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Solid State Reactions and Defects in Verneuil Laser Rubies II by P. Ballmer¹), H. Blum, W. J. Borer²), K. Eigenmann and Hs. H. Günthard

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(10. VI. 70)

Abstract. Results of new computations of crystal field spectra of Cr^{+3} in the interstitial site of the α -Al₂O₃ structure are presented. The results are used to support an assignment of the absorption band at 315 nm ascribed to a typical defect in Verneuil grown laser rubies.

1. Introduction

In a recent paper, W. Borer et al. [1] reported crystal field analysis results of a defect observed in Verneuil laser rubies. This defect is characterized by an absorption band near 315 nm and has been assigned to transitions between crystal field levels of Cr^{+3} at the interstitial site b in the α -Al₂O₃ structure [2]. In the meantime extensive crystal field calculations for transition metal ions have been made at this laboratory, based on α -Al₂O₃ crystal structure data given by Newnham [3], whereas earlier calculations were based on data published by Pauling et al. [4]. The use of the newer data led to significant changes of the crystal constants c_{lm} at sites b, c and e. In this paper we wish to report the corrected values for this constants and the energy levels for Cr^{+3} at site b.

2. Calculation of Crystal Field Constants

Using the same assumptions for the calculation of the crystal field parameters c_{lm} as in *I*, but basing on Newnhams crystal structure data for α -Al₂O₃, the results collected in Table I are obtained. With respect to the crystallographic data it should be mentionned, that Newnham's data were first transformed to rhombohedral axes³). In these axes system the structural parameters for α -Al₂O₃ are⁴)

 $a = 5.128 \pm 0.0034$ Å, $\alpha = 55^{\circ}17' \pm 3'8''$.

- ²) Present address: Dept. of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881, USA.
- ³) Loc. cit. [2], p. 20, c.f. Figure 2.5.3.
- 4) Error derived from Newnham's data.

¹) Address: Djévahirdjian S.A., Monthey, Switzerland.

The following remarks concerning the crystal field coefficients listed in Table I seem to be in order

- the coefficients $c_{0,0}$ are uncertain to the limits given owing to the well known convergence difficulties for the unipole terms,

the coefficients $c_{+4,-3}$, $c_{4,3}$ of sites b and c and $c_{1,\pm 1}$, $c_{2,\pm 2}$ of site e show considerable differences to earlier published values⁵). In part the discrepancies originate from the new crystallographic data in part from the change in phase of the angle φ originating from the new choice of crystallographic axis and in part however from errors in the earlier computations. Since all coefficients c_{lm} , $m \neq 0$, depend on the choice of phase of the angle φ , the choice adapted for this paper is shown in Figure 1.

Table I

Lattice potentials	at	the	various	sites	of	the	corundum	structure.
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Site	Rhombohedral coordinates	l	т	Coefficient real part	c _{lm} ^{a)b)c}) imag. part
		0	0 ^d)	-8.628 ± 0.009	0
		2	0	0.06717	0
С	-0.148, -0.148, -0.148	4	- 3	+0.235078	0.044656
		4	0	0.188189	0
		4	+ 3	-0.235078	0.044656
		0	0 d)	-0.349 ± 0.008	0
		2	0	0.91569	0
b	0, 0, 0	4	- 3	-0.2044556	-0.05278977
		4	0	0.463771	0
		4	+ 3	0.2044556	-0.05278977
		0	0 d)	6.878 ± 0.009	0
		1	-1	-0.07824	0
		1	0	0	0
		1	+1	+0.07824	0
е	0.055998, -0.555998, 0.250001	2	-2	+0.0759626	0
		2	-1	0	-0.475755
		2	0	0.0743679	0
		2	+1	0	-0.475755
		2	+ 2	0.0759626	0

^a) c_{lm} are the coefficients of the expansion $V(r, \vartheta, \varphi) = e_0 \sum_{l,m} c_{lm} r^l Y_l^m(\vartheta, \varphi)$ for the lattice potential. Their dimension is Å^{-(l+1)}.

^b) Only those coefficients are given, which are necessary for a certain site symmetry and a certain electron configuration.

c) The lattice sums were carried out over a nearly spherical region of 50 Å radius.

^d) The confidence interval given in this table for c_{00} represents the standard deviation of the constant calculated for twenty statistically selected values of r within 47.5 and 50 Å.

3. Crystal Field Energy Levels of Cr⁺³ in the Interstitial Site b

Using the same technique for the computation of the crystal field levels as in I the results shown graphically in Figure 2 are obtained. Only few comments should be made

⁵) Loc. cit. [1], Table 6.

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Figure 1

Rhombohedral unit cell of α -Al₂O₃. The definitions of the spherical coordinates used in this work are given. Notation of sites is as given in Ref. [2].

- (i) the general pattern of the crystal field levels shows marked differences to that obtained in I,
- (ii) the newly obtained levels fulfil the Kramers degeneracy to within better 0.1 cm^{-1} . In I much larger discrepancies were obtained.

4. Assignment of the Defect Absorption Bands

Basing on Figure 2, the absorption band of the defect near $315 \text{ nm} (31750 \text{ cm}^{-1})$ may be related to the transitions collected in Table 2.

Energy of level [cm ⁻¹] ^a)	Assignment to free ion levels						
33042.2	4F - 4P		anner i anna an e				
33138.9	4 F - 4 P						
33237.1	4 F - 4 P						
33336.8	4 F - 4 P						

Table 2 Calculated transitions in the UV/VIS region, which explain the observed $315 \text{ nm band} [31746 \text{ cm}^{-1}]$

^a) Every level is doubly degenerate, according to Kramers theorem.

The results may be commented upon as follows:

- (i) the transitions assigned are both symmetry and spin allowed (in the free ion picture),
- (ii) the assignment proposed in I is not changed by the newly calculated crystal field levels for $Cr^{+3}(b)$.



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