Growth of CaF_2 crystals by using multi-crucible set in vacuum Bridgman-Stockbarger(BS) method

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Abstract

The growth method using multi-crucible set is very useful for mass production of optical crystals such as CaF_2, LiF, BaF_2 etc. CaF_2 crystals of various diameter(42, 54 and 68mm) could be grown by means of multi-crucible set in one running operation and they were investigated to the formation of grain boundary as the cone-angle of crucibles. The qualities of crystal were evaluated by observing grain number and dislocation density. The transmittance was analyzed by using UV-Visible-NIR spectrometer.

1. Introduction

Calcium fluoride(CaF_2) crystal shows superior characteristics including low refractive index, low dispersions, high transmittance and wide transmittance range than conventional optical glasses. CaF_2 crystal, consequently, give a effect in photographic applications as an achromatic lens, which is eliminated secondary chromatic aberration. After Stockbarger[1] had grown CaF_2 crystals for aerial camera and telescope systems, CaF_2 crystals have been used for various fields of optical components. CaF_2 crystal is used for the lens of the astronomical telescopes and the analytical microscopes. Especially the refractive astronomical telescope used with CaF_2 crystal lens has high resolution relatively in same aperture, comparing with general telescopes. In addition, it is fit for the use of cell windows in order to analyze liquid samples with FT-IR spectrometry because of low solubility(<0.0001g/100g H_2O), and the useful wavelength range for spectrometric analysis is 4,000 ~ 1,140cm^{-1}. CaF_2 crystal has been grown by using vacuum Bridgman and/or Stockbarger method.[2, 3] But, in general growing methods, the amount of grown crystal was only one piece, and the diameter of crystal was one kind. This study using multi-crucible set technique is for producing CaF_2 a crystal of various diameter and high quality in one growing process.

2. Experimental Procedures

The crucibles of non-seed type for growing CaF_2 crystal are manufactured by isotropic graphite materials. The cone angles of crucible concerning on 42 and 54mm in diameter crystals were composed to 60°, 90° and 120° in order to investigate the formation of grain boundary as the change of cone angle. A crucible for 68mm diameter crystal is located in the central position and the other crucibles of 8 pieces for 42mm and 54 mm diameter crystals are alternatively settled round a crucible for 68mm diameter crystal. Therefore the grown crystals of 9 pieces can be produced by using this method. CaF_2 raw material of 99.3% in purity was packed into the crucible with PbF_2 like scavenger additive of 1wt% for crystal growth. The growing temperature was 1420°C in vacuum condition of about 10^{-6} torr, and the growth rates were 3mm/h and 5mm/h.

The grown CaF_2 crystals were characterized to crystal and optical quality. First, the light scattering portion was determined by using He-Ne laser(632.8nm in wavelength, 10mW, manufactured by Uniphase, USA) to be red beam. Second, the quality of grown crystals were determined by observing grain number and EPD(etch pit density), and the preferential growth

plane of poly-grain crystal was analyzed by means of x-ray diffraction(XRD) method. Finally the transmittance was characterized by using spectrometer(Shimazu UV-3100, Japan) in the range of UV-Visible-NIR, and the spectrometric analysis for the actual test was carried out using acrylic regin(test sample) by using of FT-IR spectrometer(MIDAC Co.)

3. Results and Discussions

3.1. The effect of cone angle of crucible

In Fig. 1 (a) and (b), the CaF_2 crystals of 42mm in diameter(42mm crystal) were occasionally grown to two grains, and the crystals of 54mm in diameter(54mm crystal) were ceaselessly formed to two to four grains in crucible position near heating element. Yet the crystals of 68mm in diameter(68mm crystal) was perfectly grown to single grain as Fig. 1(c) whenever 68mm crystal was grown.

It seems that the poly-grain is formed from the wall of crucible near the heating element because the heat loss at the wall of crucible near heating element is faster than that at the center of crucible.

