resistivity at 44 K, and its resistivity at room temperature strongly decreases (13 m $\Omega$ -cm) compared with  $\text{La}_2\text{CuO}_4$  before oxidation (0.30  $\Omega$ -cm).

**Infrared spectroscopy.** The influence of the oxygen content on the phonon modes is prominent in the IR spectra. The IR phonon modes of oxidized materials heated between 25  $^\circ\text{C}$  and 250  $^\circ\text{C}$  are compared with those of  $\text{La}_2\text{CuO}_{4.1\delta}$  before oxidation and of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (Figure 3).

The IR spectrum of  $\text{La}_2\text{CuO}_4$  before oxidation (Figure 3a) is markedly different from that of  $\text{La}_2\text{CuO}_4$  after oxidation (Figure 3b). In particular, the mode at 680  $\text{cm}^{-1}$  which corresponds mainly to Cu-O stretching in the basal plane,<sup>30-33</sup> is absent for oxygen-enriched  $\text{La}_2\text{CuO}_{4.1}$ . This spectral evolution of phonon mode at 680  $\text{cm}^{-1}$  can not be interpreted in terms of a phase transition from orthorhombic to tetragonal as demonstrated by *in-situ* IR measurements. When heating  $\text{La}_2\text{CuO}_{4-\delta}$  after oxidation up to 250  $^\circ\text{C}$  (*i.e.* above the orthorhombic-tetragonal transition<sup>34</sup>) followed by cooling down to room-temperature, the same spectrum is observed either at 250  $^\circ\text{C}$  (Figure 3c) or at 25  $^\circ\text{C}$  (Figure 3d).

It should be also pointed out that the strontium doped compounds which has a tetragonal symmetry, does not exhibit a phonon mode at 680  $\text{cm}^{-1}$  (Figure 3e). As previously reported,<sup>3</sup> TGA measurement confirmed this transformation: a complete weight loss of electrochemically oxidized  $\text{La}_2\text{CuO}_{4-\delta}$  was observed around 250  $^\circ\text{C}$ . Thus, this irrever-

**Figure 3.** IR spectra of  $\text{La}_2\text{CuO}_4$  before oxidation at 25  $^\circ\text{C}$  (a), electrochemically oxidized  $\text{La}_2\text{CuO}_4$  at 25  $^\circ\text{C}$  (b), electrochemically oxidized  $\text{La}_2\text{CuO}_4$  at 250  $^\circ\text{C}$  (c),  $\text{La}_2\text{CuO}_4$  measured at 25  $^\circ\text{C}$  (d) after cooling from spectrum (c), and  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  at 25  $^\circ\text{C}$  (e).**Figure 4.** Room-temperature IR spectra of electrochemically oxidized  $\text{La}_2\text{CuO}_4$  (a) as a function of polarization time at 450 mV and of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (b).

sibility as depicted in Figure 3 demonstrates that the spectral evolution at  $680\text{ cm}^{-1}$  is not due to a phase transition but should rather result from oxygen releasing.

Therefore, one may assume the intensity of this band to be related to the hole concentration or in other words to the amount of  $\text{Cu}^{3+}$ . The hole concentration for the Sr-doped material is about 15%, and about 16% for electrochemically oxidized  $\text{La}_2\text{CuO}_{4+\delta}$ . This concentration decreases with increasing temperature for electrochemically oxidized  $\text{La}_2\text{CuO}_{4-\delta}$ , which likely means that the lower the hole concentration is, the more intense this band is.

