Bridgman growth of $LiYF_4$ single crystal in nonvacuum atmosphere

Qishu Fang (方奇术), Hongbing Chen (陈红兵)*, Fang Xu (徐 方), Sujing Wang (王苏静), Zhe Liang (梁 哲), and Chengyong Jiang (蒋成勇)

State Key Base of Functional Materials and Its Preparation Science, Institute of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

**E-mail: chenhongbing@nbu.edu.cn*

Received February 25, 2010

Using LiF and YF_3 as starting materials, we prepare feed material from fluorides according to the molar ratio of LiF:YF_3 = 51.5:48.5. The anhydrous $LiYF_4$ polycrystalline material is synthesized via the fluoridation process with a dried HF flow at elevated temperature. By charging the feed material and adding a small amount of active carbon powder in a sealed platinum crucible, the crystal can be grown via the vertical Bridgman method in a nonvacuum atmosphere. This is possible because the oxidization and volatilization of the melt is avoided. Using optimum conditions, that is, a growth rate of 0.5–0.6 mm/h and a temperature gradient of 25–30 °C/cm across the solid-liquid interface under a furnace temperature of 920–930 °C, the colorless crystal $LiYF_4$ with the size of $\phi 25 \times 50$ (mm) is successfully grown. The optical transmittance of the crystal is as high as 85% above the absorption edge at 190 nm. The induced absorption bands are observed below 700 nm in the transmission spectrum after the crystal is subjected to a high dose of γ-ray irradiation.

OCIS codes: 160.0160, 160.4670.

doi: 10.3788/COL20100811.1071.

Since the 1970s, interest in $LiYF_4$ crystals has continued to increase mainly because of their application as a laser active medium. The host crystal $LiYF_4$ is an incongruently melting compound with a scheelite structure. This compound is suitable for the introduction of trivalent rare-earth ions, which serve as a substitute for the Y^{3+} ion. $LiYF_4$ crystals doped with rare-earth ions have been proven to be efficient tunable all-solid-state lasing media that cover varied wavelength regions[1−5]. Nd^{3+}-doped $LiYF_4$ crystal has been applied in infrared (IR) solid-state lasers with emissions ranging from 1.047 to 1.053 μm. With the use of an ultraviolet (UV) laser crystal Ce^{3+}:$LiYF_4$, a tunable laser output ranging from 306 to 330 nm can be achieved. In addition to being an excellent laser medium, pure $LiYF_4$ crystal can also be a valuable window material. The fluoride crystal may be used as a suitable optical material for lenses and other optical components because of its high optical transparency in a wide wavelength range from IR to UV.

The use of the Czochralski method or Bridgman technique to grow $LiYF_4$ crystals has been previously reported[6−8]. The main difficulties encountered in growing $LiYF_4$ crystals include the preparation of high-purity feed material without absorbed moisture, and the oxidation and volatilization of the melt during growth. In previous studies, $LiYF_4$ crystals needed to be grown in a vacuum or in a CF_4 or HF atmosphere. A modified vertical Bridgman process is applied in our laboratory for the successful growth of $LiYF_4$ crystals under a nonvacuum atmosphere. The anhydrous $LiYF_4$ polycrystalline material is synthesized via a fluoridation process at elevated temperature. The process is confirmed to be a favorable technique for overcoming the difficulties encountered in crystal growth. Recent results on the Bridgman growth of $LiYF_4$ crystals are reported in this letter. The transmission spectra of $LiYF_4$ crystal under γ-ray irradiation are also characterized.

