

Infrared spectra of the phases $\text{YSr}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7+\delta}$, with $\text{M} = \text{Mo}, \text{W}, \text{Re}$ and $x = 0.2\text{--}0.3$

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Since the discovery of high-temperature cuprate superconductors much effort has been put into stabilizing new metastable phases by chemical substitution [1]. A good example of such processes is the stabilization of $\text{YSr}_2\text{Cu}_3\text{O}_7$ at ambient pressure. It is well known that in spite of the fact that this material can only be prepared under high-pressure [2], its stabilization can be achieved at ambient conditions if other metals substitute part of the copper [3–6].

In a previous paper we reported cell parameter refinement and discussed the IR spectroscopic behavior of $\text{YSr}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7\pm\delta}$ substituted phases, where $\text{M} = \text{Ti}, \text{Fe}, \text{Co}, \text{Al}, \text{Ga}$ and Pb [7]. In order to attain a wider insight into the spectroscopic properties of such substituted materials we have now investigated the incorporation of hexavalent Mo, W and Re in the $\text{YSr}_2\text{Cu}_3\text{O}_7$ lattice.

A series of materials of this type has been recently prepared and investigated by single X-ray crystallography and powder neutron diffraction [6]. They belong to the tetragonal P4/mmm space group. It was found that the M(VI) ions substitute preferentially for the chain Cu (1) sites and that they substantially disrupt the Cu–O chain structure. On the other hand, and although not completely demonstrated, it is believed that the M(VI) substitution increases the oxygen stoichiometry and, consequently, the effective oxidation state of copper. This increase in oxidation state plays a crucial role in the stabilization of the cuprate structure, reducing the structural strain and generating superconductivity at T_c values of about 50 K [6].

Polycrystalline samples of nominal composition $\text{YSr}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7\pm\delta}$ ($\text{M} = \text{Mo}, \text{W}, \text{Re}$ and $x = 0.3$ for Mo and 0.2 for W and Re) were synthesized from intimately ground mixtures of high purity (>99.9%) Y_2O_3 , SrCO_3 , CuO and the respective metal trioxides as starting materials, in stoichiometric ratios. The powdered mixtures were initially heated in platinum crucibles at 900 °C, in air. The product was reground, pressed into pellets and heated at 1050 °C for 24 h in air. During this second heating stage the pellets were reground two times and repelletized to facilitate reaction progress. Finally, the pellets were slowly cooled in the furnace.

The purity of the samples was checked by X-ray powder diffraction. These measurements were carried out

using an automated PW model 3710 Philips diffractometer, with graphite monochromated $\text{Cu } K_\alpha$ radiation. The indexing of the powder diagrams and the refinement of the cell constants were made by a least square procedure employing a locally modified version of the program PIRUM of Werner [8].

The infrared spectra were recorded with a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. The results were also confirmed with the Nujol-mull technique.

The X-ray powder diagrams of the three materials, which confirm the generation of single phased materials, resemble that of trivalent and tetravalent metal substituted 123-YSrCu materials studied in the previous paper [7] confirming the tetragonal pseudoperovskite structure, typical of $\text{YBa}_2\text{Cu}_3\text{O}_7$, space group P4/mmm . The lattice constants obtained from our refinements are in excellent agreement with those previously reported [6] as it can be seen from Table I.

Phases containing W(VI) and Re(VI) with the same substitutional degree show very similar cell constants. However, the c -parameter in the rhenium compound is smaller than in the tungsten compound, as it may be expected from the smaller cationic size of hexavalent rhenium. The unit cell of the molybdenum containing material presents the greater cell constants in agreement with a higher amount of substitution.

As stated above, the foreign cations are located on the Cu(1) sites, generating MO_6 units, with disruption of the chain arrangement. Therefore, we recognize in these materials the following metal-oxygen polyhedra: square planar CuO_4 units, square pyramidal CuO_5 units and MO_6 octahedral units.

The infrared spectra of the three materials are very similar to those previously reported for the structurally related systems [7]. As it can be seen from Fig. 1, the

TABLE I Unit cell parameters (in Å) of the investigated $\text{YSr}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7+\delta}$ materials^a

$\text{YSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7+\delta}$	$\text{YSr}_2\text{Cu}_{2.8}\text{W}_{0.2}\text{O}_{7+\delta}$	$\text{YSr}_2\text{Cu}_{2.8}\text{Re}_{0.2}\text{O}_{7+\delta}$
$a = 3.819$ (3.814)	$a = 3.808$ (3.804)	$a = 3.813$ (3.809)
$c = 11.558$ (11.526)	$c = 11.552$ (11.551)	$c = 11.540$ (11.510)

^aValues in parentheses correspond to literature data [6].

TABLE II Infrared spectra of the investigated materials (band position in cm^{-1})

$\text{YSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7+\delta}$	820 m	620 vs	575 sh		520 w	366 s	335 vs
$\text{YSr}_2\text{Cu}_{2.8}\text{W}_{0.2}\text{O}_{7+\delta}$		645 s	583 s	556 s	514 vs	367 s	339 vs
$\text{YSr}_2\text{Cu}_{2.8}\text{Re}_{0.2}\text{O}_{7+\delta}$		643 vs	580 s	558 s	532 w	371 vs	339 vs

vs: very strong; s: strong; w: weak; sh: shoulder.

spectral patterns of the tungsten and rhenium containing phases are almost identical presenting the characteristic two band structure centered at around 600 and 380 cm^{-1} , with splittings. In the case of the molybdenum containing material, an additional weak band at ca. 820 cm^{-1} is observed.