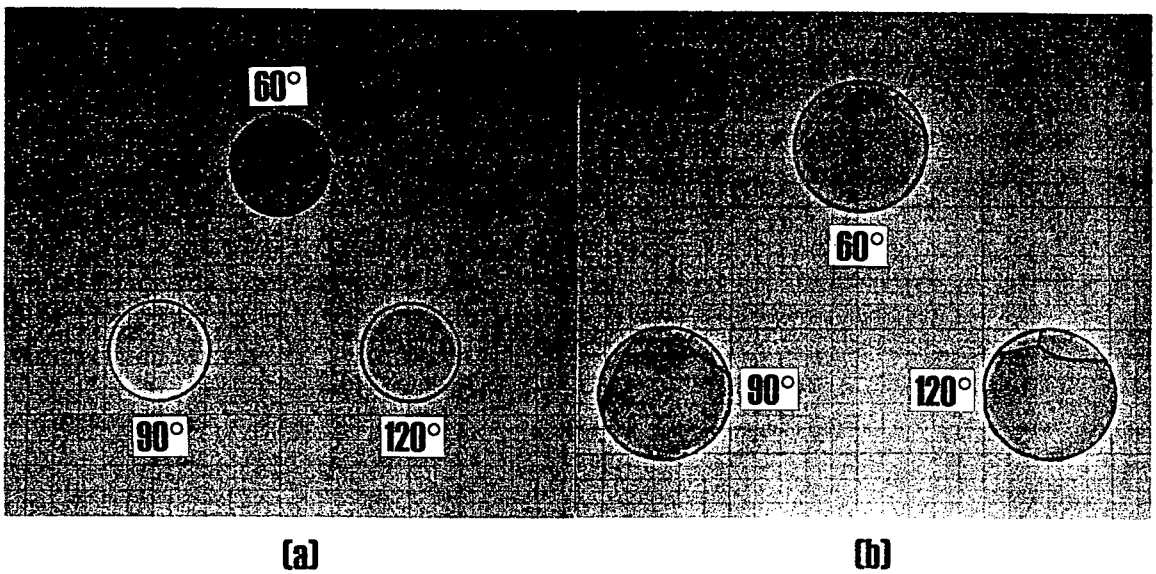

Fig 1. Photographs of the grown crystals ; (a) 42mm diameter, (b) 54mm diameter

As a shown in Fig. 2, the 42mm crystals were grown in two grains. Each grain was characterized to the preferential growth plane by means of XRD analysis. By the result of XRD analysis, the preferential growth plane of two grains was (111), so that the boundary between two grains is confirmed to be form to "twin boundary".

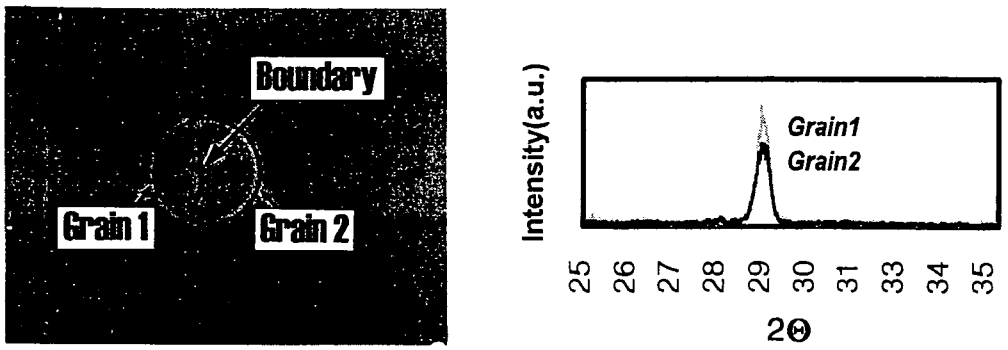

Fig 2. Photograph and XRD patterns of 42mm diameter crystal having two grains

Meanwhile the 68mm crystal grew to single grain all the time because it locates in the center of multi-crucible set. This result expects that the SL (solid/liquid) interface was flatten by the homogeneous thermal loss between "melt to solid" and "melt to crucible" because the wall of crucible don't come close to the heating element.

Also it is confirmed that the cone angles of crucible don't give a effect to the formation of polycrystalline, but the polycrystalline is formed by the inappropriate thermal stabilization as the structure of crucible setting and the crucible position which the crucible get near heating element.

