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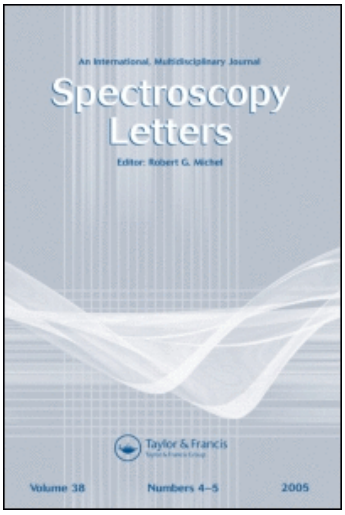

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Optical Absorption Spectra of Gd_2BaCoO_5 and Y_2BaCoO_5

J. M. Martin-Llorente[a]; E. Rodríguez[a]; R. Sáez-Puche[b]; J. Hernández-Velasco[b]
[a] Dpto. de Química Inorgánica, Universidad de Salamanca Facultad de Química, Salamanca, SPAIN [b] Dpto. de Química Inorgánica I, Universidad Complutense. Facultad de Ciencias Químicas, Madrid, SPAIN

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OPTICAL ABSORPTION SPECTRA OF Gd_2BaCoO_5 and Y_2BaCoO_5

Key words: R_2BaCoO_5 oxides, polymorphism, electronic transitions.

J. M. Martín-Llorente*, E. Rodríguez
Dpto. de Química Inorgánica, Universidad de Salamanca
Facultad de Química, 37008 Salamanca, SPAIN.

R. Sáez-Puche. J. Hernández-Velasco
Dpto. de Química Inorgánica I, Universidad Complutense.
Facultad de Ciencias Químicas, 28040 Madrid, SPAIN.

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ABSTRACT

The marked differences found in the optical spectra of the brown coloured Gd_2BaCoO_5 and the green coloured Y_2BaCoO_5 oxides, have been explained taking into account the different crystal structures that they present. While Gd_2BaCoO_5 shows orthorhombic symmetry, space group Immm, with the cobalt located at distorted octahedral coordination (CoO_6), the Y_2BaCoO_5 crystallizes with orthorhombic symmetry, space group Pnma, in which the cobalt is surrounded by five oxygen atoms, forming distorted square pyramids (CoO_5) which have C_{4V} as point symmetry.

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INTRODUCTION

R_2BaMO_5 oxides, where R is a trivalent lanthanide cation and M = Co, Ni, Cu and Zn, form a large family of compounds for different structural-types have been reported[1].

The R_2BaCoO_5 oxides, where R = Nd - Tm, crystallize with the Nd_2BaNiO_5 - type, showing orthorhombic symmetry, space grupe Immm. On the other hand, when R = Dy - Lu and Y, the Sm_2BaCuO_5 -type structure has been found for these oxides, and orthorhombic symmetry, space group Pnma, is presented by them[2-5].

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From these results it is obvious the existence of polymorphism in these compounds[5-6], and they are similar to those earlier reported for the isostructural Tm_2BaNiO_5 oxide[7].

The main structural feature of the Immm-R_2BaCoO_5 oxides is the existence of isolated chains of vertex-sharing flattened octahedra (CoO_6) which run parallel to the a-axis, as it happens in the case of the Gd_2BaCoO_5.

Nevertheless, in the Pnma-R_2BaCoO_5 oxides, like Y_2BaCoO_5, the main characteristic is the presence of isolated distorted square pyramids (CoO_5) along the b-axis.

The marked differences in these structures have a critical influence on their magnetic properties; in the case of the Immm-R_2BaCoO_5 oxides, one-dimensional interactions in the Co^{+2} sublattic has been found above the room temperature, analogous that we have reported earlier in the isostructural R_2BaNiO_5 oxides[8,9]. However, in the isostructural

R_2BaCoO_5 oxides, both rare earth and cobalt sublattices appears to be 3D-antiferromanetic ordered at very low temperatures, as it occurs in the isostructural R_2BaCuO_5[10,11].

In the present paper, the optical absortion spectra for both Gd_2BaCoO_5 and Y_2BaCoO_5 oxides are studied.

