

## Cr<sup>3+</sup> Luminescent centers in BeAl<sub>6</sub>O<sub>10</sub> crystal

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**Abstract** - The fluorescence emission spectrum of Cr<sup>3+</sup> doped BeAl<sub>6</sub>O<sub>10</sub> crystals at 300 K contains a broad band, three R-like lines and another emission lines. It has been identified by a lifetime resolution spectroscopic technique that there are three kinds of single-Cr<sup>3+</sup> centers, Cr(I), Cr(II), Cr(III), in this crystal. Cr(I) and Cr(II) are high-crystal field centers responsible for the three main "R-lines", and Cr(III) is a low-crystal field center responsible for the main broad band emission. The structures of these luminescent centers are reported.

**Keywords** - Luminescent centers, Cr<sup>3+</sup> ions, Low-crystal field, BeAl<sub>6</sub>O<sub>10</sub> (BHA) crystal

### 1. Introduction

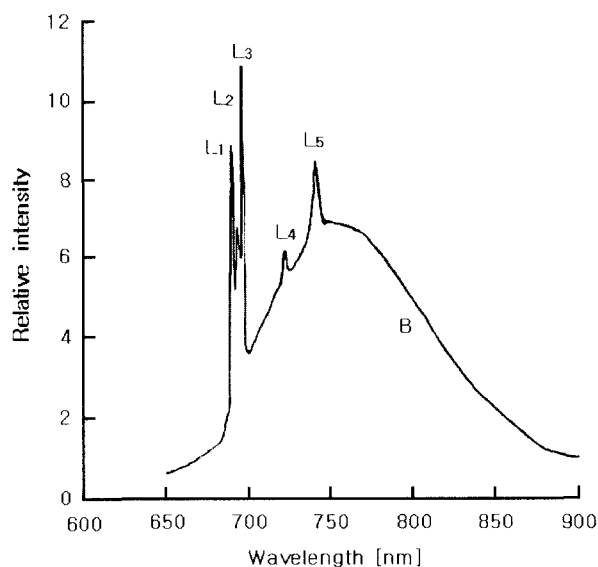
Trivalent chromium ions in crystals have been widely studied for theory of the transition-metal ion and laser applications<sup>[1]</sup>. The luminescence spectra of Cr<sup>3+</sup> ions in crystals may be narrow emission lines and their side-band, such as in ruby, or broad vibronic band, such as in LiCaAlF<sub>6</sub><sup>[2]</sup>, KZnF<sub>3</sub>, MgO, and GSGG<sup>[3]</sup>, that depends on the crystal field strength interactive with the chromium ions. For an intermediate crystal field strength, such as in Alexandrite crystals, the luminescence spectrum mainly consists of double R-lines and a broad band, which come from same mirror-centers and have the same fluorescence lifetime at room temperature<sup>[4]</sup>. Sometimes, different and distinctive Cr<sup>3+</sup>-centers (multi centers) exist simultaneously in a material and together contribute to the main feature of luminescence. In case of multi centers, the fluorescence properties may be more complex due to different properties of the centers. An instance of multi centers is MgO: Cr<sup>3+</sup>, in which exists simultaneously a high-field Cr center and a low-field Cr center.

Cr<sup>3+</sup>-doped beryllium hexa-aluminate crystal (Formula BeAl<sub>6</sub>O<sub>10</sub>:Cr<sup>3+</sup>, abbr. BHA:Cr<sup>3+</sup>) is a promising tunable laser material. Owing to the limitation of toxicity of the raw material (BeO powder), few laboratories in the world synthesized the single crystals as samples. It was reported that these crystal samples have complex luminescence feature with characteristic three R-like lines and a broad emission band, also two N-like lines<sup>[5]</sup>. This is obviously a multi-center feature. In this paper we report the origin of these spectral components and the structure of the luminescent Cr-centers in BHA crystal.

### 2. Experiment and results

The BHA:Cr<sup>3+</sup> crystals were congruently grown with Czochralski method in an airtight single furnace in china, using Al<sub>2</sub>O<sub>3</sub> ( 99.99 % purity ) and BeO ( 99.9 % ) raw materials. Cr<sub>2</sub>O<sub>3</sub> concentration of the samples in the experiment is about 0.1wt%. The single crystal samples were processed in size of 4 x 5 x 8 (mm). Crystalline structure analysis of our BHA:Cr sample has been carried out on a four-element diffractometer and the data used for discussing the structures of luminescent centers.

