IR-spectroscopic characterization of some impurity phases generated during the synthesis of $YBa_2Cu_3O_{7-\delta}$-type superconductors

E. J. BARAN, G. P. CICILEO
Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calles 47 y 115, 1900-La Plata, Argentina

The high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ is one of the stable phases in the ternary system $Y_2O_3/BaO/CuO$. This system has all the classical complexities of ternary oxide systems and a number of binary and ternary phases have been characterized in it [1-3].

We have previously reported the vibrational [4] and electronic [5] spectra of the so called "green phases" of composition Ln_2BaCuO_5, one of the stable phases in this ternary system and one of the main impurity phases generated during the synthesis of $YBa_2Cu_3O_{7-\delta}$ and related superconducting materials [6]. As a continuation of these studies, and in order to obtain a wider insight into the general properties of all the materials which can be generated as impurity phases during the synthesis of these superconducting oxides, we have now investigated the infrared spectra of some other phases which exist in the above mentioned ternary oxide system. Raman spectra of some of these phases have been previously reported [7, 8] but without any band assignment.

The following materials were prepared: $BaCuO_2$, BaY_2O_4 and $M_2^{III}Cu_2O_5$ (with M^{III} = Y, Dy, Er, Ho, Lu, In), using conventional solid state reactions.

$BaCuO_2$ was obtained by firing an equimolecular mixture of CuO and $BaCO_3$ at 800° C for 48 h [9]. BaY_2O_4 was prepared by reaction of BaO_2 with Y_2O_3 at 950° C for 12 h [10]. The $M_2^{III}Cu_2O_5$-phases were obtained from stoichiometric mixtures of CuO and M_2O_3 oxides, heated at between 950 and 980° C for 45 to 50 h.

All materials were characterized by X-ray powder diffraction. Despite the fact that it was usually accepted that $In_2Cu_2O_5$ is isotypic with $Dy_2Cu_2O_5$ and $Er_2Cu_2O_5$ but different from $Lu_2Cu_2O_5$, $Ho_2Cu_2O_5$ and $Y_2Cu_2O_5$ (cf. for example [11]), our powder patterns, which are very similar for all these phases, suggest similar or, at least, very closely related structures (cf. also [12]).

The IR spectra were recorded with a Perkin Elmer 580B spectrophotometer using the KBr pellet technique or measuring the finely powdered materials as suspensions in Nujol between CsI plates.

The crystal structure of $BaCuO_2$ belongs to the cubic system, space group O_h^9 and $Z = 92$, and is characterized by a very complicated framework structure [13]. The Cu(II) ions are in square planar oxygen environments and six of such units are bonded together by double edge sharing generating unusual six-membered rings of composition $[Cu_6O_{12}]^{12-}$.

Despite this complex arrangement, the material exhibits a very simple IR spectrum, which is shown in Fig. 1. All the observed bands can surely be related to Cu–O vibrations. The well structured band centred at $525 cm^{-1}$ and the medium intensity component at $455 cm^{-1}$ can be probably correlated with the $\nu_6(E_u)$ antisymmetric stretching of a simple square CuO_4-vibrator [14]; therefore the shoulder at $585 cm^{-1}$ can be assigned to the corresponding symmetric stretching mode $\nu_1(A_{1g})$, in agreement with the position of a strong Raman line located in the same region [7]. The remaining band, at $320 cm^{-1}$, must be, essentially, a deformation mode of the CuO_4-groups, probably coupled with Ba–O modes.

In the case of the $M_2^{III}Cu_2O_5$ phases, and accepting that all these materials belong to the same structural types, i.e., that of $Ho_2Cu_2O_5$ [11], the orthorhombic space group C_{2v}^9 with $Z = 4$ can be assumed.

