**I. INTRODUCTION**

The trivalent praseodymium ion (Pr\(^{3+}\)) in solids has an intricate energy level scheme with energy gaps of various magnitude and rich emission spectral lines in UV, visible, and infrared regions. In the past decades, various Pr\(^{3+}\)-doped materials have been investigated thoroughly in relation with several potential applications, such as the fiber laser amplifier [1], quantum cutting [2], red-emitting phosphors [3], up-conversion laser [4], and solid-state lasers [5]. They are widely employed in scintillators [6], fluorescent lamps [7], optical amplifiers for fiber-optic communication [8], 3D displays [9] long persistent luminescence application [10, 11] and optical frequency converters. Very recently, Pr\(^{3+}\) doped Cs\(_2\)NaYF\(_6\) was fabricated for X-ray-activated long persistent phosphors featuring strong (short-wavelength ultraviolet light) UVC afterglow emissions [12]. It shows that the UVC persistent luminescence of this phosphor is strong enough to be used for sterilization. This work opens up new ways for a wide variety of practical applications of Pr\(^{3+}\) [13].

The optical properties of Pr\(^{3+}\) ion can be influenced by the host lattice, doping concentration, and environmental temperature [14]. Single crystals exhibit high transparency, good anti-light irradiation, good thermal, mechanical, and chemical stability, which are suitable hosts for luminescence application. LiLuF\(_4\) (LLF) is one of important fluoride compounds and firstly reported in 1960 [15]. In recent years, LiLuF\(_4\) single crystal has attracted much attention as potential laser materials because of low maximum phonon energy, high chemical stability, and high doping concentration for rare earth ions [16]. However, report on the preparation of Pr\(^{3+}\) doped LiLuF\(_4\) single crystal for above applications is scarce. In this work, we report the growth of Pr\(^{3+}\) doped LiLuF\(_4\) single crystal by Bridgman method.

**II. EXPERIMENTS**

The crystal was grown from 99.99% pure raw materials of LiF, LuF\(_3\), and PrF\(_3\). Pr\(^{3+}\) doped LiLuF\(_4\) single crystals with the molar composition of 50.5LiF-(49.5-x)LuF\(_3\)-xPrF\(_3\), where x=0.1, 0.5 and 1.5 (designated as LFP1, LFP2 and LFP3), were prepared by a Bridgman method. The specific details and processes of crystal growth were described in Ref. [17]. The typical sample with a size of \(\phi\) 10 mm x 55 mm and polished slices are displayed in FIG. 1(b). It can be clearly observed that the synthesized crystal appears in light green color, and is highly transparent.

The X-ray diffraction (XRD) measurements to identify the phase composition of the crystals were recorded by a Bruker D8 Advance (Germany). The XRD data were collected within a 2θ range of 10°–80° at a scan speed of 2°/min. The absorption spectra measure-
TABLE I The doping concentrations of Pr$^{3+}$ ions in raw materials and the number of Pr$^{3+}$ ions (N) in LiLuF$_4$ crystals.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pr$^{3+}$/%</th>
<th>N/(10$^{20}$ ions/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP1</td>
<td>0.1</td>
<td>0.056</td>
</tr>
<tr>
<td>LFP2</td>
<td>0.5</td>
<td>0.276</td>
</tr>
<tr>
<td>LFP3</td>
<td>1.5</td>
<td>0.831</td>
</tr>
</tbody>
</table>

ments for the samples were conducted by a Cary 5000 UV/VIS/NIR spectrophotometer (Agilent Co., America). Emission spectra and excitation spectra of the samples were recorded by an F-4500 spectrophotometer (Hitachi High-Technologies Co., Tokyo, Japan). The decay lifetimes of the prepared material were characterized by a Horiba Fluorolog-3 spectrophotometer with a 450 W xenon lamp. The high-temperature measurement was conducted by a TAP-02 high-temperature heating instrument (Tian Jin Orient-KOJI instrument Co., Ltd.) connecting to the Horiba Fluorolog-3 spectrophotometer to investigate the thermal quenching behavior of the grown crystal. The recording temperature varied from 298 K to 443 K. The experimental Pr$^{3+}$ concentrations in single crystals were measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc, Optima 3000). Table I lists the measured concentrations of Pr$^{3+}$ ions in single crystals and doping concentration in raw materials. All the measurements were performed in atmospheric conditions.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

FIG. 1(a) shows XRD pattern for the 0.5% Pr$^{3+}$ doped sample. All the diffraction peaks can be assigned to the standard profile of LiLuF$_4$ (JCPDS No.27-1251). No extra diffraction peak originated from impurities is detected. The Lu$^{3+}$ sites are most probable to be replaced by Pr$^{3+}$ ions due to the comparable ionic radius between Pr$^{3+}$ (1.013 Å) and Lu$^{3+}$ (0.85 Å). Hence, the introduction of Pr$^{3+}$ ions to the LiLuF$_4$ host does not significantly affect the crystal structure as confirmed from the XRD characterization. The lattice parameters calculated from the XRD pattern are $a=b=0.5137$ nm, $c=1.0542$ nm.