Stavola and co-workers have obtained the IR spectra for  $\text{La}_2\text{CuO}_4$  (between  $135\text{ }^\circ\text{C}$  and  $300\text{ }^\circ\text{C}$ ) and  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (between  $5\text{ K}$  and  $295\text{ K}$ ). They observed that the tetragonal-to-orthorhombic phase transition has little effect on the

intensities or frequencies of the mode.<sup>20</sup> However, it is presumed that a systematic IR study at low temperature would give us valuable informations on  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  as the superconducting transition temperature,  $T_c$  is about  $40\text{ K}$ . Moreover, we have a new preparation technique, the electrochemical oxidation which can allow us to control the oxygen content in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ . Figure 4 represents room-temperature IR spectra of electrochemically oxidized  $\text{La}_2\text{CuO}_4$  (as a function of polarization time at  $450\text{ mV}$  vs.  $\text{Hg}/\text{HgO}$  reference electrode) and of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (as a function of Sr-substitution rate). The IR spectra of the electrochemically oxidized  $\text{La}_2\text{CuO}_4$  reveal that the intensity of the phonon at  $680\text{ cm}^{-1}$  is gradually decreased with the oxygen content increased by electrochemical oxidation, and this phonon is completely disappeared for  $O_x = 4.04$ . For  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , the

