

Growth, characterization and optical quality of calcium fluoride single crystals grown by the Bridgman method

HANA IBRAHIM ELSWIE^a, SLOBODANKA KOSTIĆ^b, VESNA RADOJEVIĆ^a, NEBOJŠA Ž. ROMČEVIĆ^b,
BRANKA HADŽIĆ^b, JELENA TRAJIĆ^b, ZORICA Ž. LAZAREVIĆ^{b,*}

^aFaculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

^bInstitute of Physics, University of Belgrade, P.O. Box 68, Belgrade, Serbia

Calcium fluoride - CaF₂ single crystals were grown using the Bridgman technique. By optimizing growth conditions, <111>-oriented CaF₂ crystals up to 20 mm in diameter were grown. Number of dislocations in CaF₂ crystals which were made by the method of Bridgman was $5 \times 10^4 - 2 \times 10^5$ per cm². In this paper we used XRD, Raman spectroscopy and the measurement of transmission in the mid IR-range to investigated structural and optical properties of obtained CaF₂ single crystals.

(Received November 2, 2015; accepted August 3, 2016)

Keywords: CaF₂, Optical materials, Crystal growth, XRD, Raman spectroscopy

1. Introduction

A calcium fluoride (here after abbreviated as CaF₂) single crystal has excellent transmission characteristics down to the vacuum ultraviolet region, and it is utilized as a lens material in the wafer-stepper of semiconductor lithography technology together with synthetic quartz. CaF₂ single crystals of more than 10 in diameter are required for the lens materials. Such large CaF₂ single crystals are grown by the Czochralski method [1, 2] or the vertical Bridgman method [3, 4]. Extremely high material performances are required for the lens material in the wafer-stepper to achieve high resolution of lithography. Among them, the reduction of birefringence caused by the residual stress is one of the technical problems. In the Czochralski method, residual stress is induced in the crystal by thermal stress, where as, in the vertical Bridgman method, residual stress is induced not only by thermal stress but also due to mechanical stress caused by the contact of the crystal and crucible. Generally as-grown single crystals with larger diameter have larger residual stress, which results in larger birefringence in as-grown crystals. Therefore, annealing after single-crystal growth is in dispensable process, when CaF₂ single crystals are used for the lens material in the wafer-stepper. Such annealing reduces the residual stress and suppresses the birefringence at a low level, but a very long annealing period is required to reduce the birefringence to the target value. Numerical simulations of residual stress and birefringence play an important role for searching effective annealing conditions.

CaF₂ is an ionic crystal with the fluorite structure. The lattice is a face centered cubic (*fcc*) structure with three sublattices. The unit cell of the material is most easily described as a simple cubic lattice formed by the F⁻ ions where a Ca²⁺ ion is contained in every second cube.

The remaining empty cubes (called interstitial or hollow sites) are important for defect formation and diffusion, but also for the accommodation of unwanted impurities like rare earth ions and dopants. The lattice constant is $a = 5.4626 \text{ \AA}$ [5] (Fig. 1).

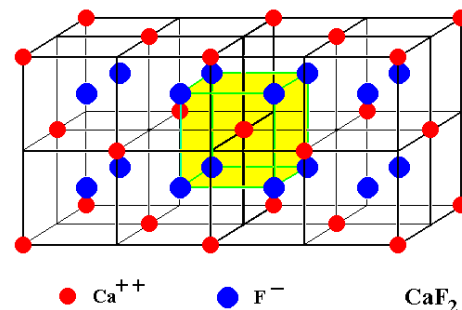


Fig. 1. Unit cell representation of CaF₂ structure

Single crystal CaF₂ used in the optical device can be of natural origin - fluorite, under which name is often referred to in literature [6] and synthetic single crystal CaF₂ which is usually obtained growth from the melt. By its chemical and physical properties of the single crystal CaF₂ is very different from other materials that have been developed techniques to obtain single crystals. The relatively high melting point (over 1300 °C), high chemical aggressiveness of fluorine at these temperatures, relatively small chemical compounds CaF₂ stability at high temperatures and very strong ability to react CaF₂ with traces of water vapor, require the use of special growth conditions to obtain quality crystals. Therefore, the growth of a single crystal CaF₂ may take place either in vacuum or in an inert gas atmosphere (argon or helium) at purity of at

least 99.99% in order to prevent the presence of traces of moisture or oxygen.

