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Comparative analysis of crystal field effects and energy level scheme of six-fold coordinated Cr^{4+} ion in the pyrochlores, $Y_2B_2O_7$ ($B=Ti^{4+}$, Sn^{4+})

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ABSTRACT

The electronic energy levels of the six-fold coordinated Cr^{4+} ion in the pyrochlores $Y_2B_2O_7$ ($B=Sn^{4+}$, Ti^{4+}), have been computed using the exchange charge model of crystal field theory. The calculated Cr^{4+} energy levels and their trigonal splitting are in good agreement with experimental spectra. Calculations of the crystal field parameters show that the higher crystal field strength in $Y_2Sn_2O_7$ (in comparison with $Y_2Ti_2O_7$) arises from increased orbital overlap effects between the Cr^{4+} ion and the nearest oxygen ions, which are located at the 48f crystallographic position of the pyrochlore lattice. The increased overlap in $Y_2Sn_2O_7$ occurs despite the fact that the Cr^{4+}–O^{2-} bond distance in $Y_2Sn_2O_7$ is longer than in $Y_2Ti_2O_7$. This is attributed to a lack of hybridization (covalent bonding) between the filled 2p orbital of oxygen ion occupying the 48f site of the pyrochlore lattice and the filled Sn^{4+} $4d^{10}$ orbital. As a result, a stronger crystal field is experienced by Cr^{4+} ions in $Y_2Sn_2O_7$, even if the Cr^{4+}–O^{2-} distances are greater in this case, when compared to those in $Y_2Ti_2O_7$.

1. Introduction

Although the optical and electronic properties of the Cr^{4+} (d^2) ion in four-fold coordination have been extensively investigated ([1–4] and references therein), the archival literature is lacking in the experimental and theoretical data pertaining to the optical properties of this ion in six-fold coordination. In the pyrochlores, $Y_2Ti_2O_7$ and $Y_2Sn_2O_7$, the Cr^{4+} ion substitutes for the tetravalent Ti^{4+} and Sn^{4+} ions that occur in a six-fold coordination of oxygen ions (trigonal antiprism) [5]. Therefore, the pyrochlore lattice provides us with a unique opportunity of investigating the optical properties of the Cr^{4+} ion in a six-fold coordination (it is well-known that Cr^{4+} in a vast majority of cases are found in crystals in the 4-fold tetrahedral coordination).

Analysis of the optical data of Cr^{4+} activated $Y_2B_2O_7$ ($B=Sn^{4+}$, Ti^{4+}) shows that: (1) the average cubic crystal field splitting (10*Dq*) of the six-fold coordinated Cr^{4+} ion is larger in $Y_2Sn_2O_7$ than in $Y_2Ti_2O_7$ [Dq ($Y_2Sn_2O_7$; 1971–1984 cm^{-1}) > Dq ($Y_2Ti_2O_7$; 1827–1973 cm^{-1})] and (2) the Cr^{4+}–O^{2-} bond is slightly more covalent in $Y_2Sn_2O_7$ [5]. These results are in variance with the expectation of the electrostatic model of crystal field since the Cr^{4+}–O^{2-} bond distances in $Y_2Ti_2O_7$ and $Y_2Sn_2O_7$ are 194 and 203.5 pm, respectively [5]. The qualitative explanation advanced in Refs. [6,7] associated the reduced crystal field in $Y_2Ti_2O_7$ relative to $Y_2Sn_2O_7$ to the electronic configurations of the Ti^{4+} {[Ar]$3d^0$} and Sn^{4+} {[Kr]$4d^{10}$}ions. In the crystal structure of pyrochlores, the Ti^{4+}/Sn^{4+} ions are present in a six-fold coordination of oxygen ions that occupy the 48f crystallographic position of the pyrochlore lattice (O^{2-}_{48f}). Here and in what follows the notations of the crystallographic sites correspond to the standard symbols from International Tables of Crystallography. The overlapping of the empty $3d^0$ orbital of the Ti^{4+} ion with the filled O^{2-}_{48f} 2p orbital induces electron sharing (covalent bonding) whereas the Sn^{4+} ion does not participate in such chemical bonding due to its filled $4d^{10}$ orbital [8,9]. The transfer of charge out of the O^{2-}_{48f} 2p orbital to the Ti^{4+} $3d^0$ orbital polarizes the O^{2-}_{48f} electron density away from the luminescent ion site. The resulting increase in the distance between the Cr^{4+} ion and the center of charge density on the O^{2-}_{48f} anion is responsible for the reduced crystal field strength at the Cr^{4+} center in $Y_2Ti_2O_7$ [6,7]. This bonding difference also explains the slightly higher covalence of the Cr^{4+}–O^{2-} bond in $Y_2Sn_2O_7$ relative to that in $Y_2Ti_2O_7$.

