



Temperature-dependent evaluation of Nd:LiCAF optical properties as potential vacuum ultraviolet laser material



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ABSTRACT

We investigate the temperature-dependent optical properties of Nd³⁺-doped LiCaAlF₆ (Nd:LiCAF) in the vacuum ultraviolet (VUV) region. The 172-nm absorption edge does not seem to experience any significant blue shift as temperature is decreased from room temperature down to 30 K. This is confirmed by excitation spectra for the same temperature range. Several energy levels in the excited state configuration are observed. Based on these energy levels, the dominant emission peak at 177 nm is assigned to the allowed dipole transition from the 4f²5d configuration of Nd³⁺ and the ⁴I_{11/2} level of the 4f³ ground state configuration. The position of the dominant 177-nm emission peak appears to be fixed across the temperature range considered. Our results suggest that the spectral overlap between the excitation and emission spectra should not increase as temperature is raised, possibly making Nd:LiCAF a potential VUV laser gain medium operating at room temperature.

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1. Introduction

There is much interest in the development of a solid-state vacuum ultraviolet (VUV) laser because of the challenges posed by conventional light sources such as F₂ or Ar₂ gas lasers, synchrotron radiation, and free electron lasers. A VUV solid-state laser is easier to maintain, more cost-efficient, and more robust than the conventional sources mentioned above. Moreover, a broad bandwidth VUV solid-state laser will extend the wavelength available for applications in this short-wavelength region.

Fluorides are excellent host materials for potential VUV laser media because of their wide band gap, which is typically greater than 6 eV, enabling them to have good transparency down to nearly

100 nm [1]. Moreover, the nature of the inter-configurational 4fⁿ⁻¹ → 4fⁿ transitions responsible for the short-wavelength emission in rare-earth (RE)-doped fluorides gives rise to broad fluorescence bandwidths. For instance, it has been demonstrated that Ce³⁺-doped LiCaAlF₆ (Ce:LiCAF) is an excellent laser medium in the UV region [2–5] because of its tunability from 288 nm to 315 nm and an impressive efficiency of as high as 39% [2]. The broadband laser emission from Ce:LiCAF also makes it an excellent medium for UV chirped pulse amplification [3]. However, despite the encouraging results delivered by Ce:LiCAF, transition energies are not large enough for VUV emission. Emission from Ce³⁺ activators typically arise from the 5d → ²F_{5/2} transitions whose maximum energy lies at about 265 nm.

Pr³⁺, Tm³⁺ and Ho³⁺ activated fluorides are among those that have been studied as optical materials below 200 nm. However, lasing action has not been demonstrated from any of them. Only in the case of Nd³⁺-doping of LaF₃ (Nd:LaF₃) was lasing in the VUV

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region achieved. This was demonstrated using F₂ laser excitation over twenty years ago [6,7]. In recent years, interesting developments with Nd:LaF₃ have been reported. For example, VUV fluorescence from Nd:LaF₃ excited by 290 nm fs pulses from a Ti:Sapphire laser [8] have been reported. Also, Nd:LaF₃ thin films have been grown for LED or LD applications [9]. Despite this progress, no other VUV laser action has been reported since the demonstration of the Nd:LaF₃ laser over twenty years ago. It is apparent that the development of new and efficient solid-state emitters in the VUV spectral region is an important and promising field of research. An integral step towards this goal is the characterization of the optical properties of various combinations of wide band gap hosts and doping ions displaying optical activity in the VUV region.

In this paper, we investigate the temperature-dependent optical properties of Nd³⁺-doped LiCAF (Nd:LiCAF). Nd:LiCAF has been researched as optical material for F₂ laser lithography [10] and as scintillator for detecting radiation [11,12]. We did not observe a shift in the transmission edge and the excitation spectra at temperatures from 300 K to 30 K, as opposed to the blue-shift observed in Nd:LaF₃ [13,14] at low temperatures.

