

## Infrared spectra of mixed oxides of the type $\text{Ln}_2\text{BaCoO}_5$

A. E. LAVAT

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

E. J. BARAN\*

*Química Inorgánica (QUINOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina*

R. SAEZ-PUCHE, J. HERNANDEZ-VELASCO

*Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain*

$\text{Ln}_2\text{BaMO}_5$  oxides (Ln = trivalent lanthanide;  $\text{M}^{\text{II}} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) present very interesting structural, magnetic and spectroscopic properties and, when  $\text{M}^{\text{II}} = \text{Cu}$ , they are generated as by-products or impurities (the so-called “green phases”) during the syntheses of the  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ -type superconductors [1, 2].

Despite their identical stoichiometries, the  $\text{Ln}_2\text{BaMO}_5$  materials belong to four different structural types, depending on the LN(III) and/or M(II) cations present in the lattices [3]. Besides, during the past few years, it has also been shown that some of them present temperature dependent dimorphism.

In previous papers, we have investigated the vibrational spectroscopic behaviour of different materials of this type containing Cu [4, 5], Zn [6, 7] and Ni [6, 8]. As phases containing cobalt as the divalent cation have only recently been characterized in detail, their spectroscopic behaviour remain to be clarified.

Structural characterization of  $\text{Ln}_2\text{BaCoO}_5$  materials showed that phases containing the smallest lanthanide cations (Dy, Ho, Er, Tm, Yb, Lu) and yttrium belong to the orthorhombic space group Pnma with  $Z = 4$ . They are green in colour and the Co(II) ions are present as isolated  $\text{CoO}_5$  square pyramidal units [9–12]. On the other hand, compounds containing greater lanthanides (Pr, Nd, Sm, Eu, Gd) are brown and belong to the orthorhombic Immm space group with  $Z = 2$ . In these materials the Co(II) ions form infinite  $\text{MO}_6$  octahedral chains, which run parallel to the  $a$  axis of the unit cell [13, 14]. Interestingly, the phases containing Dy, Ho, Er and Tm can be obtained in both structural types, by regulating adequately the maximum temperature during their syntheses [11, 15].

Polycrystalline samples of all the investigated materials were obtained by solid state high-temperature reactions from stoichiometric amounts of high purity  $\text{Ln}_2\text{O}_3$ ,  $\text{CoCO}_3$  and  $\text{BaCO}_3$ , under an argon flow, as described in detail in the previous papers

[11–15]. The infrared (IR) spectra were recorded on a Nicolet-Magna 500 Fourier transform infrared (FTIR) instrument, up to  $300\text{ cm}^{-1}$ , using the KBr pellet technique.

As typical examples of the spectra of the two different structural types adopted by these materials, Fig. 1 shows those corresponding to  $\text{Ho}_2\text{BaCoO}_5$  and  $\text{Nd}_2\text{BaCoO}_5$ . These spectra are very similar to that previously measured for the other structurally related materials of the same type [6]. As can also be seen from Fig. 1, IR spectroscopy constitutes an excellent tool for the rapid and straightforward differentiation of both structural types.

The exact IR band positions for the green materials belonging to the Pnma space group are given in Table I. As discussed earlier [4, 6], the weak high frequency band located around  $560\text{--}570\text{ cm}^{-1}$  and the first strong doublet may be assigned with confidence to virtually “pure” stretching vibrations of the square pyramidal  $\text{CoO}_5$  units, whereas all the other bands originate in very strongly coupled motions of all the metal–oxygen polyhedra present in these lattices.

Table II shows the band positions measured for the brown materials belonging to the Immm space group. As in the case of the structurally related materials containing Ni(II) instead of Co(II) [6], these spectra are dominated by a strong and unusual high-frequency band, located above  $700\text{ cm}^{-1}$ . This band is undoubtedly related to the stretching vibration of the short Co–O apical bonds, which constitute the  $\text{CoO}_6$  octahedral chains [6]. The second higher frequency band, which is seen as a very weak feature in all spectra, can probably be related to the symmetric stretching of the longer  $\text{CoO}_4$  equatorial bonds. The third one, an intense and broad band found above  $400\text{ cm}^{-1}$ , probably has a more complex origin but includes, surely, the corresponding antisymmetric stretching of the mentioned equatorial bonds.

