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Infrared spectra of Nd_2BaPdO_5 and Nd_2BaPtO_5

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Abstract

The infrared spectra of the mixed oxides Nd_2BaPdO_5 and Nd_2BaPtO_5, containing Pd(II) and Pt(II) in a square-planar oxygen-coordination, were recorded and approximately assigned on the basis of factor-group arguments. Some comparisons with related materials are made. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Mixed oxides of overall stoichiometry $Ln_2BaM^{II}O_5$ (Ln=trivalent lanthanide or yttrium, M^{II}=Co, Ni, Cu, Zn, Pd, Pt) have been of great interest in the last years due to their relation to the new high temperature superconducting materials [1]. Despite their identical stoichiometry, they belong to different structural types depending on the involved Ln(III) and/or M(II) cations (cf. Ref. [2] and references therein). In most of these compounds the M(II) cations present square-pyramidal or octahedral oxygen coordination whereas tetrahedral or square-planar environments are less frequent.

In a previous paper, we have demonstrated that it is possible to differentiate unambiguously these different structural types by means of infrared spectroscopy [2].

The known examples with a square-planar M(II) coordination are the Cu(II) oxides with Ln=La, Nd [3–5], the Pt(II) oxides with Ln=Nd, Sm, Eu, Gd [6,7] and those of Pd(II) with Ln=La, Pr, Nd, Sm, Gd, Tb [6,8].

Considering that from these systems only the vibrational behavior of Nd_2BaCuO_5 has been investigated in detail [2,9–11], we have now prepared two of the oxides containing Pd(II) or Pt(II), in order to analyze the spectroscopic characteristics of the materials containing heavy transition metal cations and to compare their behavior with that of the lighter first-row cation Cu(II).

2. Experimental

The two investigated materials, Nd_2BaPdO_5 and Nd_2BaPtO_5, were obtained in the form of micro crystalline powders, by standard solid state reactions, heating stoichiometric 1:1:1 mixtures of $BaCO_3$, PdO (or Pt-metal powder) and Nd_2O_3, in corundum crucibles in air, and up to 1000°C, as described earlier [6,8]. The purity of the obtained oxides was checked by X-ray powder diffractometry (Philips PW 3710 diffractometer, Cu Kα radiation), confirming the generation of single-phased products.

The infrared spectra were recorded on a Nicolet-Magna 550 FTIR instrument, using the KBr pellet technique. Suspensions of the finely powdered samples in Nujol, between CsI plates, gave identical results.

3. Results and discussion

The investigated oxides belong to the tetragonal space group D_{4h}^5 — $P4/mbm$ with $Z=2$ [6,8]. The structure consists of a three-dimensional array of face- and edge-sharing BaO_{10} and NdO_8 polyhedra with relatively isolated square planar PdO_4 or PtO_4 units between them. The BaO_{10} coordination polyhedron is a square prism capped on both ends by tetragonal pyramids, while the NdO_8 coordination polyhedron is a trigonal prism capped on two of the three rectangular faces.

It is expected that the highest energy region is dominated by vibrations involving the shortest bonds [11] and, therefore, it seems possible to attain approximate infor-

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mation on the characteristics of the $M^{II}O_4$ vibrations on the basis of the irreducible representation of a square-planar D_{4h}-molecule [12], i.e.:

$$\Gamma_{D4h} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$

Three of these components (A_{1g}, B_{1g}, B_{2g}) are only Raman-active, another three (A_{2u}, $2E_u$) are infrared-active and the remaining one (B_{2u}) is inactive. The two infrared active E_u species correspond to the antisymmetric stretching and bending modes of the $M^{II}O_4$ units, whereas the A_{2u} species corresponds to its out-of-plane deformation. Therefore, in the IR absorption spectrum one may expect a strong and relatively broad band, located at the highest energies, essentially related to the antisymmetric stretching of the M–O bonds.

On the other hand, the irreducible representation of the optically active modes, given by a factor group analysis [13,14], at $\mathbf{k}=0$ are $3A_{1g}+2B_{1g}+3B_{2g}+4E_g+5A_{2u}+10E_u$ [11]. On the basis of symmetry considerations, it can be shown that the IR-active phonons ($5A_{2u}+10E_u$) involve all the ions present in the unit cell [10,11]. Therefore, one must expect important factor group effects in compounds belonging to this structural type.

The FTIR spectra of both materials are similar, but not identical, as shown in Fig. 1. These spectra show interesting similarities with that of the isostructural Nd_2BaCuO_5 oxide [2,9] but also with those of Nd_2CuO_4 and Pr_2CuO_4 [15] and of the n-type $Nd_{2\text{-}x}M_x^{IV}CuO_4$ superconductors [16,17], materials which also possess square planar CuO_4 coordination polyhedra, and with the $M_2CuO_2X_2$ oxohalides, in which Cu(II) is present in a strongly distorted octahedron conformed by a CuO_4 basal plane with two halogen atoms in the apical positions [18]. The measured band positions are presented in Table 1.

