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Study on a multifunctional crystal $LiMnBO_3$

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ABSTRACT

Single crystal of high temperature phase of $LiMnBO_3$ in the hexagonal (*h*) lattice has been grown by slow-cooling method with $LiBO_2$ as flux. The transmission spectrum reveals that *h*-$LiMnBO_3$ is highly transparent from 680 to 3000 nm and its absorption bands in the visible and ultraviolet regions are assigned to *d*–*d* transitions of Mn^{2+} ions. Second-harmonic generation (SHG) was measured with a fundamental light at 2090 nm using the Kurtz and Perry technique, which showed that its effective SHG coefficient was about half that of LiB_3O_5(LBO). AC impedance spectroscopy shows that along the crystallographic *b* axis the conductivity presumably due to Li ion migration is 1.1×10^{-7} S cm^{-1} at 394 °C and the activation energy E_a is 0.599 eV. Together with its chiral magnetic ground state, present study shows that *h*-$LiMnBO_3$ is an interesting multifunctional material to possess also nonlinear optic and ionic conducting properties.

1. Introduction

In recent years, wide arrays of multifunctional materials have been proposed because of their integrated electrical, magnetic, optical and mechanical properties. For instance, the commercial piezoelectric materials, α-quartz (SiO_2) and lead titanate ($PbTiO_3$) are the core materials in a great number of devices such as actuators, sensors, and transducers [1,2]. As typical magnetic-optical materials, Yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) and doped-YIG have been widely applied in tunable microwave devices, circulators, isolators, phase shifters, nonlinear devices, etc. [3,4]. Lithium niobate ($LiNbO_3$) and lithium tantalite ($LiTaO_3$) have found significant applications that exploit their electro-optic characteristic, such as electro-optic modulation [5,6].

$LiMnBO_3$ was first synthesized by Legagneur et al.; they explored the possibility of using the boron-based compound $LiMnBO_3$ as a candidate electrode material for lithium ion battery [7]. Since then, many efforts have been continuously made to improve the discharge capacity, electrochemical activity, cycling performance of $LiMnBO_3$ [8–10]. However, up to now, as an electrode material $LiMnBO_3$ was synthesized only by solid-state reaction method and there has been no report on the electrochemical properties of bulk $LiMnBO_3$ crystals. As a matter of fact, $LiMnBO_3$ exists in two polymorphs: the low-temperature monoclinic form *m*-$LiMnBO_3$ which was synthesized below 400 °C in hydrothermal conditions [11], and the high-temperature hexagonal form *h*-$LiMnBO_3$ [7] with space group P 6/bar and lattice parameters of $a = 8.172$ Å and $c = 3.1473$ Å which is related to the present work. Magnetic neutron diffraction results reveal that *h*-$LiMnBO_3$ contains antiferromagnetic (AFM) MnO_5 chains along *c* direction and orders in a novel chiral ground state in the *ab* plane consisting of a mixture of one ferromagnetic (FM) Mn_3 triangle and two normal 120° frustrated AFM Mn_3 triangles [12].

In addition to the interesting Li transport and Mn–Mn magnetic interactions, the arrangement of the borate group BO_3 in the structure is critical in achieving significant nonlinear optical (NLO) effects. Within the *ab* plane, all of the three BO_3 groups are approximately aligned in the same direction (Fig. 1). According to the anionic group theory which assumes the macroscopic NLO coefficients can be obtained by directional summation of the contributions from the anionic groups within the unit cell of a given crystal [13,14], such an arrangement of BO_3 groups in $LiMnBO_3$ can be identified as a favourable factor to produce a large second harmonic generation (SHG) response. It is well established now the borate crystals are the best candidate NLO materials for high power laser frequency conversions since the discovery of BaB_2O_4 (BBO) and LiB_3O_5 (LBO) crystals [15,16] due to their large NLO coefficients and high damage threshold. Therefore, efforts were made herein to grow bulk single-crystal $LiMnBO_3$ and investigate its electro-chemical and optical properties.

2. Experimental

h-$LiMnBO_3$ single-crystals were prepared from MnO and $LiBO_2$ by spontaneous nucleation using the slow-cooling method according to a two-step process. The starting powders were

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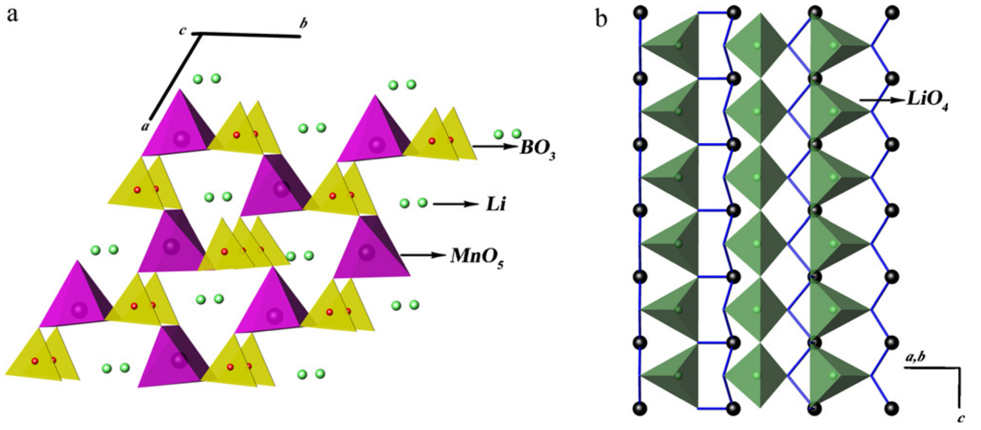

Fig. 1. (a) Crystal structure of $LiMnBO_3$ along *c*-axis. (b) Crystal structure of $LiMnBO_3$ on *ac* plane.

analytical reagent (AR) grade Li_2CO_3, MnO and H_3BO_3. $LiBO_2$ was first prepared from Li_2CO_3 and H_3BO_3 with the molar ratios of Li_2CO_3:H_3BO_3 = 1:1 by heating at 900 °C for 4 h. In the second step, MnO and $LiBO_2$ with the molar ratios of MnO:$LiBO_2$ = 1:1.33 were placed in a platinum crucible and first heated for 24 h at 950 °C to ensure homogeneity of the melt, and then cooled from 850 to 800 °C at a rate of 2 °C/day, followed by cooling to room temperature at a rate of 10–30 °C per hour. The crystal growth process was kept in a reducing atmosphere of H_2(10%)/N_2. Well-faced transparent purple crystals in millimetre-size were obtained at the surface of the content in the Pt crucible.