In these types of mixed oxides, with highly complicated structures, most of the vibrational modes are of complex origin, involving coupling of the different metal-oxygen polyhedra. Nevertheless, an approximate assignment of some of the IR bands can be attempted assuming that spectral frequencies should present an approximate correlation with the strengths of the different metal-oxygen bonds present in these materials. Taking into account that the foreign M(VI)-O units should present stronger bonds than the Cu-O polyhedra,

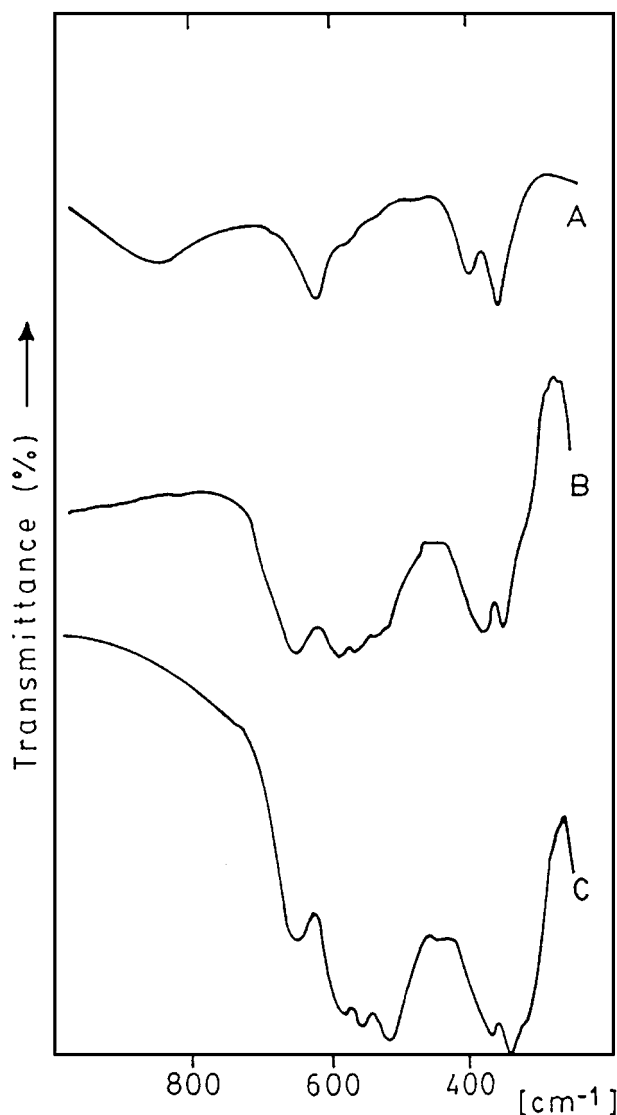


Figure 1 FTIR spectra of $\text{YSr}_2\text{Cu}_{2.7}\text{Mo}_{0.3}\text{O}_{7+\delta}$ (A), $\text{YSr}_2\text{Cu}_{2.8}\text{Re}_{0.2}\text{O}_{7+\delta}$ (B) and $\text{YSr}_2\text{Cu}_{2.8}\text{W}_{0.2}\text{O}_{7+\delta}$ (C).

it should be possible to distinguish some bands related to these M(VI)O_6 moieties.

To make this analysis, we used the site symmetry approximation [9, 10], correlating the O_h symmetry of the “free” MO_6 units with its site-symmetry (D_{2h}) in space group $P4/mmm$. This analysis shows that a total removal of degeneracies occurs for the two originally IR active modes, the antisymmetric stretching (ν_3) and deformation (ν_4) motions. Besides, the deformational mode ν_6 becomes IR-active.

On the other hand, a comparison with related systems allows to establish some typical absorption ranges for the other two building blocks (CuO_4 and CuO_5 units). In the so-called “green phases” of composition $\text{Ln}_2\text{BaCuO}_5$ main IR absorptions of the isolated CuO_5 pyramids are found at 600, 500 and 300 cm^{-1} [11, 12]. $\text{Nd}_2\text{BaCuO}_5$ and similar oxides containing isolated square planar CuO_4 moieties, present typical IR spectra consisting of a strong band at ca. 600 cm^{-1} and a doublet around 370 cm^{-1} [12, 13]. On the other hand, MO_6^{n-} -anions containing the three metals investigated in the present study, usually present their ν_3 bands between 600 and 650 cm^{-1} and the corresponding ν_4 vibrations between 350 and 450 cm^{-1} [9].

The measured band positions are presented in Table II and the above data allow an approximate assignment to be given, as follows:

- For the W and Re containing materials, the well defined and highest energy band, centered at around 640 cm^{-1} , as well as that located at 620 cm^{-1} in the case of the Mo compound must be related, essentially, to ν_3 -components of the MO_6 units, coupled to some extent with vibrations of the other two polyhedra.

- In the case of the molybdenum-substituted phase, the low intensity band at ca. 820 cm^{-1} is not easy to assign. However, its position suggests the presence of a rather short Mo-O bond in some of the MO_6 -polyhedra [14]. If such a short M-O bond is also present in the other materials, the other bands in the $650\text{--}500\text{ cm}^{-1}$ range apparently overlapped it.

- The band multiplet between 580 and 500 cm^{-1} may be related to the different stretching motions of the two types of CuO_n -polyhedra.

- The remaining bands, below 400 cm^{-1} , contain all the deformational modes of the different polyhedra.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones científicas y Técnicas de la República Argentina (CONICET), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires and the Secretaría de Ciencia y Técnica de la Universidad Nacional del Centro de la Provincia de Buenos Aires. E. J. B. is a member of the Research Career of CONICET.

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Received 22 October 1999
and accepted 1 February 2000