The most interesting and remarkable difference with the spectra of the above mentioned materials is the splitting of the first, higher-energy, band. This splitting is only insinuated as a weak shoulder in the case of the palladium oxide, but is clearly seen in the case of the isostructural platinum compound.

This doublet structure can surely be assigned to the factor-group split antisymmetric stretching vibration of the $M^{II}O_4$ squares. In the IR-spectrum of the related copper oxide, Nd_2BaCuO_5, only one band is seen in this region [2,9] suggesting that the factor-group effects are enhanced by the presence of a higher mass metal cation in the center of the vibrating square units. On the other hand, this vibration is found at a somewhat higher energy in the present materials, despite the fact that the Pd–O [8] and Pt–O [19] bonds are slightly longer than the respective Cu–O bonds [5]. A comparison with related materials, presented in Table 2, shows the same behavior, i.e. all the compounds containing CuO_4 planar units have this first band at relatively lower energies than that observed in the two materials investigated here. This apparent rein-

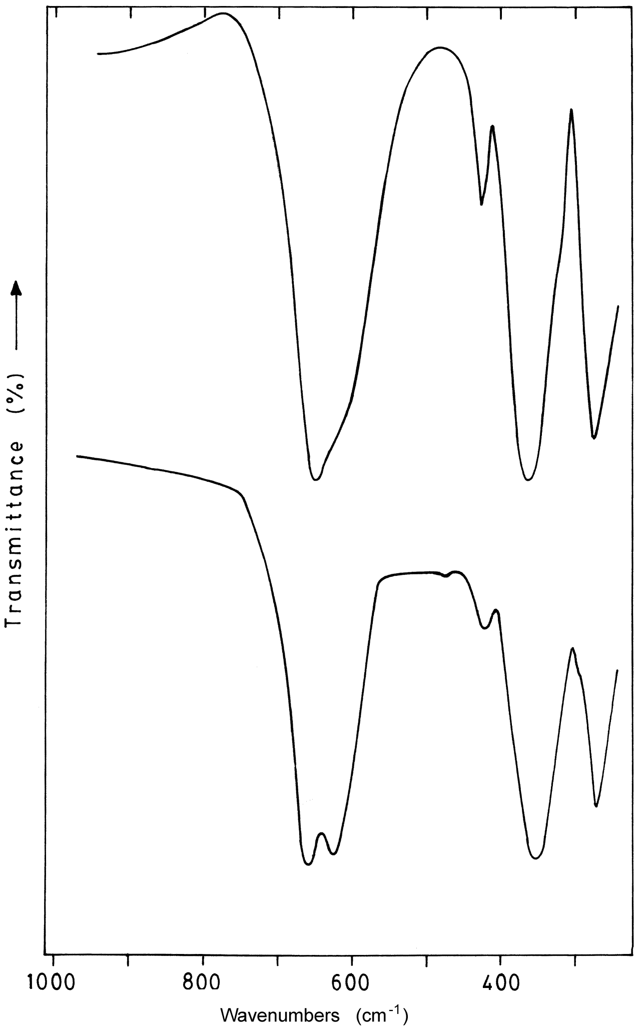

Fig. 1. Infrared spectra of Nd_2BaPdO_5 (top) and Nd_2BaPtO_5 (bottom).

Table 1
Measured wavenumbers and intensities[a] of the infrared spectra of the two investigated materials[a]

Oxide	Wavenumbers					
Nd_2BaPdO_5	645 vs	620 sh	424 m	368 sh	350 vs	274 s
Nd_2BaPtO_5	657 vs	622 vs	415 w	351 vs	338 sh	270 s

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Table 2
IR spectra of mixed oxides containing CuO_4 planar units[a]

Oxide	Wavenumbers				Ref.
Nd_2BaCuO_5	592 vs	348 vs		275 s	[2,9]
Nd_2CuO_{4-x}	528 vs	365 s	327 s		[16,17]
$Nd_{1.9}Ce_{0.1}CuO_{4-x}$	518 vs	360 s	320 s		[16]
$Nd_{1.9}Th_{0.1}CuO_{4-x}$	520 vs	355 s	322 s		[17]
Pr_2CuO_{4-x}	510 vs	340 vs	310 sh		[17]
$Pr_{1.9}Th_{0.1}CuO_{4-x}$	503 vs	335 vs	310 sh		[17]
$Ca_2CuO_2Cl_2$	611 vs	345 vs			[18]
$Sr_2CuO_2Cl_2$	564 vs	354 vs			[18]

[a] vs, very strong; s, strong; sh, shoulder.

forcement of the metal–oxygen bonds may be also a consequence of the heavier central atom, and of the concomitant coupling effects.

