A comparative infrared spectroscopic study of electronic superconductors of the type $Ln_{2-x}M^{IV}_xCuO_{4-y}$

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Before 1989 it was assumed that the charge carriers responsible for superconductivity in all high-T_c ceramic materials with $T_c > 30$ K were mobile holes confined to the conducting CuO_2 planes, the characteristic building units of these materials [1, 2]. However, this view has been challenged by the discovery of new superconducting oxides by Tokura and co-workers [3, 4] in which the charge carriers involved in the superconductivity appear to be electrons.

These electron-doped superconducting materials are obtained by doping the parent compound Ln_2CuO_{4-y} in a variety of ways. All of these dopings appear to donate electrons to the CuO_2 planes from sites either within or outside the planes. The largest group of these materials has the chemical formula $Ln_{2-x}M^{IV}_xCuO_{4-y}$, where M^{IV} ions substitute the Ln(III) ions. Superconductivity has been found with $M^{IV} = Ce$, in the pairs Pr/Ce, Nd/Ce, Sm/Ce and Eu/Ce [3, 5], and with $M^{IV} = Th$ in Pr/Th, Nd/Th and Sm/Th [5–7]. Another material of this type is $Nd_2CuO_{4-x}F_x$ in which F⁻ substitutes O²⁻ ions [8]. Finally, another type is represented by materials of composition $Nd_{2-x}Ce_xCu_{1-z}M^{III}_zO_{4-y}$, in which Ga(III) or In(III) ions substitute Cu(II) ions within the CuO_2 planes [9, 10].

After their discovery, all of these new materials were subjected to a great number of physical studies and measurements. Recently, we investigated the infrared spectra of a series of phases of this type, of composition $Nd_{2-x}Ce_xCuO_{4-y}$ [11] and $Nd_2CuO_{4-x}F_x$ [12]. In order to extend these studies and to obtain a more general picture of the vibrational behaviour of these materials, in this study we investigated the infrared spectra of a great number of phases containing different pairs of tetravalent and trivalent cations.

The investigated samples were synthesized by solid-state reactions, starting from stoichiometric mixtures of the corresponding oxides. The well-mixed powders were fired at 950 °C overnight. After grinding, they were heated again for 30–35 h at 1000–1050 °C and finally annealed under argon at 900 °C for 10–12 h, then brought to room temperature at the cooling rate of the furnace. The

samples were characterized by X-ray powder diffractometry, which showed the formation of single-phase materials. The infrared spectra were recorded with a Perkin–Elmer 580B spectrophotometer, using nujol suspensions of the powdered samples, between CsI plates.

All of the investigated materials belong to the so-called T′ form of K_2NiF_4 (tetragonal, space group I4/mmm [13, 14]), shown in Fig. 1. Usually, the lattice parameter c decreased linearly with increasing doping, whereas the value of the lattice parameter a remained nearly constant. As can be seen from the crystal structure (Fig. 1), the lattice constant of the c-axis is expected to be sensitive to the ionic radius of the atom at the Nd-site. On the other hand, the lattice constant of the a-axis is expected to change little with dopant concentration, because it is controlled mainly by the Cu–O bond length in the CuO_4 planes [15].
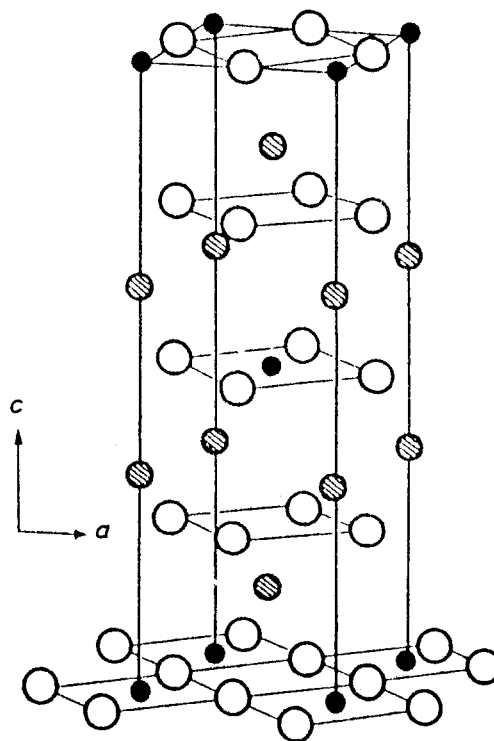

Figure 1 Crystal structure of Nd_2CuO_4: (●) Cu, (◈) Nd and (○) O.