Several experimental methods can be used for identification of the fluorescence spectra of multi centers materials. The first method is selective excitation technology. In case of BHA:Cr, however, due to total overlap of excitation spectra of the Cr<sup>3+</sup> centers, the luminescence spectrum still can not be obviously identified by the selective excitation technology. The most of the spectral components still present under selective excitation and only the relative intensities of the spectral components change. The second method, time-resolution spectroscopic technology, is a powerful tool in multi center study. For information about all luminescent centers in BHA:Cr, the time-resolution measurement needs a widely wavelength-tunable and intensity-switched laser (like as OPO laser) and a Boxcar with very long time gate of  $\mu$ S~mS, because of the very different excitation wavelength and fluorescence lifetime of the multi centers. These conditions are inconvenient for our laboratory. In our experiment, another simple time-resolution method for multi center study, so-called "Chrono spectroscopic technique"( a lifetime-resolution spectroscopic technique )<sup>[6,7]</sup> was employed. The measuring equipment used in this technique is ordinary, which includes an excitation light source (500 watts xenon lamp), an optical chopper, 0.5 m grating monochromator, PMT detector and a lock-in amplifier. Since the chopper speed is perfectly suitable for the fluorescence lifetimes of BHA:Cr, excellent experimental results have been obtained. Fig. 1 shows the total luminescence spectrum of BHA:Cr crystal

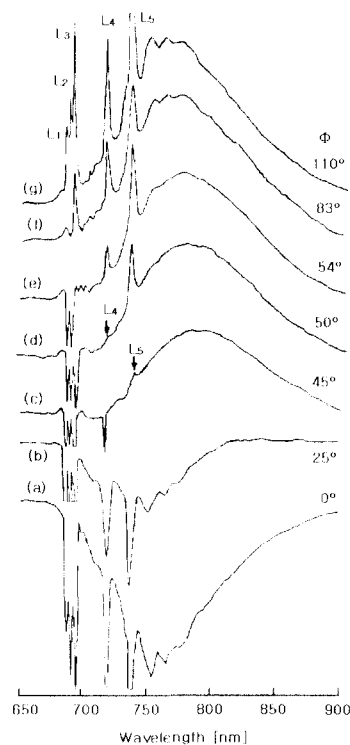


**Fig. 1** Total luminescence spectrum of BHA: 0.1 wt % Cr sample, 300 k

at room temperature under excitation of the xenon lamp light of 350 nm~650 nm through a  $\text{CuSO}_4$  solution filter. This spectrum was obtained as the chopper was placed near the entrance slit of the monochromator, resulting in less dependence on the luminescence lifetimes of the multi centers. The main feature of the luminescence in Fig.1 is characterized as three R-like lines ( $L_1$ ,  $L_2$ ,  $L_3$ ), two additional lines ( $L_4$ ,  $L_5$ ) and a broad band (B). At lower temperature some weaker emission lines appear. The three R-like lines imply there are multi  $\text{Cr}^{3+}$ -centers in BHA:Cr crystal.

The lifetime-resolved measurement results (Chrono results) of BHA:Cr at 80 K are shown in Fig. 2 and Table 1. For these measurements, the chopper was placed between the excitation source and the sample to modulate the excitation light. Therefore, the fluorescence was also modulated indirectly with some phase delay. Because the phase delay is different for the different luminescent center with different fluorescence lifetime, several spectral components disappeared from the measured luminescence spectrum as the lock-in phase of the amplifier was adjusted to a certain phase angle, that called the "null point phase" of the disappeared spectral components. The spectral components with the same null point possibly came from same kind of Cr centers.

The curve (b) in Fig. 2 was obtained at  $25^\circ$  null point where the broad emission band (B) disappeared, and  $L_{1,2,3,4,5}$  lines along with their side-band still existed ( in counter-phase ). This implied that the broad band (B) alone could be contributed to one kind of centers. At  $45^\circ$  and  $50^\circ$ , respectively,  $L_5$  and  $L_4$  disappeared at their own null points, as shown in Fig. 2, (c) and (d). Fortunately, the three "R-like lines",  $L_1$ ,  $L_2$ ,  $L_3$ , had very different null points in the Chrono results:  $L_3$  disappeared alone at  $54^\circ$  ( Fig. 2, (e) ), and  $L_1$  and  $L_2$  simultaneously disappeared at  $83^\circ$  ( Fig. 2,(f) ).



**Fig. 2** Lifetime-resolved luminescence spectra of BHA:0.1 wt % Cr at 80 K, Chopper frequency 69,9 Hz, null point phase angles given relatively to an arbitrary zero.