3.2. The effect of growth rate

The grain number and region of 42mm and 54mm crystals were increased with the increase of growth rate(from 3mm/h to 5mm/h). However, the 68mm crystal was a single crystalline, regardless to low and high growth rate. Also the violet color was produced in all of crystals which were grown under the growth rate of 5mm/h. The region of violet color was formed to the top of crystal body, and the light scattering phenomenon was investigated by He-Ne laser radiation(632.8nm in wavelength, 10mW, red beam) in the whole region of crystals of 68mm, 54mm, and 42mm in diameter.

Nassau [4] suggested that the coloration is generated by growing the crystal in the condition of excess calcium. In this study, but, the violet colored crystal was produced not because it was grown by only excess Ca ions, but because it was grown by excess Ca ions and the generation of electron charged trap in F ions site vacancy. The absorption spectrum was analyzed by means of UV-Visible spectrometer at 190~230nm and 495~610nm, concerning on the violet colored crystal having the atomic ratio between Ca and F (1: 1.2)and growing under 5mm/h, whereas the absorption spectrum was not analyzed in visible range on the non-colored crystal having the similar atomic ratio (Ca : F = 1: 1.25) and growing under 3mm/h.

In the grown crystal under growth rate of 5mm/h, in accordance, the violet color may be generated because the electron charged in the absent fluorine ion site is supplied by high solidification rate.

3.3. Characterizations of the grown crystals

The 42mm crystal grown by multi-crucible set method was characterized from the dislocation distribution as the axial and the radial distance. Three samples of disk shape were prepared from cone(sample A), middle(sample B) and end(sample C) region of crystal body. The cleaved plane prepared for the radial and axial dislocation distribution was etched in the solution of H_2SO_4(97%) for 60 to 90sec at 50°C and observed by using optical microscopy(Olympus, Japan) in magnification of 200.

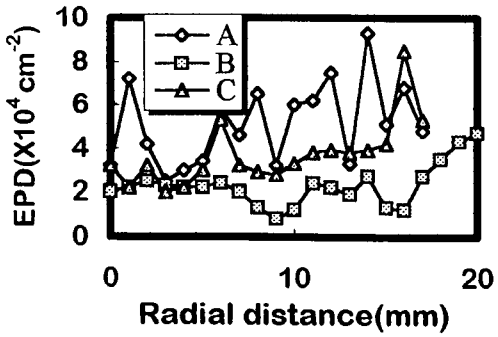

Fig 3. Radial distributions of dislocation density in case of 42mm crystal

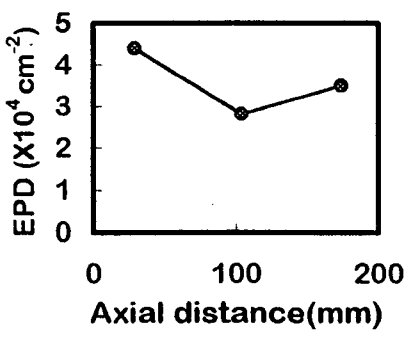

Fig 4. Axial distribution of dislocation density in case of 42mm crystal

Fig. 3 illustrates the radial dislocation distributions. Radial dislocation distributions tend to increase as the radial distance, and it shows the typical " W " distribution in Bridgman-

Stockbarger method or VGF method. Gault[5] investigated the increasing tendency of dislocation as the radial distance(from center to edge) in GaP crystal grown by VGF method.

Casagrande[6] , also, exhibited that the initial and end region have many dislocation amount while the middle region has small number of EPD in CdTe crystal. Fig. 4 shows the axial dislocation distribution. The EPD of initial portion (sample A) of crystal was much more generated than that at the other portions (sample B and C). Therefore it is confirmed that the middle portion is comparatively low EPD region in this study.

The crystal transparency was evaluated by means of UV-Vis-NIR spectrometer. The samples were selected to cone(sample A) and middle(sample B) of crystals body. As a shown in Fig. 5, the transmittance in each sample was up to 93% at above 300nm wavelength, and the transmittance in the range of 190 ~ 300nm shows the decreasing tendency sharply.
However sample A has more low transmittance than sample B in UV wavelength, and the EPD of sample A has much more than that of sample B. So the decreasing transmittance in UV wavelength region depend on the dislocation density. Meanwhile the analyzed transmittance is high in the range of Visible-NIR, so that it can be used for optical grade application such as camera lens, optical microscope lens and cell windows for FT-IR analysis, etc.