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The spectra of all prepared materials were very similar to that of the pure undoped parent Ln_2CuO_{4-y} compounds. They possess the typical two band structure discussed earlier for oxides belonging to the above mentioned structural type [16, 17]. As typical examples of the investigated series, Fig. 2 shows the spectra of the phases of composition $Pr_{1.9}Ce_{0.1}CuO_{4-y}$ and $Sm_{1.9}Th_{0.1}$-CuO_{4-y}, which are characteristic for the cerium- and thorium-containing materials, respectively.

The exact band positions for all of the materials are shown in Table I, in which we have also included our previous results for the $Nd_{2-x}Ce_xCuO_{4-y}$ phases [11] and, in order to facilitate discussion, also the ionic radii of the involved cationic species with co-ordination number 8 [18].

As discussed previously, the main infrared band located above $500\ cm^{-1}$ can be assigned to an antisymmetric stretching vibration of the Cu–O bonds of the square CuO_4 units present in this structural type. The second band, which appears always split in one of the two forms shown in Fig. 2, is more difficult to assign. However, the higher-energy component can probably be assigned to an
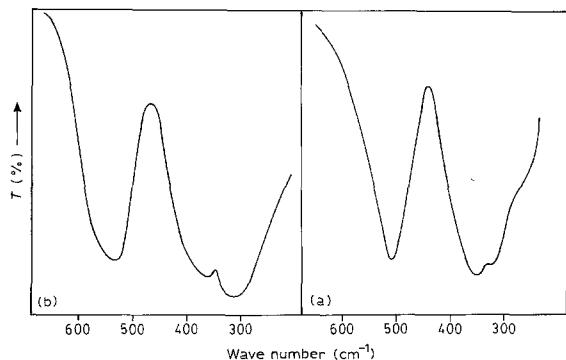

Figure 2 Infrared spectra of (a) $Pr_{1.9}Ce_{0.1}CuO_{4-y}$ and (b) $Sm_{1.9}Th_{0.1}CuO_{4-y}$.

TABLE I Infrared frequencies for the investigated materials and ionic radii for the Ln(III) and M(IV) ions (from [18])

Material	Frequencies (cm^{-1})		
Nd_2CuO_{4-y}	528	365	327
$Nd_{1.95}Ce_{0.05}CuO_{4-y}$	525	365	325
$Nd_{1.90}Ce_{0.10}CuO_{4-y}$	518	360	320
$Nd_{1.85}Ce_{0.15}CuO_{4-y}$	515	360	320
$Nd_{1.80}Ce_{0.20}CuO_{4-y}$	513	360	320
$Nd_{1.95}Th_{0.05}CuO_{4-y}$	520	355	320
$Nd_{1.90}Th_{0.10}CuO_{4-y}$	520	355	322
$Nd_{1.85}Th_{0.15}CuO_{4-y}$	520	355	320
$Nd_{1.80}Th_{0.20}CuO_{4-y}$	520	357	320
Pr_2CuO_{4-y}	510	340	310
$Pr_{1.90}Ce_{0.10}CuO_{4-y}$	505	335	315
$Pr_{1.80}Ce_{0.20}CuO_{4-y}$	505	335	305
$Pr_{1.90}Th_{0.10}CuO_{4-y}$	503	335	310
$Pr_{1.80}Th_{0.20}CuO_{4-y}$	503	335	310
Sm_2CuO_{4-y}	535	365	320
$Sm_{1.90}Th_{0.10}CuO_{4-y}$	532	360	310
$Sm_{1.80}Th_{0.20}CuO_{4-y}$	532	360	315

Ionic radii (in nm), for co-ordination number 8
Pr(III) 0.114, Nd(III) 0.112, Sm(III) 0.109, Ce(IV) 0.097, Th(IV) 0.106

Ln–O stretching mode and the other component to a deformational mode of the CuO_4 polyhedra (cf. [19] and references therein).