As the first stretching band is the most characteristic and probably the “purest” motion of the  $\text{CoO}_6$  octahedra, we have attempted to correlate its position with some of the structural characteristics of the

\* Author to whom all correspondence should be addressed.

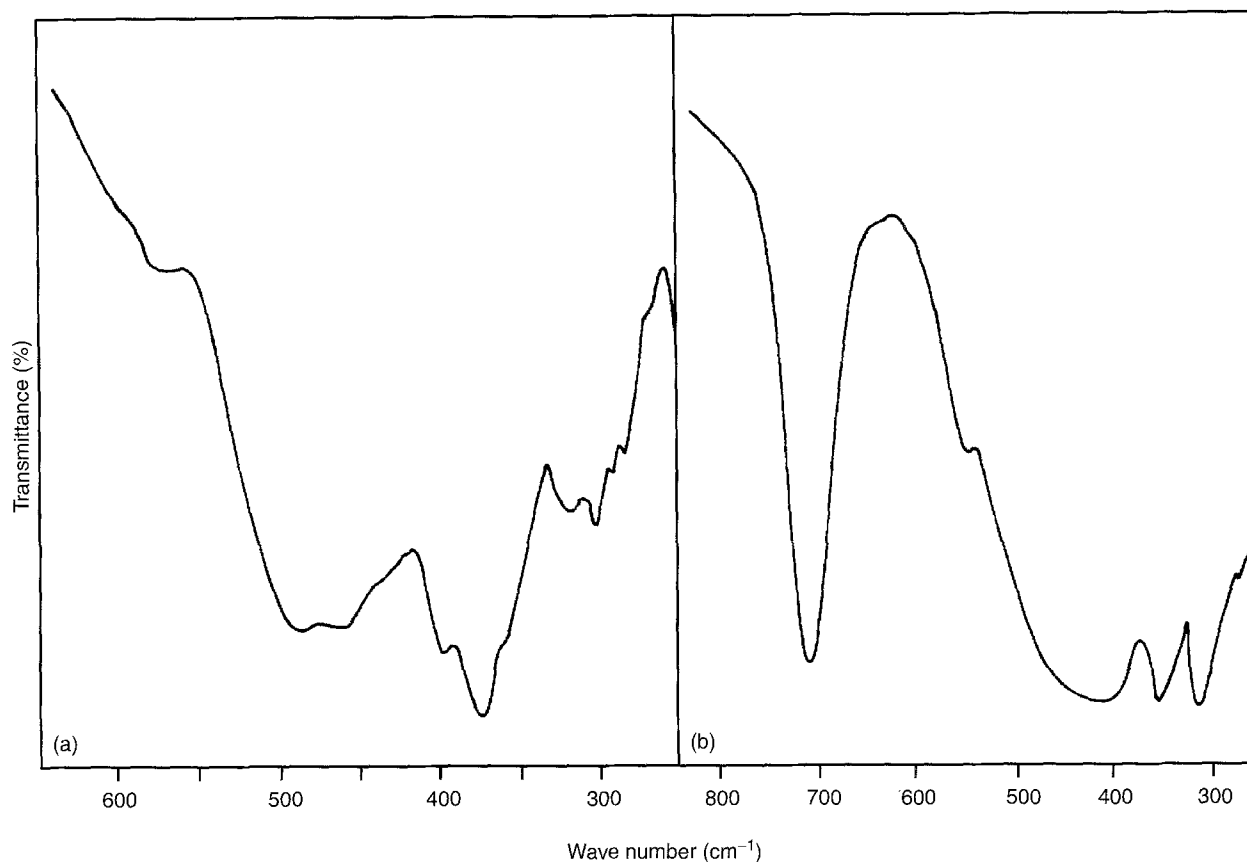


Figure 1 Infrared spectra of (a)  $\text{Ho}_2\text{BaCoO}_5$  and (b)  $\text{Nd}_2\text{BaCoO}_5$ .

