

PROPERTIES OF EXCITED STATES OF Cr^{3+} IN ALEXANDRITE CRYSTAL*

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I. INTRODUCTION

Alexandrite is a hopeful laser crystal not only because the sharp R -line shows laser action, as in ruby, but also the vibronic sideband is involved in the lasing of this crystal, in this case the system is of four-levels and is widely tunable (700 nm—800 nm)^[1,2]. We have studied the dynamic properties of the excited states of Cr^{3+} in BeAl_2O_4 . The relaxation of the system within the excited states reveals the dynamics of the interactions of the ion defects with phonons. As the time of relaxation is very short, being 1—10 ps for strong coupling of crystal and luminescence center, several hundred ps for weak coupling^[3], picosecond technique should be used in detecting the relaxation process.

II. ENERGY DIAGRAM

The energy diagram of the transition metal ion $\text{Cr}^{3+}(3d^3)$ in O_h field is shown in Fig. 1. In $\text{BeAl}_2\text{O}_4: \text{Cr}^{3+}$, instead of Al^{3+} Cr^{3+} goes into two different crystal sites, i. e. mirror sites C_s and inversion sites C_i which introduce different distortions in O_h field and arouse different splittings of corresponding energy levels. From the

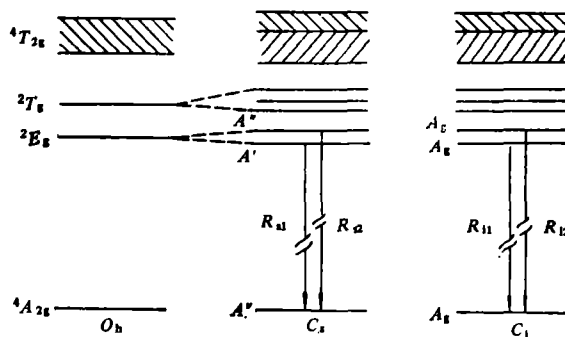


Fig 1. Energy diagram of C_i and C_s site.

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group theory and absorption spectrum, we can determine the energy diagrams of different luminescence centers^[4], shown in Fig 1. About 75% Cr^{3+} ion goes into C_s sites, the rest into C_i sites. From group theory, we know that the R-lines in C_s site, e.g. R_{s1} , R_{s2} (${}^2E - {}^4A_2$) are electric-dipole transition, while R_{i1} , R_{i2} (${}^2E - {}^4A_2$) in C_i site are magnetic-dipole transition.

III. EXPERIMENT SET-UP

The spectrum measurement was carried out by means of an Ar^+ -laser, a T-800 Raman spectrometer (resolution: 0.25 cm^{-1}) and low temperature system (10 K—100 K).

The time-resolved measurement: active-mode-locked YAG laser (pulse width 100 ps), high speed streak camera (time resolving power: 2 ps), interference filter ($\Delta\lambda \approx 7 \text{ nm}$), low temperature system, time delay system. The sample was BeAl_2O_4 , doped with 0.3% Cr^{3+} ions.

IV. RESULTS AND ANALYSIS

1. Luminescence Spectrum

The sample was excited by 488 nm (Ar-laser) and the luminescence spectrum was measured at different temperatures from 300 K to 10 K. The spectrum at room

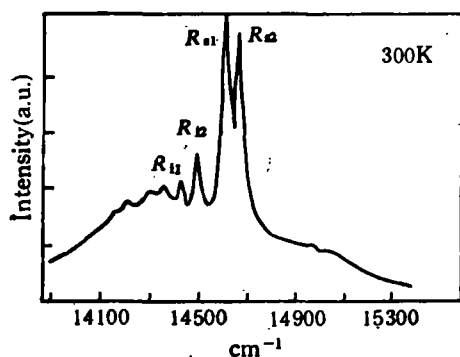


Fig 2. Luminescence spectrum of $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$ at room temperature.