The goal of this paper is to provide a quantitative elucidation of the optical properties of Cr^{4+} doped $Y_2B_2O_7$ ($B=Sn^{4+}$, Ti^{4+}) spectra. This is achieved by determination of energy levels of the Cr^{4+} ion in both crystals and by performing detailed analysis of the effects of chemical bonding on the crystal field. The Cr^{4+}

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energy levels were obtained by diagonalization of the crystal field Hamiltonian in the space of all wave functions of the Cr^{4+} $3d^2$-electron configuration. To the best of our knowledge, the present paper represents the first consistent crystal field analysis of optical properties of the Cr^{4+} ion in these pyrochlores.

2. Crystal structure of $Y_2Ti_2O_7$ and $Y_2Sn_2O_7$

The cubic pyrochlore structure, with the chemical formula $A_2B_2O_7$ (space group Fd-3m; $Z=8$) can be considered to be derived from the fluorite structure (CaF_2) by removing one-eighth of the anions so that the composition can be written as $A_2B_2O_7V_a$ where V_a is the anion vacancy [10,11]. In the pyrochlore structure there are two types of oxygen ions: the oxygen ions on the 48f site (O^{2-}_{48f}), which are bonded tetrahedrally to two A and two B ions and the oxygen ions on the 8b sites (O^{2-}_{8b}) that are bonded tetrahedrally to four A ions (see Fig. 1). The large A-ions, occupying the 16d site, are coordinated to eight oxygen ions. The coordination, which can be described as a scalenohedron contains two O^{2-}_{8b} ions at very short distance and six O^{2-}_{48f} ions at longer distance. The small B-ions occupy the 16c site and are coordinated to six oxygen ions forming trigonal antiprism. The two pyrochlores under investigation crystallize in the cubic structure, with lattice parameter $a=10.0896$ for $Y_2Ti_2O_7$ [12] and $a=10.3723$ Å for $Y_2Sn_2O_7$ [13].

3. Method of calculations

The energy levels of impurity ions with an unfilled d-shell (in our case, Cr^{4+} ion with $3d^2$ electron configuration) in a crystal field of arbitrary symmetry can be represented by eigenvalues of the following CF Hamiltonian ([14], or any standard book on crystal field theory)

$$H=\sum_{p=2,\,4}\sum_{k=-p}^{p} B_p^k O_p^k, \tag{1}$$

where O_p^k are the suitably chosen linear combinations of the irreducible tensor operators acting on the angular parts of the impurity ion's wave functions (exact definition of the operators used in the exchange charge model (ECM) can be found in [14]; in fact, the operators O_p^k correspond to the extended Stevens operators [15,16]), and B_p^k are the crystal field parameters (CFPs), which can be calculated from the crystal structure data and thus, in general, they include all the structural and geometrical informations about the host lattice and in particular reflect in a certain sense arrangement of the host lattice ions around the impurity site. The Hamiltonian (1) is defined in the space spanned by all wave functions of the free ion's LS terms (which arise due to the Coulomb interaction between electrons of an impurity ion). In the ECM, the CFPs are written as a sum of two terms [14]

$$B_p^k = B_{p,\,q}^k + B_{p,\,S}^k, \tag{2}$$

where the first term

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta_i,\varphi_i)}{R_i^{\,p+1}}, \tag{3}$$

