

# Spectroscopic behaviour of some superconducting materials containing tetraoxoanions

A. E. LAVAT, M. A. TREZZA

*Departamento de Ingeniería Química, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, 7400 Olavarría, Argentina*

E. J. BARAN\*

*Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina.*

*E-mail: baran@dalton.quimica.unlp.edu.ar*

A number of materials of composition  $YSr_2Cu_{2.8}(XO_4)_{0.2}O_y$  ( $X = S, P, V$ ) and others in which Y (III) was partially replaced by Sr(II) and/or Ca(II) were prepared by solid state reactions. Their unit cell parameters were determined and refined from X-ray powder data. The infrared spectra of the different tetraoxoanions incorporated in these materials were analyzed and discussed in detail. The vibrational modes of the other structural units present in these lattices were also approximately assigned in comparison with known spectral data of related materials. © 2001 Kluwer Academic Publishers

## 1. Introduction

Since the discovery of superconductivity in mixed metal oxides with perovskite-type structures, considerable efforts have been directed to the synthesis and characterization of new superconducting materials. One particularly interesting result of such work has been the observation that small oxo-anions, such as  $CO_3^{2-}$ ,  $BO_3^{3-}$ ,  $SO_4^{2-}$  or  $PO_4^{3-}$ , can partially substitute the small cations in materials with the perovskite structure, including superconducting cuprate phases [1–8].

On the other hand, it is also known that the ambient pressure synthesis of  $Sr_2Cu_3O_7$  [10] becomes possible, substituting copper in the “chain” sites by small foreign cations [11, 12].

In previous papers, we have investigated some aspects of the structural and spectroscopic behaviour of some of such substituted  $YSr_2Cu_3O_7$  phases [13, 14]. As an extension of these studies we have now investigated the spectroscopic characteristics of materials in which a part of the Cu(II) cations of  $YSr_2Cu_3O_7$  is replaced by  $SO_4^{2-}$  or  $PO_4^{3-}$ . It was also possible to prepare two new similar materials, incorporating  $VO_4^{3-}$  as the substituting anion.

As demonstrated by Slater *et al.* [7], the substitution of copper by sulfate and phosphate, generating materials of nominal composition  $YSr_2Cu_{3-x}(XO_4)_xO_{7-y}$ , is possible and single phased compounds with perovskite structure are obtained for  $0.2 < x < 0.32$ . These materials showed antiferromagnetic behaviour ( $T_N \approx 12$  K). However, similar samples containing Sr(II) or Ca(II) ions on the Y(III) sites became diamagnetic on cooling

exhibiting bulk superconductivity, with broad transitions and onset temperatures in the range 45–60 K.

## 2. Experimental

Polycrystalline samples of the investigated materials were prepared by conventional solid state reactions, firing intimate stoichiometric mixtures of yttrium (III) and copper(II) oxides with strontium (and eventually calcium) carbonate. Sulfate was incorporated from  $Y_2(SO_4)_2 \cdot 8H_2O$  and phosphate from  $(NH_4)_2HPO_4$ . The mixtures were heated in air during 24 hs at  $1065^\circ C$ , with numerous intermediate grindings to facilitate the reaction progress. The obtained powders were pressed into pellets and heated again during 12 hs. more at the same temperature, under oxygen. Finally, they were slowly cooled (ca. 20 hs.) up to room temperature, maintaining the oxygen flow.

The two new materials, incorporating  $VO_4^{3-}$  as the tetrahedral oxoanion, were prepared in a similar way, using  $(NH_4)VO_3$  as the vanadate source. They could also be obtained using nitrate precursors.

The purity of all the obtained materials was checked by X-ray diffractometry, using an automated PW model 3710 Philips diffractometer, with graphite monochromated  $Cu-K_\alpha$  radiation.

Unit cell parameters of the new reported materials containing vanadates, as well as that of the previously not indexed  $YSr_2Cu_{2.8}(SO_4)_{0.2}O_y$  phase, were obtained with the aid of a locally modified version of the program PIRUM of Werner [15].

\* Author to whom all correspondence should be addressed.

Infrared spectra were recorded on a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. Suspensions of the powdered samples in Nujol showed identical results.

