# Synthesis and Characterization of New Mixed Oxides of the Type $Ln_2Ba_2CuPtO_8$ ($Ln$ = Ho–Lu)

Marta B. Vassallo and Enrique J. Baran[1]

*Química Inorgánica (QUINOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina*

Polycrystalline samples of mixed oxides of the type $Ln_2Ba_2CuPtO_8$ (with $Ln$ = Ho–Lu) have been obtained by solid state reactions of platinum metal powder with appropriate $Ln_2O_3$/CuO/BaCO$_3$ mixtures. They are isostructural with the previously known $Y_2Ba_2CuPtO_8$ phase. Crystallographic data for the new oxides were obtained from X-ray powder measurements. Their IR spectra were also recorded and briefly discussed. © 1995 Academic Press, Inc.

## INTRODUCTION

It is well known that, if the synthesis of YBaCuO-type superconductors is carried out in platinum crucibles, by reaction of the pertinent oxide mixtures at high temperatures, some impurities may be generated at the crucible walls as a consequence of the basic attack of the crucible material. These impurities have been identified as platinum containing mixed oxides.

Two of the most common stoichiometries so far reported for these new systems are $Y_2Ba_2CuPtO_8$ and $Ln_2Ba_3Cu_2PtO_{10}$. The structure of $Y_2Ba_2CuPtO_8$ has been solved by different groups (1–2) and for the second type of materials, phases containing Y (3, 4), Ho (4), and Er (5) as the rare earth have been reported and structurally characterized. On the other hand, a structurally related phase of stoichiometry $Y_2(Ba,Sr)_2SrCu_2PtO_{10}$ has also been prepared (6).

Since it seemed interesting to verify if other rare earth cations apart from yttrium could be incorporated in the $Y_2Ba_2CuPtO_8$ lattice, we have investigated the behavior of the smaller lanthanide cations and found that actually five other cations, namely Ho(III), Er(III), Tm(III), Yb(III), and Lu(III), generate similar phases which retain the structural type of the Y(III) compound. Besides, the greater Dy(III) cation does not generate a material of this type.

[1] To whom correspondence should be addressed.

## EXPERIMENTAL

We have developed a new synthesis procedure to obtain large quantities of polycrystalline samples of the materials. It consists of the direct reaction of platinum powder (Aldrich, 99.99%) with an adequate mixture of the pertinent metallic oxides and working in alumina crucibles.

Stoichiometric mixtures of BaCO$_3$, CuO, Pt, and the respective rare earth oxide, $Ln_2O_3$, were mixed and homogenized. Then, they were heated in alumina crucibles in air for ca. 10 days, with frequent intermediate grinding of the reaction mixtures, at temperatures between 1000 and 1100°C. The reactions were followed by X-ray powder diffractometry until the characteristic pattern of $Y_2Ba_2CuPtO_8$ was obtained.

Usually, as shall be discussed below, some small reflections assignable to minor quantities of different by-products were also identified. The difficulty in achieving single phase products, in spite of very long reaction times, arises from inhomogenities produced by partial melting during the firing, as well as from the low reactivity of nonattacked platinum metal powder.

The powder diffractograms were obtained by means of a Philips-PW-1710 diffractometer with CuK$\alpha$ radiation. Diffraction data were collected by step scanning over an angular range of $5° < 2\theta < 70°$ in increments of 0.02° and a counting time of 2 sec for each step. Unit cell parameters were obtained using the program TREOR (7) and refined with a locally modified version of the program PIRUM (8).

The infrared spectra of the materials were recorded with a Bruker FTIR model 113v instrument, with the powdered samples dispersed in KBr discs.

## RESULTS AND DISCUSSION

### Crystallographic Data

$Y_2Ba_2CuPtO_8$ presents a very complex condensed structure (1, 2). It crystallizes in the orthorhombic space group *Pnma* with $Z$ = 4. The coordination of Cu(II) is square pyramidal and that of Pt(IV) is octahedral. The CuO$_5$ pyramids and the PtO$_6$ octahedra are joined by edge shar-
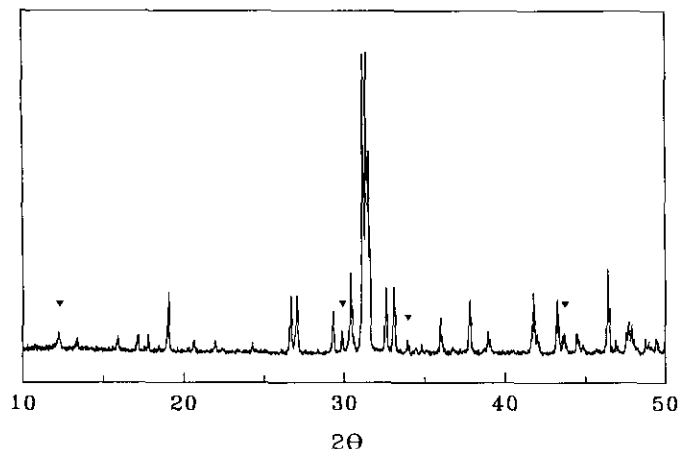
FIG. 1. X-ray diffraction powder pattern of $Er_2Ba_2CuPtO_8$ (▼ identifies $Er_2BaO_4$ reflections).

