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Challenge and study for developing of novel single crystalline optical materials using micro-pulling-down method

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Abstract

Micro-pulling-down (μ-PD) method is a useful tool to search for new materials. This method allows us to prepare single crystalline materials quickly and relatively inexpensively. Grown crystals are of sufficient dimensions for all the necessary characterization by optical and luminescence methods, including photo- and radio-luminescence, decay kinetics and light yield measurements. Recent results obtained for laser and scintillator materials at Pr-doped $Y_3Al_5O_{12}$, $Lu_3Al_5O_{12}$, $YAlO_3$, Y_2SiO_5, Lu_2SiO_5, fluorides like Ce-doped PrF_3, mixed binary fluorides AEF_2–REF_3, (Ce:AE:(Gd,Y)F_3, AE = Ba, Sr, Ca) and Yb- and Tm-doped RE_2O_3 (RE = Y, Lu, Sc) are summarized here. Practical importance of μ-PD method follows also from the shaped crystal growth aspect. It is possible to grow shaped and/or device-size crystals from the melt using a single step process. Recent improvement of μ-PD method makes the quality of μ-PD crystals comparable with those prepared by Czochralski (Cz), Bridgeman, or other classical growth techniques.

Keywords: Crystal growth from the melt; Oxide; Fluoride; Luminescence; Emission; Decay time; Laser; Scintillator; Micro-pulling-down method

1. Introduction

Study of emission centers in different crystal host is an active area of the research, which is addressed by many researchers. Thus, understanding of driving factors of the optical processes in the crystals with different concentrations of dopants are often needed. Interaction between dopant ions and lattice phonons, asymmetric crystal field perturbations or the energy transfer processes are typical examples on which the research effort is focused. Furthermore, the distribution of the dopant ions in the crystals is very important factor to determine the spectral and temporal properties of the emission [1,2]. For this purpose, we need crystals with variety of dopant concentrations having similar (high) crystalline perfection.

The micro-pulling-down (μ-PD) method allows growing a single crystal using small amount of row material, typically less than 1 g, in 5–12 h because of very high growth speed typically 0.05–1 mm/min. This very high growth speed makes the μ-PD method the unique tool for single crystalline materials screening.

The μ-PD is melt growth technique and can be categorized as one of the shaped crystal growth methods, so called Stepanov method [3]. In the case of μ-PD, crucible plays an important role. It is not only container of the melt but also the shaper (die) for the shaped crystal growth. Therefore, the possibility of producing device-size matched crystals in the form of fibers, rod-, plate- and tube-shaped elements to reduce the loss due to machining is also the advantage of this system.

The μ-PD method was proposed by Dr. Ohnishi at the Electrotechnical Laboratory, in Tsukuba, Japan and established at the Fukuda Laboratory, Institute of Materials Research, Tohoku University in Sendai, Japan [4,5].

In this paper, the result of our efforts to develop novel single crystalline optical materials using μ-PD method is

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reviewed showing the recent 5 year results achieved at both oxide and fluoride systems.

2. Crystal growth apparatus and procedures

2.1. μ-PD method with resistive heating

Schematic of the μ-PD apparatus with resistive heating is given in Fig. 1 [4,5]. Electric power is applied directly to the crucible container made of platinum or platinum/rhodium foil and pipe. The crucible is heated due to resistive heating of the crucible material. The crystals are normally grown under air atmosphere with pulling down rate ranged from 0.1 to 1.0 mm/min. The position and size/shape of solid/liquid interface is adjusted manually by selection of suitable magnitude of electric currents flowing through the crucible and the afterheater. The pulling rate is additional variable allowing control and correction of the crystal size/shape and quality.

The crystal/nozzle diameter ratio can be adjusted in the range of 0.2–1.0 for the system shown in Fig. 1. After the growth procedure, the crystal is separated from the molten zone, pulled down with the rate corresponding to cooling rate of about 10–50 °C/min, and removed from the holder. In opposite to bulk crystals very slow cooling of the fiber materials after growth is generally not necessary because difference between the temperatures in core and peripheral parts of the fiber is low due to small diameter. Heating of the seeds before growth is also made with relatively high rate.

