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Development of novel growth methods for halide single crystals

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ABSTRACT

We developed novel growth methods for halide scintillator single crystals with hygroscopic nature, Halide micro-pulling-down [H-μ-PD] method and Halide Vertical Bridgman [H-VB] method. The H-μ-PD method with a removable chamber system can grow a single crystal of halide scintillator material with hygroscopicity at faster growth rate than the conventional methods. On the other hand, the H-VB method can grow a large bulk single crystal of halide scintillator without a quartz ampule. $CeCl_3$, $LaBr_3$, Ce:$LaBr_3$ and Eu:SrI_2 fiber single crystals could be grown by the H-μ-PD method and Eu:SrI_2 bulk single crystals of 1 and 1.5 inch in diameter could be grown by the H-VB method. The grown fiber and bulk single crystals showed comparable scintillation properties to the previous reports using the conventional methods.

1. Introduction

Radiation detectors using a scintillator crystal and a photo acceptance unit have been used for various applications such as survey meter, medical and security devices, resource exploration and so on. In these applications, there are some required properties for the scintillator crystals which are the high light yield and energy resolution, small decay time and suitable density in order to achieve the high spatial resolution, reduction of noise and dead time, high sensitivity to radiation and others. To fulfill the requirements for the scintillator crystals, some single crystals have been investigated as a scintillator in the world and many novel scintillator materials have been developed. In the material research, halide scintillator crystals, chloride, bromide and iodide materials, are especially attracting worldwide attentions due to the big potential as a scintillator with the high light yield and high energy resolution. The halide materials have relatively small band gap compared to the oxide and fluoride materials and the light yield of scintillator material is inversely proportional to the band-gap according to the reported theoretical formula [1]. Therefore, the high light yield of halide materials originates from the small band gap. In addition, the high light yield provides the high energy resolution.

However, many halide materials have strong hygroscopicity and it is difficult to grow their single crystals with high crystallinity and transparency because the starting materials can't be handled in air without some harmful influences. Therefore, these halide single crystals have been grown just by the Vertical Bridgman [VB] method with a sealed quartz ampoule or the Czochralski [Cz] method in a dry room. Typical growth conditions of the VB method for halide materials are described in the previous reports [2–5].

On the other hand, we have developed various novel oxide and fluoride scintillator crystals by the micro-pulling-down [μ-PD] method [6–10]. The μ-PD method has several advantages compared to the conventional methods. One of the advantages is various shape-controlled single crystals, such as fiber, columnar, plate, tube and so on, can be grown using a custom-designed crucible [11–13]. Secondary, a single crystal can be grown at approximately ten times as fast as the conventional method. In addition, only small quantities of starting materials, less than 1 g, are required for the crystal growth and it is suitable for the material research composed of high-cost materials. Therefore, the μ-PD method has been mainly used for the novel material research of single crystal.

On the above background, we tried to develop a halide μ-PD [H-μ-PD] method for material research of the halide single crystals. However, the typical μ-PD method can't grow a single crystal of the material with hygroscopic nature which can't be handled because

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the setting of the starting materials, crucible, insulator and others are performed in air. Therefore, the H-μ-PD method has a removable chamber which can separate the inside of the chamber from outside atmosphere. On the other hand, the μ-PD method can grow just fiber crystals which typical maximum diameter is approximately 10 mm and the μ-PD method haven't been used for the applications of mass production with some exceptions. Therefore, we also developed a halide VB [H-VB] method for the crystal growth of halide bulk single crystal using the H-μ-PD furnace.

2. Development of the novel growth methods

2.1. Development of the H-μ-PD method

Fig. 1(a) is a schematic of the H-μ-PD method. The removable chamber can be separated from a vacuum pump and it can be entered in a glove box through the pass box without exposing the inside of the chamber to outside atmosphere. The size of the pass box limited the maximum length of the grown single crystal. In the glove box, concentrations of oxygen and moisture are controlled less than 1 ppm and it is filled with high-purity Ar gas. This system enables to grow single crystals of the hygroscopic halide materials without exposing to outside atmosphere in all processes from the setting of crystal growth to taking out the grown crystal. The H-μ-PD furnace is shown in Fig. 1(b). The furnace is composed of the removable chamber, the turbo molecular pump, the high-frequency [HF] induction coil for the heating of the crucible and the Charged Couple Device [CCD] camera for the observation of the liquid-solid interface during crystal growth.