### TABLE 1
#### Crystallographic Data for the $Ln_2Ba_2CuPtO_8$ Oxides

| $Ln(III)$ | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $r$ (Å)$^a$ |
|---|---|---|---|---|---|
| Lu | 13.106(4) | 5.628(2) | 10.246(2) | 755.7(4) | 1.001 |
| Yb | 13.110(4) | 5.633(2) | 10.245(2) | 756.5(4) | 1.008 |
| Tm | 13.153(4) | 5.655(2) | 10.278(2) | 764.4(4) | 1.020 |
| Er | 13.180(3) | 5.671(1) | 10.304(2) | 770.1(2) | 1.030 |
| Y | 13.195(3) | 5.678(1) | 10.310(2) | 772.4(2) | 1.040 |
| Ho | 13.204(3) | 5.681(1) | 10.320(2) | 774.1(2) | 1.041 |

$^a$ Ionic radii from R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976) and for CN = 6.

ing to form a zigzag chain parallel to [010]. Two such chains are connected through common oxygen atoms and generate a $CuPt_8O$ column. The Ba(II) and Y(III) ions are located within the column.

The new five prepared oxides of the same stoichiometry, containing the heavier lanthanides (Ho–Lu) instead of Y, present powder patterns which closely resembled that of $Y_2Ba_2CuPtO_8$. As a typical example of the obtained diagrams, Fig. 1 shows that corresponding to $Er_2Ba_2CuPtO_8$. In this figure we have also marked the reflections arising from $Er_2BaO_4$, the main impurity present in this phase.

All the diagrams could be indexed in the same way, confirming the generation of an isostructural series of mixed oxides of the same type and stoichiometry in this range of rare-earth sizes (1.041 to 1.001 Å). Attempts to prepare a similar phase with the slightly greater Dy(III) ion ($r = 1.050$ Å) failed, pointing to a limitation in the size of the rare-earth cation for the formation of this structural type. These cations occupy two different crystallographic sites in the structure (1, 2). They are coordinated by seven oxygen atoms, six of which form a trigonal-prismatic arrangement whereas the remaining one is located over one of the prismatic faces. Apparently, the generated holes can only be occupied by cations with ionic radii equal to or smaller than 1.041 Å.

The careful comparison of the obtained powder patterns shows the presence of some weak reflections, originated from secondary impurity phases, which were discarded in the subsequent indexing and refining cycles. Interestingly, some of the generated impurities could be identified from these additional reflections. The main impurity was identified as $Lu_2Ba_4O_7$ for the Lu(III) compound and as $Tm_4Ba_3O_9$ for the Tm(III) phase, as suggested by the respective ICDD files. For the materials containing Y(III), Yb(III), and Er(III) traces of the $Ln_2BaO_4$ oxides (9–11)

could be confirmed. In the case of $Ho_2Ba_2CuPtO_8$, the impurities could not be identified with certainty.

The crystallographic data, refined from our powder diagrams, are presented in Table 1.

In order to test the consistence and quality of these data we have plotted the unit cell volume against $r^3$ (cf. for example (12, 13)). As it is shown in Fig. 2 a good linear relation is obtained.

### Infrared Spectra

In order to characterize further the new series of mixed oxides, we have also recorded and analyzed their infrared spectra. These spectra present, essentially, two broad and not well-defined bands, located between 700–520 and 450–300 cm$^{-1}$, respectively.
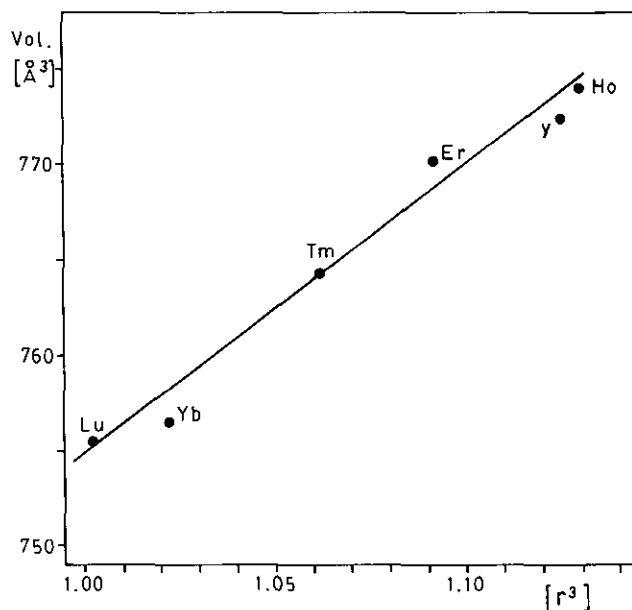