Anhydrous feed material with high purity is very important in growing $LiYF_4$ crystals. However, commercially obtained fluorides tend to absorb moisture in air. These absorbed hydrates in the fluoride reagents are extremely harmful to crystal growth. If the feed material containing the hydrates is used in crystal growth, the grown crystal would contain much optical scattering or would even be opaque because of the oxyfluorides generated by the hydrolysis reactions. The hydrolysis reaction can be presented as

$$3LiF + H_2O \rightarrow Li_3OF + 2HF,$$
$$YF_3 + H_2O \rightarrow YOF + 2HF.$$

According to the phase diagram of the system LiF-YF_3, $LiYF_4$ is an incongruently melting compound with the composition of 49 mol% YF_3 and 51 mol% LiF at the peritectic temperature of 819 °C[9]. To ensure crystallization of the desired phase, the feed materials for crystal growth were prepared with a slight excess of LiF. Using LiF (99.99%) and YF_3 (99.99%) as initial materials, the material for the crystal growth was prepared according to the molar ratio of LiF:YF_3 = 51.5:48.5. The fluoride reagents were weighed and thoroughly mixed. To synthesize anhydrous $LiYF_4$ polycrystalline material, the

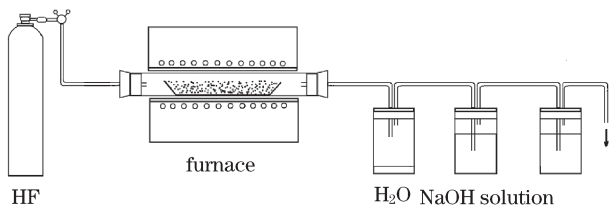

Fig. 1. Apparatus for fluoridation process at elevated temperature.

fluoride mixture was subjected to a fluoridation process at elevated temperature.

The fluoridation process was performed using the apparatus shown in Fig. 1. A total of 200–400 g mixture was charged in a vessel-shaped platinum crucible, and placed into a platinum pipe in a tubular resistance furnace. A bottled HF gas with high purity (99.95%), available commercially from a chemical company, was used as the gas source. With the dried HF continuously piped into the system, the mixture was heated at 600–800 °C for 5–6 h simultaneously. In the fluoridation process, the possible hydrolysis reaction was suppressed in dried HF ambient condition, and the moisture contained in the mixture removed with the flowing HF gas. As the fluoridation process was completed, the HF flow was terminated and the furnace cooled. After the residual HF was removed by nitrogen gas, a white anhydrous polycrystalline bar was obtained. The polycrystalline material was verified by X-ray powder diffraction to be the fluoride $LiYF_4$ without any other phases.

$LiYF_4$ single crystals were grown in a resistively heated vertical Bridgman furnace, as shown in Fig. 2. The furnace was adjusted using a WJK-100A fine temperature controller with an accuracy of ±0.5 °C. The furnace chamber can be divided into three zones according to axial temperature distribution: the high-temperature zone, the gradient zone, and the low temperature zone. During the crystal growth, the melt was homogenized in the crucibles in the high-temperature zone, whereas the grown crystal was annealed in the low-temperature zone. The solid-liquid interface was located in the gradient zone. The temperature of the melting zone was controlled to 920−930 °C or to about 100−110 °C higher than the melting point of the crystal. The horizontal temperature distribution was kept as uniform as possible.

The platinum crucibles used in the crystal growth were 25 mm in diameter and 150−200 mm in length with a 10-mm seed well. The feed material of 100−200 g was charged into the crucibles for crystal growth. To obtain the seed crystal, the initial attempts at growing the crystal were conducted using spontaneous nucleation from the seed wells. Several 10 × 40–50 mm transparent single crystals were used as the seeds after the crystals were oriented, cut, and ground. The seed was mounted onto the seed well and the feed material was charged in the crucible. The growth orientation was directed along the a-axis using an oriented seed crystal. The assembled crucible was sealed to prevent the volatilization of the melt during crystal growth. The crucible was installed in a refractory tube filled with Al_2O_3 powder to isolate it from external temperature fluctuation.

After the furnace was heated to the controlled temperature, seeding was performed by adjusting the crucible to a position in which only the top of the seed was melted. The charge was kept in this state for 3−4 h to allow a stable solid-liquid interface to be established at the top region of the seed. To detect the axial temperatures along the crucible, the crucible was fitted with two Pt-Pt/Rh 10% thermocouples. The temperature gradient near the solid-liquid interface was adjusted to around 25–30 °C/cm. The growth process was driven by lowering the crucible at a rate of 0.5−0.6 mm/h. The furnace was cooled to room temperature at a rate of 30−40 °C/h after the growth was completed. The grown crystal was obtained by cutting and stripping the crucible after removal from the refractory tube.

