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Ultraviolet irradiation effect of Ce^{3+}-doped $BaMgF_4$ crystals

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Abstract

Ce^{3+}-doped $BaMgF_4$ (BMF) crystals have the absorption and luminescence spectra in the vacuum ultraviolet (VUV) and ultraviolet (UV) ranges. Strong excitation of the fourth harmonic (266 nm) of a pulsed Nd:YAG laser colours the BMF crystal brown and produces a new luminescence spectrum with double peaks at 445 and 500 nm and a lifetime of less than 10 ns. When the sample temperature is elevated up to 200 °C, the crystal colour is changed from brown to green. The colouration is due to localized electrons and holes created by the strong UV excitation, which are identified by the electron spin-resonance (ESR) technique. This new luminescence may be due to Ce^{3+} perturbed by the colour centres.

Keywords: Ce^{3+}; $BaMgF_4$; Non-linear material; Laser material

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1. Introduction

Ce^{3+}-doped ionic crystals attract attention to applications in scintillators and tunable lasers [1,2]. Laser operations in the ultraviolet (UV) region were achieved using the Ce^{3+}-doped fluoride crystals $LiYF_4$ [3] and $LiCaAlF_6$ [4]. Recently, laser materials operating at around 200 nm are required. In order to satisfy this requirement, a frequency doubling method using a non-linear effect is useful.

$BaMgF_4$ (BMF) crystals are expected to be a candidate for tunable laser materials with a non-linear effect [5]. Kodama et al. grew the BMF crystal and crystalline optical properties [6,7]. Although laser operation of BMF:Ce^{3+} using intense UV laser light obtained from the fourth harmonic (266 nm) of a pulsed Nd:YAG laser was tried, it could not be achieved but the crystal was coloured brown. Strong UV excitation also produced a new luminescence spectrum with double peaks at 445 and 500 nm and a lifetime of less than 10 ns in the coloured BMF crystal at low temperatures.

In this paper, we report the origin of the colouration and the new luminescence centre estimated using the optical and electron spin-resonance (ESR) techniques.

2. Experimental procedure

Ce^{3+}-doped BMF crystals were grown in a vacuum-tight Czochralski system. The details were described in the previous papers [6,7]. The BMF crystals were co-doped with 0.5 at.% Ce^{3+} ions and 0.5 at.% Na^+ ions as charge compensators.

Absorption, excitation and luminescence spectra in the vacuum ultraviolet (VUV), UV and visible ranges of 100–600 nm were measured at the UVSOR facility of the Institute for Molecular Science. Visible luminescence spectra excited using a Xe-lamp were also measured using an Ocean Optics USB2000 fiber multi-channel spectrophotometer. Excitation spectra were measured by monitoring luminescence intensities using a Hamamatsu Photonics R943-02 photomultiplier tube (PMT) at the exit slit of a 1/4 m monochromator at 15 K. A sample was put on a cold

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finger in a cryostat with temperature control in the range of 15–300 K.

Lifetimes of the luminescence were measured using the 266 nm laser light and a PMT connected with a Yokogawa DL 1740 digital-oscilloscope in the temperature range of 15–300 K.

ESR measurements were made using a JEOL FA-100 X-band spectrometer with a microwave frequency of 9.431 GHz at 300 K in the Instrumental Analysis Centre, Gifu University.

3. Results and discussion

Fig. 1 shows the absorption, excitation and luminescence spectra of the BMF:Ce^{3+} crystal measured at 15 K, which are extended toward the VUV range compared with those reported in Refs. [6,7]. The excitation spectrum is clearly resolved into five broadbands at 178, 197, 232, 247 and 257 nm, which are due to the optical transitions from the 4f^1 ground state to the five non-degenerated Kramers doublets of the 5d^1 excited state of Ce^{3+} occupying the ordinary sites in the BMF crystal [6,7]. The UV excitation at 248 nm produces the luminescence of Ce^{3+} with double peaks at 293 and 310 nm. The relation between the optical properties and crystal structure were described in the previous papers [6,7].

