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Growth and scintillation properties of pure CsI crystals grown by micro-pulling-down method

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ABSTRACT

Single crystals of pure cesium iodide (CsI) have been grown from the melt using micro-pulling-down (μ-PD) method. Two kinds of crucible (graphite one and quartz one) were used for the growth and the grown crystals were investigated by X-ray diffraction (XRD) and X-ray rocking curve (XRC) analysis. The XRD analysis did not confirm any impurity phases and a sub-grain structure was observed for each sample in the rocking curve measurement. Under X-ray irradiation, strong STE emission peaks around 300 nm were observed together with some luminescence related to unintentionally present impurities. The STE emission peaks are characterized by fast decay times of several ns and about 20 ns which are interpreted as the on-center-type STE (V_K + e) and off-center type STE (H + F) recombinations, respectively. The light yield of the STE-related emissions has been estimated to be 3000 ph/MeV. Other emission peaks were observed at 410 nm and 515 nm. The former one can be related to Br-contamination and it is characterized by a relatively slow decay time of 6 μs. Concerning the latter one at 515 nm, similar luminescence was observed for the water-doped CsI grown by Bridgman method.

1. Introduction

The μ-PD method is a relatively novel method for crystal growth from the melt [1] and it has several advantages compared to some conventional methods such as Czochralski (Cz) and Bridgman (BS) methods. In the μ-PD, the shape of crucible plays an important role, because it is not only container of the melt but also the shaper for the grown crystal. The shape of the crystal is strongly depended on the configuration of the die part of the crucible positioned at the bottom and the die has a hole to allow liquid transport from the crucible. Crystals in the form of fiber, column, plate, and tube can be grown with a special shaped crucible [2]. Furthermore, from the aspect of material research, the fast growth speed of typically 0.05–1 mm/min is considerably attractive for a material screening. Many functional crystals including for example Pr-doped $Lu_3Al_5O_{12}$ [3] for gamma-ray detection and rare-earth-doped $LiCaAlF_6$ [4] for neutron measurements were developed using this convenient method so far. One of the most important factors is the wettability between the crucible and the melt. When the wettability is good, the solid/liquid interface is formed under the crucible and the shape of grown crystal is formed by the shape of the die. Otherwise, solidification occurs inside the crucible and the diameter of grown crystal can be determined by the shape and dimensions of the hole. From the point of view of pulling the melt, namely the difficulty of crystal growth, it would be defined that good conditions for the μ-PD crystal growth method are "good" or "poor" wettability between the melt of materials and crucibles. Generally, metal crucibles made of Pt, Ir or Re are used for an oxide crystal growth and graphite crucibles are used for a fluoride crystal growth. One unique feature of the crystals grown by the he μ-PD method is uniform distribution of dopants or impurities along the growth direction [5], thus superior properties are expected (e.g. energy resolution in scintillator materials). However, most halide crystals except the fluoride ones can be grown only by the B.S. method with a sealed quartz ampoule [6] or the Cz method in a dry environment due to the increased hygroscopicity. Therefore, we developed a modified μ-PD method with a removable chamber system for the growth of hygroscopic halide crystals.

CsI is a well known fast scintillator with an emission peaking at 300 and 340 nm with a fast time response characterized by a decay time of 10 ns. It has been suggested by Nishimura et al. [7], that the

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300 and 340 nm peaks are related to the intrinsic luminescence decay of the on-center-type STE (V_K + e) and off-center type STE (H + F), respectively. It also has been observed that the crystals with poor quality exhibit the increase of slow component in longer wavelength range and decrease of scintillation light yield [8]. In the recent years, much effort was devoted to obtain better scintillation characteristics of pure and Tl-doped CsI single crystals. In this study, we grew pure CsI crystals by the modified μ-PD method using two kinds of crucibles made of graphite and quartz material, then the crystallinity and scintillation properties were investigated. Actually, when trying to use platinum crucible the crystal could not be grown due to the corrosive nature of CsI and its unsuitable wettability. Then the crystalline and the scintillation properties were investigated. Water-doped CsI was also prepared by a vertical BS method to clarify the origin of impurity luminescence.

2. Experiment

2.1. Crystal growth and crystalline properties

Schematic drawing of μ-PD crucible and the growth procedure for the system with radio-frequency (RF) heating is given in Fig. 1. The crucibles are placed on an alumina pedestal in a vertical quartz tube and are heated using RF generator. When the quartz crucible is used, carbon pedestal is inserted as a heater. The modified μ-PD crystal growth furnace for halides has a removable chamber system, which can be moved in a glove box filled with Ar gas [9]. Preparation of a starting material and setup of crucible, seed and insulators were carried out inside the glove box with an atmosphere control to keep the oxygen and water moisture concentrations below 1 ppm. High purity (99.999%) CsI powder from Chemetall Company was used as a starting material. This starting material was weighed and charged into the crucibles. Fig. 2 displays these crucibles made of graphite and quartz. These crucibles had a cylindrical shape and were equipped with a hole of 1 mm in diameter. Pt wire with 0.5 mm in diameter was used as a seed instead of a seed crystal.

