Infrared Spectroscopic Evidences for the Superconductivity of La₂CuO₄-related Compounds: A Superconductivity Probe

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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 La₂CuO₄-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 La₂CuO₄-related compounds. For La$_{2-x}$Sr$_x$CuO₄ (x = 0.00, 0.03, 0.07, 0.10, and 0.15) and electrochemically (or chemically) oxidized La₂CuO₄, the intensities of the transverse oxygen mode around 680 cm^{-1} which corresponds mainly to Cu-O(1) stretching vibration in the basal plane of CuO₆ octahedron, are decreased and disappeared depending on the Sr-substitution rate and the amount of excess oxygen, while the longitudinal oxygen mode around 510 cm^{-1} corresponding to the Cu-O(2) stretching in the basal plane of CuO₆ 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 cm^{-1} are blue shifted by about 13-15 cm^{-1}, while the phonons around 510 cm^{-1} are nearly constant. The introduction of the charge carrier by doping would give rise to the small contraction of CuO₆ octahedron as Cu^{3+} requires a smaller site than 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 La₂Li$_{0.5}$Cu$_{0.5}$O₄ which exhibits an insulator behavior despite the Cu^{3+} of nearly 100%, corroborate our IR interpretations. The mode around 710 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 CuO₂ planes of La₂CuO₄-related superconductors screen more effectively the transverse oxygen breathing mode around 680 cm^{-1} depending on the concentration of the doped charge carrier in La₂CuO₄-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, La₂CuO₄-related compounds.

La₂CuO₄-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 La₂CuO₄-related compounds can be depicted as charge accepting CuO₂ planes and charge donating La₂O₂ layers which is called the blocking layer.[1] So, the charge carrier concentrations in two different reactions can be transferred from La₂O₂ layers to CuO₂ layers as follows;

i) La₂CuO₄ after electrochemical oxidation[2,3]
   [La₂O₂]$^{2+}$[CuO₂]$^{2-}$ → [La₂O$_{2+x}$]$^{+2-2x}$[CuO₂]$^{-2+2x}$
ii) La$_{2-x}$Sr$_x$CuO₄ as prepared [4,5]
   [La₂O₂]$^{2+}$[CuO₂]$^{2-}$ → [La$_{2-x}$Sr$_x$O₂]$^{+2-x}$[CuO₂]$^{-2+x}$

For electrochemical oxidation, the electronic structural evolution of La₂CuO₄ 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 CuO₂ planes varies from 2 to 2 + 2x depending on the amount of excess oxygen intercalated into the La₂CuO₄ lattice by electrochemical oxidation. In case of Sr^{2+}-substitution for La^{3+}, the charge of CuO₂ planes changes from 2 to 2 + x in proportion to the substitution ratio of Sr^{2+}.

The La₂CuO₄ 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 La₂CuO₄ reveal that a Fermi energy E_f lies between a broad σ* band and the top of a π* band.[6-8] The * band that is primarily Cu-3d$_{x^2-y^2}$ in character, results from the covalent mixing of Cu-3d$_{x^2-y^2}$ and O-2p σ orbitals, while the π* band that is primarily O-2p π in character is formed by the covalent mixing between Cu-3d$_{xy}$ and O-2p π orbitals.[9,10] Carrier doping into CuO₂ planes by oxygenation reaction, such as high oxygen pressure and electrochemical oxidation,[2,3,11] would give rise to the correlation splitting of the σ* band which is above the top of the π* 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 CuO₂ 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 La_2CuO_4-related compounds crystallized in the tetragonal K_2NiF_4 structure belongs to I4/mmm (D^{17}_{4h}) with $z = 2$, and the primitive unit cell consists of one formula unit.[12,13] 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 La_2CuO_4-related compounds.[14-17] The infrared spectra of La_2CuO_4-related compounds have been also reported.[18-22] Despite several IR and Raman Studies on La_2CuO_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 La_2CuO_4-related compounds as a function of hole concentration (or the concentration of 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 $La_{2-x}Sr_xCuO_4$.