### 3. Results and discussion

#### 3.1. Structural characteristics of the materials

The structure refinement of a material of nominal composition  $[Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.78}(SO_4)_{0.22}O_{6.12}$  from neutron diffraction data, using the Rietveld method, shows that it belongs to the orthorhombic space group Pmmm, with a complete occupancy of the Cu(1) “chain” sites of the ideal  $YBa_2Cu_3O_7$  structure by Cu and S [7]. The  $SO_4^{2-}$  groups present two long (1.54 Å) and two short (1.27 Å) oxygen bonds. The superconducting layers contain square planar  $CuO_4$ – and square pyramidal  $CuO_5$ – units.

As the X-ray powder diagrams of all the prepared materials were similar to that of  $[Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.78}(SO_4)_{0.22}O_{6.12}$  one can infer that all of them present similar structural characteristics. Table I shows the composition of the prepared materials together with the calculated unit cell dimensions. As the a and b parameters of these orthorhombic cells are nearly identical and the powder diagrams of the orthorhombic materials are very similar to those of the tetragonal ones [8], it is not easy to differentiate between both possibilities.

Notwithstanding, the powder diagrams for the materials of composition  $YSr_2Cu_{2.8}(XO_4)_{0.2}O_y$  ( $X = S, V$ ) could be indexed on the basis of an orthorhombic unit cell, as was also the previously investigated phase with  $X = P$  [8]. On the other hand, and as shown earlier [8], tetragonalization apparently occurs when part of the Y(III) is substituted for Sr(II) and/or Ca(II).

Whereas the sulfate containing materials present the smallest unit cells, only the incorporation of  $VO_4^{3-}$  anions generates an important increment in the c-parameter of the respective lattices, in comparison with the other two types of compounds investigated.

#### 3.2. Infrared spectra

This spectroscopic technique is very useful to determine the structural characteristics of the tetraoxoanions and to attain a wider insight into the vibrational behaviour of the other structural units present in these lattices.

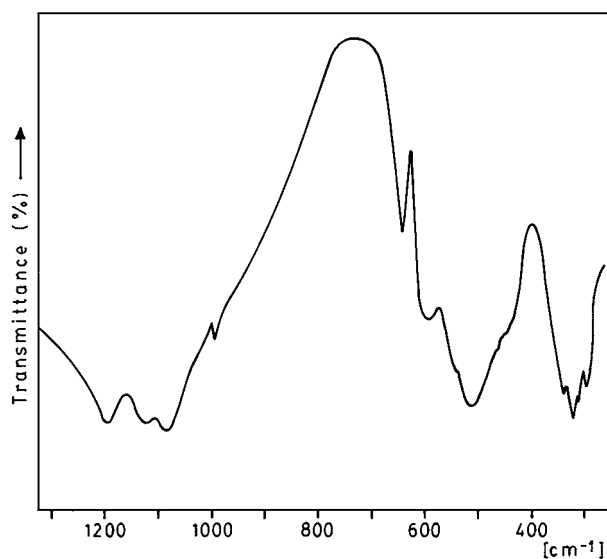


Figure 1 Infrared spectrum of  $Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.8}(SO_4)_{0.2}O_y$ .

As commented above, in the case of  $[Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.78}(SO_4)_{0.22}O_{6.12}$  the  $SO_4^{3-}$  groups show two types of S–O bonds [7], i.e., they present local  $C_{2v}$  symmetry. The “free” tetrahedral tetraoxoanions present one symmetric ( $\nu_1, A_1$ ) and one antisymmetric ( $\nu_3, F_2$ ) stretching modes as well as one symmetric ( $\nu_2, E$ ) and one antisymmetric ( $\nu_4, F_2$ ) bending modes, from which only the two triple degenerated  $\nu_3$  and  $\nu_4$  modes are IR-active vibrations [16, 17]. In the crystal lattice, and under  $C_{2v}$  symmetry, a total activation and removal of degeneracies of all the fundamental vibrations of the tetrahedral  $XO_4^{n-}$  groups is expected [16, 17].

