CaF_2 crystal growth for using optical components of laser

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Abstract

Large vacuum Bridgman-Stockbarger (BS) equipments was composed for growing large diameter CaF_2 crystals. The CaF_2 crystal of 4.5-inch was grown under the conditions of freezing temperature gradient of 12°C/cm and growing rate of 3mm/hr. Also the 6-inch crystal was grown by using thermal stabilization method under freezing temperature gradient of 14°C/cm and growing rate of 2mm/hr. The dislocation density was characterized for evaluating the quality of crystals. And the optical properties such as transmittance, refractive index and fluorescence were analyzed in order to investigate on the applications of optical components.

1. Introduction

CaF_2 crystal having low chromatic aberration is used for the broadcasting camera lens for HDTV, lens for refractive astronomical telescope and camera lens for specialists because the refractive index are very little changed with visible wavelength. CaF_2 crystal is also suitable to fabricate lens, windows and prisms for eximer laser such as ArF (193nm), XrF (248nm) laser and so on, in short VUV and UV wavelength [1], and is expected to use to the optical components of the lithography machine using eximer laser. CaF_2 crystals are also commonly used as host crystals for laser (CaF_2 : Eu), gamma radiation detectors (CaF_2 : Eu) and thermoluminescent dosimeters (CaF_2 : Mn, CaF_2 : Dy and CaF_2 : Tm). CaF_2 single crystals with doped rare earth elements of U^{3+}, Dy^{2+} and Eu^{2+} are used as laser sources in the regions of near infared to infared wavelength (0.7~2.5μm) [2]. CaF_2 crystals are used for epitaxial growth of IV-VI compound semiconductors such as PbS, PbTe, etc.[3]

In this study, we have to compose a modified high vacuum Bridgman-Stockbarger (BS) furnace, to choose a profitable conditions for crystal growth. And we grew CaF_2 single crystal of 4.5-inch and 6-inch in diameter that have a good optical properties in range of UV-Visible-IR wavelength and characterized their properties.

2. Experimental

2.1. CaF_2 single crystal growth

A crucible of non-seed type having cone angle of 90° for growing 4.5-inch and 6-inch CaF_2 crystal is machined by the isotropic graphite material with same thermal conductivity and same mechanical strength as the each direction. For this study we used CaF_2 starting material of 99.3% in purity (the granule shape of 2 ~ 4mm in size) and the scavenger additive [4] of PbF_2(Cerac Co., <325mesh, purity 99.9%). The amounts of scavenger additive were 1wt% to total weight of CaF_2 raw material. Before the crystal growth, we have tried to determine the soaking and growing temperature for automatic program control through the several melting experiments. First, in 4.5-inch crystal growth, growth rate was 3mm/hr and vacuum level was 10^{-6} torr in chamber. Molybdemn (Mo) plate for thermal reflection was composed below a conical tip of crucible, and their effects were examined as the use of Mo plate of umbrella shape.

In case of 6-inch crystal growth, second, a graphite screen playing a roll of thermal stabilization was covered round the outer wall of crucible. The purity of CaF_2 granules which is 99.3 wt% was filled 10kg in graphite crucible with PbF_2 (100g). The 6-inch crystals were grown with and without graphite screen.

Each sample was grown under the growth rate of 2mm/hr, and the monitored temperature for melting the raw material was about 1327±3°C at the conical tip of crucible. The monitoring thermocouple, TCa, to measure the temperature at conical tip of crucible and the other thermocouple, TCb, at near heating element were settled to a distance of about 50mm, and their data were used to explain the shape of solid-liquid (SL) interface indirectly.

2.2. Characterizations

The melted aspect of conical tip of grown crystal was evaluated with visible inspection, and the formation of boundary was observed as cutting conical portion vertically to the growing direction. He-Ne laser (632.8nm in wavelength, 10mW power, manufactured by Uniphase, USA) was used for inspecting the light scattering phenomenon by internal inclusions such as bubble and other cavity, etc. The samples for EPD(etch pits density) method were prepared to etch the cleaved surface in 97% H_2SO_4 solution at 50°C for 60 ~ 90 sec. The dislocation and their density in cleaved plane of CaF_2 crystal was evaluated with observing etch pits using optical microscope (Olympus, Japan). In order to analyze optical transmittance, the crystal blank (disk type ; 4.5 inch diameter × 13mm thickness) was vertically cut on the grown direction of crystal body and optically polished using diamond slurry and automatic polisher (15-inch plate, automatic atomization set, Engis, Korea) as follows ; lapping (15um) - pre-polishing (3um) - final polishing (0.5um).