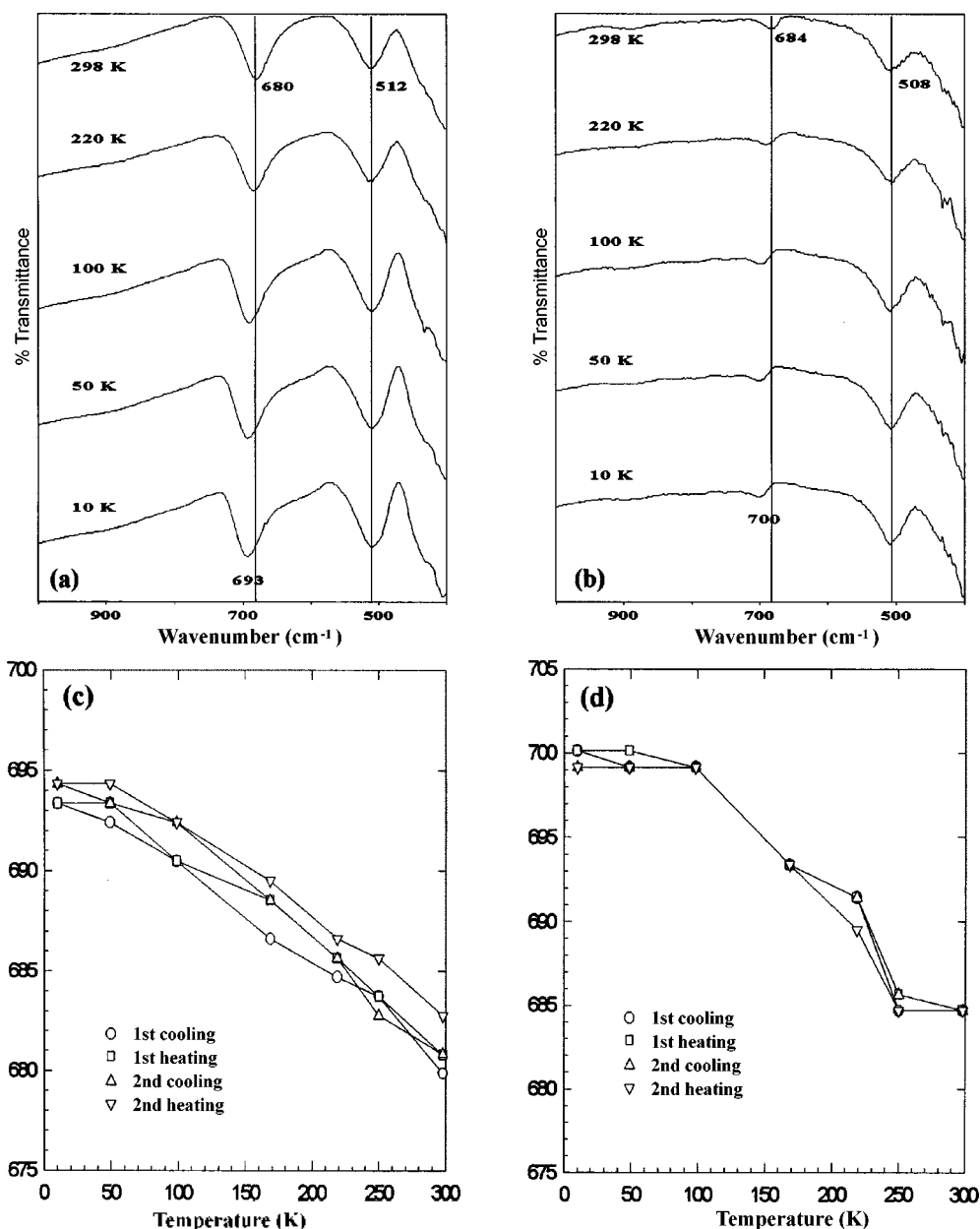


Figure 5. IR spectra of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$   $x = 0.00$  (a) and  $x = 0.03$  (b), and variation of phonon frequency on heating and cooling cycle of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$   $x = 0.00$  (c) and  $x = 0.03$  (d).

intensity of the phonon at  $680\text{ cm}^{-1}$  is reduced, and this phonon is also dramatically disappeared for  $x = 0.10$ . In two cases, it is clearly revealed that the hole concentration is increased by electrochemical oxygen intercalation and the Sr-substitution for La, so the formed conduction electrons within  $\text{CuO}_2$  planes screen more effectively the transverse oxygen breathing mode around  $680\text{ cm}^{-1}$  than the longitudinal oxygen mode around  $510\text{ cm}^{-1}$ . Infrared spectra for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $x = 0$  and  $0.03$ ) obtained between  $10\text{ K}$  and  $298\text{ K}$  are shown in Figure 5. For IR spectra of  $\text{La}_2\text{CuO}_4$ , the phonons at  $680\text{ cm}^{-1}$  are blue shifted by about  $13\text{ cm}^{-1}$  ( $\nu_{10\text{K}} - \nu_{298\text{K}}$ ) as the measuring temperature is lowered, while the phonons around  $510\text{ cm}^{-1}$  are nearly constant. It is generally accepted that the phonon around  $680\text{ cm}^{-1}$  corresponds to the stretching vibration of oxygen atoms in  $\text{CuO}_2$  plane ( $E_u$  symmetry vibration) and the phonon around  $510\text{ cm}^{-1}$  is assigned to the  $A_{2u}$  stretching vibration of apical oxygen atoms in  $\text{CuO}_6$  octahedron.<sup>30-33</sup> As the high concentration of charge carriers exists in  $\text{CuO}_2$  plane, lattice vibrations in this plane may be characterized by a strong electron-phonon coupling. Thus, it can be expected that the charge carriers in  $\text{CuO}_2$  plane will have a greater effect on the phonon around  $680\text{ cm}^{-1}$  compared with the phonon around  $510\text{ cm}^{-1}$ . For  $\text{La}_{1.97}\text{Sr}_{0.03}\text{CuO}_4$ , the intensity of  $680\text{ cm}^{-1}$  is severely reduced compared with that of  $\text{La}_2\text{CuO}_4$ , and this mode is blue shifted with decreasing temperature ( $\nu_{10\text{K}} - \nu_{298\text{K}} = 15\text{ cm}^{-1}$ ), but there is no frequency shift for around  $510\text{ cm}^{-1}$  mode. However, it is remarkable that the mode around  $510\text{ cm}^{-1}$  is red shifted compared with that of  $\text{La}_2\text{CuO}_4$ , which is consistent with that of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as a function of Sr-substitution rate as depicted in Figure 4. It should be mentioned that the charge carrier doping by the Sr-substitution or electrochemical oxidation would give rise to the small contraction of the  $\text{CuO}_6$  octahedron as  $\text{Cu}^{3+}$  requires a smaller site than  $\text{Cu}^{2+}$ , which corresponds to the shortening of the  $\text{Cu-O}(1)$  bond length and the  $\text{Cu-O}(2)$  bond length with the increased  $\text{La-O}(2)$  bond length. And also, it can be said that the blue shift of the mode around  $680\text{ cm}^{-1}$  with decreasing temperature may be due to the contraction of  $\text{CuO}_6$  octahedron as well as the stability of  $\text{Cu}^{3+}$  at low temperature. Figure 6 represents the IR spectra of  $\text{La}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$  and  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  as a function of temperature between  $10\text{ K}$  and  $298\text{ K}$ . For two compounds, there appears only one mode around  $510\text{ cm}^{-1}$  with no evolution even as a function of temperature, which means that the conduction electrons formed by Sr-substitution screen completely the phonon mode around  $680\text{ cm}^{-1}$  and that conduction electrons have no effect on the phonon mode around  $510\text{ cm}^{-1}$  as mentioned above. Figure 7 represents the IR spectra of electrochemically and chemically ( $\text{KMnO}_4$ ) oxidized  $\text{La}_2\text{CuO}_4$  as a function of temperature between  $10\text{ K}$  and  $298\text{ K}$ . For  $\text{KMnO}_4$ -oxidized  $\text{La}_2\text{CuO}_4$ , the mode around  $680\text{ cm}^{-1}$  is blue shifted by about  $14\text{ cm}^{-1}$ , and the mode around  $510\text{ cm}^{-1}$  is nearly constant within the resolution range ( $4\text{ cm}^{-1}$ ). For the electrochemically oxidized  $\text{La}_2\text{CuO}_4$ , the mode around  $680\text{ cm}^{-1}$  is disappeared due to the screening effect, and the mode around  $510\text{ cm}^{-1}$  is clearly splitted into two peaks and is not changed with decreasing

