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ANALYSIS OF THE LASER-INDUCED FLUORESCENCE IN CRYSTAL $Cr:Mg_2SiO_4$

GUO XIANG-YI(郭祥义), YANG BAO-CHENG(杨宝成), SHEN GUO-TU(沈国土), and LIN YUAN-QI(林远齐)
Department of Physics, East China Normal University, Shanghai 200062, China
ZHU SHENG-XIANG(祝生祥)
Department of Physics, Tongji University, Shanghai 200092, China
PAN PEI-CONG(潘佩琮)
Shanghai Institute of Ceramics, Academia Sinica, Shanghai 200050, China

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Observation of the 532 nm-laser-induced fluorescence spectra of two kinds of $Cr:Mg_2SiO_4$ crystalline samples grown in different atomsphere are reported. The experiments were conducted at both room temperature and liquid-nitrogen temperature. The fluorescence spectra of the two kinds of samples were different with respect to the polarizing direction of the inducing laser, and two emission bands with different polarized characters and various enhancement in intensity at low temperatures were also found. In the light of the calculated results by Ms-X_α method, the main experimental results are explained.

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I. INTRODUCTION

Chromium-doped forsterite ($Cr:Mg_2SiO_4$) is a new type of laser crystals from which Q-switched tunable laser had been obtained both at home and abroad[1]. Different characteristics of the fluorescence spectra of the crystal, however, have been reported up till now because the methods of crystal growth used are different[2-4]. Besides, attention has been focused on the influence of the relative direction of the exciting-light polarization to the crystal axis upon the structure of the fluorescence spectra. Though exhibition of polarization of the laser output of $Cr:Mg_2SiO_4$ was noticed by Petricevic *et al.*[5] while they were studying its laser performance, no systematic study has been made on the polarization of the induced fluorescence of the crystal. We have made a systematic experimental study on the laser-induced fluorescence of two kinds of $Cr:Mg_2SiO_4$ crystals grown in different shielding gases by Czochralski method. The experiment showed that the fluorescence of the crystals exhibits polarization character at both room temperature and liquid nitrogen temperature, and two emission bands exist which show different polarization features, and the general features of the fluorescence spectra of the two kinds of samples are similar to those of the samples grown by LHPG method under similar shielding gases by Jia *et al.*[6], but the spectra showed some different characters in structure. In this paper the experimental results are reported and the mechanism of the characters of the laser-induced fluorescent spectra is discussed.

II. EXPERIMENTAL CONDITIONS

The Cr:Mg_2SiO_4 crystal samples were grown by Czochralski method. The parameters of the two samples, with each face cut perpendicular to one of the crystal axes and polished, are listed in Table 1.

Table 1. Parameters of the samples.

Sample number		No.1	No.2
Shielding gases		Nitrogen	Oxygen
Dimension (mm^3)		7.8×7.5 × 9.5	7.5×5.5 × 8.7
Content of chromium ions (wt%)		0.02	0.02
Concentration of chromium ions (cm^{-3})		10^{18}	10^{18}
Color	along axis *a*	light blue	deep blue
	along axis *b*	light purple	deep purple
	along axis *c*	light green	deep green

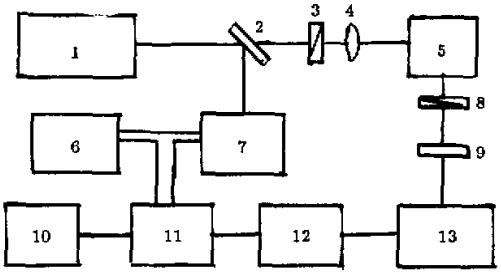
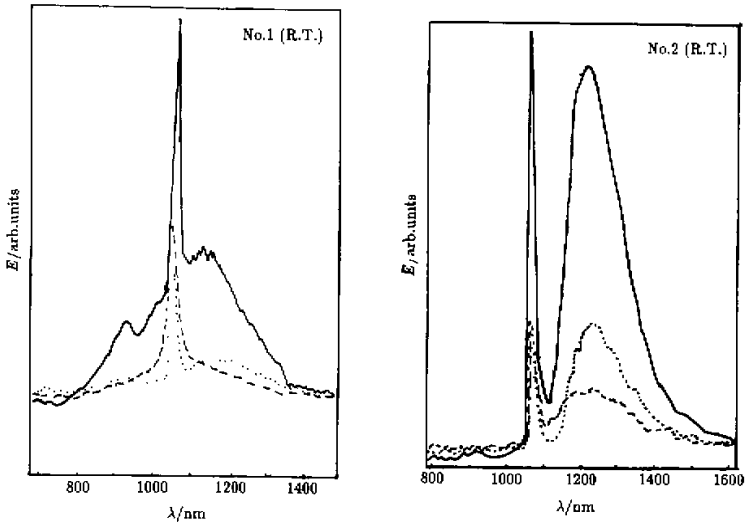