The aim of the present work was to obtain single crystal CaF_2 optical quality. The structural and optical properties obtained crystal was characterized using XRD, Raman and FTIR spectroscopic characterization.

2. Experimental procedures

The Bridgman method of crystal growth is relatively simple and allows operation in a vacuum, and also in an inert atmosphere. In this method, the crucible uses a cylindrical shape with a conical bottom. The procedure consisted of the following: the crucible cylindrical shape with melted batch CaF_2 down from the upper hot chamber of the furnace in the cooler lower chamber of the same furnace. The bottom of the crucible was in the shape of a cone and that in the formation of germs and begins the process of crystallization. The crucible was from spectroscopically pure graphite [2-8]. One of the main drawback of this method is that in the course of growth can be seen the process of crystal growth, so that if it comes to the appearance of polycrystalline, this can be concluded only after the completion of the process of growth and cooling crystals.

To obtain single crystals of CaF_2 by the Bridgman method in a vacuum has been used device BCG 356. Initial samples of single crystals were mostly clear and transparent, but some were cracked. Because of the small temperature gradient there were a sudden crystallization process and the appearance of dendrites in the lower part of the crucible, and therefore made changes to the structure of the crucible. With this change we have achieved that cone of the lower part of the crucible is in the form of a tube. Therefore we have achieved that by the sudden crystallization takes an extended part of the crucible, thus avoiding the occurrence of dendrites. The crystals that were obtained on the crucible constructed in this way were of better quality. However, when grinding the upper surface of the crystal, because the dirt that clung to that, there have been cracks crystal along a plane of cleavage.

Experiments have been performed with CaF_2 in the form of a powder. Since this device works in a vacuum, there was a danger that the air contained in the powder CaF_2 , when you turn on the vacuum pump, disperses the powder throughout the apparatus. Therefore, the CaF_2 powder was compaction and sintered in the form of pills. With such obtained pills could easily and quickly be filled crucible. Power generator was initially $P_{\text{gen}} = 3.8$ kW, and was later increased to $P_{\text{gen}} = 3.94$ kW. The crystal growth rates were 6 mm h^{-1} , 12 mm h^{-1} , 24 mm h^{-1} and 48 mm h^{-1} .

The observations relating to the dislocation were recorded by observing an etched surface of CaF_2 crystal, using a Metaval of Carl Zeiss Java metallographic microscope with magnification of 270x. To test the dislocations were used CaF_2 samples that are obtained by cleaving the crystals CaF_2 per plane splitting $\langle 111 \rangle$. The samples were etched with concentrated sulfuric acid from

10 to 30 min. It has been shown that the best results are obtained on the sample crystal is etched for 15 min.

The crystal structure of CaF_2 single crystal was approved using the X-ray diffractometer (XRD, Model Philips PW 1050 diffractometer equipped with a PW 1730 generator, 40 kV x 20 mA, and using $\text{CuK}\alpha$ radiation of 1.540598 \AA at the room temperature. Measurements were done in 2θ range of $10\text{-}90^\circ$ with scanning step width of 0.05° and 10 s scanning time per step.

The Raman scattering measurements of CaF_2 crystal was performed in the backscattering geometry at room temperature in the air using a Jobin-Yvon T64000 triple spectrometer, equipped with a confocal microscope (100x) and a nitrogen-cooled charge coupled device detector (CCD). The spectra have been excited by a 514.5 nm line of Coherent Innova 99 Ar^+ - ion laser with an output power of less than 20 mW to avoid local heating due to laser irradiation. Spectra were recorded in the range from $100 - 800 \text{ cm}^{-1}$.

The transmission a spectrum of CaF_2 sample (powdered and pressed in the disc with KBr) was obtained by transmission Fourier transforms infrared (FTIR) Hartmann&Braun spectrometer, MB-series. The FTIR spectrum was recorded between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} .