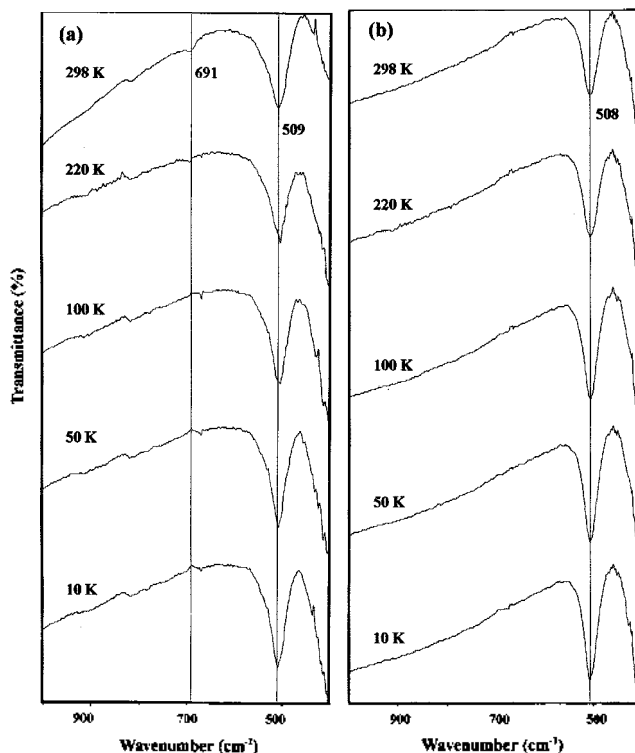


Figure 6. IR spectra of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,  $x = 0.07$  (a) and  $x = 0.15$  (b) as a function of temperature.

