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Crystal growth and spectral properties of pure and Co^{2+}-doped $Mg_3B_2O_6$ crystal

Hongyan Wang [a,b], Guohua Jia [a,b], Yan Wang [a], Zhenyu You [a], Jianfu Li [a], Zhaojie Zhu [a], Fugui Yang [a,b], Yanping Wei [a,b], Chaoyang Tu [a,*]

[a] Fujian Institute of Research on the Structure of Matter, State Key Laboratory of Structural Chemistry, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China
[b] Graduated School of Chinese Academy of Sciences, Beijing 100039, PR China

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Abstract

Novel pure and cobalt-doped magnesium borate crystals ($Mg_3B_2O_6$) have been grown successfully by the Czochralski technique for the first time. Crystal growth, X-ray powder diffraction (XRD) analysis, absorption spectrum, fluorescence spectrum as well as fluorescence decay curve of Co^{2+}:$Mg_3B_2O_6$ (MBO) were described. From the absorption peaks for the octahedral Co^{2+} ions, the crystal-field parameter Dq and the Racah parameter B were estimated to be 943.3 cm^{-1} and 821.6 cm^{-1}, respectively. The fluorescence lifetime of the transition $^4T_1(^4P) \rightarrow {}^4T_2$ centered at 717 nm was measured to be 9.68 ms.

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Keywords: Spectroscopic characteristics; Czochralski technique; Co^{2+}; $Mg_3B_2O_6$ crystal

1. Introduction

Birefringent crystals as important materials in the optical communication industry have received a great deal of interest in the past decades in the fields such as optical polarizing components, optical isolators, circulators and beam displacers [1,2]. Magnesium borate as a birefringent crystal is now attracting a practical interest because it can be utilized for a thermo-luminescence phosphor [3], an excellent anti-wear substance as well as a reduce-friction additive [4]. Magnesium borate nanobelts have been prepared by heating mixed powders of boron and MgO under flowing Ar/H_2O gases at 1100 °C by Zhang et al. [5]. Co^{2+}-doped crystals such as $MgAl_2O_4$, $LiGa_5O_8$ and $ZnGa_2O_4$ which process broad luminescence bands [6–8] have been found to be possible candidates for tunable solid-state lasers in the visible and near infrared spectral regions. The radii of the magnesium ions and the cobalt ions are comparable. Therefore, the MBO single crystal doped with cobalt ions might act as a potential host lattice for laser applications, which prompted us to study the optical properties of this crystal.

The MBO single crystal belongs to orthohombic system with the space group of P_{mnn}. The Mg^{2+} ions are surrounded by six oxygen atoms and the nearest neighbor Mg–O distances are about 2.049 Å. The cell parameters are as follows: $a = 5.398(2)$ Å, $b = 8.416(2)$ Å, $c = 4.497(2)$ Å [5], $\alpha = \beta = \gamma = 90°$, $V = 204.3$ Å^3, $Z = 2$.

The preparation of polycrystalline magnesium borate activated by dysprosium has been reported at first in 1974 [9]. However, a detailed growth method of pure and cobalt-doped magnesium borate single crystals, to our knowledge, has not yet been reported. Present paper was devoted to pure and cobalt-doped magnesium borate

* Corresponding author. Tel.: +86 591 8371 1368/2122; fax: +86 591 8371 4946.
E-mail address: tcy@fjirsm.ac.cn (C. Tu).

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crystals growth from melt by the Czochralski method. Crystal growth, X-ray powder diffraction (XRD) analysis, absorption spectrum and fluorescence spectrum analysis were described.

2. Experimental

Pure and Co^{2+}-doped MBO crystals were grown by the Czochralski technique. The polished Co^{2+}-doped MBO crystal is shown in Fig. 1. The concentration of cobalt ions in the crystal was 0.102 wt% measured by the inductively coupled plasma-atomic emission spectrometry (ICP–AES) method, thus the Co^{2+} concentration in the crystal was $0.98 \times 10^{19}\ cm^{-3}$.

XRD investigations were carried out with a CAD4 diffractometer equipped with CuK_α radiation ($\lambda = 1.054056$ Å). The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2θ range of 5–85°. The XRD pattern (shown in Fig. 2) was in good accordance with the standard JCPDS card of $Mg_3B_2O_6$ (No. 77-0048).