Experimental Section

Sample preparation. For preparing the polycrystalline samples of $La_{2-x}Sr_xCuO_4$ ($x = 0, 0.03, 0.07, 0.10$, and 0.15), stoichiometric amounts of La_2O_3, $SrCO_3$, and CuO were mixed in an agate mortar, then calcined at 800 °C for 24 hours in air. This powder was finely ground, and pressed as pellets, then sintered in air at 1050 °C for 16 hours, and finally sintered in the same condition for 16 hours. For $La_2Li_{0.5}Cu_{0.5}O_4$, stoichiometric La_2O_3, CuO, and Li_2CO_3 were heated at 1000 °C for 20 hours with an intermittent grinding, and then pressed pellets were treated at 1100 for 6 hours in air and allowed to cool in furnace.

Electrochemical and chemical oxidation. In order to control the oxygen content of La_2CuO_4, the electrochemical oxidation was performed as previously reported.[2,3] In this experiment, sintered pellets ($\phi = 8$ mm, 2 mm thickness) were embedded in epoxy resin to form rotating disk electrodes. Based on the cyclicvoltammogram of La_2CuO_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 La_2CuO_4 in an aqueous solution of $KMnO_4$.[23,24] La_2CuO_4 powder (1 g) was put into the saturated $KMnO_4$ solution (20 cc), then was maintained at 50 °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 Cu K_α radiation. The oxygen contents of $La_{2-x}Sr_xCuO_4$ before and after oxidation were determined by iodometric

titration.[25] 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 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 $La_{2-x}Sr_xCuO_4$ ($x = 0.00$ and 0.15), La_2CuO_4 after oxidation, and $La_2Li_{0.5}Cu_{0.5}O_4$ are displayed in Figure 1. For La_2CuO_4 as prepared, the splitting of (200) and (020) peaks which can be considered as the degree of the orthorhombicity, is appeared. For La_2CuO_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 La_2CuO_4 as prepared.

For $La_{2-x}Sr_xCuO_4$ 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. $La_2Li_{0.5}M_{0.5}O_4$ (M = Co, Ni, Cu, and Au) compounds have been reported.[26-29] Among them, $La_2Li_{0.5}Cu_{0.5}O_4$ has been widely mentioned as Cu^{3+} in CuO_2 planes is stabilized by the direct substitution of lithium for copper in La_2CuO_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, $La_2Li_{0.5}Cu_{0.5}O_4$ compound can be considered as an adequate reference material for Cu^{3+}.

The refined lattice parameters obtained from XRD data of $La_{2-x}Sr_xCuO_4$ and $La_2Li_{0.5}Cu_{0.5}O_4$ are listed in Table 1.

The temperature dependence of the electrical resistivity is shown in Figure 2 for La_2CuO_4 before and after electro-
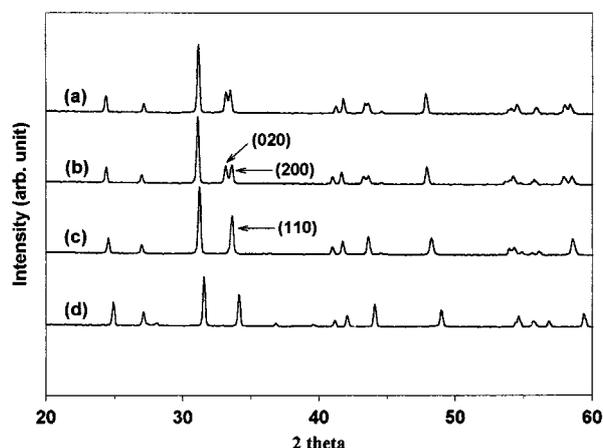
Figure 1. X-ray diffraction patterns of La_2CuO_4 before electrochemical oxidation (a), La_2CuO_4 after electrochemical oxidation (b), $La_{1.85}Sr_{0.15}CuO_4$ (c), and $La_2Li_{0.5}Cu_{0.5}O_4$ (d).