TABLE I Infrared frequencies for the (green coloured) materials belonging to the space group  $\text{Pnma}$ , containing  $\text{CoO}_5$  groups

Material	IR frequencies <sup>a</sup> ( $\text{cm}^{-1}$ )							
$\text{Dy}_2\text{BaCoO}_5$	567w	482s	450sh	393m	374vs	317m	304w	292sh
$\text{Ho}_2\text{BaCoO}_5$	568w	484s	463m	397m	373vs	317m	302m	
$\text{Er}_2\text{BaCoO}_5$	571w	492s	459m	399m	374vs		304m	283w
$\text{Tm}_2\text{BaCoO}_5$	570w	492sh	459vs	400sh	384vs		304m	281w
$\text{Yb}_2\text{BaCoO}_5$	575w	500sh	460vs	398sh	357s	317m		274w
$\text{Lu}_2\text{BaCoO}_5$	576w	507m	467s	410sh	388vs	315vs		294sh
$\text{Y}_2\text{BaCoO}_5$	561w	492s	458s	402sh	380vs	312m		285w

<sup>a</sup>vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

TABLE II Infrared frequencies for the (brown coloured) materials belonging to the space group  $\text{Immm}$ , containing  $\text{Co-O-Co}$  chains

Material	IR frequencies <sup>a</sup> ( $\text{cm}^{-1}$ )				
$\text{Nd}_2\text{BaCoO}_5$	708vs	552vw	394vs	356s	311s
$\text{Sm}_2\text{BaCoO}_5$	734vs	559w	407vs	364s	316vs
$\text{Eu}_2\text{BaCoO}_5$	745s	561w	404vs	370s	319s
$\text{Gd}_2\text{BaCoO}_5$	756s	565m	416vs	368s	322vs
$\text{Dy}_2\text{BaCoO}_5$	776s	575m	414vs	370s	322s

<sup>a</sup>vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

materials. As can be observed in Fig. 2, a direct dependence of this stretching mode from the unit cell volumes could be established, i.e. the reinforcement of the energy of the  $\text{Co-O}$  apical bond parallels the diminution of the unit cell volumes.

Besides, careful analysis of the data presented in Table I and Table II shows a similar trend for most of the IR bands. Most of the values of the  $\text{Y(III)}$  compound also lie near to those found in  $\text{Ho}_2\text{BaCoO}_5$ , in

agreement with their similar unit cell dimensions [11]. This behaviour is usually observed in series of isostructural lanthanide compounds, and was discussed in detail in previous papers [4, 6, 16–18].

From the dimorphic materials only  $\text{Dy}_2\text{BaCoO}_5$  could be obtained in both modifications with a degree of purity high enough to justify its spectroscopic study. Its IR data are included in Table I and Table II.

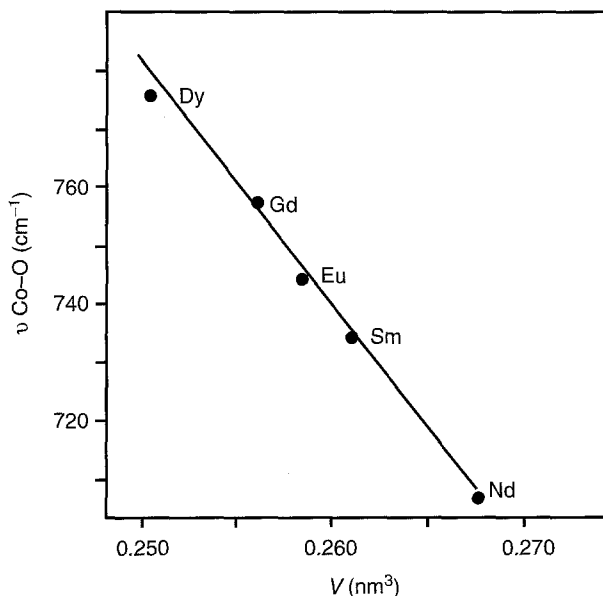


Figure 2 Correlation between the stretching frequency of the apical Co—O bonds and unit cell volumes for the Immm-type materials.

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