3. Results and discussion

CaF_2 single crystals are obtained by the vertical Bridgman method in vacuum. Experiments were carried out with the crystal growth rate of $6\text{-}48 \text{ mm h}^{-1}$. The best result was obtained with a crystal growth rate of 6 mm h^{-1} . If the growth rate of the single crystal CaF_2 larger, experiments showed that these crystals contain more stress and that in this case it is more likely to obtain polycrystals. Stresses in single crystals we have tried to eliminate annealing of crystals. The process of annealing was carried out on the plate and bulk crystal CaF_2 . The temperature of annealing of the plate was at 1000°C for 3 h, and the temperature of annealing of the bulk crystal was at 1000°C and 1080°C for 1 - 3 h. Annealing is carried out under an inert atmosphere of argon. It was noticed that after annealing, plate CaF_2 did not have enough stress. Annealing bulk single crystal CaF_2 had less stress than non-annealing. The obtained single crystals of CaF_2 was 20 mm in diameter and 90 mm in length. A polished plate of CaF_2 with a diameter of 20 mm is displayed in Fig. 2.

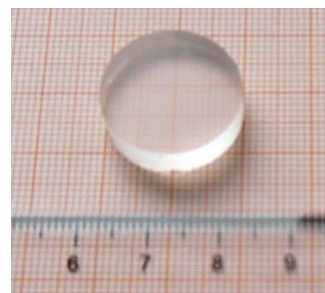


Fig. 2. Photographs of Bridgman-grown CaF_2 single crystals

The general conclusion is that in all samples was observed relatively high dislocation density (ranging from 60000 to 140000) as a consequence of greater internal stresses, which have emerged in the process of cooling. From the Fig. 3 it can be observed dislocations on CaF₂ single crystal. Etch pits have the shape of a three-sided pyramid. Number of dislocations in CaF₂ crystals which were made by the method of Bridgman was $5 \cdot 10^4 - 2 \cdot 10^5$ per cm² (Fig. 3).

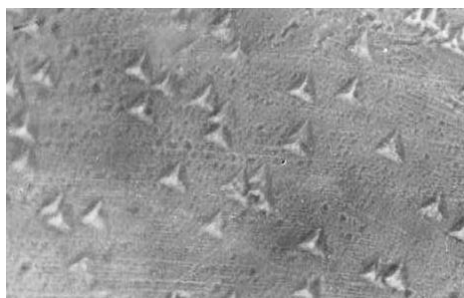


Fig. 3. The microscopic image of the surface CaF₂ crystal plate in the direction $\langle 111 \rangle$. Magnification of 270x

The sample of CaF₂ single crystal was of cubic structure with the $Fm\bar{3}m$ space group [9]. XRD pattern (Fig. 4) was indexed by using JCPDS database (card no. 87-0971). The XRD pattern was found to match exactly with those reported in the literature [10, 11]. The displayed peaks correspond to $(h k l)$ values of (1 1 1), (2 2 0), (3 1 1), (4 0 0), (3 3 1) and (4 2 2). Using the $(h k l)$ values of different peaks, the lattice constant (a) of the sample was calculated. Their lattice parameter was calculated from the equation of plane spacing for cubic crystal system and Bragg's law for diffraction [12]. The lattice parameter was 5.452 ± 0.011 Å, calculated from the obtained XRD diagram, which was in good agreement with the literature [5, 13].

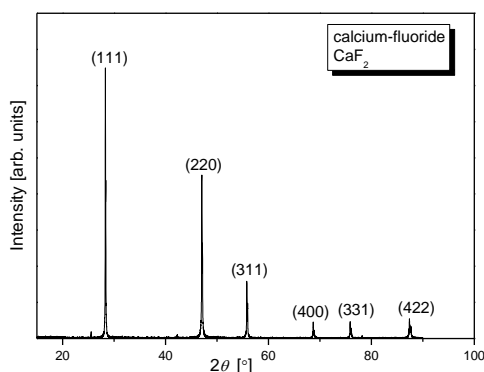


Fig. 4. X-ray diffraction pattern of the CaF₂ powdered sample

Three atoms in cubic O_h^5 ($Fm\bar{3}m$) primitive cell of the CaF₂ crystal are given nine fundamental vibrations, described by the following O_h -irreducible representations (at $k = 0$): $\Gamma = 2T_{1u} + T_{2g}$. According to several comprehensive work (see, e.g. [14-19]), their distribution