Strong irradiation of the 266 nm lasers light causes colouration of the BMF crystal. Fig. 2 shows the absorption, luminescence and excitation spectra of BMF:Ce^{3+} in the range of 300–900 nm at 15 K after colouration. The absorption spectrum consists of several bands in the range of 300–600 nm. Two different luminescence bands with peaks at 600 and 780 nm are observed. The excitation spectrum of the 600 nm luminescence is composed of two bands at 420 and 460 nm, while that of the 780 nm luminescence is composed of three bands at 350, 465 and 500 nm. The similar absorption and luminescence spectra in the visible range were observed in LiCaAlF$_6$ irradiated by X-ray, which is assigned to colour centres [8].

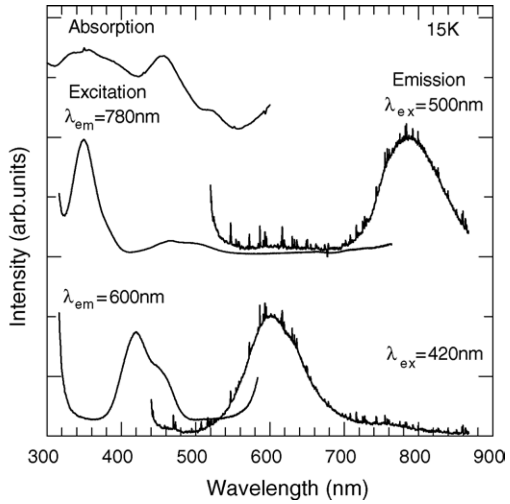

Fig. 2. Absorption, excitation and emission spectra of BMF:Ce^{3+} in the visible range at 15 K after colouration.

In order to identify the colour centres produced through the UV irradiation in BMF:Ce^{3+}, ESR measurements were performed. Fig. 3 shows the ESR spectrum of the BMF crystal measured with magnetic field B parallel to the crystalline *c*-axis consisting of broad and sharp lines at 0.3063 and 0.3370 T with the peak-to-peak widths of 13 and 1 mT, respectively. The ESR line at 0.3370 T is isotropic in the *ac* plane, whereas the ESR line at 0.3063 T shifts to high magnetic field and the intensity is weakened with magnetic field away from the *c*-axis. The *g* values of the ESR lines at 0.3063 and 0.3370 T with B//c are estimated to be 2.199 and 1.999, respectively, which are identified as holes and electrons trapped at lattice defects. In order to examine the

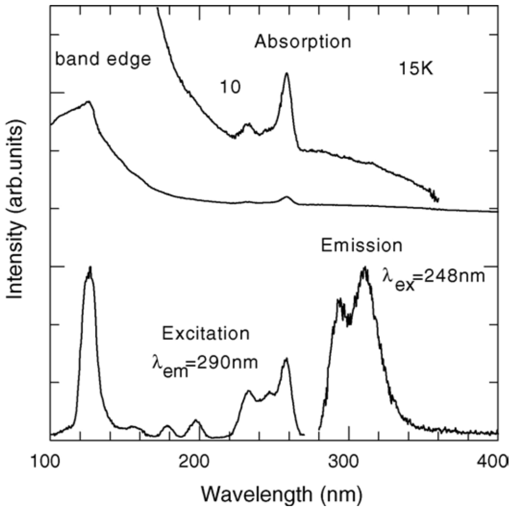

Fig. 1. Absorption, excitation and emission spectra of the as-grown BMF:Ce^{3+} crystal measured at 15 K in the VUV, UV and visible ranges.

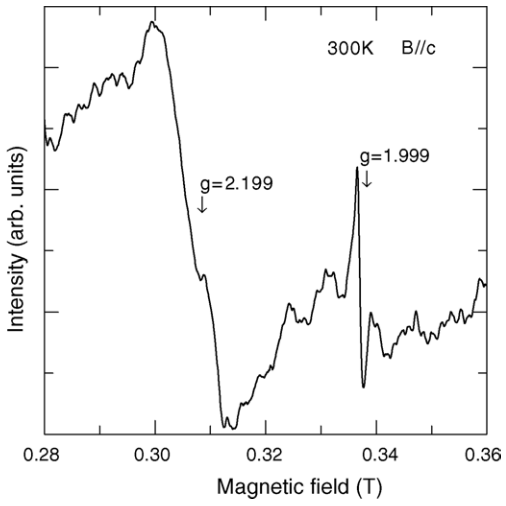

Fig. 3. ESR spectrum measured with B//c at 300 K.