Table 1. Refined lattice parameters and orthorhombicity for $La_{2-x}Sr_xCuO_4$ compounds

| Compound	a (Å)	b (Å)	c (Å)	2(a-b)/(a+b)
La_2CuO_4	5.372	5.420	13.188	0.89%
La_2CuO_4 after oxidation	5.332	5.402	13.204	1.30%
$La_{1.97}Sr_{0.03}CuO_4$	5.364	5.403	13.196	0.71%
$La_{1.93}Sr_{0.07}CuO_4$	5.362	5.374	13.218	0.23%
$La_{1.90}Sr_{0.10}CuO_4$	3.792	3.792	13.263	–
$La_{1.85}Sr_{0.15}CuO_4$	3.785	3.785	13.282	–
$La_2Li_{0.5}Cu_{0.5}O_4$	3.717	3.717	13.156	–
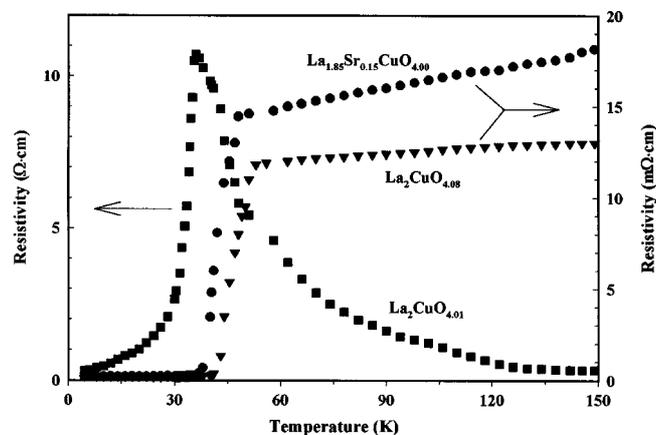
Figure 2. Thermal evolution of the electrical resistivity of La_2CuO_4 before and after oxidation, and of $La_{1.85}Sr_{0.15}CuO_{4.00}$.

chemical oxidation, and the electrical resistivity of $La_{1.85}Sr_{0.15}CuO_4$ as prepared is also displayed. The material prepared by electrochemical oxidation, $La_2CuO_{4.08}$ reveals zero resistivity at 44 K, and its resistivity at room temperature strongly decreases (13 mΩ·cm) compared with La_2CuO_4 before oxidation (0.30 Ω·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 °C and 250 °C are compared with those of $La_2CuO_{4+\delta}$ before oxidation and of $La_{1.85}Sr_{0.15}CuO_4$ (Figure 3).