2.2. μ-PD method with RF heating using Pt and Ir crucible

Schematic presentation of μ-PD crucible and growth procedure for the system with radio-frequency (RF) heating is given in Fig. 2. The crucible is placed on an alumina pedestal in a vertical quartz tube and is heated using RF generator. The calibrated orifice of about 0.3–1.0 mm in diameter is made in the crucible bottom to allow the melt flow to the direction of solid/liquid interface. The crucible temperature was controlled by power of the RF coil. The

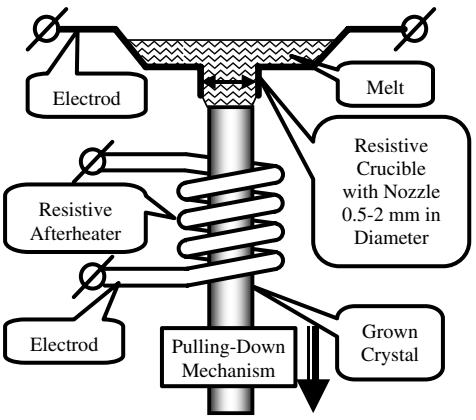

Fig. 1. Schematic of μ-PD system with resistive heating.

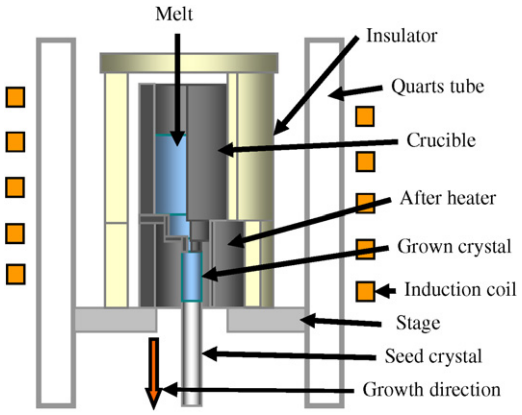

Fig. 2. Schematic of μ-PD system with RF heating.

crucibles were charged for up to 100 vol% regarding powder of starting materials or about 5–20 vol% regarding the melt. High density and high purity (99.7%) alumina ceramic was used to surround the crucible for the thermal insulation [6].

Crystal growth conditions such as temperature and atmosphere particularly depend on crucible material. In the case of Pt or Pt–Rh, oxidizing atmosphere is acceptable, however, the temperature is limited up to 1700 °C. Ar atmosphere is used to prevent oxidation of the crucible. In the case of Ir, the temperature can be up to 2100 °C, however, atmosphere should be non oxidizing to protect the crucible. Visual observation of solid/liquid interface, and the crystals is made by CCD camera and monitor. Spatial resolution of the observations is in the range of 50–100 μm.

2.3. Precise atmosphere control μ-PD method for fluorides

Fluoride materials are under systematic investigation, as they found applications in various fields, such as laser host, optical materials for VUV as well as IR regions, resistant window materials for excimer lasers etc. Recently, we have started to investigate fluoride crystals in view of their usage in the scintillation detectors. We are also realizing the necessity of a new preparation method to facilitate remarkably the screening of fluoride host lattices, dopant concentration and optimization of the growth parameters for new crystalline materials. The μ-PD method introduces a suitable innovative concept of single crystal growth and material screening.

As for fluoride crystal growth, two articles were presented at the same time [7,8]. Chamber, which can be evacuated down to 10^{-5} Torr by rotary and diffusion pumps was proposed in order to remove all the possible oxygen source [7]. It was equipped with a window made of CaF_2 for visual observation of the meniscus region, solid/liquid interface, etc. using CCD camera with monitor. Carbon or platinum were used for crucible material. The crucibles were surrounded by refractory carbon and inductively heated using a RF generator.

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Starting materials were prepared from the stoichiometric mixture of high purity chemicals. They were thoroughly mixed and put into the crucible. Chamber was evacuated up to 10^{-4} Torr. Then, the crucible was heated up to 600 °C and kept about 1 h at this temperature in order to remove oxygen traces caused by moisture of raw materials and adsorbates on the chamber surface. During this baking procedure, the chamber was further evacuated down to 10^{-5} Torr. After the baking, the recipient was filled with high purity Ar (99.999%) until ambient pressure. The crucible was heated up to the melting temperature [7,9].

2.4. μ-PD method with RF heating using Re crucible

For the ultra-high melting temperature materials like rare-earth sesquioxides (Y_2O_3, Lu_2O_3 and Sc_2O_3), rhenium (Re) is used as crucible. As the temperature is too high, nothing can be used as an insulator and therefore, a space is required between Re crucible and zirconia ceramics. Atmosphere is the mixture of Ar and 1–5% H_2. The role of H_2 is to suppress Re oxidization [10]. As for the seed at the initial experiment, most of all metals cannot be used because of high melting temperature of these oxides (over 2400 °C). Only Re or Re/W wire can be used for this purpose, and after a crystal is obtained, it can be used as a seed.

