

Characterization of Fluoride Phosphors for Diode Pumped Solid-State Lighting Applications

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Abstract

Phosphor coated diodes are critical to the lighting industry. Rare-earth doped fluoride phosphors are characterized in this work. Spectroscopy and lifetime measurements of CaF_2 : Dy^{3+} , LaF_3 : Eu^{3+} and Tb^{3+} -doped LaF_3 and CaF_2 crystals were performed by irradiating the samples with 405 and 375 nm diode lasers. Chromaticity diagrams are developed from spectral measurements. Dy^{3+} -doped CaF_2 revealed bright white light emission having peaks at 492, 570 and 654 nm. The measured color coordinates are $x = 0.322$ and $y = 0.340$ for Dy^{3+} -doped CaF_2 and these values are close to those of sunlight and the coordinated color temperature is 6147 K, under 405 m laser excitation. Eu^{3+} -doped LaF_3 revealed twenty emission peaks in the visible wavelength region. The color coordinates measured for LaF_3 : Eu^{3+} are $x = 0.283$ and $y = 0.293$ under 405 nm diode laser excitation and the color temperature is 9557 K. Eu^{3+} -doped LaF_3 provides cool white-light, under 405 nm diode laser excitation. Tb^{3+} -doped fluoride crystals revealed bright white light under low power diode laser excitation. The measured color coordinates for Tb^{3+} -doped CaF_2 are $x = 0.329$ and $y = 0.558$ and the color temperature is 7713 K. The color coordinates for LaF_3 : Tb^{3+} are $x = 0.342$ and $y = 0.365$ and the coordinated color temperature is 5370 K. These values are close to those of sunlight.

Keywords

Rare-Earth Spectroscopy, White-Light Emission, Color Coordinates, Coordinated Color Temperature, Fluoride Materials, Laser Induced Fluorescence, Europium, Terbium, Dysprosium Ions

1. Introduction

About 20 percent of the electricity supplied to homes is used in lighting. One of

the current research areas is the design of all solid-state white-light emitters which are energy efficient, robust and free from pollution [1]. There is an ongoing global effort to design efficient solid-state white-light sources. For this purpose, both organic and inorganic materials are being investigated which emit white-light under electrical pumping [2] [3] [4]. In the category of inorganic materials, semiconductor diodes, quantum dots and diode pumped phosphor materials are under consideration. One class of materials that emit white light is diode pumped phosphors which are embedded with inorganic ions [5]-[11]. Light emitting diodes (LED) consume less energy, do not pollute the environment and last much longer than their counterparts. Some of the rare-earth ions possess numerous energy levels and emit in the visible and infrared wavelength regions. Depending on the energy level structure, a rare-earth ion may absorb certain discrete lasers wavelengths. Because of these characteristic spectral features, materials embedded with single, double or triple dopants, emit different colors. White-light sensation occurs whenever the three primary colors are mixed in various combinations. Accordingly, any material that emits red, green and blue light in appropriate combinations generates white light. In this paper, rare-earth doped fluoride phosphors that produce white light under diode pumping are discussed. Materials used for solid-state lighting are characterized by measuring the color rendering index or the color coordinates. The ability of a light source to reveal the colors of different objects is expressed in terms of color rendering index. Luminous efficacy, expressed in Lumens/Watt, is the radiant power, in the visible part of the spectrum. Higher index values are preferred in lighting industries. Another way of measuring the source performance is to measure color coordinates and coordinated color temperature (CCT). CCT is a measure of the source color appearance. In this manuscript, we evaluated the materials by measuring the color coordinates and CCT.

Rare-earth ion doped materials were investigated because of their applications in the laser development, luminescent devices, optical refrigeration, optical memories, temperature measurement and others [12] [13] [14] [15] [16]. LaF_3 and CaF_2 possess high melting points 1550°C and 1450°C respectively. These crystals have wide transmission range covering the visible and infrared regions. The space group of LaF_3 is trigonal and the dopant ions occupy the isovalent La sites [17]. Spectroscopy and X-ray diffraction studies revealed a single type of site, C_2 for the dopant ions. CaF_2 is a cubic material and the trivalent dopant ions occupy bivalent cationic sites. Consequently, the dopant ions occupy multiple sites in the CaF_2 host [18]. Conventional spectroscopy work revealed five types of major sites for the dopant ion whereas a high resolution spectroscopy work revealed numerous sites for the dopant ion. The crystal field splittings are smaller than the spin-orbit coupling. The centers of gravity of the multiplets do not change much from one host to another host material. The number of crystal field components of a multiplet depends on the site symmetry of the rare-earth ion. Eu^{3+} and Dy^{3+} -doped materials were not used in the laser development.