The IR spectrum of La_2CuO_4 before oxidation (Figure 3a) is markedly different from that of La_2CuO_4 after oxidation (Figure 3b). In particular, the mode at 680 cm^{-1} which corresponds mainly to Cu-O stretching in the basal plane,[30-33] is absent for oxygen-enriched La_2CuO_{4+}. This spectral evolution of phonon mode at 680 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 $La_2CuO_{4+\delta}$ after oxidation up to 250 °C (*i.e.* above the orthorhombic-tetragonal transition[34]) followed by cooling down to room-temperature, the same spectrum is observed either at 250 °C (Figure 3c) or at 25 °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 cm^{-1} (Figure 3e). As previously reported,[3] TGA measurement confirmed this transformation: a complete weight loss of electrochemically oxidized $La_2CuO_{4+\delta}$ was observed around 250 °C. Thus, this irrever-
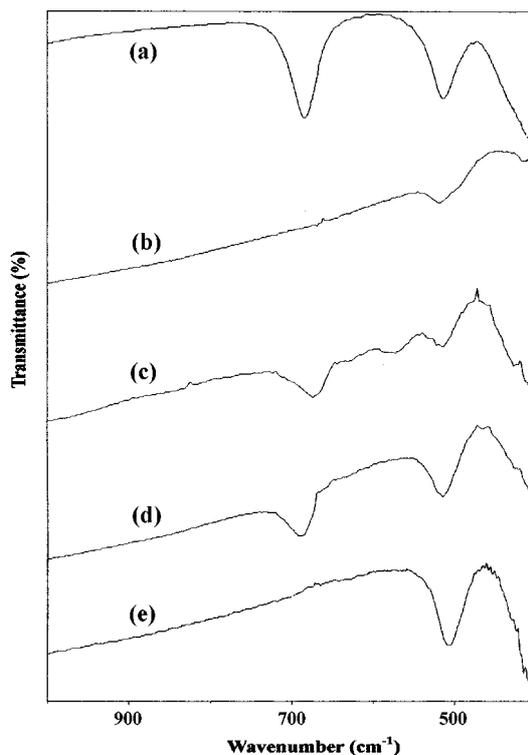
**Figure 3**. IR spectra of La_2CuO_4 before oxidation at 25 °C (a), electrochemically oxidized La_2CuO_4 at 25 °C (b), electrochemically oxidized La_2CuO_4 at 250 °C (c), La_2CuO_4 measured at 25 °C (d) after cooling from spectrum (c), and $La_{1.85}Sr_{0.15}CuO_4$ at 25 °C (e).
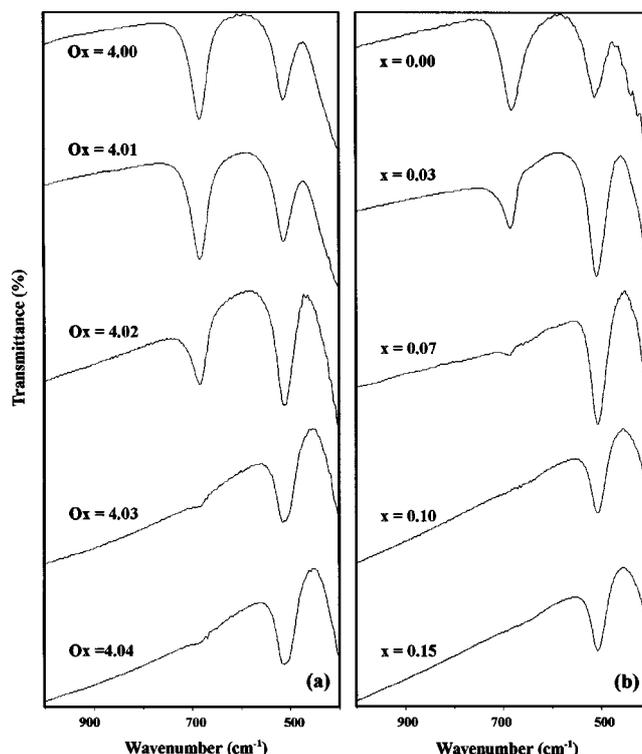
Figure 4. Room-temperature IR spectra of electrochemically oxidized La_2CuO_4 (a) as a function of polarization time at 450 mV and of $La_{2-x}Sr_xCuO_4$ (b).