Fig. 1. Schematic diagram of the experiment. 1: frequency-doubled output of *Nd*:YAG; 2: beam-splitter; 3: polarizer; 4: lens; 5: sample cell; 6. oscilloscope; 7: photodiode; 8: analyser; 9: filter; 10: recorder; 11: boxcar integrator; 12: Ge detecter; 13: monochromator.

The experimental setup is schematically shown in Fig.1. The laser used is the Q-switched YAG/Dye system of Quantel Corporation, and the laser beam is frequency-doubled to 532 nm exciting light, which is polarized and focused on a position 20 cm in front of the sample by a lens with 70 cm focal length. The transmitted laser beam is blocked by a filter while the fluorescence signals from the sample, after going through an analyser and the 0.5 m grating monochromator, are detected by a Ge photoelectronic diode and processed by the boxcar integrator; then the signals are fed into an oscilloscope for monitoring and into a recorder as well. The sample cell is a home-made glass Duwar bottle which can be operated at room temperature and at liquid nitrogen temperature quite easily.

III. EXPERIMENTAL RESULTS



(a) Fluorescence spectra of sample No.1 at room temperature with the wavelength of the inducing laser being 532 nm.

(b) Fluorescence spectra of sample No.2 at room temperature with the wavelength of the inducing laser being 532 nm.

Note: $k \parallel c$, $E_i \parallel b$. —: non-polarized; - - - : $E_0 \parallel a$; ···: $E_0 \parallel b$. k and E_i are the propagating direction and the polarizing direction of the inducing laser respectively. E_0: the polarizing direction of the fluorescence. a, b, c: the crystal axis

The narrow peak in the figure near 1064 nm, used as the identification line, is the secondary spectrum of the inducing laser.

Fig.2.

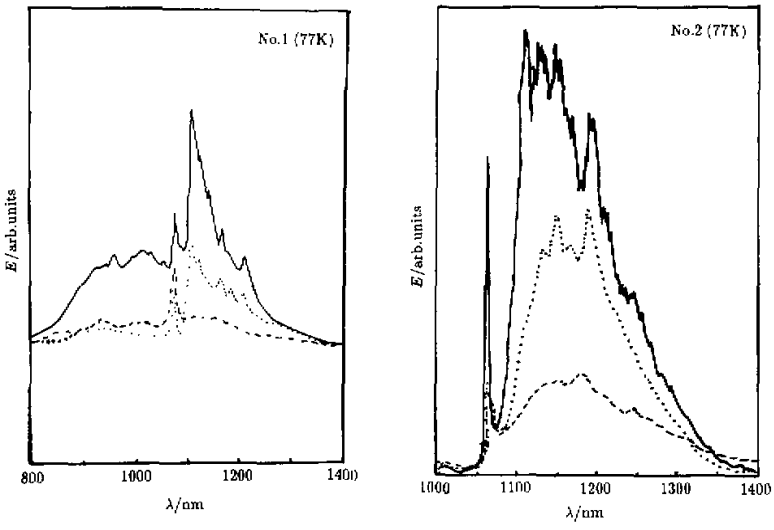
Excited by the 532 nm laser, a series of fluorescence spectra of the Cr:Mg_2SiO_4 crystals were obtained, the part of which at room temperature is shown in Fig.2, and the part of which at liquid nitrogen temperature is shown in Fig.3. In these figures, $\boldsymbol{k}$ and $\boldsymbol{E}_i$ are the wave vector and the electric vector of the inducing laser respectively, $\boldsymbol{E}_0$ is the electric vector of the fluorescence. The symbol $\boldsymbol{E}_i \parallel b$ indicates that the polarizing direction of the inducing light is parallel to the crystal axis b while the symbol $\boldsymbol{E}_0 \parallel b$ means that the polarizing direction of the fluorescence is parallel to axis b. For convenience, we refer to the fluorescent band with wavelength of the main peak shorter than 1064 nm as S band and to the other with wavelength of the emission peak longer than 1064 nm as L band.