The optical transmittance was analyzed using UV-Visible spectrometer (Hitachi U-2001, Japan, a range of 200 ~ 900nm, scan speed is 120nm/min.) for considering the quality of transparency in range of UV (200 ~ 360nm) specially, and the optical refractive index in visible wavelength were analyzed as the portions of ingot. For analyzing a fluorescence concerning on 4.5-inch crystal we searched a high absorption spectrum and then analyzed an emission peak occurred by fluorescence. Spectrofluorometer (Model SPEX 1681 Fluordog) using Xenon arc lamp (400W) was used for observing fluorescence with 0.5nm resolution.

3. Results and Discussions

3.1. Growth of CaF_2 single crystal of 4.5-inch in diameter

We obtained the vertical temperature gradient of 12°C/cm and determined the growing (1440°C) for 4.5-inch (112mm) CaF_2 crystal growth. The grown CaF_2 crystals of 4.5-inch in diameter were clear, and they were not contained any color, observed with visible inspection. However the melted aspects of conical tip were different as selecting the use of Mo thermal reflector. CaF_2 starting materials melted perfectly with using Mo reflector of umbrella shape (about 15° angle), while the raw material didn't melt at the tip of cone without the Mo reflector at the same conditions (controlled growing temperature = 1440°C, location of crucible = 450mm is from base plate to tip of crucible). It seems to suggest that the supplied heat from heating element is reflected by Mo plate of umbrella shape because the thermal radiation has a reflective property like light, so that the thermal radiation will be concentrated to the cone of crucible. Also, the SL (solid-liquid) interface is expected to form a convex by the concentration of thermal energy at cone during crystal growth. By Chang et al. [5], the SL interface becomes convex when the crucible receives the thermal energy from heating element during crystal growth. The SL interface of crystal grown by applying Mo thermal reflector was more planer or convex than the case without Mo thermal reflector. It can be proved from results that the grown crystal with Mo thermal reflector was a single crystalline, whereas the poly-grain was not eliminated in the grown crystal without Mo thermal reflector in Fig. 1.

3.2. Growth of CaF_2 single crystal of 6-inch in diameter

The pulling rate of 2mm/hr in each crystal growth was fixed, and the temperature at conical tip was 1327 ± 3°C. In case of sample NGS which don't use a graphite screen, the grown crystal was clear and colorless, and the melted aspect of conical tip was good. Yet this crystal was the polycrystalline having two grains. In Fig. 2 , a grain boundary was formed on the vertical cutting planes to the growth direction, and it was progressed toward the inner portion of ingot during the crystal growth. In this case, the radial temperature gradient (TCb-TCa) monitored by thermocouple TCa and TCb is about 70°C, which TCb is very higher than TCa in initial state of growth. Also, during the crystal growth, the change of temperature (TCa) at tip was smaller than that (TCb) at edge of crucible. Exactly the thermal energy at the wall of crucible is faster deprived than the inner portion of crucible during crystal growth. Accordingly two nuclei were formed at tip and edge of cone at the same time during the crystal growth because of the fast heat loss from melt to crucible, and then the boundary formed between two grains moved toward the inner portion of ingot because the SL interface is shaped to the concave shape (the convex isotherm) from large radial thermal gradient. When the crucible receive the heat from the exterior such as heating element, also, the SL interface becomes more convex. [5] As the thermal conductivity of graphite crucible is larger than that of CaF_2 material, however, the heat loss for crystal growth at melt/crucible interface become greater than that at the center of crystal/melt interface. Jasinski and Witt [6] introduced on the crucible effect through simulation in Ge and CdTe crystal growth. Accordingly the heat loss at the wall of crucible must be controlled by a treatment for minimizing the radial temperature gradient. The graphite screen is very available to minimize the radial temperature gradient in crucible, so that the graphite screen was adopted between the crucible and the heating element.