sibility as depicted in Figure 3 demonstrates that the spectral evolution at 680 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 Cu^{3+}. The hole concentration for the Sr-doped material is about 15%, and about 16% for electrochemically oxidized $La_2CuO_{4+\delta}$. This concentration decreases with increasing temperature for electrochemically oxidized La_2CuO_{4+}, 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 La_2CuO_4 (between 135 °C and 300 °C) and $La_{1.85}Sr_{0.15}CuO_4$ (between 5 K and 295 K). They observed that the tetragonal-to-orthorhombic phase transition has little effect on the

intensities or frequencies of the mode.[20] However, it is presumed that a systematic IR study at low temperature would give us valuable informations on $La_{2-x}Sr_xCuO_{4+\delta}$ as the superconducting transition temperature, T_c is about 40 K. Moreover, we have a new preparation technique, the electrochemical oxidation which can allow us to control the oxygen content in $La_{2-x}Sr_xCuO_{4+\delta}$. Figure 4 represents room-temperature IR spectra of electrochemically oxidized La_2CuO_4 (as a function of polarization time at 450 mV *vs*. Hg/HgO reference electrode) and of $La_{2-x}Sr_xCuO_4$ (as a function of Sr-substitution rate). The IR spectra of the electrochemically oxidized La_2CuO_4 reveal that the intensity of the phonon at 680 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 $La_{2-x}Sr_xCuO_4$, the
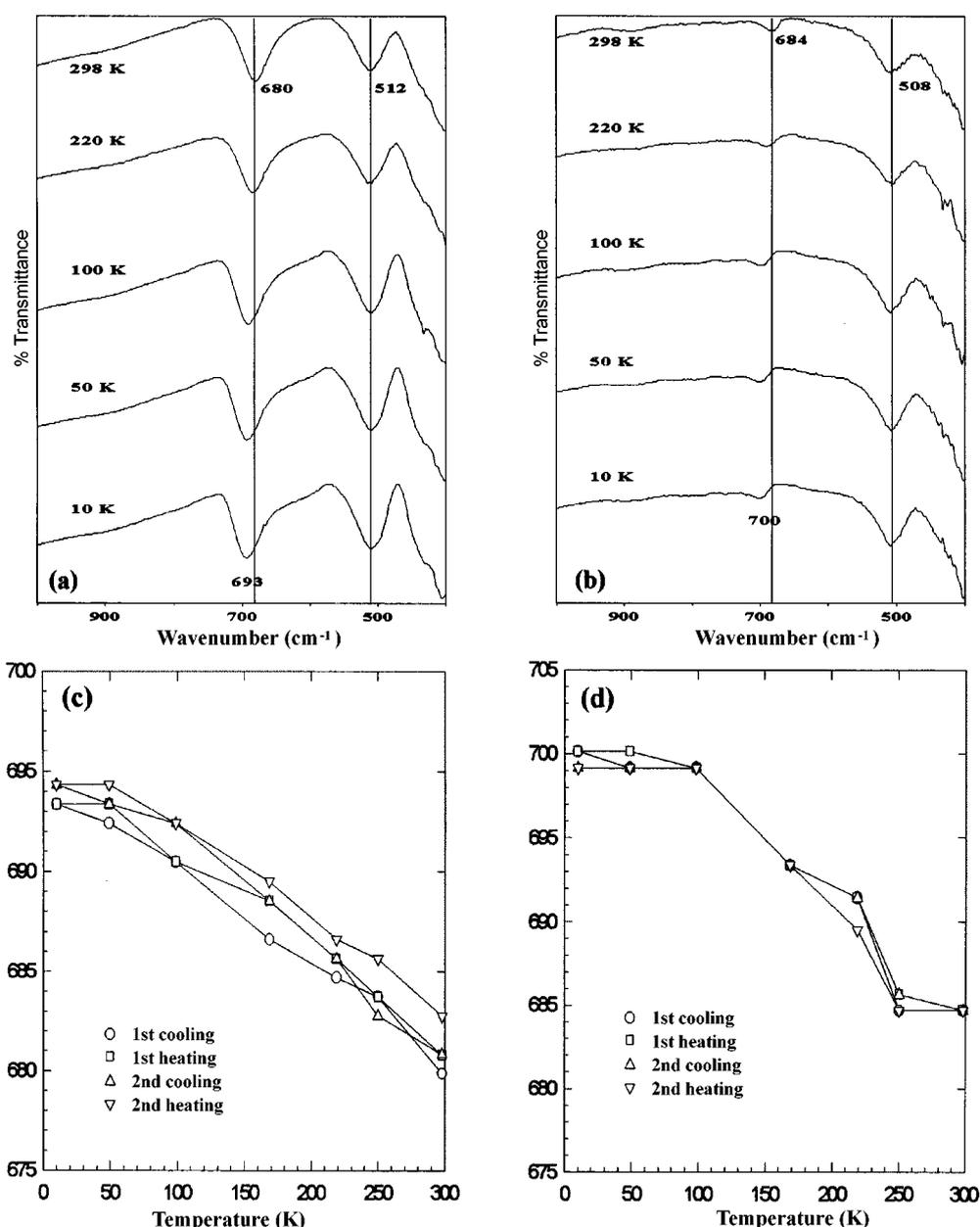
Figure 5. IR spectra of $La_{2-x}Sr_xCuO_4$ $x = 0.00$ (a) and $x = 0.03$ (b), and variation of phonon frequency on heating and cooling cycle of $La_{2-x}Sr_xCuO_4$ $x = 0.00$ (c) and $x = 0.03$ (d).