However, Eu^{3+} -doped materials were extensively investigated because their possible applications in optical hole burning memory devices [16]. Published literature on Dy^{3+} -doped materials is far less than that for Er^{3+} -doped materials because the latter is used in the laser development. Moreover, at higher doping levels concentration quenching dominates in Dy^{3+} -doped materials. Lately, rare-earth doped materials are being investigated for possible applications in solid-state lighting [19]-[24]. Rare-earth doped LaF_3 and CaF_2 are relatively stable when compared to other materials, because of their high melting points. Crystal growth of CaF_2 is a mature technology and large windows are grown for infrared applications. In the current study the suitability of these materials for solid-state lighting applications is discussed. In a solid, excited rare-earth ions relax radiatively and non-radiatively [25]. The former depends on the transition probabilities which are calculated using Judd-Ofelt intensity parameters which, in turn, are derived from the absorption spectrum. The radiative probabilities are independent of temperature. The non-radiative relaxation is temperature dependent and its value depends on the energy gap between the levels and the cut-off phonon frequency [26]. The cut-off phonon frequency depends on the reduced mass of the molecule and force constants. The phonon structure is revealed by Raman and infrared spectral measurements. The cut-off phonon frequency of LaF_3 and CaF_2 crystals are 360 and 380 cm^{-1} respectively.

2. Experimental Details

The crystals used for this investigation were obtained from Optovac, Inc. The crystals are of the size 8x6x4 mm^3 and were polished for optical studies. Optical absorption spectroscopy measurements were performed by a Cary 3E spectrophotometer. The fluorescence spectroscopy measurements were performed using a Stellarnet spectrometer. Luminescence was generated from the samples by exposing them to Coherent OBIS 375 or 405 nm diode lasers. For lifetime measurements the laser beams were chopped at 100 Hz by a mechanical chopper to generate laser pulses. The luminescence was acquired by a fiber bundle whose other end was connected to an Acton Research Corporation, Spectra Pro 500 spectrometer (Figure 1). The spectrometer output was detected by a Hamamatsu R928 photomultiplier tube (PMT). The PMT output was amplified and then acquired by a Stanford Research Corporation, SRC 430 multichannel scaler. The resulting decay signals were fitted to single exponentials to derive the lifetimes of the excited levels. For the measurement of color coordinates and CCT the spectra were acquired by a Stellar Net spectrometer.

3. Results and Discussion

3.1. CaF_2 : Dy^{3+} (0.17%)

A partial energy level diagram was generated from the absorption spectral measurements (Figure 2). The energy levels are identified by comparing the spectral

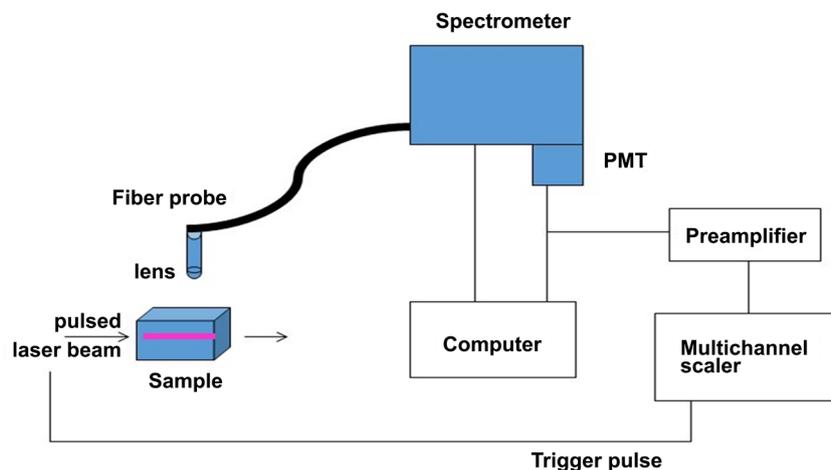


Figure 1. A block diagram of the experimental setup used for lifetime measurement.