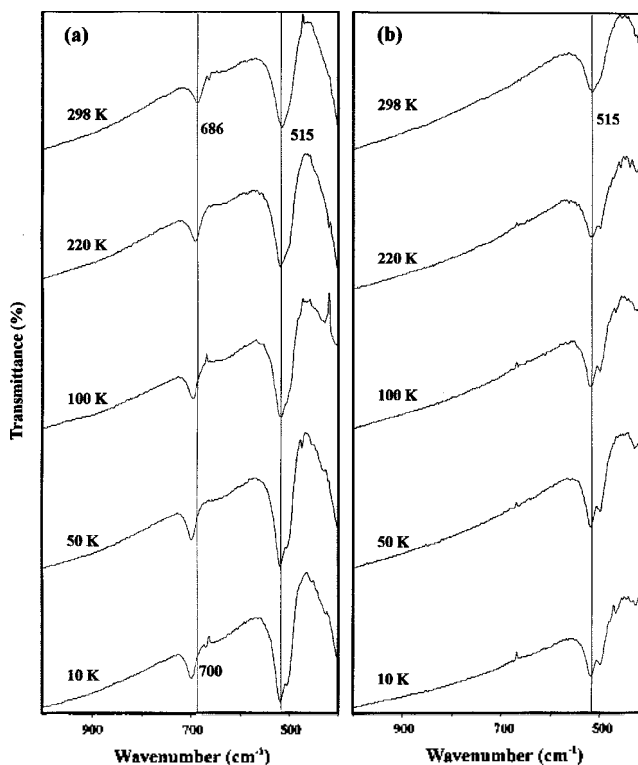
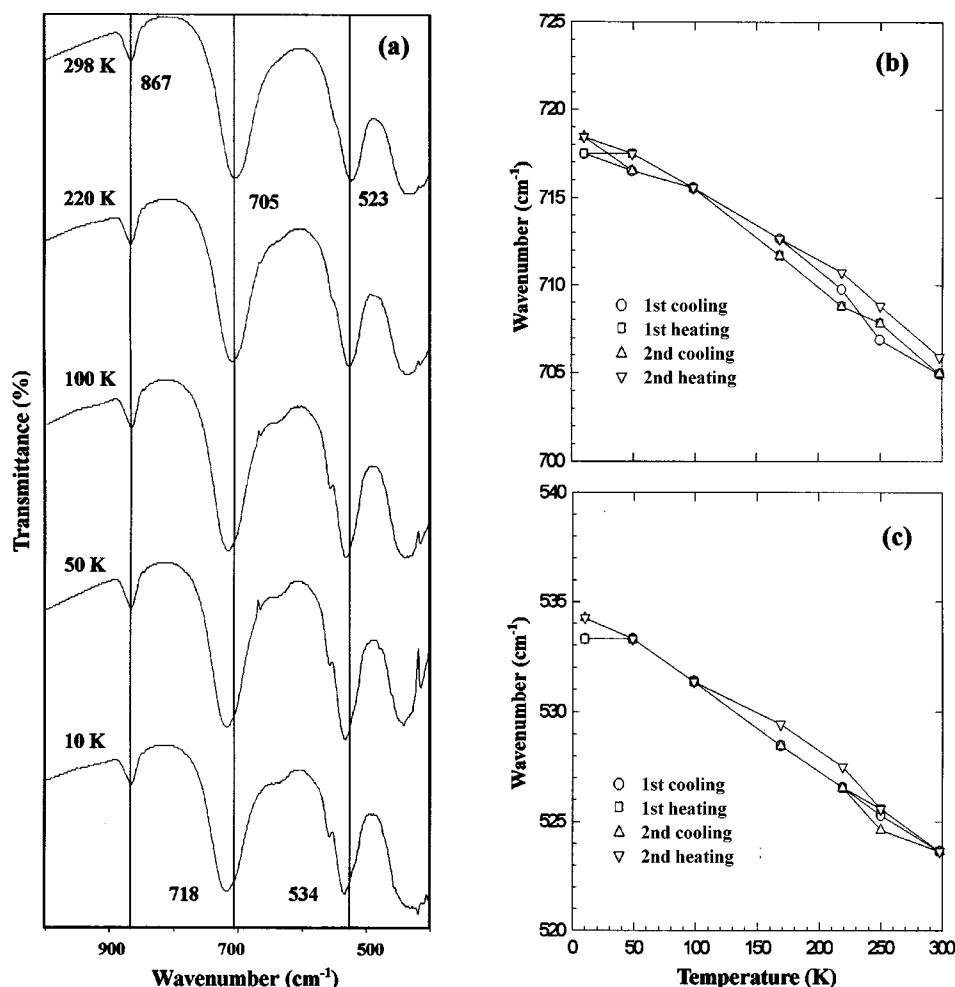