As can be seen from Table I, the band positions show a small shift to lower energies in going from pure Nd_2CuO_{4-y} to the Ce(IV)-substituted samples. This behaviour is very interesting because the volume of the unit cell decreases with increasing Ce(IV) content, due to the smaller size of Ce(IV) compared with Nd(III) (cf. [15, 20]). Therefore, a slight reinforcement of the Cu–O bonds could be expected in the same direction with a concomitant displacement of the Cu–O stretching vibration to higher energy (cf. for example [21, 22]), in disagreement with the experimental data. This somewhat unexpected behaviour is probably related to the fact that the Cu–O distances become slightly enlarged in the superconducting samples, in comparison with in the pure Nd_2CuO_{4-y}. This result shows that the strength of the Cu–O bonds apparently overrides the unit-cell size effects. In this context it is interesting to note that a detailed neutron and electron diffraction study of the phase $Nd_{1.845}Ce_{0.155}CuO_{4-y}$ has clearly shown that the Cu–O distance is slightly longer than those normally found in hole-doped superconducting copper oxides. This suggets a higher electronic density along the Cu–O bonds in the electron superconductors [23], which could be responsible for the observed Cu–O bond weakening.

In the case of the Nd/Th phases, the unit-cell volumes remain practically unchanged, although a small decrease in both the c lattice dimension and the c/a ratio with increasing Th(IV) substitution is observed [24]. Although the ionic radius of Th(IV) is close to that of Nd(III), as is that of Ce(IV), the effect of the substitution is even more pronounced in the case of the Nd/Th materials, suggesting the generation of somewhat longer Cu–O distances in these phases. However, interestingly, practically no changes can be observed between the different members of the $Nd_{2-x}Th_xCuO_{4-y}$ series.

A structural study of some Pr/Ce phases with x-values ranging between 0.05 and 0.18 also showed a diminution of the c-values, whereas the a-values remained practically constant [25]. A similar behaviour could be expected for the $Pr_{2-x}Th_xCuO_{4-y}$ materials [5].

As can be seen in Table I, the substitution of Pr(III) by both Ce(IV) and Th(IV) also generated a diminution of the Cu–O stretching frequency in comparison with the value measured in undoped Pr_2CuO_{4-y}. In these cases both Ce(IV) and Th(IV) doping produced effects of similar magnitude on the Cu–O bonds.

Finally, the two investigated $Sm_{2-x}Th_xCuO_{4-y}$ materials also showed a very small decrease of the Cu–O stretching frequency after doping.

To conclude, this spectroscopic investigation has clearly shown that doping of pure Ln_2CuO_{4-y} materials belonging to the T'-K_2NiF_4 structural type with M(IV) cations on the Ln(III) sites produces a marked weakening of the Cu–O bond strengths. As

in all the investigated cases the greater Ln(III) cations were substituted by a smaller M(IV) ion, a continuous decrease in the unit-cell volume may be expected with increased substitution. On the other hand, increased M(IV) incorporation with the simultaneous decrease in unit-cell volume generates a higher electron density along the Cu–O bonds [formally, more $Cu(d^{10})$ appear on the Cu sites] producing a weakening of this bond. This proposed generation of Cu^+ ions is also supported by other types of measurements [26–29].

As recently discussed by Rosseinsky et al. [30], the crystal chemistry of T'-materials is strongly dependent on geometrical factors, originating from longer Cu–O bonds in that structural type, in comparison with those usually found in the orthorhombic K_2NiF_4 structure. In this context, it becomes evident that the T'-structure will also favour lower copper oxidation states [30].

Finally, it should be emphasized that in the cases investigated the weakening of the Cu–O bond strength clearly overrides the unit-cell size effects, which are usually observed in isomorphous series of lanthanide compounds.

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