As it can be seen from Fig. 1, the stretching vibrations of the  $SO_4^{2-}$  groups, located in the spectral region above  $900\text{ cm}^{-1}$ , clearly fulfill these expectations, as the four predicted vibrations could be clearly identified. The assignment of the bending modes is not so straightforward. They are expected to lie around  $450$  ( $\nu_2$ ) and  $600$  ( $\nu_4$ )  $\text{cm}^{-1}$  [16] and they are surely partially overlapped with vibrations related to the  $CuO_n$ –polyhedra, lying in the same region, as discussed below. Interestingly, also the materials containing  $PO_4^{3-}$  and  $VO_4^{3-}$  groups show a similar behaviour in the stretching region, pointing to similar structural characteristics for them.

The IR spectra of the three materials of composition  $YSr_2Cu_{2.8}(XO_4)_{0.2}O_y$  are compared in Fig. 2. The assignment of the vibrations of the tetraoxoanions of all the materials is presented in Table II. The stretching vibrations of the sulfate and phosphate groups are

TABLE I Unit cell parameters of the investigated materials

Composition	a[Å]	b[Å]	c[Å]	Ref.
$YSr_2Cu_{2.8}(SO_4)_{0.2}O_y$	3.811(4)	3.862(2)	11.335(3)	this paper
$[Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.8}(SO_4)_{0.2}O_y$	3.8254	3.8436	11.2572	[7]
$YSr_2Cu_{2.8}(PO_4)_{0.2}O_y$	3.824	3.843	11.35	[8]
$[Y_{0.7}Ca_{0.3}]Sr_2Cu_{2.8}(PO_4)_{0.2}O_y$	3.824		11.360	[8]
$YSr_2Cu_{2.8}(VO_4)_{0.2}O_y$	3.817(3)	3.843(8)	11.507(5)	this paper
$[Y_{0.74}Sr_{0.1}Ca_{0.16}]Sr_2Cu_{2.8}(VO_4)_{0.2}O_y$	3.816(1)		11.494(2)	this paper

TABLE II Assignment of the IR spectra of the  $\text{XO}_4^{n-}$  groups present in the investigated materials (band positions in  $\text{cm}^{-1}$ )

Material	$\nu_3$	$\nu_1$	$\nu_4$ (*)
$\text{YSr}_2\text{Cu}_{2.8}(\text{SO}_4)_{0.2}\text{O}_y$	1187 s, 1116 s, 1083 s	992 w	643 s
$[\text{Y}_{0.74}\text{Sr}_{0.1}\text{Ca}_{0.16}]\text{Sr}_2\text{Cu}_{2.8}(\text{SO}_4)_{0.2}\text{O}_y$	1193 s, 1123 s, 1084 s	993 w	644 s
$\text{YSr}_2\text{Cu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_y$	1072 s, 1031 vs, 1010 sh	947 w	654 s
$[\text{Y}_{0.7}\text{Ca}_{0.3}]\text{Sr}_2\text{Cu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_y$	1073 s, 1031 vs, 1018 sh	947 w	654 s
$\text{YSr}_2\text{Cu}_{2.8}(\text{VO}_4)_{0.2}\text{O}_y$	868 s, 815 sh, 806 vs	840 w	—
$[\text{Y}_{0.74}\text{Sr}_{0.1}\text{Ca}_{0.16}]\text{Sr}_2\text{Cu}_{2.8}(\text{VO}_4)_{0.2}\text{O}_y$	869 s, 812 sh, 806 vs	840 w	—

\*partially overlapped with  $\text{CuO}_n$  -vibrations.

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

TABLE III Band positions in the spectral range between 600 and  $250\text{ cm}^{-1}$

Material								
$\text{YSr}_2\text{Cu}_{2.8}(\text{SO}_4)_{0.2}\text{O}_y$	595 m	557 sh	503 s	445 sh	395 sh	334 s	310 sh	276 w
$[\text{Y}_{0.74}\text{Sr}_{0.1}\text{Ca}_{0.16}]\text{Sr}_2\text{Cu}_{2.8}(\text{SO}_4)_{0.2}\text{O}_y$	583 m	543 sh	513 vs	440 sh	338 sh	320 s	311 sh	297 w
$\text{YSr}_2\text{Cu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_y$	592 s	561 s	506 vs	442 w	360 sh	346 vs	301 sh	
$[\text{Y}_{0.7}\text{Ca}_{0.3}]\text{Sr}_2\text{Cu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_y$	591 s	560 sh	518 vs	450 w	345 w	332 vs	316 sh	
$\text{YSr}_2\text{Cu}_{2.8}(\text{VO}_4)_{0.2}\text{O}_y$	633 m	543 vs	492 sh	400 m	335 sh	321 vs		298 m
$[\text{Y}_{0.74}\text{Sr}_{0.1}\text{Ca}_{0.16}]\text{Sr}_2\text{Cu}_{2.8}(\text{VO}_4)_{0.2}\text{O}_y$	587 m	529 vs		440 sh	360 w	319 vs		299 w