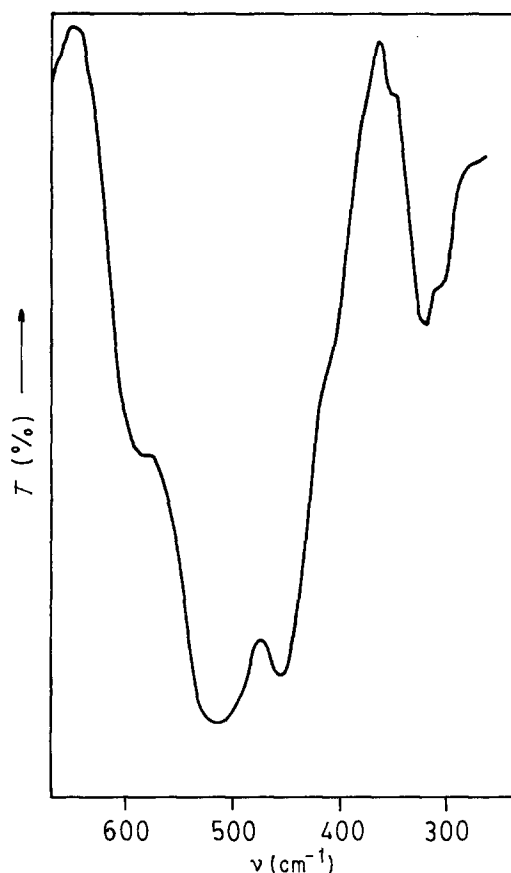In these phases the Cu(II) ions are also in strongly distorted square-planar oxygen coordination. These

Figure 1 IR spectrum of $BaCuO_2$.

TABLE I Infrared spectra of the investigated $M_2^{III}Cu_2O_5$-phases (values in cm^{-1})

$Y_2Cu_2O_5$	$Dy_2Cu_2O_5$	$Ho_2Cu_2O_5$	$Er_2Cu_2O_5$	$Lu_2Cu_2O_5$	$In_2Cu_2O_5$
630 w	635 w	635 w	630 w	640 w	632 w
565 s	570 s	570 s	565 s	580 s	575 s
535 w	535 w	530 w	∼530 sh	540 w	545 w
490 s	495 s	500 s	500 s	505 s	500 s
450 s	450 s	450 s	450 s	460 s	∼470 w, sh
415 s	412 s	410 s	405 s	420 m	425 m
360 sh	∼370 sh	∼365 sh	∼365 sh	∼380 sh	–
340 s	340 m	340 w	∼335 w	350 s	370 s
310 w	305 w	∼300 sh	–	∼320 w	345 w
220 s	220 s	220 s	220 s	–	235 m

s: strong; m: medium; w: weak; sh: shoulder

square units generate double Cu_2O_6-polyhedra by sharing one edge, and the double units share also one terminal oxygen with similar units, forming deformed Cu_2O_5-chains which run parallel along the a-axis of the unit cell [11, 12].

As an example of the IR spectra of this series, Fig. 2 shows that of $Y_2Cu_2O_5$. The measured frequencies for all the prepared materials of this type are presented in Table I. The strong similarities between all these spectra reinforce our supposition of a common structural type for all of these compounds. Our spectra also show strong similarities to those recently reported for $Y_2Cu_2O_5$ and $Ho_2Cu_2O_5$, using reflectivity measurements [8].

All the bands located above $400\,cm^{-1}$ can be related to Cu–O modes and an approximate assignment of some of them can be proposed based on the vibrational modes of a "free" square unit [14] and taking advantage from Raman data available for the yttrium and holmium compounds [8].

The strong and broad IR band at $565\,cm^{-1}$ can be related to the antisymmetric stretching mode $v_6(E_u)$ of these square units; the Raman counterpart would be the medium-intensity doublet located at $593/568\,cm^{-1}$. The strong Raman line at $520\,cm^{-1}$ and the
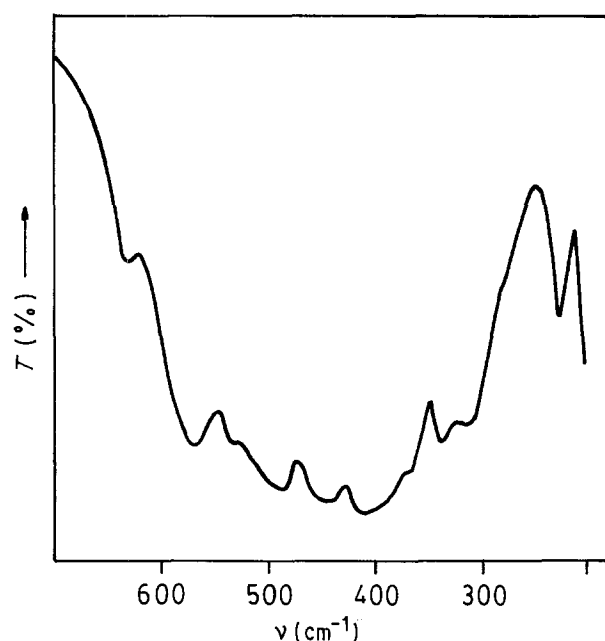
weak IR band at $535\,cm^{-1}$ could be the corresponding symmetric stretching $(v_1(A_{1g}))$. The other strong IR band at $490\,cm^{-1}$ must be probably a bridge vibration coupled with the other stretching mode of the square, $v_4(B_{2g})$. Bands at 450 and $415\,cm^{-1}$ are surely deformation vibrations of the CuO-polyhedra.