3. Optical materials grown by the μ-PD method

3.1. Pr doped single crystals for scintillator application

Recently, Pr-doped scintillators were re-recognized and attracted the interest of device designers. Fast and intense emission is expected from the 5d–4f transition of the Pr^{3+} ion when the host lattice have medium–strong crystal field, which shifts the lowest 5d state below the $^1S_0$ level of Pr^{3+} and makes the 5d–4f radiative transition possible.

Pr-doped $Lu_3Al_5O_{12}$ (LuAG), $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), Y_2SiO_5 (YSO) and Lu_2SiO_5 (LSO) were prepared by the μ-PD method and the radioluminescence spectra are shown in Fig. 3. We found that Pr:LuAG is most efficient among the above crystals. Energy spectra of Pr:LuAG excited using γ-ray are shown in Fig. 4.

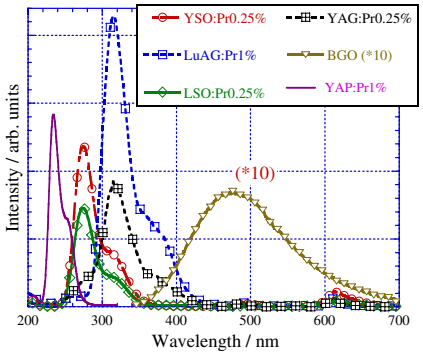

Fig. 3. Radioluminescence spectra of Pr-doped LuAG, YAG, YAP, YSO and LSO grown by the μ-PD method (exc. X-ray, RT).

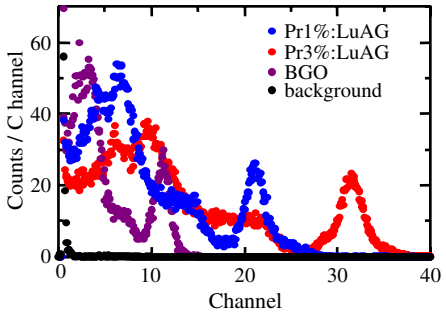

Fig. 4. Energy spectra of Pr:LuAG using γ-ray from ^{137}Cs (spectrally uncorrected).

3.2. Ce:PrF_3 crystals

Single crystals of $Pr_{1-x}Ce_xF_3$ with $x = 0.0$, 0.001, 0.005, 0.01, 0.03, 0.05, 0.10, 0.20, 0.6, 0.8, 1.0 were grown by the μ-PD method. 4N fluoride powders were used for the growth experiments. The grown crystals were transparent and of greenish color (except CeF_3:colorless), 3 mm in diameter and 15–50 mm in length. Neither visible inclusions nor cracks were observed. Radioluminescence spectra were measured. When the concentration of Ce^{3+} increased, the emission intensity of Pr^{3+} decreased (Fig. 5). This is due to the energy transfer process from $^1S_0$ level of Pr^{3+} to the Ce^{3+} 5d states [7,11].

3.3. Design of new host crystal for optical materials

Fedorov and Sobolev [12] studied crystal structure and phase transition temperature for trifluorides, which systematically change with rare-earth atomic number or RE^{3+} ionic radii. From LaF_3 to SmF_3, it is stable as tysonite structure and there are no phase transition between melting temperature and room temperature. From TbF_3 to HoF_3, it is also stable as β-YF_3 type structure and there are no phase transitions between melting and room temperatures. However, two groups of trifluoride compounds (Sm, Eu, Gd and Er, Y, Tm, Yb, Lu) have phase transitions. Thus,

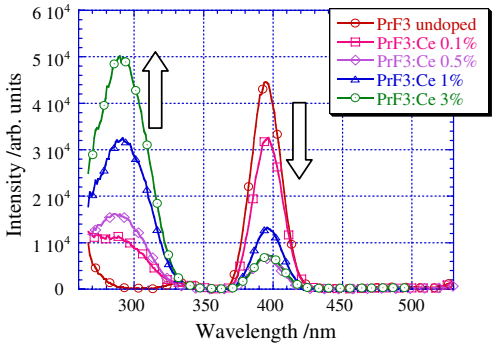

Fig. 5. Emission spectra of Ce:PrF_3 (exc. X-ray, RT).