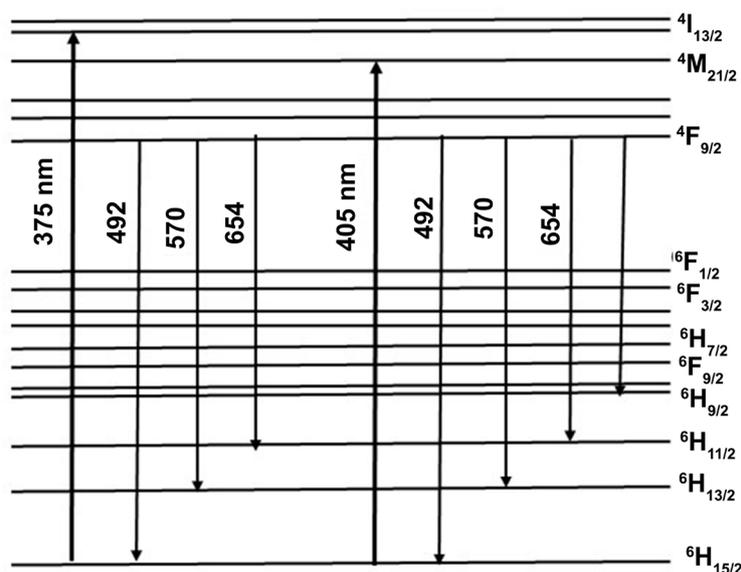


Figure 2. Partial energy level diagram of Dy^{3+} ion depicting emission transitions, under 375 and 405 nm diode laser excitations.

wavelengths with those of literature values. The 405 nm diode laser resonantly excites the ${}^4\text{M}_{21/2}$ level, whereas the 375 nm laser resonantly excites ${}^4\text{I}_{13/2}$ level. Excited ions relax non-radiatively in cascade to ${}^4\text{F}_{9/2}$. The energy gap between ${}^4\text{F}_{9/2}$ and its lower level is very large and hence ${}^4\text{F}_{9/2}$ relaxes radiatively to the lower levels with 100% quantum efficiency, in the absence of concentration quenching effects. The fluorescence spectrum observed under a 375 nm diode laser is shown in **Figure 3** and the sample color is shown in the inset. **Figure 3** reveals emission peaks at 492 (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$), 570 (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$) and 654 nm (${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$); the spectral identifications are given in parentheses. The fluorescence contains blue, green and red colors and hence the sample color is white along the beam path. The emission spectrum is identical even for 405 nm excitation. The measured lifetime of ${}^4\text{F}_{9/2}$ level is 1.3 ± 0.1 ms. Each emission peak is a

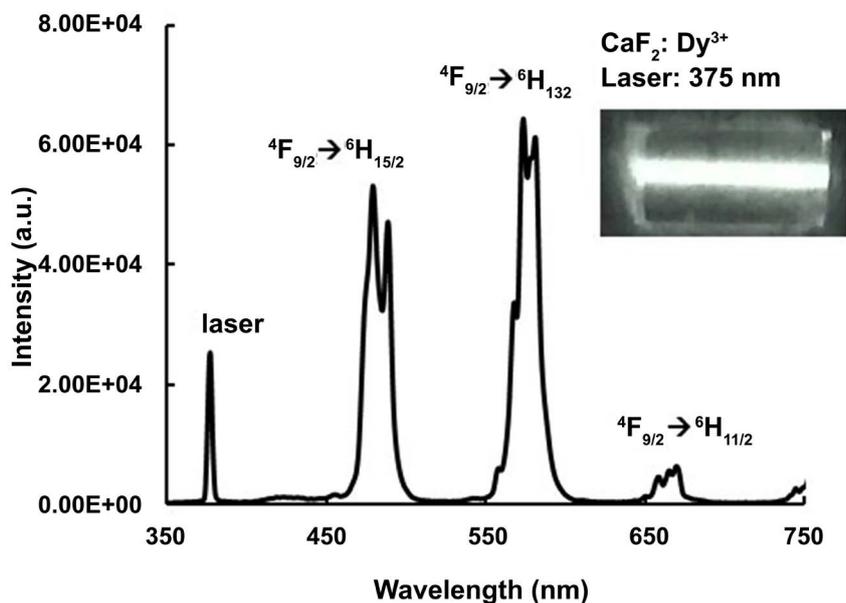


Figure 3. Emission spectrum of $\text{CaF}_2:\text{Dy}^{3+}$ observed under 375 nm laser excitation. Inset in the figure is the sample photograph depicting the emission color.