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

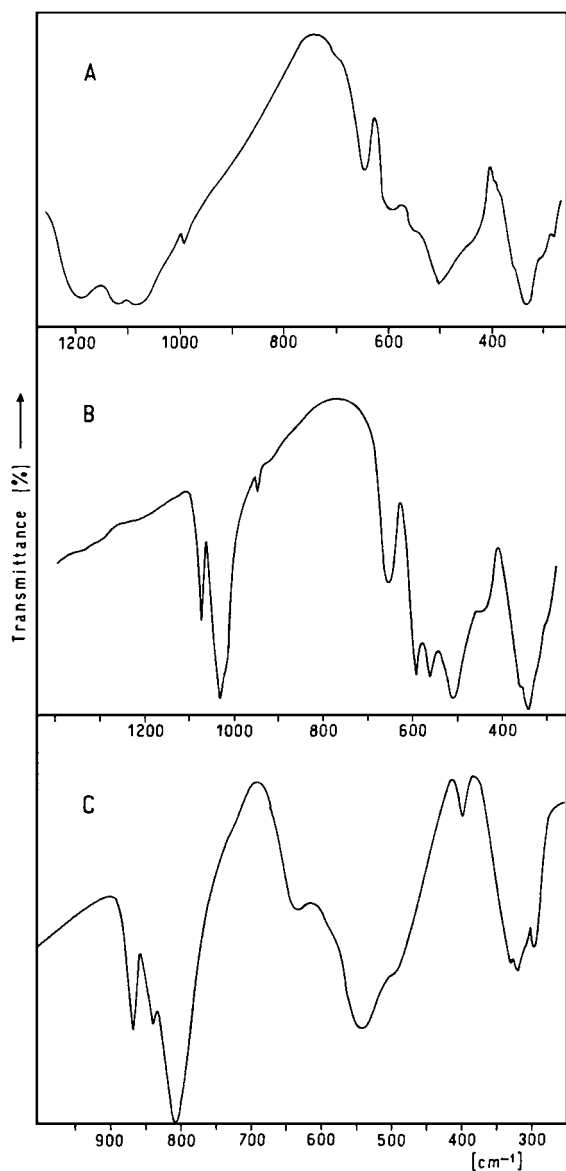


Figure 2 Infrared spectra of  $\text{YSr}_2\text{Cu}_{2.8}(\text{SO}_4)_{0.2}\text{O}_y$  [A];  $\text{YSr}_2\text{Cu}_{2.8}(\text{PO}_4)_{0.2}\text{O}_y$  [B] and  $\text{YSr}_2\text{Cu}_{2.8}(\text{VO}_4)_{0.2}\text{O}_y$  [C].

clearly displaced to higher wavenumbers, in comparison with “free” anion values [16]. In the case of the vanadate groups this effect is not so important and also the splitting of the  $\nu_3$  mode is not so clear to visualize as in the other two cases. On the other hand, the antisymmetric bending mode,  $\nu_4$ , is practically unobservable, as it clearly lies at lower frequencies in comparison with its position in the other two tetraoxoanions [16, 18]. But, interestingly, in this case the symmetric stretching mode,  $\nu_1$ , appears intercalated between two of the  $\nu_3$  components. This behaviour has often been observed in numerous pure crystalline vanadates [17, 19–21].

Finally, comparisons with some other related systems allow to establish some typical vibrational ranges for the  $\text{CuO}_4$  and  $\text{CuO}_5$  units present in the investigated lattices. In the so called “green phases” of composition  $\text{Ln}_2\text{BaCuO}_5$  main IR absorptions of the  $\text{CuO}_5$  pyramids are found at 600, 500 and  $300\text{ cm}^{-1}$  [22, 23].  $\text{Nd}_2\text{BaCuO}_5$  and similar oxides containing isolated square planar  $\text{CuO}_4$  moieties, present characteristic IR patterns consisting of a strong band at about  $600\text{ cm}^{-1}$  and a doublet at ca.  $370\text{ cm}^{-1}$  [23, 24].