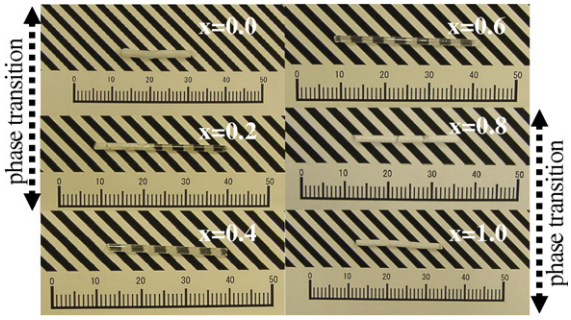

Fig. 6. Photo of $(Gd_{1-x}Y_x)F_3$ crystals grown by the μ-PD method.

single crystals of SmF_3, EuF_3, GdF_3, ErF_3, YF_3, TmF_3, YbF_3, and LuF_3 cannot be obtained directly from the melt. Therefore the solid solution with average ionic radii ranged from that of Tb to Ho cations was designed to allow melt growth of the crystals without phase transitions. Solid solution of GdF_3 and YF_3 were prepared with wide variety of ratio to find appropriate composition (Fig. 6). It was found that $(Gd_{1-x}Y_x)F_3$ with $0.4 \leqslant x \leqslant 0.6$ have no phase transition from room temperature to melting temperature. 4N fluoride powders were used for the growth experiments.

Luminescence from the perturbed Ce^{3+} can be observed in fluoride lattice when the AE^{2+} (AE = Mg, Ca, Sr, Ba) is codoped [13] i.e. in Ce:AE:(Gd,Y)F_3. Efficient energy transfer from $Gd^{3+}$to perturbed Ce^{3+} was observed and Ca^{2+} and Sr^{2+} co-doping was found the best in the perturbed Ce^{3+} creation [14].

3.4. Ultra-high melting temperature crystals

Non-doped, Yb doped and Tm doped Y_2O_3 single crystals were grown from the melt using Re crucible (Fig. 7) [10]. Non-doped, and Yb^{3+}-doped Lu_2O_3 and Sc_2O_3 single crystal were also grown with 3–5 mm in diameter and around 10 mm in length. 5N oxide powders were used for the growth experiments. As grown crystals show some color, but became colorless after annealing in air at 1400 °C for 24 h.

3.5. Device-size shaped crystal growth

As the bottom of the crucible can be used as a die, it is possible to grow shaped crystals using μ-PD method. For the precise shape control, design of the shape of the die is

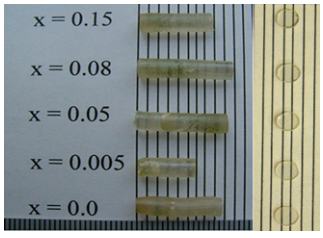

Fig. 7. $(Y_{1-x}, Yb_x)_2O_3$ single crystals grown by the μ-PD method.

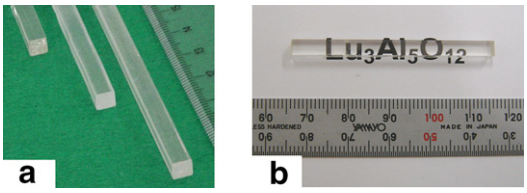

Fig. 8. Single crystal with square rod shape grown by the μ-PD method: (a) sapphire single crystals and (b) LuAG single crystal.

one of the most important parameters. It is prepared considering the wetting angle between crucible material and melt in the growth atmosphere. Recent improvements of μ-PD method allow us to consider device-size shaped crystal growth. So far, square rod , tube and plate shape single crystals were grown. As an example, LuAG and sapphire samples grown in the form of square rod are shown in Fig. 8. 5N oxide powders were used for the growth experiments. The Yb^{3+}:LuAG demonstrates best performances among garnets for Yb laser [15], and Pr^{3+}:LuAG shows best performance among Pr doped scintillators [16].

4. Conclusions and prospects

Recent development of μ-PD method is reviewed. Researches using μ-PD method are accelerated in the world and significant development has been done in recent 5 years. Especially, the following three technologies; "growth of fluoride crystal with precise atmosphere control chamber", "crystal growth of ultra-high melting temperature (above 2100 °C) materials" and "device-size shaped crystal growth" should be noted. This method can be applied to alloys, semiconductors and other important technical materials. Automation of the crystal growth process, continuous feeding system, and multi-die growth system will be established in the nearest future.

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