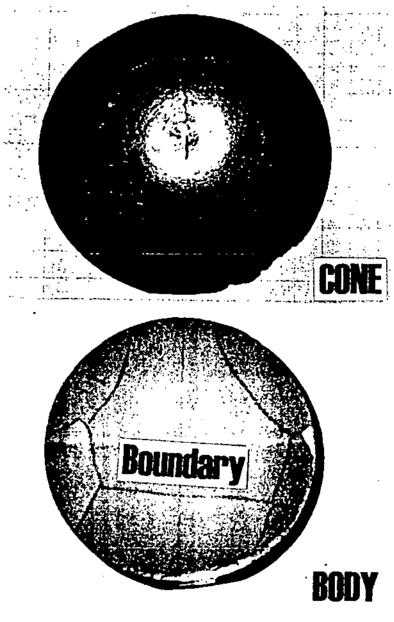

Fig. 1. The boundary aspects as the use of Mo thermal reflector without Mo reflector.

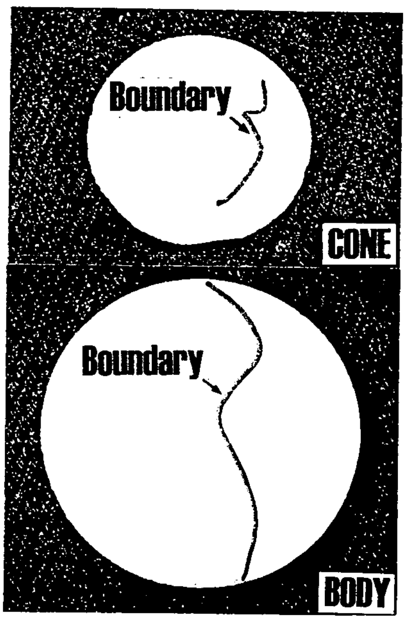

Fig. 2. Photographs of cross-section planes in sample NGS

We grew a good crystal of which is sample GS using graphite screen and ceramic warmer. This crystal was very clear and colorless, and the conical tip of ingot was completely melted. Sample GS is a single crystalline in whole region. It seems that the SL interface was nearly formed as the planer shape by using graphite screen. This estimate can be explained to small radial temperature gradient(2~4°C) profile. During the crystal growth, exactly, the temperature at the interface of crucible/crystal is similar with that at the center of crystal/melt interface by using graphite screen. It is because a graphite screen to do duty as thermal stabillization received indirectly a convection of heat flow from heating element. Since the radial temperature gradient of sample GS is very smaller than that of sample NGS, so that the isotherm have a possiblity to be flatten. Monberg et. al, [7] suggested that the polycrystalline nucleation at the crystal/crucible interface be controlled through reducing the radial temperature gradient in InP crystal growth.

3.3. Characterizations of 4.5-inch UV grade crystal

He-Ne laser (632.8nm, 10mW) was used for an inspection of internal inclusions. First of all, before an inspection by using He-Ne laser, the body of crystal must be polished for the observation of light scattering. We irradiated to one of cutting plane of the polished body in case of 4.5 inch single crystal grown by using umbrella shape of Mo reflector. The red beam is partially transmitted, then the light scattering phenomenon is occurred in internal region of crystal. Stockbarger [4] suggested on light scattering, which is caused by tiny hexagonal cavity. In our experiments, the scattered region was observed in a range of 20 ~ 40mm from the top of body because the melt containing the gas was directly solidificated by supercooling [8], so that the gaseous inclusions might be isolated in the SL interface.

The quality of crystal was determined by analyzing the dislocation density from etch pits. The etch pits are the typical shape of triangular formed in cubic structure on a (111) cleaved surface, and the average density(EPD) is $1.4 \times 10^4 cm^{-2}$, which is a good quality.

