Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Luminescence 119–120 (2006) 69–74
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Vacuum ultraviolet and ultraviolet spectroscopy of $BaMgF_4$ codoped with Ce^{3+} and Na^+

Eiji Hayashi[a], Kiyotaka Ito[a], Satoshi Yabashi[a], Mitsuo Yamaga[a,*], Nobuhiro Kodama[b], Singo Ono[c], Nobuhiko Sarukura[c]

[a]*Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan*
[b]*Department of Materials Science and Engineering, Akita University, Akita 010-8502, Japan*
[c]*Institute for Molecular Science, Okazaki 444-8585, Japan*

Available online 31 January 2006

Abstract

Ce^{3+}/Na^+-doped $BaMgF_4$ (BMF) crystals with a nonlinear property show strong absorption in the vacuum ultraviolet (VUV) and ultraviolet (UV) ranges. Three different fluorescence bands (A, B, C) at 300, 340, and 430 nm were observed when pumped at different wavelengths. Under excitation of the fourth harmonic (266 nm) from a pulsed Nd:YAG laser the BMF crystal changed its colour from transparent to brown due to formation of colour centres. The A, B and C bands are assigned to three different sites of Ce^{3+}: site A is Ce^{3+} substituting for perfect Ba^{2+} sites; site B is Ce^{3+} (Ba^{2+}) perturbed by Na^+ as a charge compensator; and site C is a complex composed of Ce^{3+} and F^- vacancies, which trapped one or two electrons.

PACS: 78.20.−e; 78.40.−q; 78.55.Hx

Keywords: Ce^{3+}; $BaMgF_4$; Nonlinear material; Laser material; Tunable laser

1. Introduction

$BaMgF_4$ crystals codoped with Ce^{3+} and Na^+ (BMF:Ce:Na) are a candidate for tunable laser materials with a nonlinear effect [1]. Kodama et al. grew the BMF:Ce:Na crystal and reported the crystalline and optical properties [2,3]. No lasing has been achieved in the BMF:Ce:Na crystal under intensive pumping with the fourth harmonic (266 nm) of a pulsed Nd:YAG laser. Under the ultraviolet (UV) irradiation the crystal changed its colour from transparent to brown. The optical absorption induced by the UV irradiation may be due to hole and electron trapping centres, for example, F_A centre (an electron trapped at a fluorine vacancy with dopants Ce^{3+} and/or Na^+ in the nearest neighbours) [4]. New fluorescence

*Corresponding author. Tel./fax: +81 58 293 3052.
E-mail address: yamaga@cc.gifu-u.ac.jp (M. Yamaga).

0022-2313/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2005.12.013

bands peaking at 445 and 500 nm with lifetime less than 10 ns were observed in the coloured BMF crystal at low temperatures [5].

In this paper, we report optical absorption, excitation and fluorescence spectra of three different Ce^{3+} sites in the BMF crystal observed in the vacuum ultraviolet (VUV), UV and visible ranges, and discuss a possibility of energy transfer from colour centres to Ce^{3+} ions.

2. Experimental procedure

The BMF crystal is reported to have orthorhombic structure with space group C_{2v} 12(C_{mc21}) [6]. The unit cell is shown in Fig. 1. Each octahedron consists of a central Mg and six nearest-neighbour F^- ligand ions. Ba^{2+} ions are located at centres of trigonal prisms. Dopants Ce^{3+} and Na^+ as a charge compensator substitute preferentially for Ba^{2+} ions because their ionic radii are close to that of Ba^{2+}, but much larger than that of Mg^{2+}. The BMF crystals codoped with 0.5 at% Ce^{3+} and 2.5 at% Na^+ were grown in a vacuum-tight Czochralski system. The details were described in the previous papers [2,3].

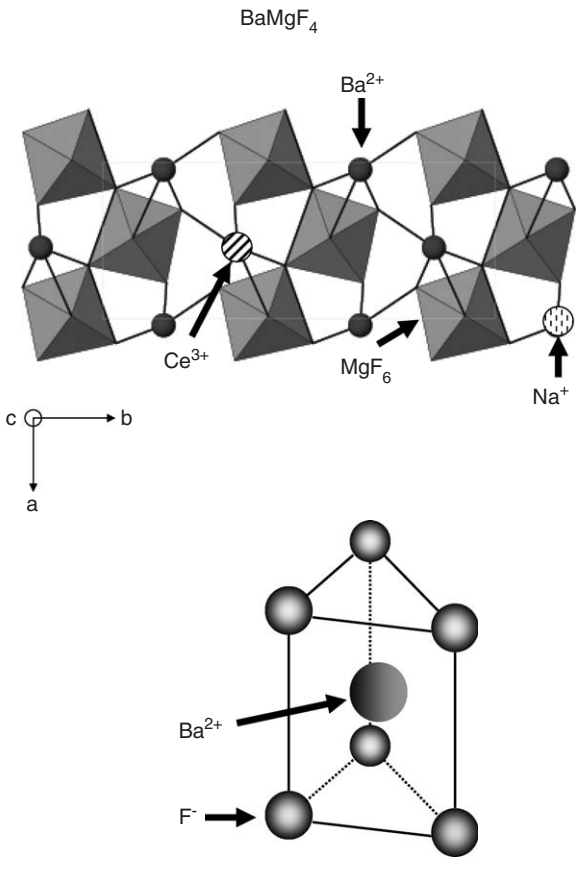

Fig. 1. Crystal structure of $BaMgF_4$ and a trigonal prism consisting of Ba^{2+} and F^-.

Optical absorption, excitation, and fluorescence spectra were measured in the spectral range 100–600 nm with the ultraviolet synchrotron orbital radiation (UVSOR) facility in the Institute for Molecular Science. The spectra were analysed with a 1-m focal-length Seya-Namioka monochromator.

Lifetimes of the Ce^{3+} fluorescence in the BMF crystal were measured at room temperature using a 10-Hz Q-switched Nd:YAG laser operated with 266-nm, 100-mJ and 10-ns pulses or using a 1-kHz Ti–sapphire regenerative amplifier with 290-nm, 80-μJ and 210-fs pulses, and a streak camera loaded with a spectrograph.

3. Results

Fig. 2(a) shows the optical absorption spectra of the BMF:Ce:Na crystal measured at 17 K before and after the UV (266 nm) irradiation, which are extended towards the VUV range in comparison with those reported in Refs. [2,3]. The spectrum before the UV irradiation consists of two intense bands at 125 and 160 nm, and five bands at 178, 199, 229, 246, and 260 nm. The peak at 125 nm is close to the band edge of pure BMF crystals. After the UV irradiation, the 160-nm broadband was strongly reduced and a new band appeared at 458 nm. The 458-nm band contributes to the colouration of the crystal.

Three different fluorescence bands denoted by A, B and C are obtained for the coloured BMF:Ce:Na crystal at 17 K when excited at 258, 299 and 160 nm, respectively. The line shapes of A and B bands are very similar except the peak shift of B band to longer wavelength. The intensity of B band increases with an increase of the Na^+ concentration (0.5 and 2.5 at%). C band has a