FIG. 2. Plot of the crystallographic cell volume of the $Ln_2Ba_2CuPtO_8$ oxides against $r^3$ of the $Ln(III)$ cations.
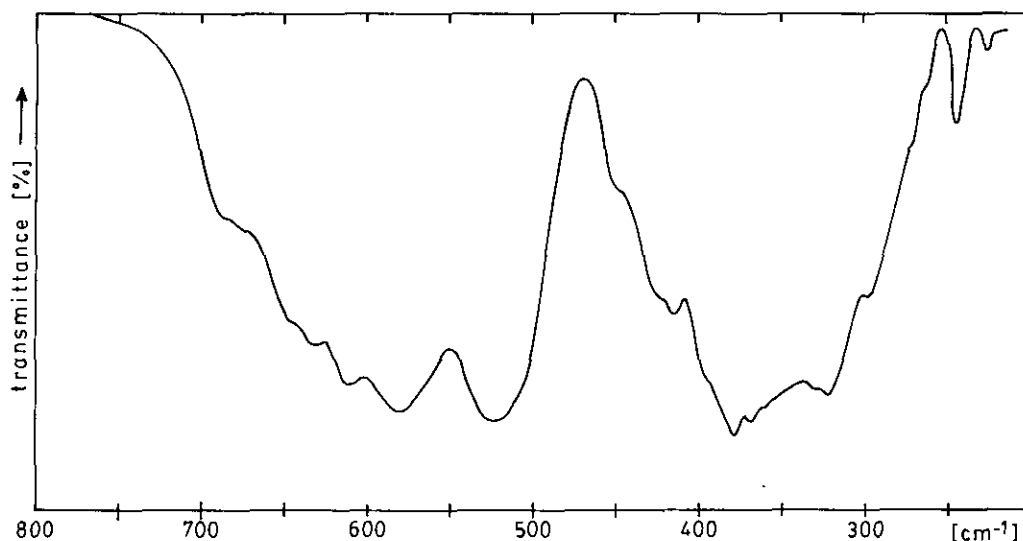
FIG. 3. FT-Infrared spectrum of $Er_2Ba_2CuPtO_8$.

As a typical example of the obtained spectra, Fig. 3 shows that corresponding to $Er_2Ba_2CuPtO_8$. The exact band positions of the spectra of the six oxides are shown in Table 2.

Although it is not possible to attempt even an approximate assignment of these complex spectra, some of its features merit further comments.

TABLE 2
Infrared Spectra of the $Ln_2Ba_2CuPtO_8$ Oxides
(Band Positions in $cm^{-1}$)

| Lu | Yb | Tm | Er | Y | Ho |
|---|---|---|---|---|---|
| 688 m | 686 m | 686 m | 686 sh | 686 sh | 684 sh |
| | | | 674 w | 675 w | 667 w |
| 656 sh | 654 m | 651 sh | 646 sh | 642 sh | 638 sh |
| 636 sh | 636 sh | 636 w | 631 w | 628 w | 627 w |
| 615 m | 611 m | 613 m | 611 m | 611 m | 609 m |
| 586 s | 584 s | 582 s | 580 s | 579 s | 579 s |
| 538 vs | 538 vs | 526 vs | 523 vs | 525 vs | 519 vs |
| 451 sh | 451 m | 449 w | 445 w | 455 w | 445 m |
| 432 w | 426 w | 426 w | 422 sh | 420 w | 425 sh |
| | | | 415 m | | 415 m |
| 399 w | 391 w | 389 sh | | 393 sh | 395 sh |
| 386 m | 380 m | 376/330 s, br | 368 w | 366 w | 368 m |
| 361 m | 361 sh | | | | 347 w |
| 332 w | 334 w | | 330 sh | 326 m | 324 m |
| 324 w | | 318 w | 322 m | | |
| 310 w | | 306 sh | | | |
| 290 m | 299 m | 285 sh | 269 sh | 270 s | 269 sh/255 w |
| | 255 w | | 264 sh | | 255 w |
| 247 m | 247 m | 245 m | 243 s | | 243 m |
| 223 w | 222 m | 221 w | 226 m | 228 s | 225 m |

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

A comparison with the spectra of the so-called "green phases" of composition $Ln_2BaCuO_5$ (14, 15) which also contains square-pyramidal $CuO_5$-units, shows some similarities in the spectral patterns of these materials and the higher frequency region of the now investigated oxides. Nevertheless, a clear displacement to higher frequencies is observed for the $Ln_2Ba_2CuPtO_8$ materials, in agreement with their more condensed nature. This comparison suggests that the bands located in the 700–550 $cm^{-1}$ region, although strongly coupled, are essentially related with Cu–O motions.