intensity of the phonon at 680 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 CuO$_2$ planes screen more effectively the transverse oxygen breathing mode around 680 cm^{-1} than the longitudinal oxygen mode around 510 cm^{-1}. Infrared spectra for La$_{2-x}$Sr$_x$CuO$_4$ ($x = 0$ and 0.03) obtained between 10 K and 298 K are shown in Figure 5. For IR spectra of La$_2$CuO$_4$, the phonons at 680 cm^{-1} are blue shifted by about 13 cm^{-1} (v_{10K}-v_{298K}) as the measuring temperature is lowered, while the phonons around 510 cm^{-1} are nearly constant. It is generally accepted that the phonon around 680 cm^{-1} corresponds to the stretching vibration of oxygen atoms in CuO$_2$ plane (E_u symmetry vibration) and the phonon around 510 cm^{-1} is assigned to the A$_{2u}$ stretching vibration of apical oxygen atoms in CuO$_6$ octahedron.[30-33] As the high concentration of charge carriers exists in 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 CuO$_2$ plane will have a greater effect on the phonon around 680 cm^{-1} compared with the phonon around 510 cm^{-1}. For La$_{1.97}$Sr$_{0.03}$CuO$_4$, the intensity of 680 cm^{-1} is severely reduced compared with that of La$_2$CuO$_4$, and this mode is blue shifted with decreasing temperature (v_{10K}-$v_{298K} = 15$ cm^{-1}), but there is no frequency shift for around 510 cm^{-1} mode. However, it is remarkable that the mode around 510 cm^{-1} is red shifted compared with that of La$_2$CuO$_4$, which is consistent with that of La$_{2-x}$Sr$_x$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 CuO$_6$ octahedron as Cu^{3+} requires a smaller site than Cu^{2+}, which corresponds to the shortening of the Cu-O(1) bond length and the Cu-O(2) bond length with the increased La-O(2) bond length. And also, it can be said that the blue shift of the mode around 680 cm^{-1} with decreasing temperature may be due to the contraction of CuO$_6$ octahedron as well as the stability of Cu^{3+} at low temperature. Figure 6 represents the IR spectra of La$_{1.93}$Sr$_{0.07}$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ as a function of temperature between 10 K and 298 K. For two compounds, there appears only one mode around 510 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 cm^{-1} and that conduction electrons have no effect on the phonon mode around 510 cm^{-1} as mentioned above. Figure 7 represents the IR spectra of electrochemically and chemically (KMnO$_4$) oxidized La$_2$CuO$_4$ as a function of temperature between 10 K and 298 K. For KMnO$_4$-oxidized La$_2$CuO$_4$, the mode around 680 cm^{-1} is blue shifted by about 14 cm^{-1}, and the mode around 510 cm^{-1} is nearly constant within the resolution range (4 cm^{-1}). For the electrochemically oxidized La$_2$CuO$_4$, the mode around 680 cm^{-1} is disappeared due to the screening effect, and the mode around 510 cm^{-1} is clearly splitted into two peaks and is not changed with decreasing
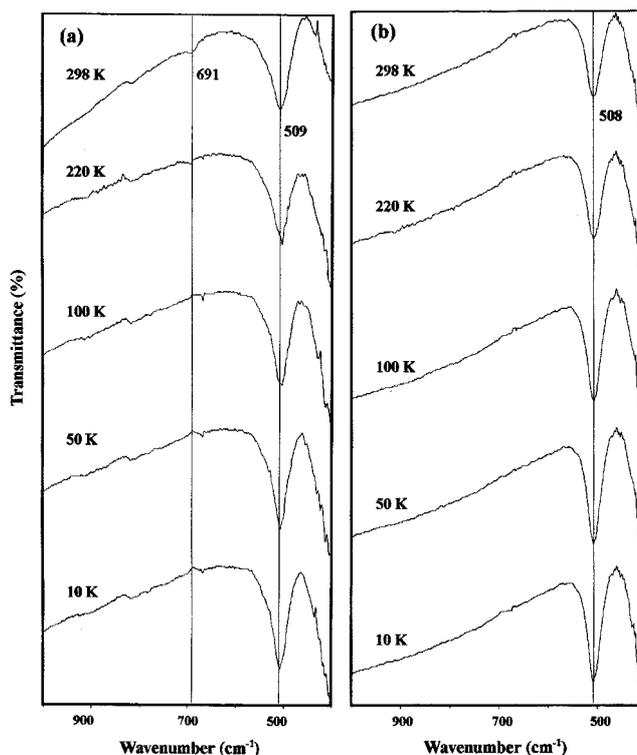

