

Preparation and scintillation properties of translucent $\text{LiCaBO}_3:\text{Ce}$ polycrystalline plates



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ABSTRACT

Translucent $\text{LiCaBO}_3:\text{Ce}$ thin plates were prepared by liquid phase sintering using LiBO_2 as a sintering aid, and their fluorescent and scintillation properties were investigated to examine the possibility to use as neutron scintillator. Since the initial part of the directionally solidified specimen contained a second phase of $\text{Ca}_3\text{B}_2\text{O}_6$, LiCaBO_3 may melt incongruently, and simple melt growth of $\text{LiCaBO}_3:\text{Ce}$ is consequently difficult. Translucent thin plates 300 μm in thickness were successfully fabricated from $\text{LiCaBO}_3:\text{Ce}$ sintered compacts. Although strong fluorescence with the peak wavelength of 390 nm was observed in photoluminescence measurement, scintillation light yield and detection efficiency by α -particle irradiation were rather poor. The diffuse reflectance spectrum of $\text{LiCaBO}_3:\text{Ce}$ revealed existence of an absorption band other than Ce^{3+} bands in the ultraviolet region. The band may correspond to defect levels, which interrupt the energy transfer from the conduction band of the host to the 5d level of Ce^{3+} resulting in the degradation of the scintillation performance.

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1. Introduction

Neutron scintillators have been used for imaging and diffraction technologies and will find other application fields such as medicine and security systems with the progress of scintillation performance. ^3He gas have conventionally been used as a gas scintillator material due to its high neutron capture efficiency [1]; however, the ^3He resources are limited, and development of alternative materials has accordingly been required. A number of solid scintillators have so far been developed, for example, $\text{LiF}/\text{ZnS}:\text{Ag}$ [2], Li-glass [3], and $\text{LiCaAlF}_6:\text{Ce}$ [4] etc. These solid materials have high densities in comparison with the gas type and highly efficient detection is expected. In neutron detection, a scintillation material is excited by the energy of the charged particles generated via the capture reactions between neutrons and nucleus of particular isotope species such as ^6Li or ^{10}B in the material. Consequently, the kind of the elements that form the host material is limited. In most solid neutron scintillators such as Li-glass and $\text{LiCaAlF}_6:\text{Ce}$ single crystals, only ^6Li is used as a neutron capturing isotope. Although the total energy of charged particle resulted from the reaction between

neutron and ^{10}B is less than that from the neutron- ^6Li reaction, neutron capture cross-section of ^{10}B is much higher than that of ^6Li , and abundance ratio of ^{10}B is larger than ^6Li . Thus B-bearing materials have also been developed as neutron scintillators [5–7]; however, the light yield of such materials were relatively small.

$\text{LiCaBO}_3:\text{Ce}$ was reported as a blue phosphor [8] based on the $5d \rightarrow 4f$ transition of Ce^{3+} substituted in the Ca^{2+} site; however, it has not been studied as a scintillation material. Since $\text{LiCaBO}_3:\text{Ce}$ is composed of relatively light elements, low sensitivity to gamma-ray from the background under neutron measurement environment is expected. Furthermore, since Ce^{3+} usually exhibits intensive light emission and short decay time in conventional scintillator materials, $\text{LiCaBO}_3:\text{Ce}$ is expected to exhibit excellent scintillation properties. According to the reported phase diagram of the pseudobinary system $\text{LiBO}_2\text{--CaO}$ [9], LiCaBO_3 melts congruently at 915 °C indicating the possibility of melt growth such as Bridgman and Czochralski techniques. On the basis of these features, $\text{LiCaBO}_3:\text{Ce}$ may be one of the candidates as a neutron scintillator material.

In this study, we attempted directional solidification of $\text{LiCaBO}_3:\text{Ce}$ to investigate the possibility of its melt growth. Liquid phase sintering was also tried to obtain translucent thin plates of $\text{LiCaBO}_3:\text{Ce}$, and their fluorescence and scintillation properties were examined to discuss the possibility as a neutron scintillator.

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2. Experimental

2.1. Solidification behavior of $\text{LiCaBO}_3\text{:Ce}$

Powders of LiBO_2 (99 up %), CaCO_3 (99.99%) and CeO_2 (99.9%) were used as starting materials. These raw materials were mixed with ethanol in agate mortar in the composition of $\text{LiCa}_{0.9925}\text{Ce}_{0.005}\text{BO}_3$. After forming under a uniaxial pressure of 100 MPa, the mixed powder was fired at 800 °C for 10 h in H_2 (4%)/Ar. The calcined compact was charged in a carbon crucible, which was then placed in a tube furnace with some tilting angle. After melting for 5 h, the melt was directionally solidified by reducing the temperature at a rate of 1.5 °C/h in N_2 atmosphere. This cooling rate corresponds to the linear growth rate of 0.5 mm/h on the basis of the temperature gradient of the tube furnace. The initial part of the obtained solidified specimen was ground and evaluated by X-ray diffraction (MiniFlex600, Rigaku).

2.2. Preparation of translucent $\text{LiCaBO}_3\text{:Ce}$ polycrystalline plates

The calcined powder of $\text{LiCa}_{0.9925}\text{Ce}_{0.005}\text{BO}_3$ prepared with the same process described above was mixed with LiBO_2 as a sintering aid. After forming pellets under a uniaxial pressure of 100 MPa, they were sintered at 800 or 820 °C for 50 or 100 h in H_2 (4%)/Ar, which was effective to reduce the tetravalent cerium to trivalent one. The obtained pellets were gray and its absorption could inhibit emission. Post-sintering annealing at 800 °C for 10 h in N_2 resulted in colorless pellets. The sintered compacts were polished to be mirror finish, followed by etching in hot water. The crystalline phases of the sintered compacts were identified by X-ray diffraction and their microstructures were observed with a scanning electron microscope (JSM-6390LVS, JEOL). The polished surfaces of the sintered compacts were adhered to glass plates with epoxy resin. The compacts were then ground to be 300 μm in thickness resulting in translucent thin plates.