2. Experiment

The Nd:LiCAF sample was prepared by the Czochralski growth method. The bulk sample was cut into 20 mm diameter with 8 mm thickness and polished for an optical finish. Nd:LiCAF was placed inside the vacuum chamber maintained at a pressure less than 5×10^{-3} Pa for temperature-dependent PL measurements. A liquid helium cryostat and a heater were used to vary the temperature from 300 K to 30 K. The crystal was irradiated with a F₂ laser operating at 157-nm and 1-mJ pulse energy. The optical path from the laser to the vacuum chamber was purged with nitrogen gas to decrease VUV absorption by oxygen. Fluorescence from Nd:LiCAF was collected and focused onto the entrance slit of a Seya-Namioka spectrometer by a couple of MgF₂ lenses. The fluorescence intensity was measured using a CCD camera (ANDOR D0434-FI-Z). For temperature-dependent PLE measurements, the vacuum chamber was kept at a pressure of less than 10^{-5} Pa. The temperature was also maintained using a liquid helium cryostat and a heater. The crystal was excited using the 100-nm to 180-nm synchrotron radiation from the BL7B line at the UVSOR facility of the Institute for Molecular Science, Japan [15]. The spectral distribution of the synchrotron radiation was obtained using a Si photodiode and the PLE spectra were corrected for the wavelength-dependent intensity variation using the Si photodiode. The 5d-4f transition fluorescence around 172 nm was selected using a band-pass filter (Peak 172 nm, FWHM 26.4 nm), and the fluorescence intensity was measured using a photomultiplier tube (Hamamatsu Photonics R6836). The optical path from the MgF₂ window of the vacuum chamber to the photomultiplier tube was also purged with nitrogen gas. The absorption spectra were measured by collecting the transmitted beam with a Si photodiode located behind the sample. The synchrotron radiation spectrum was measured in the same way. The resolution of the spectrometer used for all measurements is around 0.2 nm.

3. Results and discussion

The absorption spectra of Nd:LiCAF at 300 K, 200 K, 77 K, and 30 K are shown in Fig. 1 (a). Within experimental uncertainty, the absorption edge at 172 nm is the same for all temperatures considered. Several intense peaks are observed below the absorption edge, from 120 nm to about 170 nm, as shown in Fig. 1 (b). These peaks can be attributed to manifolds of the 4f²5d excited state configuration arising from crystal field splitting by Nd³⁺.

