Synthesis and Optical Study of Novel Nd^{3+}:$Na_2Mg_2ZnB_4O_{10}$ Single Crystal

Shivaji R. Dagdale
Department of Physics, Sant Gadge Baba Amravati University, Amravati (MS) India-444602

Abstract

A novel neodymium doped sodium magnesium zinc borate (Nd^{3+}:$Na_2Mg_2ZnB_4O_{10}$) single crystal has been grown first time by melt solid-state reaction technique. Obtained single crystal was characterized using ultraviolet visible (UV-vis) spectrometry, which was used to determine percent transmission and absorption and to identify various transition states of the crystal. The optical band gap of the grown crystal has also been reported. The photoluminescence study was carried out to determine absorption and emission bands.

KEYWORDS: Crystal growth; Non-linear optics; Photoluminescence; Transparency; UV-vis spectroscopy.

Introduction

Now a day, laser beams in the ultraviolet and visible (UV-vis) regions are used for several industrial, signal processing, medical surgeries, optical data storage devices, optical data communication, color displays and entertainment purposes [1-4]. Borate crystals have excellent linear and nonlinear optical (NLO), piezoelectric, luminescent and other useful physical properties for technical applications. Due to the reason, these crystals have received great attention of research community [5]. The grown NLO crystals required to have high NLO coefficient, moderate birefringence for phase matching, high transparency at the wavelength of interest, non-hygroscopic in nature, high-laser-damage threshold and good mechanical properties [6, 7]. As per the literature survey, the various advantageous borate based family NLO grown crystals [8] such as LiB_3O_5 (LBO) [9], $CsLiB_5O_{10}$ (CLBO) [10], $SrBe_2B_2O_7$ (SBBO) [11], $KBe_2BO_3F_2$ (KBBF) [12], $K_2Al_2B_2O_7$ (KAB) [13], their $RECa_4O(BO_3)_3$ (RECOB) [14], $YCa_4O(BO_3)_3$ (YCOB) [15], $LaCa_4O(BO_3)_3$ (LCOB) [16], $Y_2CaB_{10}O_{19}$ (YCB) [17] $Li_2Pb_2CuB_4O_{10}$ [18] with their confirmation study have been reported. Those mentioned crystals have excellent transmission properties combined with NLO behavior [6]. Since then, intense work began in developing novel crystals with other elemental combinations for NLO applications. The NLO materials in expanding the frequency range provided by the conventional laser sources was identified as a major advantage [4].

In present investigation, the crystal growth and optical study of novel Nd (5 mol%) doped sodium magnesium zinc borate (Nd:NMZB) ($Na_2(Nd_{0.05}Mg_{0.95})_2ZnB_4O_{10}$) NLO crystal has been reported. The NMZB crystal has been grown from melt using simple solid-state reaction technique at its congruent melting point. Our own search for new compounds material use Nd_2O_3-Na_2O-MgO-ZnO-B_2O_3 new phases and may provide interesting stoichiometric melt. The absorption and transmission by the crystal in ultraviolet and visible range along with its optical energy band gap were analyzed using UV-vis spectroscopy. The photoluminescence study of the material has been carried out. The results have been presented.

Experimental

Materials and methods

Sodium carbonate (Na_2CO_3) and zinc oxide (ZnO) were purchased from Fisher scientific, India. Magnesium oxide (MgO) was obtained from CDH, India. Boron trioxide (B_2O_3) was purchased from sd Fine chemicals, India. Neodymium oxide (Nd_2O_3) was procured from LOBA Chemie, India. All the chemicals used for crystal growth were of analytical reagent grade and used as received without further purification.

The single crystal was grown using high-temperature muffle furnace. UV-vis transmission and optical band gap study have been performed using Black CSR-50 StellarNet Spectrophotometer, USA and photoluminescence study has been done using FL-7000 HITACHI, fluorescence spectrophotometer Japan.

The high temperature single crystal Nd:NMZB was grown via melt solid-state reaction technique. The chemicals Na_2CO_3, MgO, ZnO and B_2O_3 with 99.99% purity used were crushed in a mortar with the help of pestle to make the homogeneous mixture. 5 mol% Nd was mixed with Na_2CO_3, MgO, ZnO and B_2O_3. Then this homogeneous mixture was taken in a silica crucible and put it in muffle furnace. On first day, the prepared material was heated at 450^oC for 5h to make the mixture homogeneous. For the decomposition of B_2O_3 from prepared material, the mixture was further heated at 550 ^oC continuously for 10 h on second day. In the same manner the resulting mixture was further heated upto 1000 ^oC just above its melting point and kept continue for 24 h. After this process, muffle furnace was turned towards slow cooling of the prepared material to a temperature 550 ^oC with a rate of 3 ^oC/h, and finally cooled to room temperature at a rate of 10 ^oC/h. The reaction takes place during the crystal growth is as;

$$½(0.05)Nd_2O_3 + (1.95)MgO + ½(1.95)Na_2CO_3 + ZnO + 2B_2O_3 \rightarrow Nd_{0.05}Mg_{1.95}Na_{1.95}ZnB_4O_{10} + ½(1.95)CO_2\uparrow$$