EXPERIMENTAL

Y_2BaCoO_5 and Gd_2BaCoO_5 oxides were synthesized as green and brown coloured powders respectively by solid state reaction from the stoichiometric amounts of high purity Y_2O_3 (99.999%), Gd_2O_3 (99.99%) $CoCO_3$ nH2O (99.999%) and $BaCO_3$ (A.R. Grade). The ground samples were heated under argon flow at 1100-1300 °C for 24 hours with some interruptions for regrinding to enhance the homogeneity of the materials. It is worth noting the instability of Co^{+2} in air at the high temperature that is neccesary to prepare these oxides.

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Magnetic susceptibility measurements were made using a fully automatic DSM8 magneto-susceptometer based on the Faraday method in the temperature range 300-4.2 K. The magnetic fiels used was 5.6 KG with $H \cdot dH/dz = 14.2\ KG^2\ cm^{-1}$. The setup was calibrated with $Hg[Co(SCN)_4]$ and $Gd_2(SO_4)_3 \cdot 8H_2O$ as standards. The data were corrected for ionic diamagnetism.

Electronic spectra of the sample were performed by diffuse reflectance in the 850-250 nm wavelenght range, using a Shimadzu UV-250 spectrophotometer with MgO as standard reference and a spectra bandwidth (slit) of 5 nm,

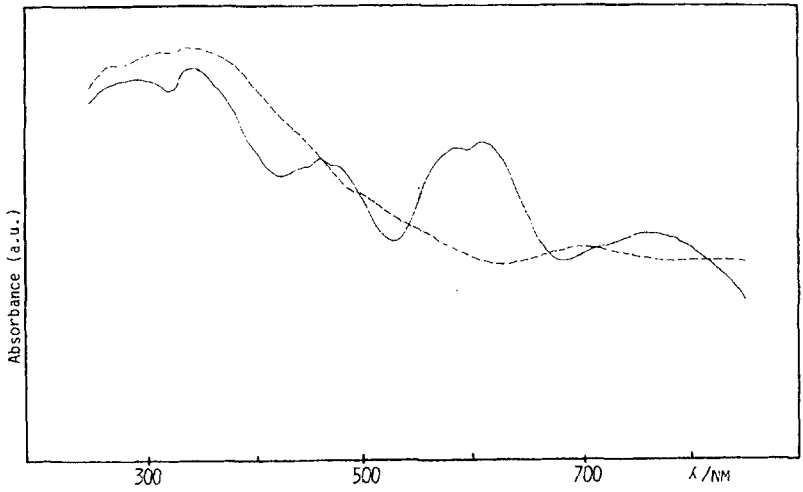

FIG. 1 Difuse reflectance spectra of Gd_2BaCoO_5 (---) and Y_2BaCoO_5 (—).

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RESULTS AND DISCUSSION

As it was mentioned earlier, in the Gd_2BaCoO_5 oxide, the Co^{+2} (d^7) ion is located at the center of an octahedral arrangement of oxygens; otherwise, in the Y_2BaCoO_5 compound, the Co^{+2} environment shows a square distorted pyramidal geometry with five oxo ligands, giving raise aproximately to the C_{4V} point symmetry.

The visible spectra of both oxides are principally due to the d-d transitions of Co^{+2}, since Gd^{+3} and Y^{+3} ions have not transitions in this range of the spectrum.(Fig. 1.)

The spectrum of Gd_2BaCoO_5 agrees well with the Co^{+2} located at an octahedral environment of oxygens, being similar to the spectrum of another complexes in which the CoO_6 chromophore is present[12], such $[Co(H_2O)_6]^{+2}$ or CoO/MgO.

TABLE 1. Electronic transitions of the Y_2BaCoO_5 oxide from the ground state ^4A (cm^{-1}).

Transitions	obs.	calc.[a]
$^4E(F)$	------	1190
$^4B_2(F)$	------	4760
$^4E(F)$	------	6900
$^4B_1(F)$	13100	13300
$^4E(P)$	16400	16900
$^4A_2(P)$	21800	22600

a) For CoO_5 (C_{4V}) symmetry. Dq=850 cm^{-1} and Oax.-Co-Obas.angle of 100°.