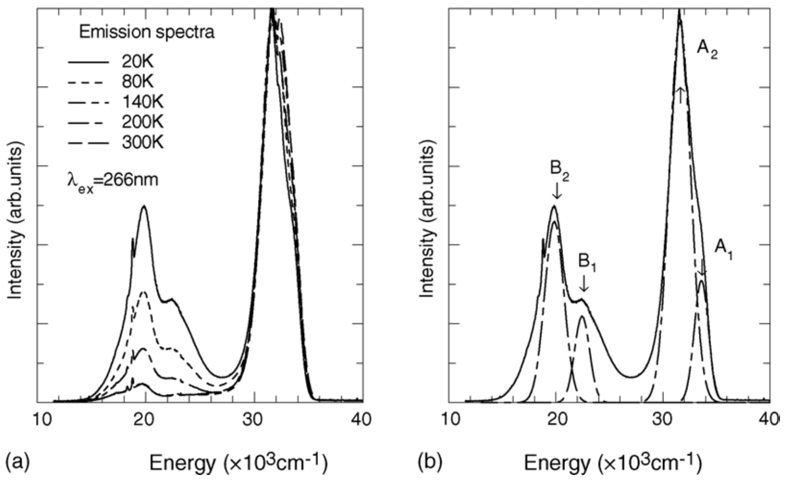

Fig. 4. (a) Emission spectra excited with the 266 nm laser light in the temperature range of 20–300 K after colouration. (b) Deconvolution of the emission spectrum at 20 K. The spectrum is composed of (A_1, A_2) and (B_1, B_2) bands.

structure of the trapped centres, further ESR experiments are required.

The strong 266 nm UV excitation also produces two groups of the broadband luminescence at (297, 316 nm) and (445, 500 nm) denoted by (A_1, A_2) and (B_1, B_2), respectively, as shown in Fig. 4. The intensities and lifetimes (30 ns) of the A_1/A_2 luminescence keep constant in the temperature range of 15–300 K. On the other hand, the intensities of the B_1/B_2 luminescence drastically decrease with an increase of temperature. The lifetime of the B_1/B_2 luminescence is less than 10 ns, which is a limit of resolution corresponding to a laser pulse width of 5 ns. Taking into account the temperature dependence of the intensity, the lifetime may be shortened by a phonon-assisted non-radiative decay process.

In order to examine the origin of the B_1/B_2 luminescence, the spectrum at 20 K is deconvoluted into two Gaussians as shown in Fig. 4(b). The energy difference in the double peaks B_1/B_2 is about 2400 cm^{-1}, which is almost equal to the ground state splitting between $^2F_{5/2}$ and $^2F_{7/2}$ of Ce^{3+}. The peak wavelengths of the B_1/B_2 bands are fairly shifted to long wavelengths, compared with those of the A_1/A_2 bands. Taking into account the large peak shift and the non-radiative decay, there is a possibility that the B_1/B_2 luminescence is due to strongly perturbed Ce^{3+} centres. A model that complex consists of Ce^{3+} and vacancy in the nearest neighbour F^- ligand ion is proposed. Although the strong excitation using the 266 nm UV laser light produces the B_1/B_2 luminescence, weak UV excitation using a Xe-lamp does not produce the B_1/B_2 luminescence. This result suggests that the strong UV irradiation simultaneously causes excitation of Ce^{3+} and creation of colour centres, followed by formation of a complex centre consisting of Ce^{3+} and colour centre.

4. Conclusions

The BMF:Ce^{3+} crystal was coloured brown by strong irradiation of the 266 nm laser light. The brownish colour of the crystal is changed to green when the sample temperature is elevated up to 200 °C where either electron or hole centres disappear at high temperature. The coloured sample shows the luminescence bands with the peaks at 600 and 780 nm. The strong excitation using the 266 nm laser light produces the new luminescence bands with the double peaks at 445 and 500 nm. The new luminescence may be assigned to a complex centre of Ce^{3+} and colour centre. However, there is a possibility that it is assigned to another colour centre different from those corresponding to bands at 600 and 780 nm. In order to confirm this assignment, further ESR experiments at low temperatures are required.

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