**Table 1** Lifetime-resolved experimental results of BHA: 0.1 wt % Cr at 80 K, null point phase angle  $\Phi$  in degree, peak wavelength  $\lambda$  in nm

Emission	$\lambda$ (nm)	$\Phi$ (deg)	Cr-center
Band	790.0	$25 \pm 1$	Cr(III)
$L_5$	735.3	$45 \pm 0.5$	$N_5$
$L_4$	716.3	$50 \pm 0.5$	$N_4$
	712.0	$65 \pm 1$	
	709.7	$57 \pm 1$	
	701.8	$25 \pm 0.5$	
$L_3$	693.0	$54 \pm 0.5$	Cr(II)
$L_2$	690.0	$83 \pm 0.5$	Cr(I)
$L_1$	687.5	$83 \pm 0.5$	Cr(I)

Thus, we can identify the different luminescent centers in BHA:Cr, labeled as Cr(I), Cr(II) Cr(III),  $N_4$  and  $N_5$  as following:

- Cr(I) center: a high-field  $\text{Cr}^{3+}$ -center ( a  $\text{Cr}^{3+}$  ion at a high crystalline field ) giving rise to  $L_1$ ,  $L_2$  (double R-lines);
- Cr(II) center: another high-field  $\text{Cr}^{3+}$ -center giving rise to  $L_3$  (single R-line);
- Cr(III) center: a low-field  $\text{Cr}^{3+}$ -center giving rise to the broad band emission;
- $N_4$  center: giving rise to the  $L_4$  emission line;

- N<sub>5</sub> center: giving rise to the L<sub>5</sub> emission line;

Some of weaker emission lines measured at 80 K also were given in Table 1.

### 3. Structure of the luminescent centers

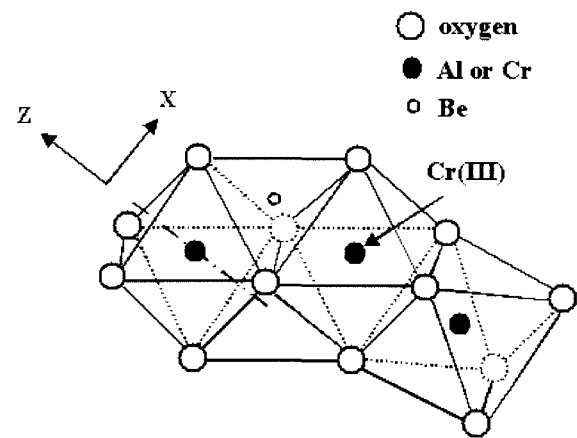
BHA crystal belongs to the orthorhombic crystal system, C<sub>2v</sub><sup>5</sup> space group. Each unit cell contains 8 BeAl<sub>6</sub>O<sub>10</sub> molecules, i.e. 80 oxygen ions, 8 Be<sup>2+</sup> ions and 48 Al<sup>3+</sup> ions. The Al-O octahedron parameters were obtained and listed in Table 2, based on the crystal structure data of our BHA:Cr sample analyzed on a four-element diffractometer. 40 Al<sup>3+</sup> sites of one unit cell are occupied by Al<sup>3+</sup> ions or possibly by Cr<sup>3+</sup> ions. Other 8 Al<sup>3+</sup> sites of Al (7) and Al (8) are not listed as they are tetrahedron Al<sup>3+</sup> sites. The 40 octahedron Al<sup>3+</sup> sites can be divided into 4 x 10 distortion manners with different Al-O bond length and O-Al-O bond angle distortion. Table 2 gives the average length  $l_{av}$  of the six Al-O bonds in each octahedron, the bond length difference  $\Delta l$  of the longest bond and the shortest bond, and the angle difference  $\Delta\alpha$  of the maximum and the minimum O-Al-O bond angles. As seen in the table, ahead 24 Al octahedrons of 4 x Al (1)~Al (6) have an average bond length distortion of  $\Delta l = 0.18 \text{ \AA}$  and bond angle distortion of  $\Delta\alpha = 12.8^\circ$ , compared respectively to only 0.07A and 2.5° for other eight Al (9) and Al (10) octahedrons. Therefore, for all practical purposes, Al(9) and Al(10) are two regular octahedrons. The last eight sites of Al (11) and Al (12) have special structure. As seen in Fig.3, they share a common face with the Be-O (or Al-O) tetrahedron, so that here the Be-Cr (or Al-Cr) distance is short of 1.6 Å ~ 1.7 Å. It is believed that the Cr(III) center is at Al (11) or Al (12) sites which adjoin Be ions. Due to the influence of Be<sup>2+</sup> at near distance, the crystalline field in these octahedron sites has been weakened on a grand scale, although oxide crystals generally have high-field. Meanwhile, Al (1) ~ Al (6) and Al (9) ~ Al (10) can form two ordinary Cr<sup>3+</sup> centers labeled