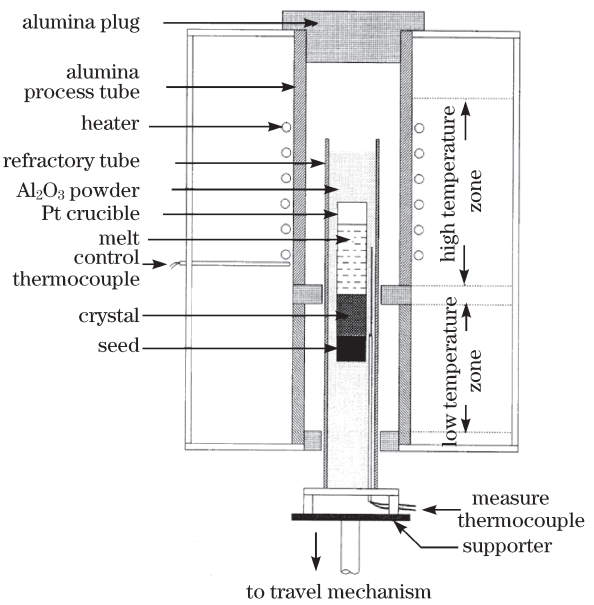

Fig. 2. Schematic of vertical Bridgman furnace.

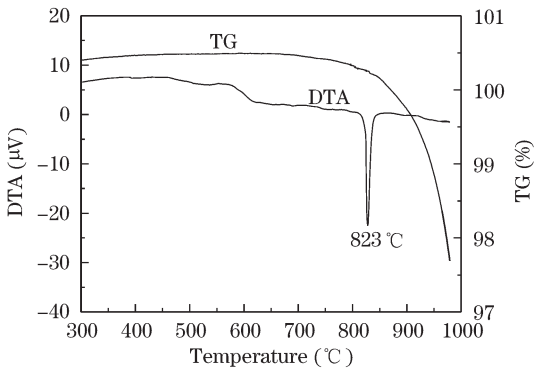

Fig. 3. DTA/TG curve of $LiYF_4$ single crystal.

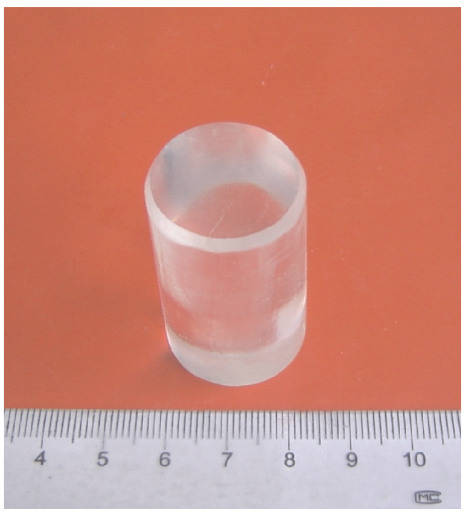

Fig. 4. $LiYF_4$ single crystal grown via vertical Bridgman process.

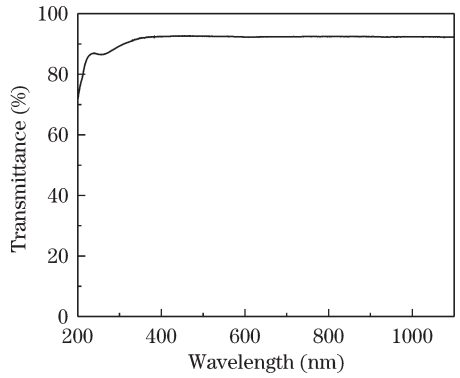

Fig. 5. Transmission spectrum of $LiYF_4$ single crystal.

