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RESEARCH ARTICLE



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Superposition model study of Cr³⁺ doped YGa₃(BO₃)₄

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ABSTRACT

Superposition model (SPM) is used to obtain zero field splitting (ZFS) parameters (ZFSPs) and crystal field parameters (CFPs). Two sites, namely substitutional and structural vacancy, for Cr^{3+} ion in YGa₃(BO₃)₄ (YGB) crystal in addition to distortion are considered. The calculated ZFSPs are in good agreement with the experimental values when distortion is taken into account. The optical energy levels for Cr^{3+} in YGB are computed using CFPs obtained from SPM and CFA package. The results indicate that Cr^{3+} ions enter YGB lattice at Ga^{3+} sites.

Keywords: Superposition model; Crystal field and zero-field splitting Hamiltonians; Optical spectroscopy; Cr³⁺ ions in YGB.

1. Introduction

Superposition model (SPM) is applicable in electron magnetic resonance (EMR) of transition ions in crystals as discussed earlier [1-2]. It gives semi-empirical modeling of the zero field splitting (ZFS) parameters (ZFSPs) in EMR [3-6] and the crystal field parameters (CFPs) in optical study [7-11]. Various Hamiltonians \mathcal{H}_{CF} , *physical* CF Hamiltonian; \mathcal{H}_{SH} , *effective* spin Hamiltonians (SH); \mathcal{H}_{ZFS} , ZFS Hamiltonian have been described in [12].

In this paper, we consider SPM/ZFS analysis to obtain ZFSPs of Cr^{3+} ions at orthorhombic sites in YGa₃(BO₃)₄ (YGB) crystal. Different distortion models have been considered to get most likely site of Cr^{3+} ions out of the substitutional and structural vacancy sites in YGB lattice. The optical energy levels for Cr^{3+} in YGB are determined using SPM/CF parameters and CFA package.

2. Crystal structure

X-ray diffraction analysis of 0.1 % Cr-doped YGa₃(BO₃)₄ (YGB) crystal shows that it crystallizes in the huntite [Mg₃Ca(CO₃)₄] structure with the space group R32. The crystals are hexagonal with unit cell parameters: a = 9.4490 Å, c = 7.4546 Å and Z = 3 [13, 14]. The coordination polyhedra of Y³⁺, Ga³⁺ and B³⁺, formed by oxygen ions, are trigonal prisms, octahedra and triangles, respectively. The Y³⁺ ions are located at the site of D₃ symmetry while Ga³⁺ ions are surrounded by six oxygen ions forming a distorted octahedron with a single symmetry element-C₂. The crystal structure of YGB is shown in Fig. 1. The local symmetry in YGB crystal is trigonal type I with the trigonal axis $C_3 ||c|/z$ - for Ga^{3+} sites. Due to doping of Cr³⁺ in YGB crystal, the site symmetry about Cr³⁺ions is lowered and may be considered to be approximately orthorhombic, as suggested by EMR spectra of Cr³⁺: YGB at room temperature [13, 14]. It should be noted that the reduction in symmetry from a trigonal point group takes to one of the monoclinic groups [15-18].



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Hence, orthorhombic site symmetry as a result of distortions of a trigonal ML_n complex is taken as an approximation of the actual site symmetry [15-18].

Since the crystallographic axis system (CAS), (a, b, c), is not Cartesian [13, 14], we take the modified crystallographic axis system CAS* (a, b^*, c) as shown in Fig. 1 (the axis *a* is perpendicular to *c* and *b**). A common axis system $(a/|x, b^*|/y, c/|z)$ is considered to simplify SPM/ZFS and SPM/CFs calculations.



Figure 1: Crystal structure of YGa₃(BO₃)₄.

The crystal structure data in spherical polar coordinates for the Cr^{3+} sites in YGB on the basis of fractional positions of ligands [14] are given in Table 1. These data are used for SPM/ZFS and SPM/CF calculations presented here for YGB: Cr^{3+} .

3. SPM calculations of ZFSPs

The energy levels of an orbital singlet ground state of transition ions doped in crystals are obtained by the spin Hamiltonian having electronic Zeeman (Ze) and ZFS terms [12, 19-22]:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{\text{Ze}} + \mathcal{H}_{\text{ZFS}} \\ &= \mu_B B.g.S + \sum B_k^q O_k^q = \mu_B B.g.S + \sum f_k b_k^q O_k^q \text{,(1)} \end{aligned}$$

where *g* is the spectroscopic splitting factor, μ_B is the Bohr magneton, **B** is the applied magnetic field , *S* is the effective spin operator and $O_k^q(S_x, S_y, S_z)$ are the extended Stevens operators (ESO) [23, 24]. B_k^q and b_k^q are the related ZFSPs, $f_k = 1/3$ and 1/60represent the scaling factors for k = 2 and 4, respectively. The ZFS terms in (1) for Cr³⁺ ion (*S* = 3/2) at orthorhombic symmetry sites are given as [12, 19-22]:

$$\mathcal{H}_{ZFS}$$

$$B_2^0 O_2^0 + B_2^2 O_2^2 = \frac{1}{3} b_2^0 O_2^0 + \frac{1}{3} b_2^2 O_2^2 = D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2),$$
(2)