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The spectrum shows the weak intensity transition $^4T_{2g}$ -----> $^4A_{2g}$ at ~14400 cm^{-1}, and a shoulder, near the charge-transfer band of the spectrum, at ~ 19000 cm^{-1}, that is probably due to the $^4T_{2g}$ -----> $^4T_{1g}(P)$ transition.

The spectrum of Y_2BaCoO_5 is concordant with a square pyramidal environment for the cobalt, and the existence of the CoO_5 chromophore. Likewise, the spectrum of this oxide is similar to that of $[Co(MeØ_2AsO)_4NO_3]^+$ which also contains the CoO_5 square pyramid polyhedron[13].

The observed and calculated transitions that correspond to a ligand field of oxo ions in a C_{4V} symmetry are included in Table 1. The theoretical values were calculated using the energy levels disgrams proposed by Ciampolini and Bertini[14], and taking 100° as the value of

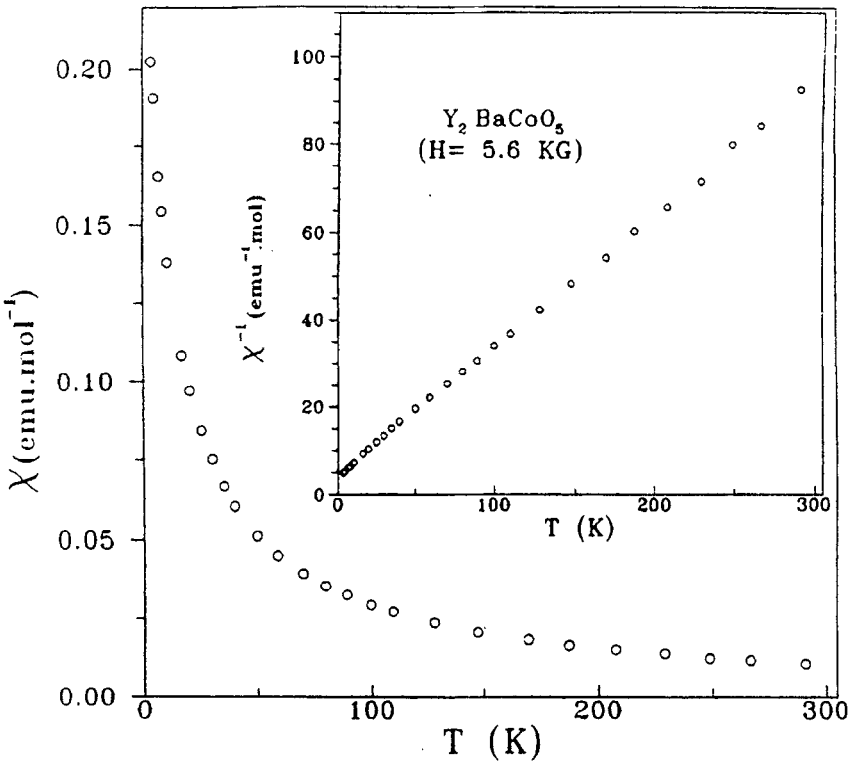

Fig. 2 Temperature dependence of the molar magnetic susceptibility for Y_2BaCoO_5. The inset shows the reciprocal magnetic suseptibility.

the O(axial) -- Co --O(basal) angle, and Dq = 850 cm^{-1}. It is noting that these diagrams are valid for Co^{+2} in a high-spin state.

The spin state of Co^{+2} for Y_2BaCoO_5 has been determined from the magnetic susceptibility measurement, which follows a Curie-Weiss behaviour in a very wide temperature range, 4.2 K-300 K, as can be observed in Fig. 2. The magnetic moment obtained is μ = 4.98 BM, that fully agrees with the expected for Co^{+2} in high-spin state.

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Only the three most energetic electronic transitions have been registered, showing a good agreement with the calculated values. The small differences found between the observed and calculated values are probably due to the distortion away from the C_{4V} symmetry, since the five Co-O distances in the pyramids are not equal[2], being Co-O_1(basal) = 1.999 Å(×2), Co-O_2(basal) = 2.098 Å(×2) and Co-O_3(axial) = 2.013 Å(×1).

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