is the point charge contribution to the CFPs, which arises from the electrostatic interaction between the central ion and the lattice ions enumerated by index i with charges q_i and spherical coordinates, R_i, θ_i, φ_i (with the reference system centered at the impurity ion itself). The averaged values $\langle r^p \rangle$, where r is the radial coordinate of the d electrons of the optical center, can be obtained either from the literature or calculated numerically, using the radial parts of the corresponding ion's wave functions. The values of the numerical factors K_p^k,γ_p (the latter appears in Eq. (4)), the expressions for the polynomials V_p^k and the definitions of the operators O_p^k can all be found in Ref. [14] and thus are not shown here for the sake of brevity. The second term of Eq. (2) is proportional to the overlap between the wave functions of the central ion and ligands and thus includes all covalent effects. It can be calculated using the following equation:

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i \left(G_s S(s)_i^{\,2} + G_\sigma S(\sigma)_i^{\,2} + \gamma_p G_\pi S(\pi)_i^{\,2} \right) \frac{V_p^k(\theta_i,\varphi_i)}{R_i}, \tag{4}$$

with $S(s)$, $S(\sigma)$, $S(\pi)$ corresponding to the overlap integrals between the d-functions of the central ion and p- and s-functions of the ligands: $S(s)=\langle d0|s0\rangle$, $S(\sigma)=\langle d0|p0\rangle$, $S(\pi)=\langle d1|p1\rangle$. The G_s, G_σ, G_π entries are dimensionless adjustable parameters of the model, whose values are determined from the positions of the first three absorption bands in the experimental spectrum. They can be approximated to a single value, i.e. $G_s=G_\sigma=G_\pi=G$, which then can be estimated from one absorption band only. This is usually a reasonable approximation [14].

The main advantages of the ECM are the following: (i) a small number of fitting parameters, (ii) opportunity to calculate the crystal field parameters and energy levels of impurities in crystals without invoking any assumptions about the impurity center symmetry, but by using only crystal structure data and (iii) the possibility to treat the covalent effects quantitatively (by calculating the overlap integrals).

ECM has been successfully applied for the calculations of energy level of rare earth ions ([14,17,18] and references therein) and transition metal ions ([19–23] and references therein).

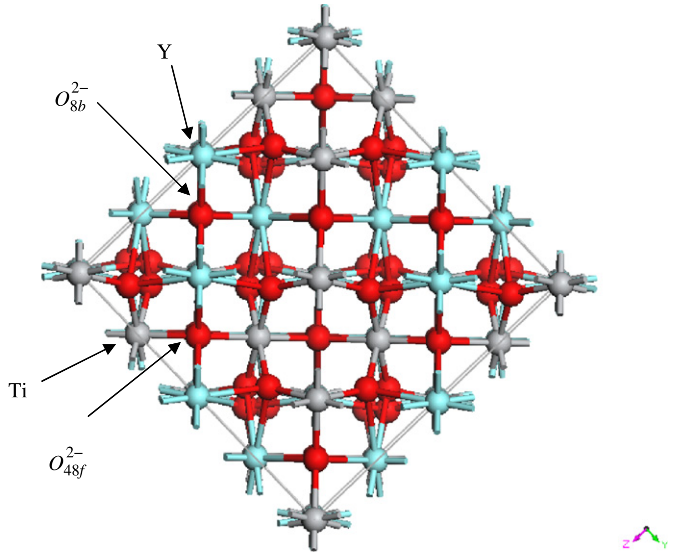

Fig. 1. A general view (from the a axis) of a unit cell of $Y_2Ti_2O_7$. The two different crystallographic positions of the oxygen ions are indicated. Crystal structure of $Y_2Sn_2O_7$ is identical and is not shown.

4. Results of calculations and discussion

Crystal structure data from Refs. [12,13] were used to calculate the CFPs values. The Cr^{4+}–O^{2-} overlap integrals needed for calculations of the exchange charge contribution to the CFPs were taken from Ref. [19]. To ensure proper convergence of the crystal lattice sums (especially for the second rank CFPs, which depend on interatomic