among optical and acoustical are: the triply degenerate T_{2g} optical phonon is Raman active and IR inactive; one of the T_{1u} representations (triply degenerate as well) corresponds to the zero frequency acoustic mode, while the other T_{1u} species is actually split into a double degenerate transverse optical mode and a nondegenerate longitudinal optical mode, all the above are IR active. The room-temperature first order T_{2g} one-band spontaneous Raman scattering spectra of CaF₂ crystal is shown in Fig. 5. In this single allowed SRS-promoting optical mode with frequency $\omega_{SRS} = 319.7$ cm⁻¹ Ca²⁺ cation remains stationary and the neighboring substitutional fluoride F⁻ ions vibrate against each other [19-21].

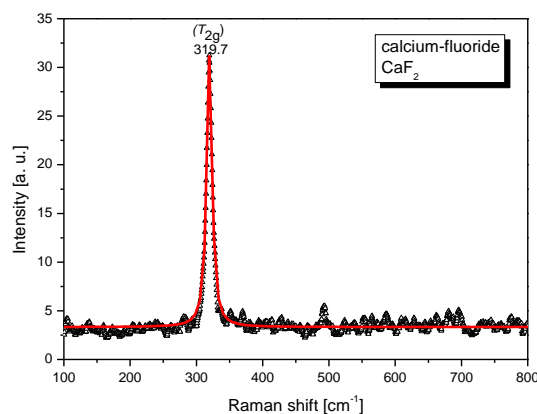


Fig. 5. Raman spectra of the CaF₂ single crystal at room temperature

FTIR transmission was measured in order to check the purity of the obtained CaF₂. As shown in Fig. 6, the sharp peaks of the absorption at 2854 cm⁻¹ and 2936 cm⁻¹ are assigned to the symmetric and antisymmetric stretching vibration of -CH₂ groups [22]. Also, the spectra shows two broad IR absorption peaks at ~3432 cm⁻¹ and 1628 cm⁻¹ are assigned to the symmetrically stretching vibration and antisymmetric stretching vibration of hydroxyl groups -OH, implying the presence of H₂O molecules [23, 24]. The peak at 671 cm⁻¹ in the FTIR spectra was assigned to the Ca-F stretching vibration of CaF₂ [25]. The band at ~2357 cm⁻¹ is due to KBr pellets used for recording FTIR spectrum [26].

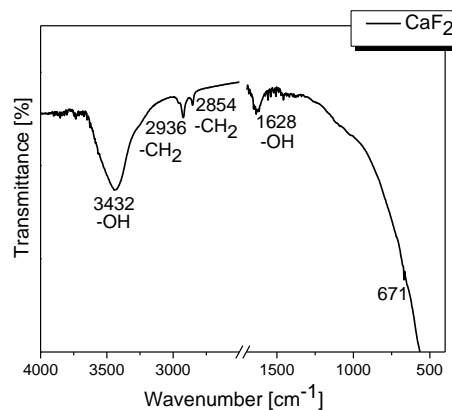


Fig. 6. FTIR spectra of CaF₂

The properties of the crystal, such as density of dislocations, crystallinity, and impurities concentrations, determine the optical quality.

4. Conclusions

CaF₂ single crystals in diameter of 20 mm are obtained by the vertical Bridgman method in vacuum. The crystal growth rate was 6.0 mm h⁻¹. Number of dislocations is of the order of 5×10⁴ - 2×10⁵ per cm². The crystal structure was confirmed by XRD. The Raman T_{2g} optical mode at 319.7 cm⁻¹ was observed. The FTIR transmission spectra indicate that there are some amounts of -CH₂, -OH or water molecules and organic groups adhering to the surfaces. Based on our work and observations during the experiment, it could be concluded that the obtained transparent single crystal CaF₂ of good optical quality, which was the goal of our work.

Acknowledgements

This research was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through Projects No. III45003 and TR34011.