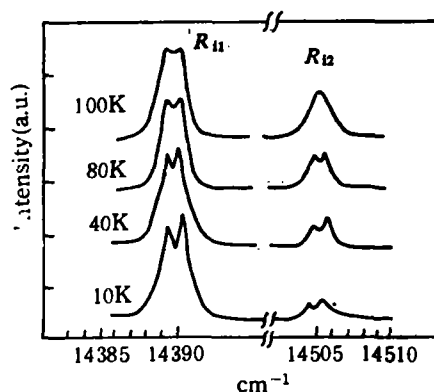


Fig 3. Luminescence spectrum of R_{11} and R_{12} at temperature from 100 K to 10 K.

temperature is shown in Fig 2. R_{s1} , R_{s2} and R_{i1} , R_{i2} appear in the same position as reported^[2]. T_1 , T_2 and T_3 are the electric-dipole transition of ${}^2T - {}^4A_2$ in C_s site. There are three pairs of phonon side-lines of R_{i1} , R_{i2} in the low energy site, they are the electric-dipole-LO phonon transitions of ${}^2E - {}^4A_2$. From the measured spectrum, the LO phonon energy is 250 cm^{-1} .

When the temperature was lowered to 100 K, we found the R_{i1} and R_{i2} lines began to split into two peaks. As the temperature was lowered further, the splitting became more obvious. Fig. 3 shows the luminescence spectrum of R_{i1} and R_{i2} from 100 K to 10 K. At 10 K the separation between these peaks is 1.2 cm^{-1} . We believe that the further splitting of spectral lines at low temperature is due to the spin-orbit interaction in C_i site. Using the crystal field theory we have found that the

ground state 4A_2 level splits into two energy levels as the result of spin-orbit interaction. The R_{11} and R_{12} lines split into two peaks correspondingly. At higher temperature, this splitting is covered by thermal noise.

2. Time-resolved Spectrum

We used the second harmonic light of YAG laser (532 nm), interference filters and streak camera to measure the time-resolved spectrum of $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$. Fig. 4 shows the normalized spectrum. 680 nm corresponds to the ordinary luminescence,

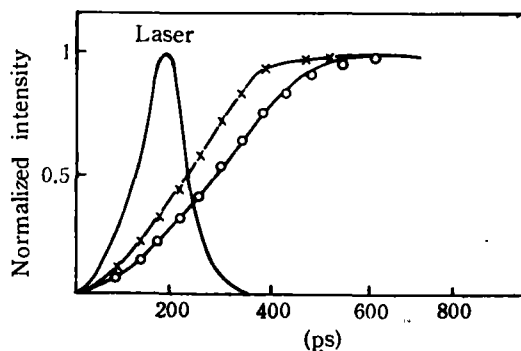


Fig 4. Time-resolved spectrum. \times , 660 nm; \circ , 680 nm.

i. e. the transition of the lowest excited state to ground state 4A_2 . 600 nm is hot luminescence, i. e. the transition of excited states where the energy is higher than 2E states by 2 vibronic quanta. From Fig. 4, we can see that after being excited, the luminescence intensity rises. As the width of the laser pulse is 100 ps, the observed rising process is the convolution of luminescence and laser pulse^[7]. By deconvolution, the rise time of luminescence at 680 nm is 100 ps. At 660 nm it is 80 ps, 20 ps faster than that at 680 nm. This means that electron relaxed through two vibronic energy levels from 660 nm to 680 nm is 20 ps.

When the sample is excited into higher excitation states, the electron (hot electron) drops back into ground states, (hot luminescence) or relaxes down to lower excitation states by emitting LO-phonons. As the emission of phonons is very quick, most of the hot electrons relax down to lower excitation states and then give ordinary luminescence^[6]. The rise time of 680 nm means that the total relaxation time from the highest energy level to the lowest excited level is 100 ps. The comparison of the rise time of 680 nm with that of 660 nm shows that 2 LO-phonon emission requires 20 ps. Thus one LO-phonon emission requires 10 ps.

V. CONCLUSIONS

In the case of C_i site of Cr^{3+} , the spin-orbit interaction causes the ground states 4A_2 to split into two energy levels, the hyperfine structure is 1.2 cm^{-1} .

The phonon process is obvious in alexandrite and the time required for the emission of 1 LO-phonon is about 10 ps. So that the crystal and Cr^{3+} ion coupling is

considered to be strong.

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