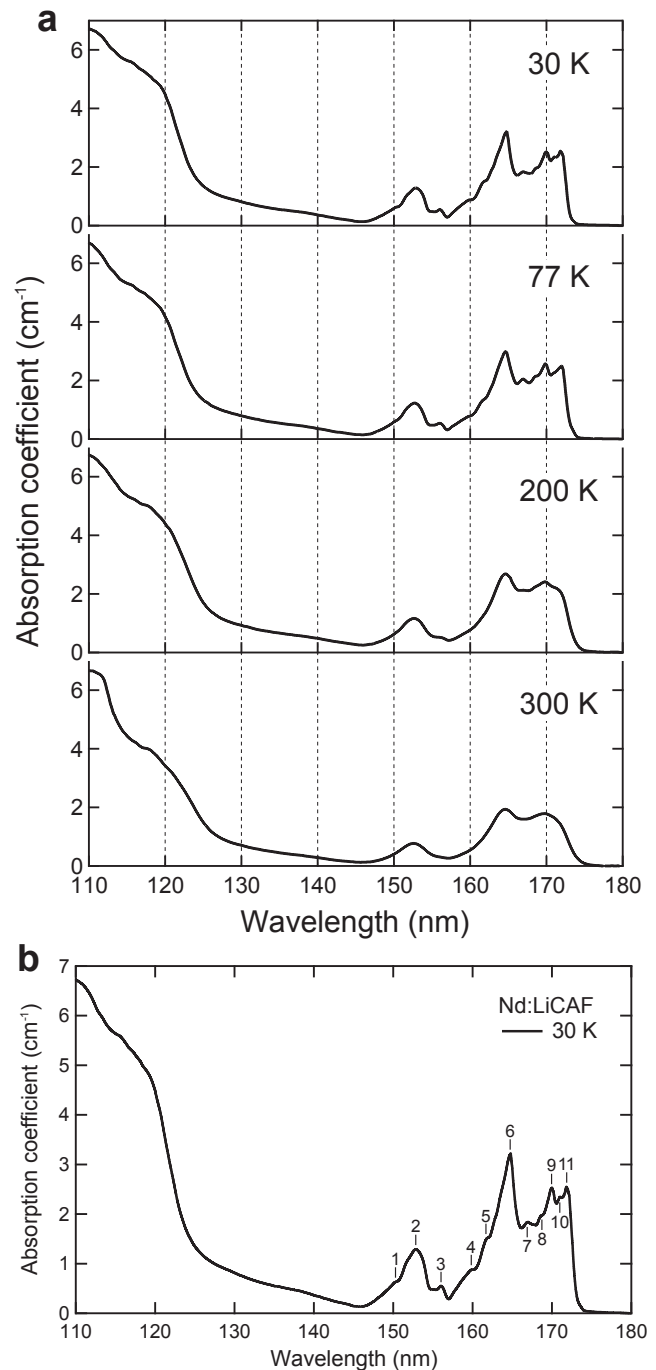


Fig. 1. (a) Absorption spectra of Nd:LiCAF at 300 K, 200 K, 77 K, and 30 K. Absorption edge appears to be fixed at 172 nm. The absorption spectra are not corrected for surface reflections, (b) Assignment of absorption peaks at 30 K whose values appear in Table 1.

Table 1 shows the position of these absorption peaks and their corresponding energy values. The lowest excited state energy level is located at about $5.821 \times 10^4 \text{ cm}^{-1}$.

Fig. 2 shows the emission spectra of Nd:LiCAF from 300 K down to 30 K when excited by the 157-nm emission of a F₂ laser. Emission peaks are observed at 177 nm, 183 nm, and 190 nm. The dominant emission peak at 177 nm is located close to the 172-nm emission from Nd:LaF₃ [6,7,13,14]. This VUV emission is therefore characteristic of the Nd³⁺ dopant and can be attributed to an allowed

Table 1
Absorption peaks corresponding to energy levels in the $4f^25d$ excited state configuration.

Peak	Wavelength [nm] ($\times 10^4$ [cm^{-1}])
1	150.3 (6.653)
2	152.8 (6.545)
3	156.4 (6.394)
4	159.9 (6.254)
5	161.8 (6.181)
6	164.8 (6.068)
7	166.9 (5.992)
8	168.6 (5.931)
9	170.0 (5.883)
10	171.0 (5.848)
11	171.8 (5.821)

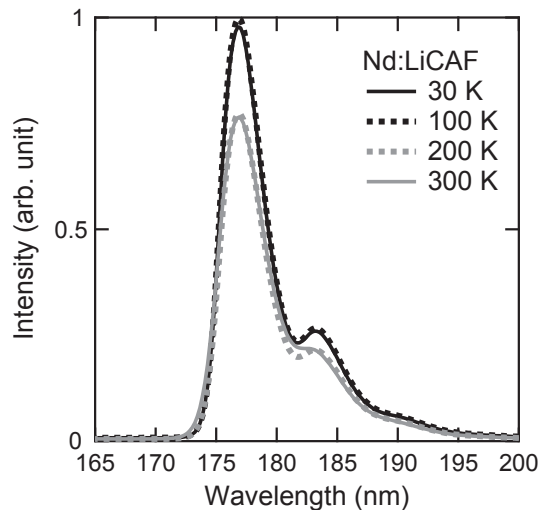


Fig. 2. Emission spectra of Nd:LiCAF from 300 K down to 30 K when excited by the 157-nm emission of a F_2 laser. Emission peaks are observed at 177 nm, 183 nm, and 190 nm. The dominant emission peak does not appear to be blue-shifted at low temperatures.

dipole transition from the mixed $4f^25d$ excited state configuration to the $^4I_{11/2}$ level of the $4f^3$ ground state configuration. It is usual to have an allowed dipole transition from the mixed $4f^25d$ excited state configuration to the lowest energy $^4I_{9/2}$ level of the $4f^3$ ground state configuration. A transition from $4f^25d$ to $^4I_{9/2}$ in Nd:LiCAF will give an emission peak at 172 nm. This is also confirmed from the absorption edge located at 172 nm as shown in Fig. 1. However, this $4f^25d \rightarrow ^4I_{9/2}$ emission peak was previously reported to be weak possibly due to self-absorption [10]. The penetration length of the 157-nm excitation light is large and emission is detected from the bulk of the crystal, which results in strong reabsorption. Photoluminescence (PL) measurements were calibrated using the zeroth order diffraction and an F_2 laser known to emit at 157 nm. Photoluminescence excitation (PLE) measurements using synchrotron radiation were calibrated using the zeroth order diffraction. The dominant peak from Nd:LiCAF does not appear to be red-shifted as temperature is increased. Moreover, it does not appear to smoothen out at high temperatures. This is contrary to what has been observed in Nd:LaF₃, where the dip in the fluorescence peak around 173.2 nm smoothen out and the dominant fluorescence peak is red-shifted at room temperature [13,14].