The origin of the strongest band, found in the 520–540 $cm^{-1}$ region, is unclear because the magnitude of the contribution of Pt(IV)–O stretchings to that of the Cu(II)–O motions is difficult to estimate.

The typical and well-defined bands, which are found in all spectra below 200 $cm^{-1}$, are surely due to the external modes of the metal–oxygen lattice.

Finally, it is interesting to comment that the present oxides show a spectroscopic behavior which is characteristic and has often been observed for the isostructural series of lanthanide compounds (14–20). An increase of the frequency values with the diminution of the unit cell volumes is observed by comparing corresponding and well-defined bands of the different spectra. This implies that, as a direct consequence of the volume decrease from Ho to Lu, the metal–oxygen bonds of the different structural building units are reinforced. This reinforcement explains the increase observed in some of the vibrational frequencies.

## ACKNOWLEDGMENTS

de Buenos Aires. The authors are also indebted to Ing. Pedro Molina (LANAIS-EFO) for generous help during the spectral measurements and to Mr. R. Vaena for valuable advice with the computer programs.

## REFERENCES

1. J. S. Swinnea and H. Steinfink, *Acta Crystallogr. Sect. C* **43**, 2436 (1987).
2. K. Kato, K. Kosuda, Y. Uchida, E. Takayama-Muromachi, and O. Fukunaga, *Acta Crystallogr. Sect. C* **44**, 794 (1988).
3. G. Calestani, C. Rizzoli, and G. D. Andreetti, *Solid State Commun.* **66**, 223 (1988).
4. U. Geiser, L. C. Porter, H. H. Wang, T. H. Allen, and J. M. Williams, *J. Solid State Chem.* **73**, 243 (1988).
5. Y. Saito, K. Ukei, T. Shishido, and T. Fukuda, *Acta Crystallogr. Sect. C* **47**, 1366 (1991).
6. M. Hjorth, *Acta Chem. Scand. A* **42**, 727 (1988).
7. P. E. Werner, L. Eriksson, and M. Westdahl, *J. Appl. Crystallogr.* **18**, 367 (1985).
8. P. E. Werner, *Ark. Kemi* **31**, 513 (1969).
9. G. A. Costa, M. Ferretti, M. L. Fornasini, E. A. Franceschi, and G. L. Olcese, *Powder Diffr.* **4**, 24 (1989).
10. W. Wong and B. Paretzkin, *Powder Diffr.* **6**, 187 (1991).
11. E. J. Baran, M. B. Vassallo, and C. Cascales, *An. Asoc. Quím. Argent.* **82**, 251 (1994).
12. R. D. Shannon and C. T. Prewitt, *J. Inorg. Nucl. Chem.* **32**, 1427 (1970).
13. I. L. Botto and E. J. Baran, *N. Jahrb. Mineral. Abhandl.* **142**, 320 (1981).
14. E. J. Baran, G. P. Cicileo, G. Punte, A. E. Lavat, and M. Trezza, *J. Mater. Sci. Lett.* **7**, 1010 (1988).
15. A. E. Lavat, E. J. Baran, R. Saez-Puche, A. Salinas-Sanchez, and M. J. Martin-Llorente, *Vib. Spectrosc.* **3**, 291 (1992).
16. E. J. Baran, M. E. Escobar, L. L. Fournier, and R. R. Filgueira, *Z. Anorg. Allg. Chem.* **472**, 193 (1981).
17. M. E. Escobar and E. J. Baran, *Z. Naturforsch. A* **35**, 1100 (1980).
18. A. E. Lavat, M. Trezza, I. L. Botto, D. I. Roncaglia, and E. J. Baran, *Spectrosc. Lett.* **21**, 335 (1988).
19. E. J. Baran, E. G. Ferrer, I. Bueno, and C. Parada, *J. Raman Spectr.* **21**, 27 (1990).
20. I. L. Botto, E. J. Baran, C. Cascales, I. Rasines, and R. Saez-Puche, *J. Phys. Chem. Solids* **52**, 431 (1991).