The conventional orthorhombic ZFSPs (*D*, *E*) and (B_k^q , b_k^q) are related as:

$$b_2^0 = D = 3 B_2^0, b_2^2 = 3E = 3 B_2^2$$
 (3)

Using SPM [25-28], the ZFSPs for aML_n complex may be determined (in ESO notation) for any symmetry as [2]:

$$b_{k}^{q} = \sum_{i} \overline{b}_{k} \left(R_{0} \right) \left(\frac{R_{0}}{R_{i}} \right)^{t_{k}} K_{k}^{q} \left(\theta_{i}, \varphi_{i} \right), \qquad (4)$$

where (R_i, θ, φ) provide the spherical polar coordinates of the *i*-th ligand. The intrinsic parameters \overline{b}_k give the strength of the *k*-th rank ZFS contribution from a ligand positioned at the distance R_i , while the coordination factors K_k^q provide the geometrical information. K_k^q withk = 1to 6 in the ESO notation found in [29] are relisted in Appendix A1 of [2]. The distance dependence of the intrinsic parameters for aMLn complex is given below in (5) [2, 25-28], where t_k are the power-law exponents and R_0 is the reference distance [2, 30-33].

Eq. (4) gives conventional ZFSPs, D and E as follows [2]:

$$b_{2}^{0} = D = \frac{\overline{b}_{2}(R_{0})}{2} \left[\left(\frac{R_{0}}{R_{i}} \right)^{t_{2}} \sum_{i} (3\cos^{2}\theta_{i} - 1) \right]$$
(5)
$$b_{2}^{2} = 3E = \frac{b_{2}^{2}}{3} = \frac{\overline{b}_{2}(R_{0})}{2} \left[\left(\frac{R_{0}}{R_{i}} \right)^{t_{2}} \sum_{i} \sin^{2}\theta_{i} \cos 2\varphi_{i} \right]$$

Cr³⁺ ion in YGB can be considered to enter the lattice at substitutional site, the Ga³⁺ ion site, and the structural vacancy site with similar ligand arrangementt. The local symmetry at Cr³⁺ ion site is taken to be approximately orthorhombic. In octahedral coordination of Cr³⁺ ion for LiNbO₃ having Cr³⁺-O²⁻ bond, $\bar{b}_2(R_0) = 2.34$ cm⁻¹ and t₂ = -0.12 [34] have been used to calculate b_2^0 and b_2^2 . As Cr³⁺ ion in YGB has distorted octahedral



coordination (Fig.1) with oxygen ligands, the b_K^q in the present study are calculated using the parameters $\bar{b}_2(R_0) = 2.34$ cm⁻¹ and t₂ = -1.697.

The location of metal ion and spherical coordinates of ligands given in Table 1 are used for calculation. The conventional ZFSPs, D and E of Cr³⁺ ion in YGB crystal are determined using (5). The reference distance of 0.112 nm was taken for the determination of ZFSPs [35], and the obtained values of conventional ZFSPs are |D| = 0.4649cm⁻¹ and |E| = 0.0983 cm⁻¹. The ratio b_2^2 / b_2^0 should be within the range (0, 1) for orthorhombic symmetry [36]. In this study,the ratio $|b_2^2| / |b_2^0| = 0.634$ and |E| / |D| = 0.211, which is in agreement with

above for b_2^2 / b_2^0 . However, the value of |E| is not in agreement with the experimental value. Therefore, using above values of t₂ and reference distance, the ZFSPs |D| and |E| are calculated for Cr³⁺ at the Ga³⁺ site with distortion having position Ga³⁺(0.5505, 0.4140, -0.0727).The calculated conventional ZFSPs now are $|D| = 0.4650 \text{ cm}^{-1}$, |E|= 0.0129cm⁻¹, which are in good agreement with the experimental values. The ratio $\mid b_{2}^{2} \mid / \mid b_{2}^{0} \mid$ = 0.083 and |E| / |D| = 0.028 which is consistent with above range [36]. Further using above values of t₂ and reference distance, the conventional ZFSPs |D| and |E| are calculated for Cr^{3+} at thestructural vacancy site but the values found are quite different from the experimental ones. Hence, these data are not being presented here.

Position of Cr^{3+} $R^{A}\vartheta^{0}\phi^{0}$	Ligands	Spherical co-ordinates of ligands			
ND: Substitutional	O(1)	4.7596	38.4	0	
(0.5505, 0, 0)	O(2)	3.7424	5.2	0	
	O(3)	4.2862	27.7	-54.6	
	O(4)	6.3992	54.4	0	
	O(5)	6.3992	54.4	0	
	O(6)	6.4376	53.9	0	

Table 1. Fractional coordinates of Cr^{3+} ion and spherical co-ordinates (R, θ , ϕ) of ligands in YGB crystal.

The calculated and experimental ZFSPs for Cr³⁺ ion are given in Table 2. From Table 2, it is noted that the conventional ZFSPs are in good agreement

with the experimental values [14] when the distortion is taken into account.