In order to confirm that the fluorescence peak indeed does not experience a shift with change in temperature, the excitation spectrum was obtained at the peak emission wavelength (177 nm). Fig. 3 (a) confirms that the excitation spectrum does not experience

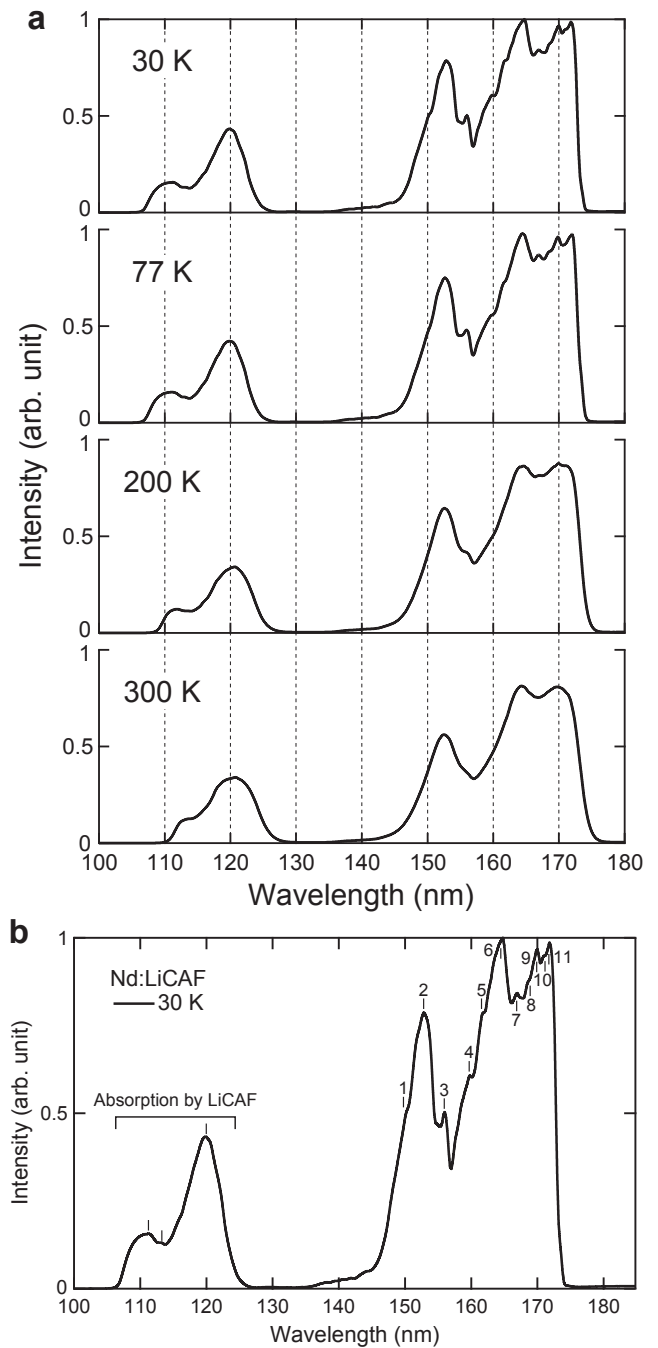


Fig. 3. (a) Nd:LiCAF excitation spectrum obtained at 300 K, 200 K, 77 K, and 30 K and at the 177-nm peak emission wavelength. (b) Assignment of excitation peaks at 30 K.

a significant shift as temperature is changed. In general, the excitation spectrum mimics the absorption spectrum. The excitation channels are also confirmed to correspond to energy levels of the $4f^25d$ excited state configuration, as shown in Fig. 3 (b). A schematic diagram of the energy levels of Nd:LiCAF with probable transitions resulting to the emission peaks observed in Fig. 2 is shown in Fig. 4. The position of the states of $4f^25d$ configuration is where the maximum absorption takes place.