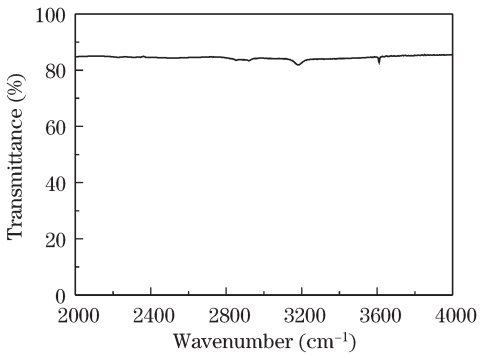

Fig. 6. IR spectrum of $LiYF_4$ single crystal.

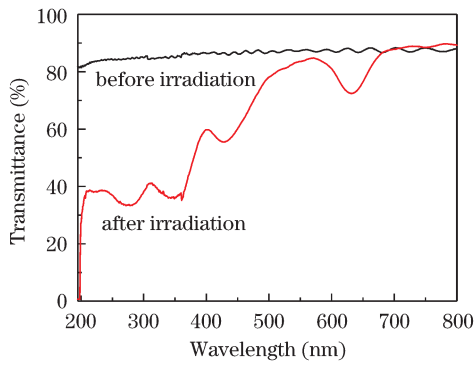

Fig. 7. Induced absorption bands in transmission spectra of $LiYF_4$ single crystal after γ-ray irradiation.

Another difficulty encountered in growing $LiYF_4$ crystals is the oxidation and volatilization of the melt during growth. To investigate the volatilization of the melt in the process, the crystal was tested by differential thermal analysis/thermal gravimetry (DTA/TG). The sample was analyzed in nitrogen ambient condition by DTA/TG using a Seiko EXSTAR 6300 thermal analyzer. The DTA and TG curves of the crystal are presented in Fig. 3. The DTA curve shows that the crystal is melted congruently at 823 °C. A distinct weight loss occurs above the melting point. As much as 2.5 wt.-% weight loss is observed on the TG curve from 823 to 1000 °C. In the modified Bridgman process, the volatilization can be effectively avoided by sealing the crucibles. No evident weight losses occurred during the growth because the vapor was enclosed in the sealed crucibles. The composition of the melts was kept constant during growth.

By sealing the platinum crucible, growing $LiYF_4$ crystal in a nonvacuum atmosphere can be realized. In a normal atmosphere, a volume of air always remains in the crucible when it is sealed. The sealed air contained only a small chemical amount of oxygen, which reacts partially with the fluoride melt during the crystal growth. Although oxidation from the remaining oxygen is not very clear due to its minimal amount, we still attempt to thoroughly eliminate the harmful effect using a simple method. A small amount of active carbon powder, estimated to be 100 ppm or so, was added to the top of the feed material to exhaust the air sealed in the crucible at elevated temperature before crystal growth was performed.

Through the growth process described above, $LiYF_4$ single crystal was grown successfully. As shown in Fig. 4, a $\phi 25 \times 50$ (mm) crystal boule is obtained. The crystal appears to be colorless and transparent with good optical transparency. It has a 3-mm-thick precipitate layer cut from the top of the boule. An examination of the crystal with a He-Ne laser shows that the crystal boule is free from optical scattering. The crystal surface shows chemical stability without any deliquescence as it was exposed to air for a long period. As a window material for practical applications, the crystal elements should be fabricated with oil grinding materials.

X-ray powder diffraction analysis of the grown crystal was performed using a Bruker D8 Focus diffractometer. The X-ray diffraction pattern of the crystal accords with the data in JCPDS 17-0874[9]. The transmission spectrum of the sample with 2-mm thickness was measured with a Perkin Elmer UV/visible spectrometer in the range of 200−2000 nm at room temperature. Figure 5 presents the transmission spectrum of the crystal platelet, in which transmittance above 220 nm reaches more than 85% without any absorption band. The IR spectrum of $LiYF_4$ crystal is shown in Fig. 6. A very weak absorption peak at 3620 cm^{-1} is observed, indicating trace amounts of OH^- contained in the crystal. The trace amounts of OH^- in the crystal can be eliminated using an even higher-purity anhydrous HF gas.

