Nd$^{3+}$: (La$_{1-x}$,Ba$_x$)F$_{3-x}$ as Vacuum Ultraviolet Scintillator and New Potential Laser Material


At present, few laser sources are available in the vacuum ultraviolet (VUV) region and most of them are either complicated or expensive. Among these are excimer lasers based on rare gas dimers [1]. However, limited tunability and the use of e-beam excitation impose serious experimental restrictions. Tunable radiation can be generated from nonlinear methods using frequency mixing in gases [2,3], metal vapors [4] and nonlinear crystals [5] but this scheme is characterized by low conversion efficiency. Current injection-type semiconductor laser diodes are more compact; however their operating wavelength cannot extend below 200 nm because of their narrow band gap. An attractive solution is to take advantage of the allowed radiative interconfigurational d-f transitions of rare earth (RE) activated ions in wide band gap dielectric crystals due to its simplicity, reliability, and efficiency. With this scheme, it is possible to obtain good quality laser beam, controlled adjustment of the spectral width, and multi-wavelength operation from only one laser oscillator [6].

Several works have studied the potential of Nd$^{3+}$-doped fluorides such as LaF$_3$ as laser materials in the VUV. Dubinskii et al and Waynant et al demonstrated the ability of Nd$^{3+}$:LaF$_3$ to lase at 172 nm by optical [7] and electron beam pumping [8], respectively. After these efforts, no successful material research for VUV laser media is reported. On the other hand, gamma ray scintillator that emits vacuum ultraviolet fluorescence is strongly needed for gas scintillation micro-wire stripped detector for high resolution PET application [9]. Material research for this application is still ongoing. To efficiently address the need for suitable materials, we use the micro-pulling down (micro-PD) method for crystal growth that enable shorter growth time at a lower cost compared with other melt growth methods like Czochralski or Bridgeman – Stockbarger [10].

In this paper, Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$ as new scintillator and laser material is explored. Single crystal was efficiently grown using the micro-PD method modified for fluoride crystal growth [11]. Compared to Nd$^{3+}$:LaF$_3$, it has higher VUV transmission, shorter transmission edge; and its fluorescence peak located at 175 nm is broader and more intense.

The sample was grown using an RF heated micro-PD apparatus with graphite crucible [11]. High purity LaF$_3$, BaF$_2$, and NdF$_3$ with 90 mol%:10 mol%:1 mol% molar ratio were used as starting materials to obtain Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$ where x = 0.1. The 20-mm long, 2-mm wide single crystal was grown with a pulling rate of 0.1 mm/min. The growth atmosphere is mixture of Ar and CF$_4$. The crystal was grown with complete solidification of the melt charged in the crucible.

Transmission characteristics are highly influenced by the host material. Figure 1 shows that the transmission edge of undoped (La$_{1-x}$,Ba$_x$)F$_{3-x}$ located at 160 nm is at a shorter wavelength compared to LaF$_3$ at 180 nm. This implies that Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$ would have better VUV transmission characteristics compared to Nd$^{3+}$:LaF$_3$.

For fluorescence measurements, excitation is from an F$_2$ laser operating at 157 nm, 100-Hz repetition rate, 1-mJ pulse energy, and 5-ns pulse duration. The sample is placed inside a vacuum chamber evacuated to 10-3 Torr. Fluorescence is collected by a MgF$_2$ lens and focused onto the entrance slit of a spectrograph (1-nm resolution), which projects the component wavelengths onto a VUV CCD detector.

Figure 2.a shows the fluorescence spectrum for Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$. The fluorescence signal is magnified 25-times with respect to the scattered excitation for emphasis. Fluorescence from 300 nm to 170 nm, with the strongest peak in the VUV at 175 nm, was observed.

Using the same set up for obtaining the Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$ fluorescence, we also obtained the fluorescence spectrum for Nd$^{3+}$:LaF$_3$ as shown in Figure 2.b. Note that both samples used have the same dimension and were grown using the same technique. VUV fluorescence peak is located at 172 nm. The shift in VUV fluorescence from 172 nm (Nd$^{3+}$:LaF$_3$) to 175 nm Nd$^{3+}$:(La$_{1-x}$,Ba$_x$)F$_{3-x}$ may be due to the effect of BaF$_2$ as the particular sample was a mixture of 90% LaF$_3$ and 10% BaF$_2$. The VUV transmission of a BaF$_2$ host is
shown in Figure 1.

Nd\textsuperscript{3+}:(La\textsubscript{1-x},Ba\textsubscript{x})F\textsubscript{3-x} offers several advantages over Nd\textsuperscript{3+}:LaF\textsubscript{3}. First, since its transmission edge is at a shorter wavelength, it is suitable as shorter wavelength solid-state material. Second, it has a broader fluorescence with a FWHM of 12 nm compared to 8 nm for Nd\textsuperscript{3+}:LaF\textsubscript{3}. The broad fluorescence provides for a more tunable operation in the VUV from 169 nm to 181 nm. Moreover, the broad fluorescence makes amplification for shorter pulses possible. Third, it has a more intense fluorescence. Therefore it is more suitable for gamma ray scintillator. Fourth, a mixed fluoride from solid-solution is generally harder than a single component material, hence Nd\textsuperscript{3+}:(La\textsubscript{1-x},Ba\textsubscript{x})F\textsubscript{3-x} is harder than Nd\textsuperscript{3+}:LaF\textsubscript{3}, making it more robust against mechanical degradation.

In summary, Nd\textsuperscript{3+}:(La\textsubscript{1-x},Ba\textsubscript{x})F\textsubscript{3-x} single crystal is successfully grown using the micro-PD method and its VUV transmission and laser induced fluorescence investigated. The short transmission edge at 160 nm together with the strong and broad 175 nm VUV fluorescence make it an attractive new VUV scintillator and potential laser material.

REFERENCES

[9] Private communication with Professor Takahashi from Tokyo University.

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