**Table 2** The structural data of the Al<sup>3+</sup> octahedrons in BHA:Cr crystal

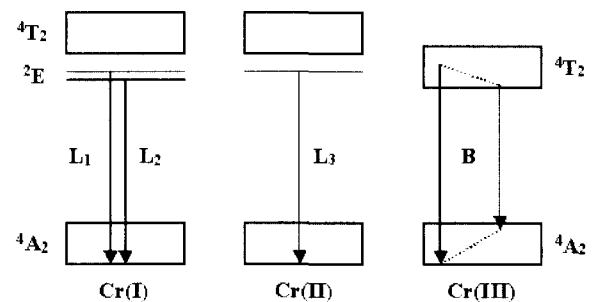
Al <sup>3+</sup>	Al-O		O-Al-O	Cr-center
	$l_{av}$ (Å)	$\Delta l$ (Å)	$\Delta\alpha$ (deg)	
4 Al (1)	2.02	0.25	16	Cr(I)
4 Al (2)	1.96	0.13	13	
4 Al (3)	2.00	0.17	13	
4 Al (4)	2.00	0.18	13	
4 Al (5)	2.00	0.19	10	
4 Al (6)	2.05	0.20	12	
4 Al (9)	1.92	0.06	3	Cr(II)
4 Al (10)	1.93	0.08	2	
2 Al (11)	1.96	0.28	6	Cr(III)
2 Al (11)	1.94	0.33	13	
2 Al (12)	1.93	0.38	10	
2 Al (12)	1.97	0.24	7	

here as Cr(I) centers and Cr(II) centers, respectively. The former is the distorted octahedron site with lower site-symmetry than symmetry O<sub>h</sub> resulting in double R-line emission of the Cr(I) center in the high-field. The latter has O<sub>h</sub> symmetry without essential energy level split, and giving rise to an unresolved R-line. Fig. 4 shows a schematic diagram of the energy levels and emission transitions of these luminescent centers.

As shown in Fig. 1 and Fig. 2(g), the relative intensity of L<sub>1</sub>/L<sub>2</sub> of the double R-lines varies exponentially with temperature of the sample. This is also an evidence of their coming from the same center.



**Fig. 3** The structure of Cr(III) center.



**Fig. 4** Schematic diagram of the luminescence origin

### 4. Discussion and conclusion

As seen in Table 2, there is an outward contradiction in the arrangement of Cr(I) and Cr(II). L<sub>1,2</sub> lines of Cr(I) are at somewhat higher energy than L<sub>3</sub> of Cr(II), but Cr(I) has been arranged to the larger octahedron sites of Al(1) ~ Al(6), where seems to be a lower crystalline field than that of Cr(II). Our argument is that the crystalline field strength in great degree also depends on the shortest bond length and the bond angle distortion in the octahedron. As demonstrated by the calculation of D<sub>q</sub>, even a small shift of 0.1 Å of the metal ion can result in D<sub>q</sub>'s variance<sup>[8]</sup>. Therefore, the field of Al (1~6) sites must not be lower than that of Al(9,10) sites. We also did not intend to arrange the Cr(I)

to the Al(11) and Al(12) positions because, in its special structure, the crystalline field may be much lower due to effect of the next-nearest cations ( tetrahedral Be or Al).

The crystal structure allows formation nearest Cr(I)-Cr(I), Cr(I)-Cr(II), even Cr(I)-Cr(III) interchange-coupled ion pairs because some Al octahedrons and tetrahedrons in the unit cell share common edge or face with decrease of Al-Al distance (about 2.8 Å). In an energy scale, the Cr-pair emission line (N-line) should be in the lower energy direction of R-line due to interchange-coupling interaction. It is possible that the main lines  $L_4$  and  $L_5$  belong to Cr-pairs and should vanish at low Cr concentration.

The assignment of Cr(III) seems reasonable. The electron affinity of Be ion often affects seriously the electric field of its neighborhoods, for example, as in Alexandrite and Emerald crystals. In our findings, the field is so low that  $^4T_2$  becomes the lowest excitation state which emits broad fluorescence from 680 nm to more than 880 nm (Fig. 1, without spectral sensitivity correction of the PMT detector). The  $^4T_2$  is the unique emission channel of Cr(III). Such a material is promising for tunable lasing and deserves detailed further study of its luminescent properties.

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