Table 2: Calculated and experimental ZFSPs of Cr³⁺ doped YGB single crystal together with reference distance.

		Calculated ZFS parameters (cm ⁻¹)	Conventional ZFS parameters (cm ⁻¹)			
Ro ^Å		$ b_2^0 $ $ b_2^2 $ $ b_2^2 / b_2^0 $	D E E / D			
ND	1.12	0.4649 0.2949 0.634	0.4649 0.0983 0.211			
		0.4650^{e} 0.0130^{e} 0.028				
WD	1.12	0.4650 0.0388 0.083	0.4650 0.0129 0.028			
		0.4650^{e} 0.0130^{e} 0.028				

ND = No distortion, WD = With distortion, $Ga^{3+}(0.5505, 0.4140, -0.0727)$ ^e = experimental.

4. SPM calculations of CFPs

The CF energy levels of transition ions in crystals [37-40], in terms of CF Hamiltonian $\mathcal{H}_{\it CF}$ [7-

11], using Wybourne operators [7,12], are expressed as:



$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^{(k)} \tag{6}$$

Using SPM [25-28], the CFPs in (6) for aML_n complex can be found for any symmetry as:

$$B_{kq} = \sum_{i} \overline{A}_{k} \left(\frac{R_{0}}{R_{i}}\right)^{t_{k}} K_{kq}\left(\theta_{i}, \varphi_{i}\right).$$
(7)

where R_0 is the reference distance for the site; R_i , θ_i , ϕ_i are the polar coordinates of the ith ligand and K_{kq} are the coordination factors [37]. To obtain B_{kq} (k =

2, 4; q = 0, 2, 4), we take.
$$A_2$$
 = 40, 400 cm⁻¹, t₂ = 1.3,

 A_4 = 11, 700 cm⁻¹ and t₄ = 3.4 from [37]. The calculated B_{kq} parameters are shown in Table 3. The ratio B₂₂/B₂₀ = -0.069, which indicates that B_{kq} parameters are standardized [36]. With the help of these B_{kq} parameters and CFA program [38, 39], the

CF energy levels of Cr³⁺ doped YGB crystals are determined. The energy levels of Cr³⁺ ion are computed by diagonalizing the complete Hamiltonian including the Coulomb interaction (in terms of the Racah parameters B and C), Trees correction, the spin-orbit interaction, the crystal field Hamiltonian, the spin-spin interaction and the spin-other orbit interaction. The computed energy values are given in Table 4. As optical study report on Cr³⁺: YGB could not be found in literature, the experimental energy values for isomorphous system Cr³⁺: YAB [41] are shown here for comparison. From Table 4, it is found that there is reasonable agreement between theoretical and experimental band position values. Thus the theoretical investigation of Cr³⁺ entering YGB lattice at Ga³⁺ sites supports the experimental conclusion [14].

Table 3. B_{kq} parameters of Cr³⁺ doped YGB single crystal.

Calculated B_{kq}^{cm-1} Parameters used for CFA package $R_0^{A}B_{20}B_{22}B_{40}B_{42}B_{44B22/B20}$							
WD	WD 1.12 6827.218 -472.762 -57.6591 -202.282 -298.018 -0.069						
WD = With distortion.							

Table 4: Experimental and calculated (CFA package) energy band positions of Cr³⁺ doped YGB single crystal.

Transition from ⁴ A _{2g} (F)	Experimentally observed band (cm ⁻¹) [41]	Calculated energy band from CFA (cm ⁻¹)
² Fa(G)	14641 14695	14170 14187
$^{2}T_{1}q(G)$	15275, 15321, 15375	14227, 14265, 14370
$^{4}T_{2}g(F)$	16950	16050, 16394, 16819,
² T ₂ g(H)	20846	18425, 18631, 18810
⁴ T₁g(F)	23750	25363, 25610, 26461,
		26685, 27193, 27327
² T1g(aD) ² Eg(bD)		38362, 38437, 41540 41958, 42673

(Racah parameters in A, B and C, spin-orbit coupling constant and Trees correction are 0, 681, 2724 (= 4B), 276 and 70 cm⁻¹, respectively)



5. Summary and Conclusions

The zero-field splitting (ZFS) parameters (ZFSPs) and the crystal field (CF) parameters (CFPs) are determined using superposition model (SPM) for Cr³⁺ ions in YGa₃(BO₃)₄ (YGB) single crystals. Cr³⁺ ions entering the YGB lattice at Ga³⁺ ion sites, structural vacancy site and distortion models are considered. The computed conventional ZFSPs for Cr³⁺ ion at Ga³⁺ sites in YGB crystal are in good agreement with the experimental values when distortion is taken into consideration. It is inferred that the Cr³⁺ ions enter the lattice substitutionally by replacing Ga³⁺ ions. The CF energy levels for Cr³⁺ ions at Ga³⁺ sites determined using CFA package and CFPs are in reasonable agreement with the experimental energy values. Thus the theoretical results support the inference drawn from the experimental investigation.

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