A. As can be seen from Fig.2(a), at room temperature the fluorescence spectra of sample No.1 display a double-peak structure. When the wave vector $\boldsymbol{k}$ of the inducing laser is parallel to c-axis and its electric vector $\boldsymbol{E}_i$ is parallel to b-axis (that is, $\mathbf{k} \parallel c$ and $\mathbf{E}_i \parallel b$), S

band and L band can be seen simultaneously, but L band is a little stronger in intensity. By close observation, it is not difficult to see that there are a number of small peaks near 960 nm in S band, while the detail of the peak of L band, which is located at 1150 nm, is almost indiscernible and the peak looks smooth.

By contrast, the fluorescence spectra of sample No.2 exhibit quite different characteristics, as can be clearly seen in Fig.2(b). Under the same experimental conditions, it is found that the signals of S band are extremely weak, while those of the L band are very strong, about more than ten times stronger than the former in intensity. Nevertheless, L band still shows broad-peak structures and no fine details can be seen. The experiments also show that when the relative direction of the polarization of the inducing laser to the crystal axis varies, the positions of the peaks change slightly too.

One common feature of the fluorescent spectra of both samples at room temperature is that when the direction of the analyser is parallel to a-axis, i.e., $\boldsymbol{E}_0 \parallel a$, the fluorescent signals of L band received is much stronger than when $\boldsymbol{E}_0 \parallel b$, and the opposite is true for those of S band. It obviously indicates that the polarization characters of the two bands are different.



(a) Fluorescent spectra of sample No.1 at liquid nitrogen temperature with the wavelength of the inducing laser being 532 nm.

(b) Fluorescent spectra of sample No.2 at liquid nitrogen temperature with the wavelength of the inducing laser being 532 nm.

Note: the same as Fig.2.

Fig.3.

B. One remarkable feature of the fluorescent spectra at liquid nitrogen temperature, as

seen in Fig.3, in comparison with those at room temperature, is that with other experimental conditions identical, S band of both samples shows only slight changes, while the intensity of L band increases considerably, at least an order of magnitude. The enhancement is so great that S band is almost lost in the noises, while the fine structures of L band will exhibit.

There are six or seven discernible fine peaks in the range of 1080 nm to 1250 nm in the spectra of sample No.1 with the maximum near 1100 nm, and the others decreasing successively in intensity. For sample No.2 there are up to more than a dozen fine peaks in the same range, the intensity of which varies but does not show decrease until the wavelength reaches 1210 nm, and the fluorescence range extends to about 1650 nm.

That the fluorescent signals of L band is much stronger when $\boldsymbol{E}_0 \parallel a$ than when $\boldsymbol{E}_0 \parallel b$ remains the common feature of the two samples, that is to say, the polarization character of L band does not vary with temperature.

C. What characterizes the fluorescent intensity of both samples at different temperatures is that the direction of the wave vector $\boldsymbol{k}$ of the inducing light relative to the axis has little influence on the fluorescent intensity, whereas that of electric vector $\boldsymbol{E}_i$ considerably affects the intensity as well as the fine structures of the fluorescence. Details about this have been reported in our previous work[7]. As to the polarization character of the fluorescence, our experiments show that, for L band, the fluorescent signal is the strongest for $\boldsymbol{E}_0 \parallel a$, becomes weaker when $\boldsymbol{E}_0 \parallel b$, and is the weakest when $\boldsymbol{E}_0 \parallel c$. But it is not the case for S band, of which the signal is the strongest when $\boldsymbol{E}_0 \parallel b$, and the weakest when $\boldsymbol{E}_0 \parallel a$. These results are consistent with the phenomenon observed by Petricevic *et al.* in their experiment on $Cr:Mg_2SiO_4$ laser, which showed that the polarization direction of laser output is parallel to b-axis.