B. Absorption and emission spectra

FIG. 2 displays absorption spectra of Pr$^{3+}$ doped LiLuF$_4$ single crystal from visible to infrared region. As shown in FIG. 2, characteristic absorption bands originated from the $^3$H$_4$ ground state to the excited energy states of Pr$^{3+}$ can be observed. Specifically, the visible absorption bands centered at 441, 464, 475, and 587

FIG. 1 (a) XRD pattern for LiLuF$_4$ single crystal doped with 0.5% Pr$^{3+}$ measured by using the powders derived from grinding the bulk crystal. (b) Photograph of 0.5% Pr$^{3+}$ doped LiLuF$_4$ single crystal, the right is the boule of single crystal, the left is polished slices. (c) Standard line pattern of the LiLuF$_4$ (JCPDS No.27-1251).

FIG. 2 Absorption spectra of Pr$^{3+}$ doped LiLuF$_4$ single crystal (a) in the visible adn (b) in the infrared region.

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from the emission spectra of FIG. 3(b), characteristic emission bands around 468, 480, 490, 522, 541, 586, 605, 638, 695, and 718 nm can be observed. Meanwhile, transitions from the \( ^3\text{H}_4 \) ground state to the \( ^3\text{P}_2, ^3\text{P}_1, ^3\text{P}_0, ^1\text{D}_2 \) excited levels, respectively. Meanwhile, transitions from the \( ^3\text{H}_4 \) to the \( ^1\text{G}_4, ^3\text{F}_4, ^3\text{F}_3, ^3\text{F}_2, ^3\text{H}_6 \) energy levels contribute to absorption peaks at 1010, 1447, 1523, 1881 and 2238 nm [18], respectively. Moreover, the absorption intensity increases almost linearly with the \( \text{Pr}^{3+} \) doping concentration, suggesting \( \text{Pr}^{3+} \) ions have replaced effectively the crystal lattice sites of the LiLuF\(_4\) single crystal.

FIG. 3 (a) Excitation spectra of 0.5\% \( \text{Pr}^{3+} \) doped LiLuF\(_4\) single crystal. (b) Emission spectra with different \( \text{Pr}^{3+} \) concentration doped LiLuF\(_4\) single crystal.

Transitions from the \( ^3\text{P}_0 \) state to the \( ^3\text{H}_4, ^3\text{H}_5, ^3\text{F}_2, ^3\text{F}_3, \) and \( ^3\text{F}_4 \) states lead to emission at 480, 541, 638, 695 and 718 nm, respectively. Meanwhile, emission at 490 and 605 nm attribute to the \( ^3\text{H}_4 \rightarrow ^3\text{P}_0 \) and \( ^3\text{P}_2 \rightarrow ^3\text{H}_4 \) transitions, respectively [22, 23]. FIG. 5 exhibits the decay curves at 480 nm (\(^3\text{P}_0 \rightarrow ^3\text{H}_4\)), 522 nm (\(^3\text{P}_1 \rightarrow ^3\text{H}_5\)) and 605 nm (\(^1\text{D}_2 \rightarrow ^3\text{H}_4\)) of \( \text{Pr}^{3+} \) doped in LiLuF\(_4\) single crystal excited by 446 nm light. The decay curves can be well fitted by a double exponential function as follows [24]:

\[
I = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}
\]

where \( I \) is the luminescence intensity, \( \tau_1 \) and \( \tau_2 \) are the
FIG. 5 Decay curves of 0.5% Pr$^{3+}$ at different sites in LiLuF$_4$.

TABLE II Comparison of the lifetime at different sites for Pr$^{3+}$ doped oxide single crystal.

<table>
<thead>
<tr>
<th>Material State</th>
<th>Material State</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbWO$_4$:Pr$^{3+}$ [26]</td>
<td>Bi$_2$ZnOB$_2$O$_6$:Pr$^{3+}$ [27]</td>
</tr>
<tr>
<td>$^3$P$_0$ 5.71</td>
<td>$^3$P$_0$ 0.95</td>
</tr>
<tr>
<td>$^3$P$_1$ 3.99</td>
<td>$^3$P$_1$ /</td>
</tr>
<tr>
<td>$^1$D$_2$ 12.22</td>
<td>$^1$D$_2$ 4.55</td>
</tr>
<tr>
<td>LiLuF$_4$:Pr$^{3+}$ (This work)</td>
<td>LiLuF$_4$:Pr$^{3+}$ (This work)</td>
</tr>
<tr>
<td>$^3$P$_0$ 38.5</td>
<td>$^3$P$_0$ 38.5</td>
</tr>
<tr>
<td>$^3$P$_1$ 37.3</td>
<td>$^3$P$_1$ 37.3</td>
</tr>
<tr>
<td>$^1$D$_2$ 36.8</td>
<td>$^1$D$_2$ 36.8</td>
</tr>
</tbody>
</table>

fast and slow components of the luminescence lifetimes, $A_1$ and $A_2$ are the weighting parameters. The average lifetime can be calculated by the following expression [25]:

$$\langle \tau \rangle = \frac{A_1 \tau^1_1 + A_2 \tau^2_2}{A_1 \tau^1_1 + A_2 \tau^2_2}$$

