Short Communication

Electronic Spectra of (Mg,Co)₂P₂O₇ Phases

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As a continuation of a series of studies on the spectroscopic properties of different oxosalts and to obtain a wider insight into the electronic characteristics of metal–oxygen chromophores, we have now investigated the electronic spectra of a series of solid solutions of the type (Mg,Co)₂P₂O₇, isostuctural with α-Mg₃P₂O₇.

The crystal structure of α-Mg₃P₂O₇ was determined in 1967 by Calvo.1 Later Krishnamachari and Calvo have shown that α-Co₃P₂O₇ is isostuctural with α-Mg₃P₂O₇.2 The monoclinic space group symmetry is B2/c (No. 14), with one distinct five- and one six-coordinated metal site (Z=8). The average metal–oxygen distances are 2.044 Å (five-coordination; range 1.985-2.120) and 2.103 Å (six-coordination; range 2.059-2.142) in α-Mg₃P₂O₇,1 and 2.049 (1.957-2.110) and 2.116 Å (2.062-2.183), respectively, in α-Co₃P₂O₇.2 The MO₃ groups are fairly regular octahedra, while the MO₂ polyhedra should rather be described as square pyramids.

Experimental

Pure diphosphates of magnesium and cobalt (II) and four α-(M₈₋₁Co₈)₂P₂O₇ solid solutions (x = 0.2, 0.4, 0.6 and 0.8) were prepared as described earlier.3 X-Ray powder diffraction data were obtained with a Guinier-Hägg camera (Cr Kα radiation, λ = 2.28975 Å, R = 50.00 mm, KCl internal standard) and evaluated with the computer program system by Nord and Forsberg4 to give the unit-cell dimensions presented in Table 1. The figures of merit are according to de Wolff.5 The electronic reflectance spectra were recorded with a Beckman ACTA-IV instrument between 250 and 870 nm, with an integrating sphere employing TiO₂ as a standard.

Results and discussion

The reflectance spectra of the (Mg,Co)₂P₂O₇ phases are similar to each other (Fig.1). A larger cobalt content implies more CoO₅ chromophores and also a better defined spectrum. Spectra of phases with lower cobalt contents show some broadening of the bands at 21.5 × 10⁵ and 19.23 × 10⁵ cm⁻¹, but the transition energies do not change significantly with the composition.

Two different chromophoric groups are present in this structure, and the observed transitions must therefore be related to the CoO₅ and CoO₆ groups. For the octahedral CoO₆ chromophore two electronic bands are expected in the measured range6 and have been assigned to the strong

<table>
<thead>
<tr>
<th>Table 1. Unit-cell dimensions for the α-(Mg,Co)₂P₂O₇ diphosphates.</th>
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<tbody>
<tr>
<td>Phase a</td>
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<tr>
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</tr>
<tr>
<td>Mg₂₀₀</td>
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<tr>
<td>Mg₀₉Co₁₀</td>
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<tr>
<td>Mg₀₈Co₁₁</td>
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<tr>
<td>Mg₀₆Co₁₃</td>
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<td>Co₁₀₀</td>
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aMg₈₀₀ stands for pure α-Mg₃P₂O₇, Mg₈₀₀Co₁₀ for α-(Mg₀₉Co₁₀)₂P₂O₇, and so forth. bN = number of reflections used in the refinements. cM(20) = figure of merit according to de Wolff.

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bands at 585 nm (17.10×10^3 cm⁻¹) and 520 nm (19.23×10^3 cm⁻¹). These are related to the \(^4F_{1g} \rightarrow ^4A_{2g}\) (F) and \(^4F_{1g} \rightarrow ^4F_{1g}\) (P) transitions, respectively. A third band, corresponding to the \(^4F_{1g} \rightarrow ^4F_{2g}\) (F) transition, is expected to lie at around 8.5×10^3 cm⁻¹ as predicted from the known relation \(v_F/v_1 = 2\) (Ref. 6).

For the assignment of the transitions of the square-pyramidal CoO₆ chromophore (C₆₃ symmetry) we have used the energy-level diagram proposed by Ciamploni and Bertini,⁷ based on the weak-field scheme with F–P term intermixing (cf. Fig. 2 and Ref. 8). According to this scheme, the following band assignments can be proposed:

465 nm (21.5×10^3 cm⁻¹) to \(^4A_1 \rightarrow ^4A_2\) (P)

585 nm (17.1×10^3 cm⁻¹) to \(^4A_1 \rightarrow ^4E\) (P)

835 nm (12.0×10^3 cm⁻¹) to \(^4A_2 \rightarrow ^4B_1\).

A fourth transition, expected at around (7–8)×10^3 cm⁻¹ and assignable to the \(^4A_2 \rightarrow ^4E\) transition, lies outside the range of our instrument.

The second transition of the CoO₆ chromophore coincides with the \(^4F_{1g} \rightarrow ^4A_{2g}\) transition of the CoO₆ group. This explains the intensity enhancement observed for this band. In an octahedral environment this band usually has a lower intensity than that corresponding to the \(^4F_{1g} \rightarrow ^4F_{1g}\) (P) transition. Moreover, in square-pyramidal environments this band generally presents an intensity comparable to that of the \(^4A_1 \rightarrow ^4A_2\) (P) transition.⁸ A similar intensity enhancement has also been found previously in cobalt-containing solid solutions isomorphous with γ-Zn₃(PO₄)₂, in which octahedral CoO₆ groups and distorted trigonal bipyramids CoO₆ are found together. The last very weak band located at 320 nm (31.25×10^3 cm⁻¹) can probably be assigned to a spin-forbidden transition which involves a level originating from higher doublet terms.⁹

The cation distribution in two (Mg,Co)₃(PO₄)₃ solid solutions has earlier been determined from X-ray diffraction data,¹⁰ showing that there is a slight tendency for Co²⁺ to enter preferably the five-coordinated site rather than the six-coordinated site (K₃=2). The metal–oxygen distances are comparable to those of the (Mg,Co) diphosphates, but the MO₆ group should rather be described as a distorted trigonal bipyramid. For instance, in (Mg₀.₃Co₀.₇)(PO₄)₃, the respective average metal–oxygen distances are 2.06 Å.


(five-coordiation; range 1.94–2.21) and 2.08 Å (six-coordi-

A comparison of the electronic spectra recorded earlier
for some (Mg,Co) orthophosphates and here reported for
four α-(Mg,Co)₃P₂O₇ phases suggests that in the latter
phases also Co²⁺ prefers to enter the five-coordinated site.
This is in accordance with Burns’ observation that Co²⁺
ions are enriched in distorted and small-dimension sites,
while magnesium seems to have a greater tendency for
octahedral sites. The present results also extend our
knowledge in relation to MO₆ and MO₅ chromophores, and
show that the spectra of CoO₅ chromophores with a square-
pyramidal configuration are, within the resolution of our
instrument, very similar to those of trigonal-bipyramidal
systems, as is known for some other Co²⁺ compounds.

References


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