References

- [1] L. Su, Y. Dong, W. Yang, T. Sun, Q. Wang, J. Xu, G. Zhao, *Mater. Res. Bull.* **40**, 619 (2005).
- [2] H. Yanagi, T. Nawata, Y. Inui, Y. Hatanaka, E. Nishijima, T. Fukuda, *Proc. SPIE 5377, Optical Microlithography XVII*, 1886 (May 28, 2004); doi:10.1117/12.556614.
- [3] N. Senguttuvan, M. Aoshima, K. Sumiya, H. Ishibashi, *J. Cryst. Growth* **280**, 462 (2005).
- [4] J. Xu, M. Shi, B. Lu, X. Li, A. Wu, *J. Cryst. Growth* **292**, 391 (2006).
- [5] G. Scholz, I. Dörfel, D. Heidemann, M. Feist, R. Stösser, *J. Solid State Chem.* **179**, 1119 (2006).
- [6] I. V. Stepanov, P. P. Feofilov, *Artificial fluorite*. In *Rost kristalov (Vol. I)*, Moscow, Russia: Akademia Nauk SSSR. (in Russian), 1957, p. 229.
- [7] G. V. Molev, V. E. Bozherolnog, *J. Cryst. Growth* **19**, 117 (1973).
- [8] K. Recker, R. Leckebusch, *J. Cryst. Growth* **9**, 274 (1971).
- [9] L. Gerward, J. S. Olsen, S. Steenstrup, M. Malinowski, S. Åsbrink, A. Waskowska, *J. Appl. Crystallogr.* **25**, 578 (1992).
- [10] B.-C. Hong, K. Kawano, *J. Alloys Compd.* **408-412**, 838 (2006).
- [11] N. D. Alharbi, *J. Nanomaterials* **2015**, Article ID 136957, 8 pages, <http://dx.doi.org/10.1155/2015/136957>.
- [12] S. Biswas, S. Kar, S. Chaudhuri, *J. Cryst. Growth* **299**, 94 (2007).
- [13] L. G. DeShazer, S. C. Rand, B. A. Wechsler, in: M. J. Weber (ed.) *Handbook of Laser Science and Technology, V, Optical Materials: Part 3*(CRC Press, Boca Raton, FL), 1988, pp.281.
- [14] R. K. Chang, B. Lacina, P. S. Pershan, *Phys. Rev. Lett.* **17**, 755 (1966).
- [15] J. R. Ferraro, H. Horan, A. Quattrochi, *J. Chem. Phys.* **55**, 664 (1971).
- [16] D. G. Mead, G. R. Wilkison, *J. Phys. C* **10**, 1063 (1977).
- [17] D. J. Oostra, H. W. den Hartog, *Phys. Rev. B* **29**, 2423 (1984).
- [18] P. C. Ricci, A. Casu, G. de Giudici, P. Scardi, A. Anedda, *Chem. Phys. Lett.* **444**, 145 (2007).
- [19] A. A. Kaminskii, S. N. Bagayev, H. J. Eichler, H. Rhee, K. Ueda, K. Takaichi, K. Oka, H. Shibata, Y. Hatanaka, Y. Matsumoto, *Laser Phys. Lett.* **8**, 385 (2006).
- [20] L. Su, J. Xu, W. Yang, X. Jiang, Y. Dong, *Chinese Optics Letters* **3**, 219 (2005).
- [21] J. P. Russell, *Proceedings of the Physical Society* **85**, 194 (1965).
- [22] J. Song, G. Zhi, Y. Zhang, B. Mei, *Nano-Micro Lett.* **3**, 73 (2011).
- [23] L. Zhou, D. Chen, W. Luo, Y. Wang, Y. Yu, F. Liu, *Mater. Lett.* **61**, 3988 (2007).
- [24] G. A. Kumar, C. W. Chen, J. Ballato, R. E. Riman, *Chem. Mater.* **19**, 1523 (2007).
- [25] K. Tahvildari, M. Esmaeili Pour, Sh. Ghamamy, H. Nabipour, *Int. J. Nano Dim.* **2**, 269 (2012).
- [26] C. Pandurangappa, B. N. Lakshminarasappa, B. M. Nagabhushana, *J. Alloys Compd.* **489**, 592 (2010).

*Corresponding author: lzorica@yahoo.com