On the other hand, and although the Pd–O and Pt–O bond distances are practically identical, within the experimental errors [8,17], the present spectroscopic results show that the Pt–O stretching vibration appears slightly stronger, suggesting a somewhat shorter bond in this last case. This behavior is not totally unexpected, because relativistic arguments predict bond shortening on going from a 5th period compound to a similar compound of the 6th period of the Periodic Table [20–22].

The origins of the other bands seen in Fig. 1 are not so easy to interpret. All are surely of complex origin involving different motions of all the coordination polyhedra [11]. As discussed in the case of the Nd_2BaCuO_5 oxide [9], the antisymmetric bending mode of the square planar units probably lies below 300 cm^{-1}. Therefore, one can assume that in the present cases the last measured band, at around to 270 cm^{-1}, may be essentially related to this bending.

A comparison with spectroscopic data of other related materials (cf. Table 2 and Refs. [16–18,23]) suggests that the other very strong band, located at around 350 cm^{-1}, may be essentially related to vibrations of the NdO_8-polyhedron. This band appears clearly split in some of the materials included in Table 2, whereas in the present cases only a very weak shoulder accompanies the main band.

Finally, the two investigated oxides present another spectral feature not observed in the related materials, i.e. the IR band located around 420 cm^{-1}, which appears very well defined in the Pd compound and as a weak band in the Pt material (cf. Fig. 1). A similar band was only observed in the $M_2CuO_2X_2$ oxohalides as a weak shoulder at about 430 cm^{-1} [18].

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References

[1] J.K. Burdett, J.F. Mitchell, J. Am. Chem. Soc. 112 (1990) 6571.

[2] A.E. Lavat, E.J. Baran, R. Sáez-Puche, A. Salinas-Sánchez, M.J. Martín-Llorente, Vibrat. Spectr. 3 (1992) 291.

[3] C. Michel, L. Er-Rakho, B. Raveau, J. Solid State Chem. 39 (1981) 161.

[4] D. Dubé, B. Champagne, Y. Le Page, Mater. Lett. 8 (1989) 283.

[5] J.K. Stalick, W. Wong-Ng, Mater. Lett. 9 (1990) 401.

[6] S. Schiffler, H. Müller-Buschbaum, J. Less-Common Met. 128 (1987) 117.

[7] H. Müller-Buschbaum, C. Lang, J. Less-Common Met. 142 (1988) L1.

[8] S. Schiffler, H. Müller-Buschbaum, Monatsh. Chem. 117 (1986) 465.

[9] E.J. Baran, A.E. Lavat, R. Sáez-Puche, A. Salinas-Sánchez, J. Mater. Sci. Lett. 11 (1992) 1087.

[10] A. de Andrés, S. Taboada, J.L. Martínez, A. Salinas, J. Hernández, R. Sáez-Puche, Phys. Rev. B 47 (1993) 14898.

[11] S. Taboada, A. de Andrés, J.L. Martínez, R.P.S.M. Lobo, P. Odier, F. Gervais, A. Salinas, R. Sáez-Puche, J. Alloys Comp. 225 (1995) 216.

[12] J.R. Ferraro, J.S. Ziomek, Introductory Group Theory, Plenum Press, New York, 1969.

[13] A. Müller, E.J. Baran, R.O. Carter, Struct. Bond. 26 (1976) 81.

[14] A. Fadini, F.M. Schnepel, Schwingungsspektroskopie. Methoden, Anwendungen, G. Thieme, Stuttgart, 1985.

[15] K.K. Singh, P. Ganguly, Spectrochim. Acta 40A (1984) 539.

[16] A.E. Lavat, E.J. Baran, J. Mater. Sci. Lett. 10 (1991) 470.

[17] A.E. Lavat, M. Trezza, E.J. Baran, J. Mater. Sci. Lett. 12 (1993) 923.

[18] A.E. Lavat, E.J. Baran, submitted for publication.

[19] S. Schiffler, H. Müller-Buschbaum, Z. Anorg. Allg. Chem. 523 (1985) 63.

[20] P. Pyykkö, J.P. Desclaux, Acc. Chem. Res. 12 (1979) 276.

[21] P. Pyykkö, Chem. Rev. 88 (1988) 563.

[22] J.B. Bersuker, Electronic Structure and Properties of Transition Metal Compounds, Wiley, New York, 1996.

[23] S.L. Herr, K. Kamaras, D.B. Tanner, S.W. Cheong, G.R. Stewart, Phys. Rev. B 43 (1991) 7847.