Also the actual test was tried by using the polished blank and water-soluble acrylic regin. The analyzing spectrum range is 4000 ~ 1000 cm^{-1}. The analyzed spectrum of acrylic regin using a grown crystal window is very similar with the spectrum using a commercial cell window.

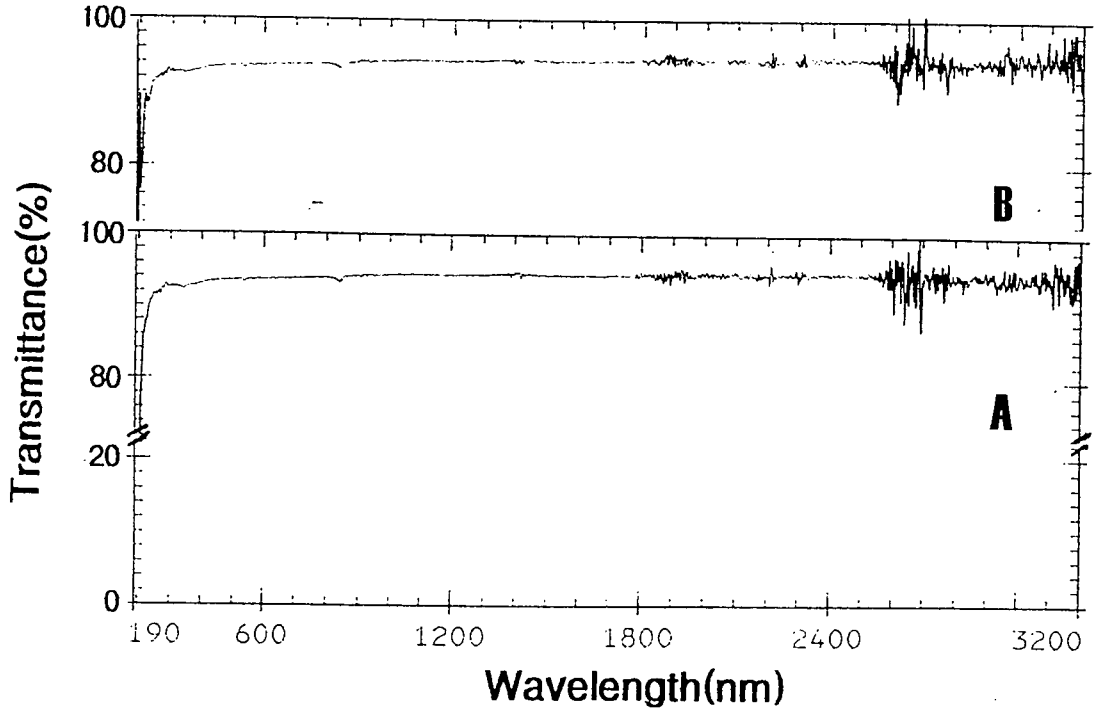

Fig 5. Transmittance of sample A and B in the range of 190~3200nm wavelength

4. Conclusion

The multi-crucible set was used for mass production and various crystal production in CaF_2 crystal growth. The crystals of various diameter were successfully grown by this method under 3mm/h and about 10^{-6}torr, and they were evaluated to have good optical quality which are high transparency of up to 93% in Visible-NIR and low dislocation density. The grown crystal quality decrease with increasing growth rate. The 42mm crystal shows the homogeneous properties such as transmittance and dislocation density. Also the actual test for using as cell window shows the successful results.

5. Reference

[1] D.C. Stockbarger, J. Opt. Soc. Am., 39(1949) 731
[2] H. Guggenheim, J. Applied Phys., 34(1963) 2482
[3] D. Nicoara and I. Nicoara, Materials Sci. and Eng. A, 102(1988) L1
[4] Kurt Nassau, Am. Mineral., 63(1978) 219
[5] W.A. Gault, E.M. Monberg and J.E. Clemans, J. Crystal Growth, 74(1986) 491
[6] L.G. Casagrande, D.J. Larson,Jr., D.D. Marzio, J. Wu and M. Dudley, J. Crystal Growth, 137(1994) 195