convolution of spectral overlap emitted by different sites. Hence the uncertainty in the measured lifetime is large. It is customary to compare the sample emission color with that of sunlight. The color is characterized by developing a chromaticity diagram to estimate color coordinates and coordinated color temperature (CCT). The color coordinates of $\text{CaF}_2:\text{Dy}^{3+}$ are $x = 0.322$ and $y = 0.340$ and the color temperature is 6147 K, under 405 nm laser excitation, which are close enough to those of sunlight values; $x = 0.33$ and $y = 0.33$. The color coordinates are $x = 0.338$ and $y = 0.36$ under 375 nm laser excitation, and the CCT is 5474 K (**Figure 4**). The pink curve in the middle of the figure represents the path of the color of a blackbody as a function of its temperature, also called Planckian locus. The color coordinates of sunlight, $x = 0.33$, $y = 0.33$ are located at the crossing of the two straight lines, called, achromatic point. Inset in **Figure 3** reveals the sample emission color, observed under 375 nm laser excitation. Though fluorescence is generated from the same upper level, $^4\text{F}_{9/2}$, for both 375 and 405 nm laser excitations, the color coordinates change slightly when the sample is excited with different diodes. Each diode laser may excite one or more sites, depending on the laser wavelength. The energy level positions and transition probabilities change from one site to another. Hence, the color coordinates and color temperature differ slightly under different laser excitations.

3.2. $\text{LaF}_3:\text{Eu}^{3+}$ (0.3%)

A partial energy level diagram of Eu^{3+} is shown in **Figure 5**. Eu^{3+} ions occupy a single type of site in this material. 405 and 375 nm lasers resonantly excite $^5\text{D}_3$ and $^5\text{L}_7$ levels, respectively. Excited ions relax radiatively and non-radiatively in cascade to the lower levels. Transition probabilities predict radiative transitions

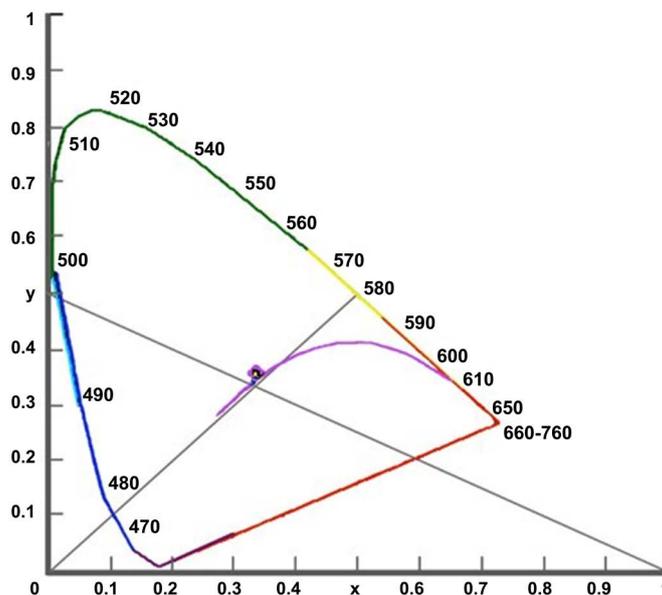


Figure 4. Chromaticity diagram of $\text{CaF}_2: \text{Dy}^{3+}$ measured with 375 nm diode laser excitation. The color coordinates are $x = 0.338$ and $y = 0.36$ and CCT is 5474 K.

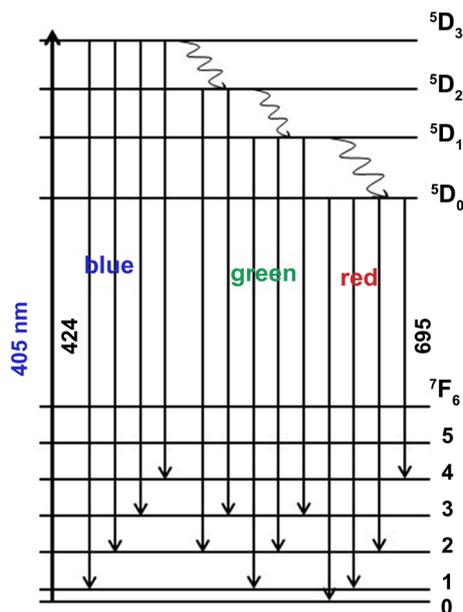


Figure 5. Partial energy level diagram of $\text{LaF}_3: \text{Eu}^{3+}$ depicting absorption and emission transitions under diode laser excitation.