In a series of lanthanide compounds it is usually possible to observe an increase in the vibrational frequencies as the volume of the unit cell decreases ($cf.$ for example [4, 15, 16]). In the present case, it was not possible to establish with certainty such a behaviour, in part, due to the fact that most of the observed bands are broad and not well defined. But, it is also possible that such effects would be more evident in the case of compounds with more isolated oxoanions.

BaY_2O_4 is orthorhombic, space group D_{2h}^{16} and $Z = 4$ [10] and is structurally related to SrY_2O_4 [17] and $CaFe_2O_4$ [18]. In this structure, the trivalent cations are located in octahedral voids whereas the divalent ions are surrounded by nine oxygen atoms in a very distorted trigonal-prismatic environment.

The IR spectrum of this material is poorly defined, showing only a broad band between 650 and $250\,cm^{-1}$ with some weak peaks at 390, 345 and $310\,cm^{-1}$. Therefore, it was practically impossible to attempt an analysis of this spectrum.

To conclude, this study allowed the IR-spectroscopic characterization of a number of interesting oxide-materials, which appear in ternary oxide systems along with the ceramic high T_c-superconductors of the type $LnBa_2Cu_3O_{7-\delta}$. The results could also be approximately interpreted on the basis of the structural characteristics of these phases and point to close structural similarities between all the investigated systems of the type $M_2^{III}Cu_2O_5$.

Acknowledgement

Figure 2 IR spectrum of $Y_2Cu_2O_5$.

References

1. H. STEINFINK, J. S. SWINNEA, Z. T. SUI, S. M. HSU and J. B. GOODENOUGH, $J.$ $Amer.$ $Chem.$ $Soc.$ 109 (1987) 3348.
2. K. G. FRASE and D. R. CLARKE, $Advanced$ $Ceramic$ $Materials,$ Spec. Issue 2 (1987) 295.
3. G. F. HOLLAND and A. M. STACY, $Acc.$ $Chem.$ $Res.$ 21 (1988) 8.
4. E. J. BARAN, G. P. CICILEO, G. PUNTE, A. E.

LAVAT and M. TREZZA, *J. Mater. Sci. Lett.* **7** (1988) 1010.

5. E. J. BARAN and G. P. CICILEO, *J. Mater. Sci. Lett.* **9** (1990) 1.

6. R. M. HAZEN, L. W. FINGER, R. J. ANGEL, C. T. PREWITT, N. L. ROSS, H. K. MAO and C. G. HADIDIAKOS, *Phys Rev.* **B35** (1987) 7238.

7. H. ROSEN, E. M. ENGLER, T. C. STRAND, V. Y. LEE and D. BETHUNE, *Phys. Rev.* **B36** (1987) 726.

8. Z. V. POPOVIC, C. THOMSEN, M. CARDONA, R. LIU, G. STANISI and W. KÖNNIG, *Z. Phys.* **B72** (1988) 13.

9. M ARJOMAND and D. J. MACHIN, *J. Chem. Soc. Dalton Trans.* (1975) 1061.

10. G. A. COSTA, M. FERRETI, M. L. FORNASINI, E. A. FRANCESCHI and G. L. OLCESE, to be published.

11. H. R. FREUND and Hk. MÜLLER-BUSCHBAUM, *Z. Naturforsch.* **32b** (1977) 609.

12. F. ROMERY and F. QUEYROUX, *Mater. Res. Bull.* **24** (1989) 275.

13. R. KIPKA and Hk. MÜLLER-BUSCHBAUM, *Z. Naturforsch.* **32b** (1977) 121.

14. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd edit. (Wiley, New York, 1978).

15. E. J. BARAN, M. E. ESCOBAR, L. L. FOURNIER and R. R. FILGUEIRA, *Z. Anorg. Allg. Chem.* **472** (1981) 193.

16. A. E. LAVAT, M. TREZZA, I. L. BOTTO, D. I RONCAGLIA and E. J. BARAN, *Spectr. Lett.* **21** (1988) 355.

17. Hk. MÜLLER-BUSCHBAUM, *Z. Anorg. Allg. Chem.* **358** (1968) 138.

18. Hk. MÜLLER-BUSCHBAUM and H. G. V. SCHNERING, *Z. Anorg. Allg. Chem.* **336** (1965) 295.