The transmittance of grown crystal was evaluated by means of UV-Visible and FT-IR spectrometer. The transmittance was above 93% in the 7500 ~ $500cm^{-1}$. The transmittance of polished crystal blank, also, is up to 93.5% in visible range and up to 91.6% in UV range(200 ~ 360nm) as a shown in Fig. 3. The transmittance result in UV to IR ranges is expected to be very suitable for lens and windows of eximer and other lasers and IR analytical cell windows. The refractive index was measured as a wavelength of visible region using at 22 ℃. It is very similar with the other commercial products, and the refractive index (n_d = 1.43378 ~ 1.43380 @587.56nm in wavelength)of grown crystal as the portions of ingot is homogeneous. Also, Abbe's constant calculated from the refractive index and the follow equation are homogeneous in the values of 94.9 to 95.1 as the portions of ingot.

$$\textit{Abbe's constant,}\quad \nu_d = (n_d - 1)/(n_F - n_c) = (n_{587.6} - 1)/(n_{486.1} - n_{656.3})$$

where, n_{number} means the refractive index at some wavelength.

High fluorescence intensity was occurred at the 420nm wavelength of violet-color spectrum in case of applying the conditions of maximum excitation at 337nm wavelength. In general the fluorescence at 420nm wavelength is occurred in natural fluorite. Fig. 4 illustrates the variation of the fluorescence intensity as the dislocation density. Peak A is a non-strained crystal of $1.4 \times 10^4 cm^{-2}$, peak B is a strained crystal of $2.0 \times 10^4 cm^{-2}$. With increasing the dislocation density, exactly, the fluorescence intensity is increased. It is possibly estimated from this that the transitions associated with defects formed by the broken ionic bond of between cation and anion and/or between anion and anion make a great contribution to the fluorescence phenomenon.

4. Conclusions

We organized the vacuum Bridgman-Stockbarger (BS) equipment which is reached to high temperature(above 1600°C) in high vacuum level(10^{-5} ~ 10^{-6} torr) for large diameter CaF_2 single crystal growth. The CaF_2 crystal of 4.5-inch diameter and 210mm length having a good quality could be grown in the conditions of growing temperature of 1440°C, growth rate of 3mm/hr and vertical freezing temperature of 12°C/cm. The CaF_2 crystal grown by using umbrella shape of Mo thermal reflector was formed perfectly to the single crystalline from bottom to top of body.

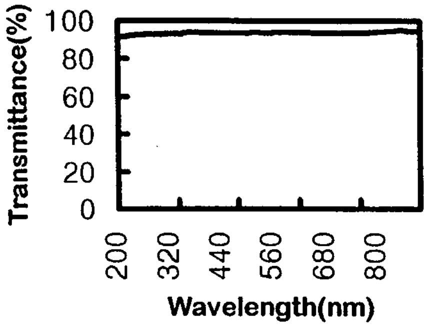

Fig. 3. Transmittance of 4.5 inch CaF_2 crystal in the range of UV-Visible (200 ~ 900nm in wavelength)

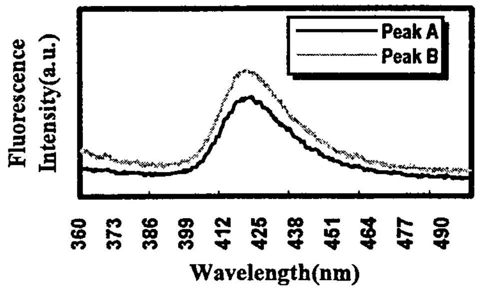

Fig. 4. Fluorescence spectra of non-strained and strained crystals

The grown 6-inch CaF_2 crystal by thermal stabilization method that use a graphite screen and a ceramic pipe was perfect single crystal, and clear and colorless under the conditions of growth rate of 2mm/hr, vertical temperature of 14°C for freezing and temperature of 1324°C at conical tip. The graphite screen contribute to form a flat SL interface by the result of radial temperature gradient of about 2 ~ 4°C. The CaF_2 crystal having dislocation density of $1.4\times10^4 cm^{-2}$ has the transmittance of above 91% in UV region, and the refractive index and Abbe's constants were similar to that of a commercial product. The fluorescence intensity was increased as increasing the dislocation density.

5. Reference

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