Figure 7. IR spectra of  $\text{KMnO}_4$ -oxidized  $\text{La}_2\text{CuO}_4$  (a) and electrochemically oxidized  $\text{La}_2\text{CuO}_4$  (b) as a function of temperature.

temperature. More especially, the transmittance of overall spectrum was considerably decreased with decreasing temperature below  $T_c$  ( $44\text{ K}$ ), which can be regarded as the sign



**Figure 8.** IR spectra of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (a) as a function of temperature, (b) and (c) variation of phonon frequency on heating and cooling cycle of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ .

of the superconducting transition. Neutron powder diffraction data corroborate our IR interpretation on the variation of  $\text{CuO}_6$  local structure. Radaelli and co-workers reported that the Cu-O(1) bond length in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  slightly decreased in proportional to the Sr-substitution and as a function of temperature,<sup>35</sup> and they observed a comparatively smaller contraction of the Cu-O(2) bond length depending on the excess oxygen content in  $\text{La}_2\text{CuO}_4$ .<sup>36</sup> The IR spectra of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  reference compound are shown in Figure 8.  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  compound is a good candidate for reference material as it is the same space group (I4/mmm) with  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compounds and exhibits very high resistivity despite the  $\text{Cu}^{3+}$  of nearly 100%. As depicted in Figure 8, the unexpected mode is appeared. The mode at  $867\text{ cm}^{-1}$  is assigned to the vibration of the trace of  $\text{Li}_2\text{CO}_3$  which was added excessively for preparing  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  and the frequency of this mode is nearly constant independent of temperature between 10 K and 298 K. Thus, this mode at  $867\text{ cm}^{-1}$  can be regarded as the mode of frequency calibration. In particular, it is remarkable that the mode around  $710\text{ cm}^{-1}$  is strongly remained with blue shift by about  $13\text{ cm}^{-1}$  ( $\nu_{10\text{K}} - \nu_{298\text{K}}$ ), and the mode around  $520\text{ cm}^{-1}$  is blue shifted by  $10\text{ cm}^{-1}$  ( $\nu_{10\text{K}} - \nu_{298\text{K}}$ ). The frequencies of two mode are slightly

higher than those of  $\text{La}_2\text{CuO}_4$ -related compounds, which is probably due to the compressed " $\text{CuO}_6$ " octahedra as  $\text{Cu}^{3+}$  requires a smaller site than  $\text{Cu}^{2+}$ , and the Cu-O(apical) distances are shorter for  $\text{Cu}^{3+}$  due to the removal of the Jahn-Teller distortion.<sup>37</sup> From the fact that the intensities of this mode which correspond mainly to Cu-O stretching in the basal plane, are not changed as the measuring temperature is lowered, it can be said that there is no interaction between conduction electrons and lattice vibrations in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  compound. It should be mentioned that in IR spectra of  $\text{La}_2\text{CuO}_4$ -related superconductors, the mode around  $680\text{ cm}^{-1}$  is suppressed and finally disappeared depending on the Sr-substitution rate or the concentration of excess oxygen.

What is the difference in the tendency of this mode between  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  and  $\text{La}_2\text{CuO}_4$ -related superconductors? It is presumed that the clear solution for this question would be the key of the origin of the superconductivity in  $\text{La}_2\text{CuO}_4$ -related superconductors.

Band structure consideration for  $\text{La}_2\text{CuO}_4$  discloses that the band gap is narrowed, and Fermi energy is shifted with Sr-substitution rate (or, the concentration of excess oxygen) in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  compound, which is in agreement with the increased concentration of mobile hole. Thus, the conduc-

tion electrons formed within  $\text{CuO}_2$  planes screen more effectively the transverse oxygen breathing mode around  $680\text{ cm}^{-1}$ , which results in the suppression and disappearance of this mode depending on the number of carriers in  $\text{CuO}_2$  planes. According to the report of Kastner *et al.*,<sup>38</sup> Li-substitution increases the degree of disorder of the  $\text{CuO}$  layers where the valence states are located. This results in the diminution of the magnitude of the order parameter written as  $\Psi = \Delta e^{-i\phi}$ , so no superconductivity is observed even a few percent of Li-substitution, which is in accordance with the nonexistence of conduction electrons. Based on the efficacy of Li-substitution, it can be explained that the mode around  $710\text{ cm}^{-1}$  is strongly remained because of no interaction between conduction electrons and lattice vibrations.