Figure 6. IR spectra of La$_{2-x}$Sr$_x$CuO$_4$, $x = 0.07$ (a) and $x = 0.15$ (b) as a function of temperature.
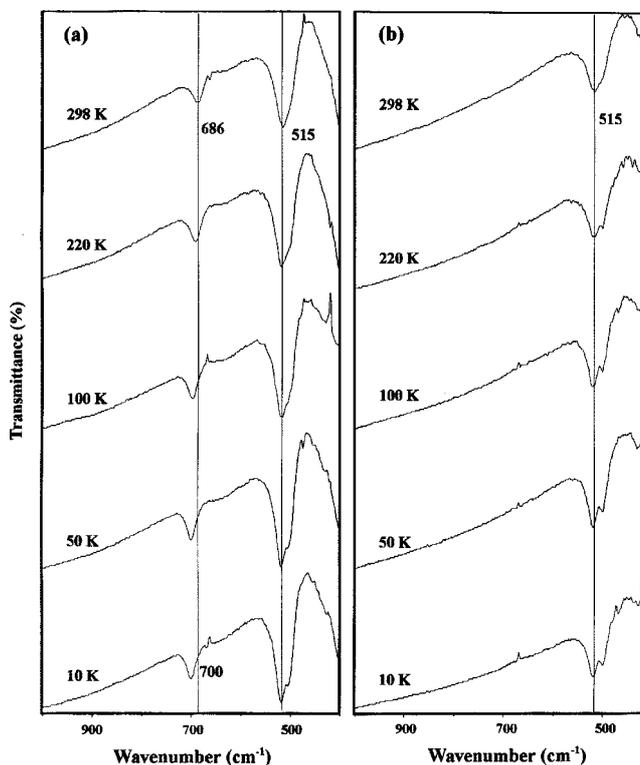
Figure 7. IR spectra of KMnO$_4$-oxidized La$_2$CuO$_4$ (a) and electrochemically oxidized La$_2$CuO$_4$ (b) as a function of temperature.

temperature. More especially, the transmittance of overall spectrum was considerably decreased with decreasing temperature below T_c (44 K), which can be regarded as the sign
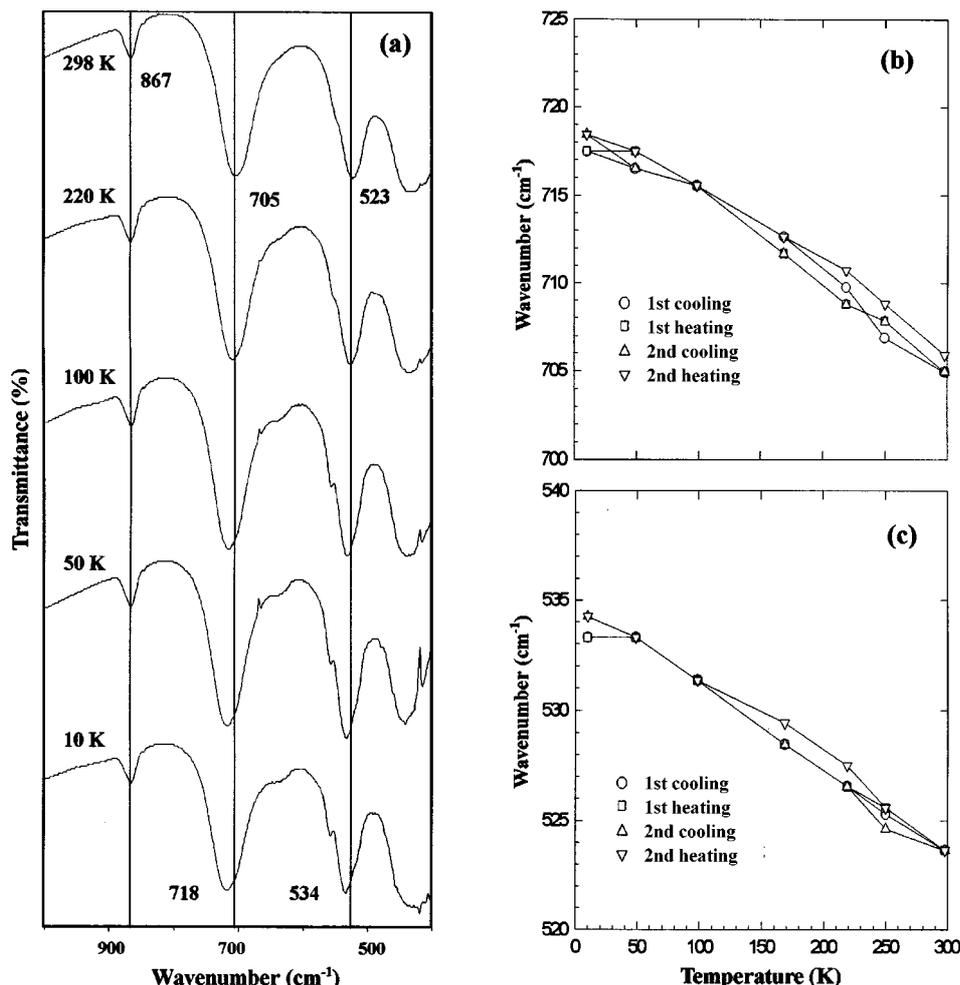
Figure 8. IR spectra of $La_2Li_{0.5}Cu_{0.5}O_4$ (a) as a function of temperature, (b) and (c) variation of phonon frequency on heating and cooling cycle of $La_2Li_{0.5}Cu_{0.5}O_4$.