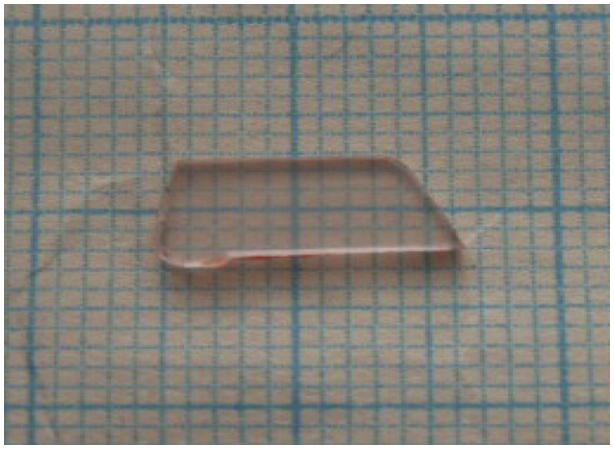

Fig. 1. Polished 0.12 cm-thick MBO:Co^{2+} crystal.

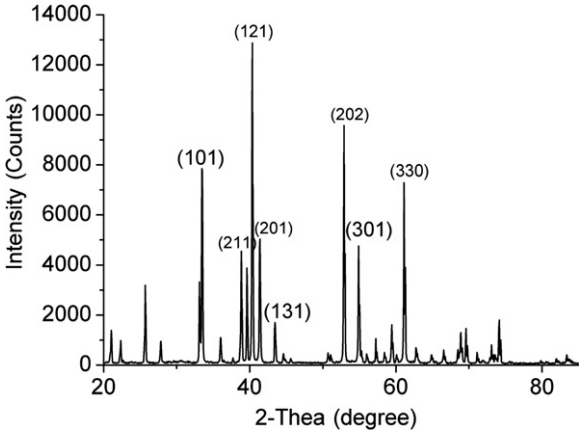

Fig. 2. X-ray powder diffraction pattern of MBO crystal.

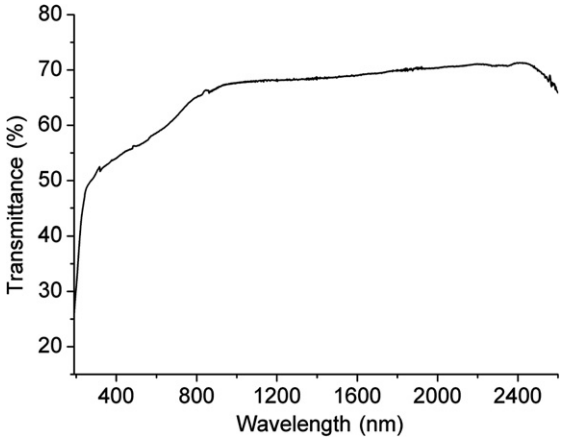

Fig. 3. Transmission spectrum of MBO single crystal.

The transmission spectrum of the MBO crystal and absorption spectrum of the Co^{2+}:MBO were measured by the Perkin–Elmer UV–VIS–NIR Spectrometer (Lambda 900) at room temperature from 190 to 3300 nm. The transmission spectrum is presented in Fig. 3 from which we can see that the ultraviolet absorption edge is at about 200 nm. High transmission of this crystal in 300–2500 nm region of the spectrum favored research on the electron transitions of cobalt ions in infrared and visible spectral regions. The emission spectrum of the crystal was recorded at room temperature by an Edinburgh Instruments FLS920 spectrophotometer.

3. Results and discussion

3.1. Crystal growth

Pure and Co^{2+}-doped MBO crystals were grown by the Czochralski technique. The compound was prepared by classical solid-state reactions. The starting materials were prepared by mixing A.R purity $MgCO_3$, H_3BO_3, $CoCl_2 \cdot 6H_2O$ powders according to the following reaction:

$$(3-3x)MgCO_3 + 2H_3BO_3 + 3xCoCl_2 \cdot 6H_2O = (Mg_{1-x}Co_x)_3B_2O_6 + (3-3x)CO_2\uparrow + (6+30x)H_2O\uparrow + 6xHCl\uparrow$$

These compounds were ground, mixed separately in the molar ratio in an agate motor and pressed into pieces. Then they were put into a platinum crucible with diameter of 80 mm and height of 80 mm. They were slowly heated to 1080 °C and maintained at this temperature for 3 days. Then they were ground, mixed and heated again. The above process was repeated to make sure that the chemicals react thoroughly. The compound was placed in the Ir-crucible and heated up to a temperature 50 °C higher than the crystallization temperature about 2–3 h so as to melt completely and homogeneously. During crystal growth, the Ir rod rotated at a rate of 16 rpm and the pulling rate was 0.4–0.7 mm/h. When these procedures were over, the