### Conclusion

We find that there are the prominent effects of temperature (between 10 K and 298 K) and of hole concentration on the frequency and intensity of characteristic phonons in polycrystalline  $\text{La}_2\text{CuO}_4$ -related superconductors using FT-IR spectroscopy. For Sr-substituted  $\text{La}_2\text{CuO}_4$  or the excess oxygen-doped  $\text{La}_2\text{CuO}_4$ , the conduction electrons within  $\text{CuO}_2$  planes are formed and screen more effectively the transverse oxygen breathing mode around  $680\text{ cm}^{-1}$  depending on the concentration of the doped charge carrier. On the contrary, for  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ , the mode  $710\text{ cm}^{-1}$  is still strongly remained even at low temperature (10 K), which means that the efficacy of Li-substitution results in the increment of the degree of disorder in the  $\text{CuO}$  layers and there is no conduction electron formed within  $\text{CuO}_2$  planes of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ .

Our results imply that the Infrared spectroscopy is one of the techniques in probing the superconductivity of  $\text{La}_2\text{CuO}_4$ -related compounds.

**Acknowledgment.** This work was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1996.

### References

- Nobumasa, H.; Shimizu, K.; Nishina, M.; Kawai, T. *Z. Phys. B* **1993**, *90*, 387.
- Wattiaux, A.; Park, J. C.; Grenier, J. C.; Pouchard, M. C. *R. Acad. Sci.* **1990**, Ser2, *310*, 1047.
- Park, J. C.; Hwang, P. V.; Rey-Lafon, M.; Grenier, J. C.; Wattiaux, A.; Pouchard, M. *Physica C* **1991**, *177*, 487.
- Bednorz, J. G.; Müller, K. A. *Z. Phys. B* **1986**, *64*, 189.
- Cava, R. J.; von Dover, R. B.; Batlogg, B.; Rietmann, E. A. *Phys. Rev. Lett.* **1987**, *58*, 408.
- Fujimori, A.; Takayama-Muromachi, E.; Uchida, Y.; Okai, B. *Phys. Rev. B* **1987**, *35*, 8814.
- Mattheiss, J. F. *Phys. Rev. Lett.* **1987**, *58*, 1028.
- Yu, J.; Freeman, A. J.; Xu, J. H. *Phys. Rev. Lett.* **1987**, *58*, 1035.
- Goodenough, J. B. *J. Mater. Education* **1987**, *2*, 620.
- Goodenough, J. B.; Manthiram, A.; Zhou, J. *Mat. Res. Soc. Symp. Proc.* **1989**, *156*, 339.
- Bellie, J.; Cabanel, R.; Chaillout, C.; Chevalier, B.; Demazeau, G.; Deslandes, F.; Etoumeau, J.; Lejay, P.; Michel, C.; Pro-