of the superconducting transition. Neutron powder diffraction data corroborate our IR interpretation on the variation of CuO_6 local structure. Radaelli and co-workers reported that the Cu-O(1) bond length in $La_{2-x}Sr_xCuO_4$ slightly decreased in proportional to the Sr-substitution and as a function of temperature,[35] and they observed a comparatively smaller contraction of the Cu-O(2) bond length depending on the excess oxygen content in La_2CuO_{4+}[36] The IR spectra of $La_2Li_{0.5}Cu_{0.5}O_4$ reference compound are shown in Figure 8. $La_2Li_{0.5}Cu_{0.5}O_4$ compound is a good candidate for reference material as it is the same space group (I4/mmm) with $La_{2-x}Sr_xCuO_4$ compounds and exhibits very high resistivity despite the Cu^{3+} of nearly 100%. As depicted in Figure 8, the unexpected mode is appeared. The mode at 867 cm^{-1} is assigned to the vibration of the trace of Li_2CO_3 which was added excessively for preparing $La_2Li_{0.5}Cu_{0.5}O_4$, and the frequency of this mode is nearly constant independent of temperature between 10 K and 298 K. Thus, this mode at 867 cm^{-1} can be regarded as the mode of frequency calibration. In particular, it is remarkable that the mode around 710 cm^{-1} is strongly remained with blue shift by about 13 cm^{-1} (v_{10K}-v_{298K}), and the mode around 520 cm^{-1} is blue shifted by 10 cm^{-1} (v_{10K}-v_{298K}). The frequencies of two mode are slightly

higher than those of La_2CuO_4-related compounds, which is probably due to the compressed "CuO_6" octahedra as Cu^{3+} requires a smaller site than Cu^{2+}, and the Cu-O(apical) distances are shorter for Cu^{3+} due to the removal of the Jahn-Teller distortion.[37] 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 $La_2Li_{0.5}Cu_{0.5}O_4$ compound. It should be mentioned that in IR spectra of La_2CuO_4-related superconductors, the mode around 680 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 $La_2Li_{0.5}Cu_{0.5}O_4$ and La_2CuO_4-related superconductors?

It is presumed that the clear soluton for this question would be the key of the origin of the superconductivity in La_2CuO_4-related superconductors.

Band structure consideration for La_2CuO_4 discloses that the band gap is narrowed, and Fermi energy is shifted with Sr-substitution rate (or. the concentration of excess oxygen) in $La_{2-x}Sr_xCuO_4$ compound, which is in agreement with the increased concentration of mobile hole. Thus, the conduc-

tion electrons formed within CuO_2 planes screen more effectively the transverse oxygen breathing mode around 680 cm^{-1}, which results in the suppression and disappearance of this mode depending on the number of carriers in CuO_2 planes. According to the report of Kastner *et al.*,[38] Li-substitution increases the degree of disorder of the 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 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 La_2CuO_4-related superconductors using FT-IR spectroscopy. For Sr-substituted La_2CuO_4 or the excess oxygen-doped La_2CuO_4, the conduction electrons within CuO_2 planes are formed and screen more effectively the transverse oxygen breathing mode around 680 cm^{-1} depending on the concentration of the doped charge carrier. On the contrary, for $La_2Li_{0.5}Cu_{0.5}O_4$, the mode 710 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 CuO layers and there is no conduction electron formed within CuO_2 planes of $La_2Li_{0.5}Cu_{0.5}O_4$.

Our results imply that the Infrared spectroscopy is one of the techniques in probing the superconductivity of La_2CuO_4-related compounds.

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