The removable chamber was installed on vacuum and gas system with a stage movable in vertical direction. When the installation of the chamber was finished, the chamber was heated up and evacuated to less than 10^{-3} Pa by a rotary pump and turbo molecular pump to remove moisture in the raw material. Then the chamber was filled with the high purity Ar gas. After these processes, the crucible was heated up to the melting temperature of CsI. The

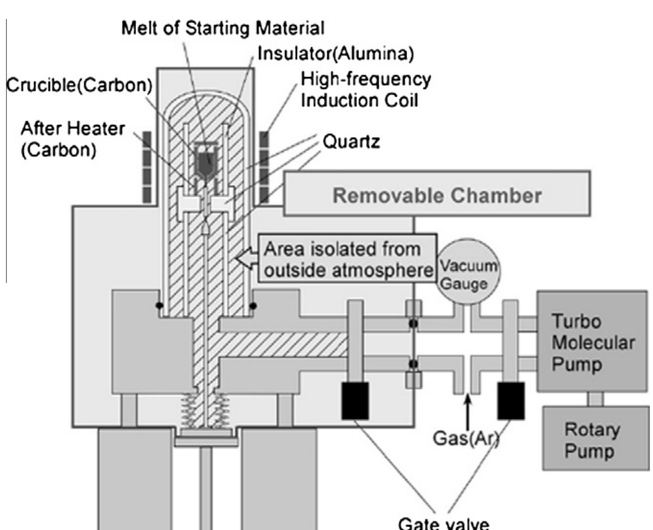

Fig. 1. Schematic diagram of the modified μ-PD method with a removable chamber system.

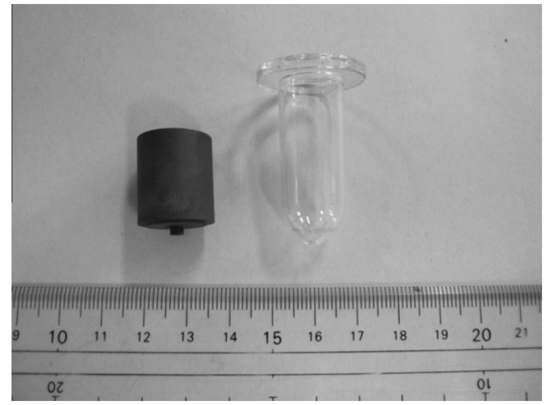

Fig. 2. Photograph of two kinds of crucible, carbon graphite (left) and quartz (right).

pulling rate was controlled between 0.01 and 0.1 mm/min. The grown crystals were cooled down to room temperature in 1 h after the pulling was finished. To examine the contaminations from the atmosphere inside the furnace, glow-discharge mass spectrometry analysis was carried out.

The phase of the grown crystals was confirmed by the X-ray diffraction (XRD) analysis (RINT-2000, Rigaku corporation) in the 2θ of 10°–90° with step of 0.02°. The X-ray was generated by Cu target using the tube voltage of 40 kV and current of 40 mA. The crystallinity was investigated by X-ray rocking curve (XRC) analysis for the (1 1 0) plane of grown crystals using a high-resolution diffractometer (Rigaku ATX) with Cu Kα1 radiation diffracted by a two-bounce Ge (2 2 0) channel monochromator. Crystallinity of the grown CsI crystals was measured by ω-scan and evaluated using the width of the peak. All the X-ray experiments were carried out at room temperature.

2.2. Scintillation evaluation

The grown crystals were cut and polished to evaluate the scintillation properties. Pulse height spectrum measurements were carried out under gamma-ray (^{137}Cs) excitation with a photomultiplier tube R7600U (Hamamatsu Photonics) connected to an ORTEC 113 preamplifier, an ORTEC 572 shaping amplifier and an Amptek Pocket MCA 8000 A multichannel analyzer for digital signal conversion. The bias voltage of the PMT was supplied at +600 V (ORTEC 556). The samples were mounted on the PMT with an optical grease (OKEN, 6262A) and covered with several layers of Teflon tape to collect scintillation photons. At the same time, decay time measurement was done using a digital oscilloscope (Tektronix TDS3052B). To evaluate the light yield, BGO crystal was used as a Ref. [10].

The radio-luminescence spectra measurement was performed at room temperature under X-ray irradiation. The excitation source was the RINT-2000 and the X-ray tube was supplied 40 kV and 40 mA. The emission spectra were measured using a Andor DU-420-OE CCD cooled down to 213 K by a Peltier module. This CCD was coupled with ORIEL INSTRUMENTS monochromator with 285 grooves/mm and 280 nm blaze wavelength. The scintillation light was sent to CCD through a 2 m optical fiber to avoid direct irradiation of CCD by the X-ray.

3. Results and discussion

3.1. Crystal growth and crystallinity

CsI crystals were successfully grown by the μ-PD method with two kinds of crucibles and they are shown in Fig. 3. Both are trans-