A comparison of the spectral patterns shown in Fig. 2, in the IR region below  $600\text{ cm}^{-1}$ , with those of the related materials of composition  $\text{YSr}_2\text{Cu}_{3-x}\text{M}_x\text{O}_y$  [13] shows a very similar arrangement. Although a detailed assignment is impossible, due to the strong coupling effects expected in this region, it is evident that the first block of bands, between 600 and  $400\text{ cm}^{-1}$  may be related essentially to stretching modes of the  $\text{CuO}_4$  units with minor contributions of the  $\text{CuO}_5$  moieties. The remaining vibrations of these last groups, together with the different kinds of expected deformational modes, should be located at lower energies. Band positions in the mentioned regions are presented in Table III, and as it can be seen, all the band blocks are located in relatively narrow and comparable energy ranges, suggesting a similar origin for all of them in the different investigated materials.

## Acknowledgements

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas de las República Argentina (CONICET) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires. E. J. B. is a member of the Research Career from CONICET.

## References

1. K. KINOSHITA and T. YAMADA, *Nature* **357** (1992) 313.
2. C. GREAVES and P. R. SLATER, *J. Mater. Chem.* **1** (1991) 17.
3. *Idem.*, *Physica C* **175** (1991) 172.
4. A. R. ARMSTRONG and P. P. EDWARDS, *J. Solid State Chem* **98** (1992) 432.
5. B. DOMENGES, M. HERVIEU and B. RAVEAU, *Physica C* **207** (1993) 65.
6. A. MAIGNAN, M. HERVIEU, C. MICHEL and B. RAVEAU, *ibid.* **208** (1993) 16.
7. P. R. SLATER, C. GREAVES, M. SLASKI and C. M. MUIRHEARD, *ibid.* **208** (1993) 193.
8. R. NAGARAJAN, S. AYYAPPAN and C. N. R. RAO, *ibid.* **220** (1994) 373.
9. P. R. SLATER and C. GREAVES, *ibid.* **223** (1994) 37.
10. B. OKAI, *Jpn. J. Appl. Phys.* **29** (1990) L2180.
11. P. R. SLATER and C. GREAVES, *Physica C* **180** (1991) 299.
12. R. L. HARLOW, G. H. KWEI, R. SURYANARAYANAN, M. A. SUBRAMANIAN, *ibid.* **257** (1996) 125.
13. A. E. LAVAT, M. C. GRASSELLI and E. J. BARAN, *Mater. Chem. Phys.* **57** (1998) 152.
14. A. E. LAVAT and E. J. BARAN, *J. Mater. Sci. Lett.* **19** (2000) 1331.
15. P. E. WERNER, *Ark. Kemi* **31** (1969) 513.
16. S. D. ROSS, "Inorganic Infrared and Raman Spectra" (McGraw Hill, London, 1972).
17. A. MÜLLER, E. J. BARAN and R. O. CARTER, *Struct. Bonding* **26** (1976) 81.
18. A. MÜLLER, E. J. BARAN and P. J. HENDRA, *Spectrochim. Acta* **25A** (1969) 1654.
19. E. J. BARAN and P. J. AYMÓNINO, *Z. Naturforsch.* **27b** (1972) 76.
20. *Idem.*, *Z. Anorg. Allg. Chem.* **390** (1972) 77.
21. E. J. BARAN, *ibid.* **427** (1976) 131.
22. E. J. BARAN, G. P. CICLEO, G. PUNTE, A. E. LAVAT and M. TREZZA, *J. Mater. Sci. Lett.* **7** (1988) 1010.
23. A. E. LAVAT, E. J. BARAN, R. SAEZ-PUCHE, A. SALINAS-SANCHEZ and M. J. MARTÍN-LLORENTE, *Vibrat. Spectr.* **3** (1992) 291.
24. E. J. BARAN, A. E. LAVAT, R. SAEZ-PUCHE and A. SALINAS-SANCHEZ, *J. Mater. Sci. Lett.* **11** (1992) 1087.

Received 14 March 2000  
and accepted 12 February 2001