- ost, J.; Raveau, B.; Sulpice, A.; Tholence, J. L.; Tournier, R. C. *R. Acad. Sci.* **1987**, Ser2, *304*, 1097.
- Wells, A. F. *Structural Inorganic Chemistry*; Oxford Univ. Press: New York, 1975.
- Burns, G.; Glazer, A. M. *Space Groups for Solid State Scientists*; Academic: New York, 1978.
- Brun, T.; Grimsditch, M.; Gray, K. E.; Bhadra, R.; Maroni, V.; Loong, C. K. *Phys. Rev. B* **1987**, *35*, 8837.
- Copic, M.; Mihailovic, D.; Zgonik, M.; Prester, M.; Biljakovic, K.; Orel, B.; Brmicovic, N. *Solid State Commun.* **1987**, *64*, 297.
- Brun, G.; Chandrashekhar, G. V.; Dacol, F. H.; Shafer, M. W. *Solid State Commun.* **1988**, *68*, 67.
- Weber, W. H.; Peters, C. R.; Wanklyn, B. M.; Chen, C. K.; Watts, B. E. *Phys. Rev. B* **1988**, *38*, 917.
- Saito, Y.; Yoshizaki, R.; Sawada, H.; Iwatani, T. E.; Abe, Y.; Matsuura, E. *Jpn. J. Appl. Phys.* **1987**, Part 2, 1011.
- Schlesinger, Z.; Green, R. L.; Bednorz, J. G.; Müller, K. A. *Phys. Rev. B* **1987**, *35*, 5334.
- Stavola, M.; Cava, R. J.; Rietman, E. A. *Phys. Rev. Lett.* **1987**, *58*, 1571.
- Orenstein, J.; Thomas, G. A.; Rapkine, D. H.; Bethea, C. G.; Levine, B. F.; Cava, R. J.; Rietman, E. A.; Johnson, Jr., D. W. *Phys. Rev. B* **1987**, *36*, 729.
- Degiorgi, L.; Kaldis, E.; Wachter, P. *Solid State Commun.* **1984**, *64*, 873.
- Taktakma-Muromachi, E.; Sasaki, T.; Matsui, Y. *Physica C* **1993**, *207*, 97.
- Taktakma-Muromachi, E.; Navrotsky, A. *Physica C* **1993**, *218*, 164.
- Harris, D. C.; Hewston, T. A. *J. Solid State Chem.* **1987**, *69*, 182.
- Blasse, G. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2683.
- Demazeau, G.; Parent, C.; Pouchard, M.; Hagenmüller, P. *Mater. Res. Bull.* **1972**, *7*, 913.
- Abbattista, F.; Vallino, M.; Mazza, D. *J. Less-Common. Met.* **1985**, *10*, 391.
- Paul Attfield, J.; Gerard Ferey, J. *Solid State Chem.* **1989**, *80*, 112.
- Bazhenov, A. V.; Fursova, T. N.; Timofeev, V. B.; Cooper, A. S.; Remeika, J. P.; Fisk, Z. *Phys. Rev. B* **1989**, *40*, 4413.
- Gervais, F.; Echegut, P.; Bassat, J. M.; Odier, P. *Phys. Rev. B* **1988**, *37*, 9364.
- Mostoller, M.; Zhang, J.; Rao, A. M.; Eklund, P. C. *Phys. Rev. B* **1990**, *41*, 6488.
- Eklund, P. C.; Rao, A. M.; Lehman, G. W.; Doll, G. L.; Dresselhaus, M. S.; Picone, P. J.; Gabbe, D. R.; Jenssen, H. P.; Dresselhaus, G. *J. Opt. Soc. Am. B* **1989**, *6*, 389.
- Jorgensen, J. D.; Dabrowski, B.; Shiyou, Pei.; Hinks, D. G.; Soderholm, L.; Morosin, B.; Schirber, J. E.; Venturini, E. L.; Ginley, D. S. *Phys. Rev. B* **1988**, *38*, 11337.
- Radaelli, P. G.; Hinks, D. G.; Mitchell, A. W.; Hunter, B. A.; Wagner, J. L.; Dabrowski, B.; Vandervoot, K. G.; Viswanathan, H. K.; Jorgensen, J. D. *Phys. Rev. B* **1994**, *49*, 4163.
- Radaelli, P. G.; Jorgensen, J. D.; Schultz, A. J.; Hunter, B. A.; Wagner, J. L.; Chou, F. C.; Johnston, D. C. *Phys. Rev. B* **1993**, *48*, 499.
- Hewat, A. W. *Neutron News* **1990**, *1*, 28.
- Kastner, M. A.; Birgeneau, R. J.; Chen, C. Y.; Chiang, Y. M.; Gabbe, D. R.; Jenssen, H. P.; Junk, T.; Peters, C. J.; Picone, P. J.; Tineke, T.; Thurston, T. R.; Tuller, H. L. *Phys. Rev. B* **1988**, *37*, 111.