IV. DISCUSSION

The study on the crystal structure of forsterite has shown that there are three possible kinds of coordinate positions for Cr ions, correspondingly, there will be three possible kinds optically active centers. Two of them are octahedron $(CrO_6)^{9-}$ created by Cr^{3+} substituting for the Mg^{2+} ions in two distinct sites: one with inversion symmetry (C_i) and the other with mirror symmetry (C_s); another one is tetrahedron $(CrO_4)^{4-}$, produced by Cr^{4+} taking the place of Si^{4+}, with the position symmetry being C_s. Generally, the ions with mirror symmetry are optically active, while dipole-transition is prohibited by parity for the ions in positions of inversion symmetry. As the tetrahedrons do not possess inversion symmetry, while the octahedrons do, the average transition probability of Cr^{4+} ions will be greater than that of Cr^{3+} ions, since part of the Cr^{3+} ions will be in the position of inversion symmetry. Therefore, when the densities of Cr^{4+} and Cr^{3+} in the crystal are about equal,

the characters of Cr^{4+} ions will be dominant in the fluorescence spectra.

We have calculated the electronic structure and energy levels of the chromium ions in different valent state with four or six ligands using MS-X_α method[8,9]. With the aid of the results calculated most experimental results can be interpreted. The fluorescence of S band was assigned to the emission of Cr^{3+} in octahedron when induced by 532 nm laser, while the Cr^{4+} in tetrahedron emits the fluorescence of L band. The calculation also indicates that, the electronic ground state of $(CrO_4)^{4-}$ in higher position symmetry such as C_{3v}, ^3E, is digenerate, as the symmetry lowers to C_s, it will split into two non-degenerate levels about 219 cm^{-1} apart, $^3A'$ and $^3A''$, being similar to Jahn-Teller effect. Another degenerate state ^1E, only 538 cm^{-1} above ^3E, will also split into two levels $^1A'$ and $^1A''$, seperated in energy by 330 cm^{-1}. These levels get nearer to one another after splitting and so result in a band-like ground state. At room temperature the population on these lower levels is small but cannot be neglected, and this limits the intensity of the fluorescence. As temperature drops, the population on these levels decreases. This can increase the population on the ground levels only a little, and the absorption intensity of the crystal shows little increase accordingly, but the population difference between the higher and the lower excited levels can increase considerably, and in consequence, the fluorescent intensity at liquid nitrogen temperature is enhanced dramatically. According to the calculation, the electronic ground state of $(CrO_6)^{9-}$ under D_{4h} symmetry is already non-degenerate $^4B_{2g}$, which cannot split further even if the symmetry lowers, and the nearest excited level is also 2500 cm^{-1} above $^4B_{2g}$. It is natural that the cluster $(CrO_6)^{9-}$ does not show temperature enhancement as $(CrO_4)^{4-}$.

The relative density of Cr^{3+} and Cr^{4+} ions in $Cr:Mg_2SiO_4$ crystal depends on the shielding gases used in growth period. For crystals grown in nitrogen, the density of Cr^{4+} ions is relatively lower than that of Cr^{3+} ions, and for crystals grown in oxygen or in atmosphere, the opposite is true. The intensity of L band of sample No.2 is clearly greater than that of S band, indicating that the Cr^{4+} density is indeed higher than Cr^{3+} density in the sample. This experimental result also confirms the theoretical conclusion. It can be concluded at the same time that to get tunable laser in the range of L band, the density of Cr^{4+} ions should be enhanced, so the method of growing the crystal in gases containing oxygen should be adopted.

The polarization features of the fluorescence are related to the characterstics of Cr^{4+} ions and Cr^{3+} ions, which are obviously different, and also to the positions and ligands around. Exerted by different ligand field, the ions may have different splitting behaviour. All these will affect the transtion probobilities of both ions in different positions. These subjects will be no doubt interesting and worth while to be studied comprehensively.

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