(2)

The average lifetimes for the emissions at 480, 522, and 605 nm are determined to be 38.5 $\mu$s, 37.3 $\mu$s, and 36.8 $\mu$s, respectively. It can be seen from Table II that the lifetimes are much longer than those in PbWO$_4$ [26] and Bi$_2$ZnOB$_2$O$_6$ [27] oxide single crystal of $^3$P$_0$→$^3$H$_4$, $^3$P$_1$→$^3$H$_5$ and $^1$D$_2$→$^3$H$_4$ transitions, which is attributed to the fluoride host lattice of LiLuF$_4$.

C. CIE chromatic coordinate

The CIE chromaticity coordinates for Pr$^{3+}$ doped LiLuF$_4$ single crystals under 446 nm excitation are illustrated in FIG. 6. The variation of CIE coordinates is not significant with $\Delta x <0.006$ and $\Delta y <0.0135$, suggesting the excellent color stability of the Pr$^{3+}$ doped LiLuF$_4$ single crystals. The correlated color temperature ($T_c$) can be estimated by the McCamy’s empirical formula [28]:

$$T_c = -437n^3 + 3601n^2 - 6861n + 5514$$

(3)

where $n = \frac{x - x_e}{y - y_e}$ and $(x_e, y_e)$ is the chromaticity epicenter which lies at $x_e=0.3320, y_e=0.1858$ [28]. The $T_c$ slightly increases from 5474 K to 5755 K with the Pr$^{3+}$ doping concentration increase from 0.1 % to 1.5 %.

Thermal stability is a key factor to evaluate the potential of materials for applications, which significantly affects the performance of luminescence, such as the light output, lifetime, chromatic, and color rendering index [29]. The thermal quenching behavior of Pr$^{3+}$ doped LiLuF$_4$ single crystal is investigated by increasing temperature from 298 K to 443 K under 446 nm excitation. As shown in FIG. 7, the emission intensity constantly decreases with the increase of temperature due to the enhancement of non-radiative quenching at high temperature. The inset in FIG. 7 illustrates the integrated emission intensity for the $^3$P$_0$→$^3$H$_4$, $^3$P$_1$→$^3$H$_5$ and $^1$D$_2$→$^3$H$_4$ transitions as a function of temperature. The $^3$P$_0$→$^3$H$_4$ transition is the most vulnerable to temperature, followed by the $^3$P$_1$→$^3$H$_5$ transition and $^1$D$_2$→$^3$H$_4$ transition.

The activation energy ($E_a$) as a crucial parameter to determine the thermal stability of the prepared materials can be calculated by the Arrhenius equation [30]:

$$I_T = \frac{I_0}{1 + Ce^{(-E_a/k_B T)}}$$

(4)

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where $I_0$ is the intensity at 298 K, $I_T$ is the intensity at temperature $T$, $C$ is a constant and $k_B$ is the Boltzmann constant ($8.617 \times 10^{-5}$ eV/K). The Arrhenius equation can be modified to yield $E_a$ by plotting $\ln([I_0/I_T] - 1)$ against $1/k_B T$. The activation energy is determined to be 0.31, 0.30 and 0.28 eV for the $^3P_0 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3H_5$ and $^1D_2 \rightarrow ^3H_4$ transitions from the optimal linear fitting to the experimental data, respectively, as illustrated in FIG. 8(b). Meanwhile, the CIE chromaticity coordinates are also influenced by the temperature. The emission color shifts to the blue region as the temperature increases, as shown in FIG. 8(a).

IV. CONCLUSION

In conclusion, Bridgman method in a completely closed environment is a favorable technical method to grow high quality Pr$^{3+}$ doped LiLuF$_4$ single crystals. The Pr$^{3+}$ can be doped effectively in the crystal lattice sites of LiLuF$_4$ single crystal inferred from the results of XRD and optical spectra. The emission spectra appears sharp emissions at 480, 522, and 605 nm when excited by 446 nm light. Increasing temperature leads to a reduction of the emission intensity and a blue-shift of the emission color for the synthesized material. The results indicate the Pr$^{3+}$ doped LiLuF$_4$ single crystal may be a potential candidate for optics applications such as UV laser and the UVC persistent luminescence.

V. ACKNOWLEDGEMENTS

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