2.3. Optical characterization of $\text{LiCaBO}_3\text{:Ce}$

As a method to easily check the light emission by photons, the sintered bodies were irradiated with handy UV lamp (AS ONE, Japan) having a wavelength of 365 nm. After that, fluorescence properties were investigated. The measurements of photoluminescence spectra were carried out using a JASCO FP-6500 (JASCO.CORDERATION, Japan).

The scintillation properties for α -particles were evaluated using ^{241}Am . The energy of α -particles emitted from ^{241}Am approximately corresponds to the energy of the charged particles generated by the capture reactions between a neutron and a nucleus of ^6Li . Accordingly, if scintillation for α -particles was observed, scintillation for neutrons is surely expected. A thin copper plate with a hole of 2 mm in diameter was placed between the α -particle source and the sample to regulate the flux of α -particles. The specimen was fixed on the photomultiplier tube with the aid of optical grease. A photomultiplier tube (H7195, Hamamatsu Photonics), a delay line amplifier (460, Ortec), a pulse stretcher (542, Ortec), and a multi-channel analyzer (WE7562, Yokogawa Electric) were used to evaluate the response for α -particles. The integration time constant of the delay line amplifier was set at 250 ns, considering the decay time of the scintillators.

3. Results and discussion

3.1. Solidification behavior of $\text{LiCaBO}_3\text{:Ce}$

Fig. 1(a) shows a directionally solidified ingot of $\text{LiCaBO}_3\text{:Ce}$.

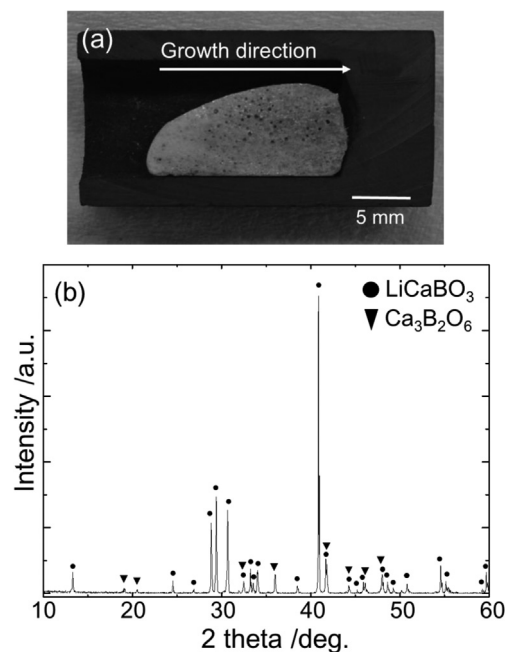


Fig. 1. (a) The solidified specimen, (b) XRD pattern of the initial part of the solidified specimen.

Since the initial part of the ingot is rounded due to the poor wettability of the melt to the carbon crucible, the definitive point from which solidification started is unclear. A large portion that is thought to surely contain the start point is therefore examined by the X-ray powder diffraction. As shown in Fig. 1(b), the major phase in the portion is $\text{LiCaBO}_3\text{:Ce}$ but formation of an appreciable amount of $\text{Ca}_3\text{B}_2\text{O}_6$ can be observed. This result indicates that LiCaBO_3 may melt incongruently and $\text{Ca}_3\text{B}_2\text{O}_6$ is the initial phase for the melt composition of LiCaBO_3 . In the reported phase diagram for the pseudobinary system of $\text{LiBO}_2\text{--CaO}$ [9], the difference in the melting temperature of LiCaBO_3 and eutectic temperature for the $\text{LiCaBO}_2\text{--CaO}$ system is very small and the eutectic composition is very close to the LiCaBO_3 composition. Since the amount of $\text{Ca}_3\text{B}_2\text{O}_6$ was small, peritectic and liquidus temperatures could be confused as eutectic and melting temperatures, respectively. Even though LiCaBO_3 melts incongruently, the single crystal of LiCaBO_3 can be grown by using an appropriate flux. In fact, relatively large LiCaBO_3 grains were obtained in the ingot; however, the crystal quality was rather poor due to the existence of numerous bubbles. The bubbles are thought to be formed by constitutional super-cooling because of the high viscosity of the borate-based melt. The purpose of the present study is to examine the possibility of $\text{LiCaBO}_3\text{:Ce}$ as a neutron scintillator and this could be done transparent or translucent specimen can be obtained. Therefore we focused to prepare sintered compact of $\text{LiCaBO}_3\text{:Ce}$ with large grains instead of single crystal growth, which is a challenging task.

3.2. Characterization of the polycrystalline thin plates

Fig. 2 shows microstructures of the sintered compacts. All the samples comprised only the LiCaBO_3 phase and no secondary phase was observed. In both samples (a) and (b) sintered at 800 °C, the grains that had particle size 20–50 μm were observed. The uniformity of the compact (b) sintered for 100 h was improved better than that of (a) sintered for 50 h. For the sintering time of 50 h, larger size of grains were observed in the sample sintered at 820 °C than that sintered at 800 °C. The relative densities of all samples

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