The main difference in luminescence properties of Nd³⁺ in LaF₃ and LiCAF is due to different electron-lattice coupling in different hosts. In the case of LaF₃ there is strong electron-lattice coupling resulting in large Stokes shift between 4f-5d absorption and 5d-4f emission spectra as well as in large broadening of respective

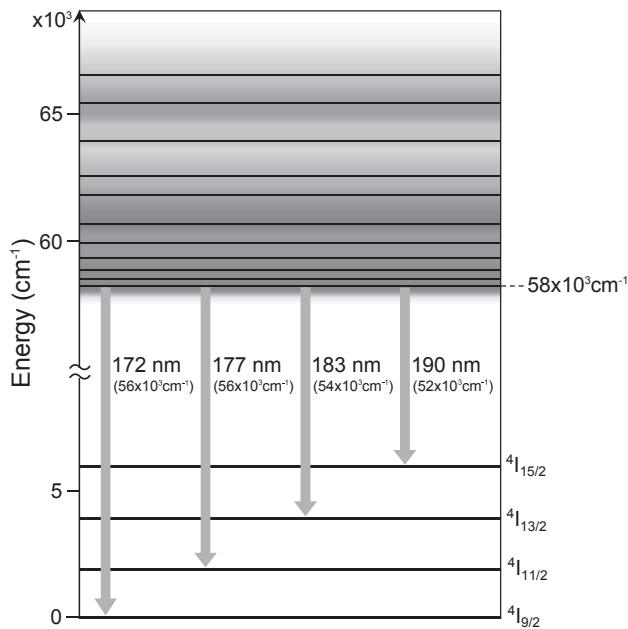


Fig. 4. Schematic diagram of the energy levels of Nd:LiCAF with probable transitions resulting to the emission peaks observed in Fig. 2. Ground state energy levels for Nd³⁺ are at 0 (⁴I_{9/2}), 1897 cm⁻¹ (⁴I_{11/2}), 3907 cm⁻¹ (⁴I_{13/2}), and 5988 cm⁻¹ (⁴I_{15/2}) [16]. The 172 nm emission arising from 4f²5d → ⁴I_{9/2} transition was too weak to be observed.

absorption and emission bands [14,17,18]. On the other hand, electron-lattice coupling in LiCAF is much weaker, leading to the appearance in the spectra of some fine structure corresponding to zero-phonon lines of respective transitions and maybe some vibronic lines, as can be seen in Fig. 3. In general, the structure of 4f-5d transitions of Nd³⁺ in both hosts is rather complicated but in the case of LiCAF matrix this structure can be revealed in the experimental spectra measured at low temperature whereas in the case of LaF₃ the structure is smeared because of broadening. The dominant fluorescence peak in Nd:LaF₃ originates from the lowest energy level of this 4f²5d excited state configuration. In the case of Nd:LiCAF, the absorption and excitation spectra (Figs. 1 and 3) show multiple 4f²5d excited state energy bands. The energy gap between the lowest excited state energy and the next higher-lying energy level is about 270 cm⁻¹. Since this energy gap is close to kT (209 cm⁻¹ at 300 K), the next higher-lying energy level can be thermally populated at increasing temperature. As a result, radiative transitions will be observed from both levels at high temperatures and hence, no significant red-shift in the dominant 177-nm fluorescence peak is observed. The spectral overlap between the excitation and emission spectra does not increase as temperature is raised. When used as a laser gain medium, the temperature of Nd:LiCAF is expected to increase during pumping and laser operation. The absence of significant spectral shift would indicate that fluorescence self-absorption does not seem to worsen as the crystal heats up. As a result, room-temperature operation should be feasible. This would make Nd:LiCAF an attractive potential gain medium.

4. Conclusion

Temperature-dependent optical properties of Nd:LiCAF in the vacuum ultraviolet (VUV) region is investigated. The absorption edge does not seem to experience significant blue shift as temperature is decreased from room temperature up to 30 K. The 172-nm absorption edge estimated at 300 K is, within experimental uncertainty, the same as that at 30 K. This is confirmed by the

excitation spectra for the same temperature range. Several energy levels in the excited state configuration of Nd:LiCAF is observed. Based on these energy levels, the dominant emission peak at 177 nm is assigned to the allowed dipole transition from the 4f²5d configuration of Nd³⁺ and the ⁴I_{11/2} level of the 4f³ ground state configuration. The emission peaks are not observed to undergo significant blue shift at 30 K. Our results suggest that fluorescence self-absorption does not seem to worsen because increasing temperature does not lead to an increase in the spectral overlap between the excitation and emission spectra.

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