A crystal plate of 4 mm × 3 mm × 0.5 mm (Fig. 2, inset) in size was chosen for optical and electrochemical properties studies. Room temperature optical transmission spectrum was recorded with a Lambda 900 UV–vis-NIR (Perkin-Elmer) spectrophotometer in the region of 185–3000 nm. The impedance measurements with an Agilent 4294A Precision Impedance Analyzer in the frequency range from 100 Hz to 100 MHz were performed in the temperature range 200–400 °C. The silver-coated single crystal plate was placed in the sample holder about 2 mm next to the thermocouple.

Though quite strong SHG signal (green light) from the single crystal was clearly observed, quantitative measurement could not be done with an Nd:YAG laser because $LiMnBO_3$ absorbs part of the SHG signal at 532 nm. The optical SHG response of the crystalline sample of the $LiMnBO_3$ was instead measured by means of the Kurtz–Perry method [17] with an fundamental light at 2090 nm, which was generated with a Q-switched Ho:Tm:Cr:YAG laser. Since SHG efficiencies are known to depend strongly on particle size, the $LiMnBO_3$ crystallites were ground and sieved into distinct particle sizes: 0–50, 50–74, 74–105, 105–150, 150–200, 200–300 μm, respectively. For comparison, powdered LiB_3O_5 (LBO) crystal of similar particle size served as a reference.

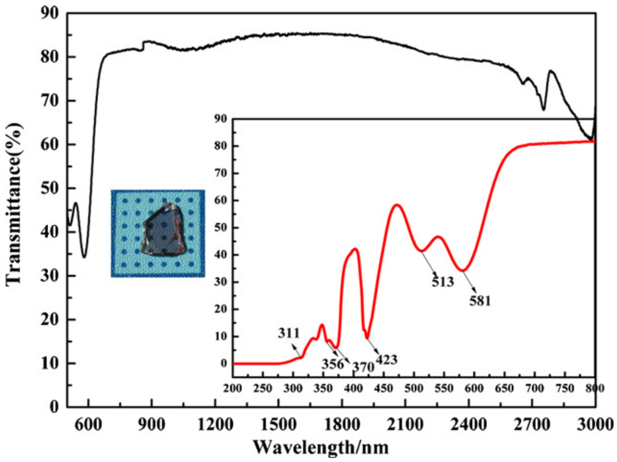

Fig. 2. The transmission spectrum of the $LiMnBO_3$ crystal.

3. Results and discussion

3.1. Transmission spectrum

The transmission spectrum of the $LiMnBO_3$ crystal, shown in Fig. 2, consists of six absorption bands: a small weak peak at 311 nm, two sharp absorption peaks at 370 and 423 nm, along with a weak shoulder peak at 356 nm, and two broad bands at 513 and 581 nm. These absorption bands can be tentatively associated to the *d*–*d* transitions of Mn^{2+} ions based on Tanabe–Sugano diagram of the d^5 configuration [18,19]: the first small, weak peak 311 nm together with the shoulder peak at 356 nm and the two higher and sharp energy peaks at 370 nm, 423 nm are attributable to the crystal-field independent or weak dependent transitions from the ground state $^6A_1(^6S)$ to the $^4T_1$ (^4P); $^4E(^4D)$; $^4T_2(^4D)$; $^4A_1$ and $^4E(^4G)$ levels, respectively. The two broad bands at 513 nm and 581 nm are assigned to transitions from the ground state $^6A_1(^6S)$ to $^4T_2(^4G)$ and $^4T_1(^4G)$ with band broadening due to crystal-field effect.

The energy levels were calculated using the Racah (*B* and *C*), the crystal field splitting (*Dq*) and the Trees correction parameters (α) [20,21]. In the present study, the same free ion value of α = 76 cm^{-1} was adopted as that for $Mg_2B_2O_5$:Mn^{2+} [21]. The energy matrices including Trees correction terms were presented by Tanabe and Sugano and Mehra [20], respectively.

The electrostatic parameters of B = 866 cm^{-1}, C = 2638 cm^{-1} and Dq = 727 cm^{-1} were evaluated using the following equations [21]:

$$B = \frac{94\alpha + \sqrt{49(T_2 - T_1)^2 - 768\alpha^2}}{49}$$

$$C = \frac{T_1 + T_2 - 27B - 26\alpha}{10}$$

$$(10Dq)^2 = (10B + 6C + 12\alpha - T_3)^2 - (C - 8\alpha)^2 - \frac{4(3B + 2\alpha)^2(10B + 5C + 20\alpha - T_3)}{19B + 7C + 10\alpha - T_3}$$

We have taken T_1 as the energy difference between $^6A_1(^6S) \rightarrow {}^4E(^4G)$, T_2 as $^6A_1(^6S) \rightarrow {}^4E(^4D)$, which are independent of crystal field interactions, and T_3 as $^6A_1(^6S) \rightarrow {}^4T_1(^4G)$.