2.2. Development of the H-VB method

Fig. 1(c) is a schematic of the H-VB method. As with the crystal growth by the H-μ-PD method, the removable chamber was used to prevent the exposure of the inside to the outside atmosphere. We designed a carbon crucible with 1 inch inner diameter and a pocket for the seed crystal at the bottom. In the glove box, a seed crystal was set in the pocket of the crucible and the starting materials were entered in the crucible above the seed crystal. The starting materials were melted by the HF induction coil and the melt was pulled down with the crucible as shown in Fig. 1(d). After the crystal growth, the crucible was cooled to room temperature for 12–36 h. Then, the chamber was entered in the glove box and the grown crystal was taken out from the crucible.

3. Experimental

To demonstrate the crystal growth of halide materials by the H-μ-PD method, we selected the $CeCl_3$, $LaBr_3$, Ce:$LaBr_3$ and Eu:SrI_2 which were well-known scintillators. Details of their crystal growths by the H-μ-PD method were described in the previous reports [14–16]. Starting materials, $CeCl_3$, $CeBr_3$, $LaBr_3$, EuI_2 and SrI_2

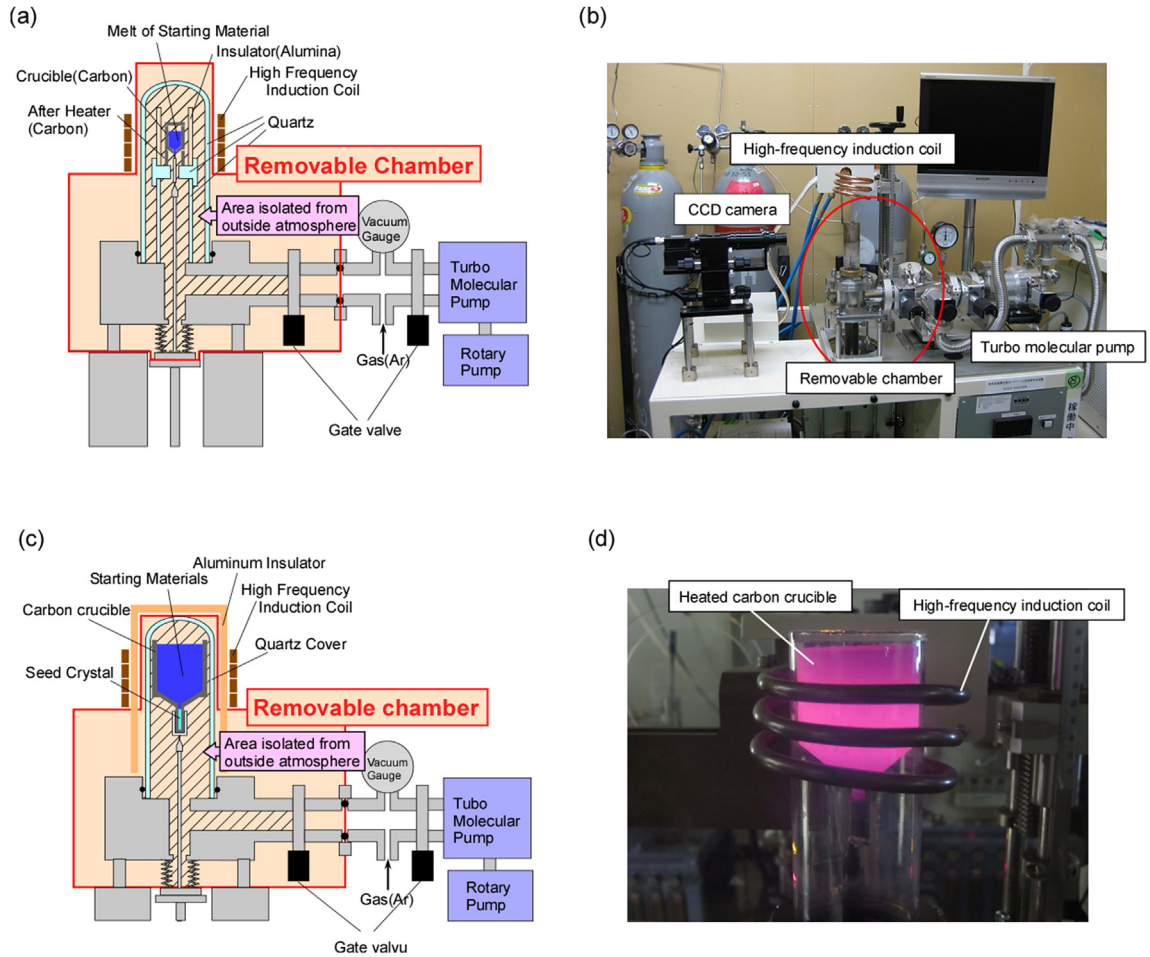

Fig. 1. (a) Schematic of the H-μ-PD method using the removable chamber and (b) the H-μ-PD furnace. (c) Schematic of the H-VB method using the removable chamber and (d) the crucible during crystal growth by the H-VB method.

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