Results and Discussion

UV-vis study

The optical transmission spectrum of Nd:NMZB crystal was recorded in the wavelength range 190 - 1083 nm and is shown in Fig. 1. The UV absorption edge for the grown crystal observed at around 213 nm cut-off wavelength. The optical transparency of grown crystal is found to >70 percent over a wide wavelength range. In addition, from the percent transmittance spectrum (Fig. 1) crystal, the absorption bands around particular wavelengths have also been determined. In the presented spectrum, the absorption bands with peaks at 360, 573, 692, and 772 nm wavelengths have been detected and may assigned to transitions from ground state $^4I_{9/2}$ to the higher excited states $^4D_{1/2}$, $^4G_{5/2}$, $^4F_{9/2}$ and $^4S_{3/2}$ respectively of Nd^{3+} $4f^3$ electronic configuration [19-21].

The energy band gap of grown Nd:NMZB crystal determined from the transmission spectra is found to be 6.10 eV. A plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ for optical band gap is as shown in Fig. 2.

Photoluminescence (PL) study

Photoluminescence is the process by which a material is bombarded with photons to excite and then emits photons back. The two excitation peaks are observed in UV-vis range at 348 and 378 nm, which may correspond to the transitions $^4I_{9/2}$ - $^4D_{3/2}$ and $^4I_{9/2}$ - $^2P_{3/2}$. In the same manner, the two emission peaks observed at 417 and 441 nm may depicts the transitions $^2P_{3/2}$ - $^4I_{11/2}$ and $^4D_{3/2}$ - $^4I_{15/2}$ as shown in Fig. 3 respectively [22, 23]. These two emission bands centered at around 417 and 441 nm belongs to violet and blue spectral region.

Conclusions

In the present report, a novel 5 mol% Nd doped $Na_2Mg_2ZnB_4O_{10}$ crystal was successfully grown. A simple melt solid-state reaction technique was used to grow crystal of large size with good optical transparency. The optical transparency of the present crystal was more than 70 percent and envisages good optical quality crystal. The absorption determined from the measured percent transmittance confirms the presence of absorption bands corresponding to the Nd-element. Grown crystal has lower cut off wavelength at 213 nm. The energy band gap of the grown crystal was found to be 6.10 eV. The photoluminescence study confirms the violet and blue emission.

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Figure Captions

Fig. 1 UV-vis transmission spectrum of Nd:NMZB crystal

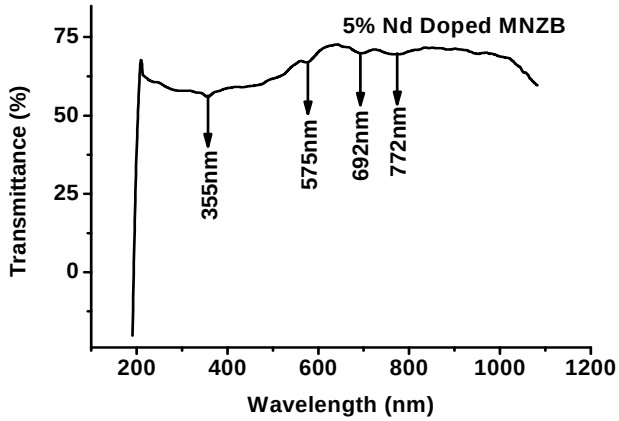

Fig. 2 A plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ (eV) of Nd:NMZB crystal

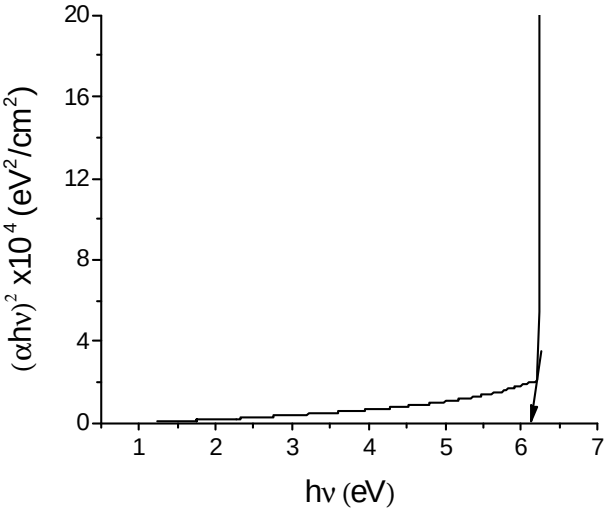

Fig. 3 PL spectrum of Nd:NMZB crystal. (a) Excitation spectra (λ_{em}-417nm) and (b) Emission spectra (λ_{ex}-378nm)