By means of a ^{60}Co gamma source with average gamma energy of 1.25 MeV, the crystal sample was subjected to γ-ray irradiation for a cumulative dose of 6×10^5 Gy. Before and after the irradiation was performed, transmission spectra of the sample were measured. After the crystal platelet was subjected to γ-ray irradiation, the sample color changes from clear to green. Figure 7 shows the transmission spectra of the sample before and after irradiation. Four induced absorption bands at about 279, 345, 426, and 630 nm are found, and no induced absorption is observed above 700 nm. Kaczmarek found five induced absorption bands (260, 330, 440, 505, and 640 nm) in γ-ray-irradiated pure $LiYF_4$ crystal grown by Czochralski method under a CF_4 atmosphere. The absorption bands in the UV and visible region originated from the color centers inside the fluoride crystals induced by γ-ray irradiation[10]. Compared with the results in previous studies, the induced absorption band at 505 nm is not observed in this experiment. The bands at 279, 345, 426, and 630 nm shift toward longer and shorter wavelengths. This reaction may be attributed to the different conditions for crystal growth.

In conclusion, $LiYF_4$ single crystal is a promising window material with desirable optical transmittance in a

wide wavelength range. Compared with other studies, this work provides an effective method for preparing anhydrous fluoride polycrystalline material and a modified process for growing $LiYF_4$ crystal in a nonvacuum atmosphere. The anhydrous $LiYF_4$ polycrystalline material with high purity can be prepared via the fluoridation process at elevated temperature. By sealing the feed material in a platinum crucible, the oxidization and volatilization of the melt can be avoided in the crystal growth. A large $LiYF_4$ single crystal is grown via the vertical Bridgman process in a nonvacuum atmosphere.

This work was supported by the Natural Science Foundation of Zhejiang Province (No. Y4090057) and the Natural Science Foundation of Ningbo City (No. 2009610016). The authors would like to acknowledge the support extended by the Personnel Training Project of the Zhejiang Education Department. This work was also sponsored by the K. C. Wong Magna Fund of Ningbo University.

References

1. N. D. Vieira, Jr., I. M. Ranieri, L. V. G. Tarelho, N. U. Wetter, S. L. Baldochi, L. Gomes, P. S. F. de Matos, W. de Rossi, G. E. C. Nogueira, L. C. Courrol, E. A. Barbosa, E. P. Maldonado, and S. P. Morato, J. Alloys and Compounds **344,** 231 (2002).
2. F. Okada, S. Togawa, K. Ohta, and S. Koda, J. Appl. Phys. **75,** 49 (1994).
3. I. F. Elder and M. J. P. Payne, Opt. Commum. **145,** 329 (1998).
4. T. Böttger, G. J. Pryde, C. W. Thiel, and R. L. Cone, J. Lumin. **127,** 83 (2007).
5. H. Peng, K. Zhang, L. Zhang, Y. Hang, J. Xu, Y. Tang, Y. Cheng, J. Xiong, C. Zhao, G. Chen, and X. He, Chin. Opt. Lett. **8,** 63 (2010).
6. S. L. Baldochi, K. Shimamura, K. Nakano, N. Mujilatu, and T. Fukuda, J. Cryst. Growth **205,** 537 (1999).
7. H. Sato, A. Bensalah, H. Machida, M. Nikl, and T. Fukuda, J. Cryst. Growth **253,** 221 (2003).
8. S. Duffy, J.-R. Wells, H. G. Gallagher, and T. P. J. Han, J. Cryst. Growth **203,** 405 (1999).
9. R. E. Thomas, C. F. Weaver, H. A. Friedman, H. Insley, L. A. Harris, and H. A. Yakel, J. Phys. Chem. **65,** 1096 (1961).
10. S. M. Kaczmarek, A. Bensalah, and G. Boulon, Opt. Mater. **28,** 123 (2006).