to several lower multiplets from each excited state. As a result, radiative relaxation occurs from $^5\text{D}_3$, $^5\text{D}_2$, $^5\text{D}_1$ and $^5\text{D}_0$ multiplets to several ground state manifolds, $^7\text{F}_j$ ($J = 0$ to 6). Fluorescence spectrum shown in **Figure 6** reveals numerous transitions from 400 to 700 nm. Hence, the sample emission is white as exhibited by the photograph (inset in **Figure 6**). Spectral identifications are shown on the same figure. Lifetime measurements confirm the spectral identifications. The lifetimes of $^5\text{D}_j$ manifolds ($J = 0, 1, 2$ and 3) are in the millisecond range.

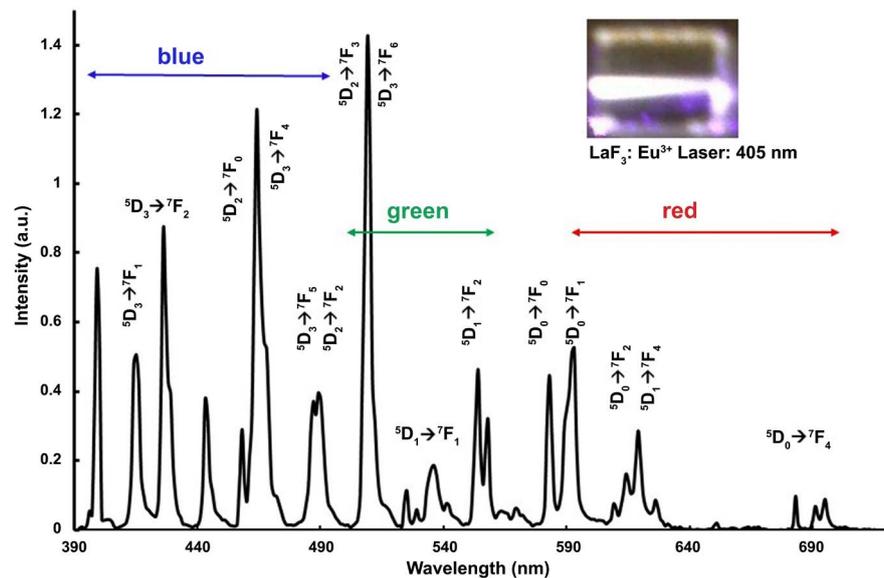


Figure 6. Fluorescence spectrum of $\text{LaF}_3:\text{Eu}^{3+}$ observed with 405 nm diode laser excitation. The inset in the figure is a photograph of the sample, which reveals white emission color.

Chromaticity diagrams are developed for this material from the emission measurements under 375 and 405 nm laser excitations. The color coordinates are $x = 0.283$ and $y = 0.293$ under 405 nm laser excitation and the coordinated color temperature is 9557 K (**Figure 7**). This indicates that the emission color of this material is cool white. Under 375 nm laser excitation the measured color coordinates are $x = 0.273$ and $y = 0.282$ and the color temperature is 11,648 K (figure not shown). The sample absorption is relatively stronger at 375 nm. The intensities of the spectral components, in the blue wavelength region 400 - 450 nm, increase for 375 nm laser excitation when compared to those observed under 405 nm excitation. Hence, the color temperature increased and the color coordinates shifted more towards cool white.

3.3. Tb^{3+} -Doped CaF_2 and LaF_3

The absorption spectrum of $\text{CaF}_2:\text{Tb}^{3+}$ (0.1%) is shown in **Figure 8**. It revealed peaks at 257 ($^5\text{K}_9$), 274 ($^5\text{F}_4$), 286 ($^5\text{F}_5$), 295 ($^5\text{H}_5$), 303 ($^5\text{H}_6$), 320 ($^5\text{D}_0$), 329 ($^5\text{D}_1$), 343 ($^5\text{G}_3$), 352 ($^5\text{G}_4$), 367 ($^5\text{L}_{10}$), 380 ($^5\text{D}_3$), and 488 nm ($^5\text{D}_4$). The symbols in the parentheses represent the corresponding spectral terms of the excited energy states. The absorption spectrum does not reveal any peak in the vicinity of 405 nm. Accordingly, the material did not reveal any fluorescence from $^5\text{D}_1$ ($J = 3, 4$) levels under 405 nm excitation. However, the sample emitted bright white light under 375 nm laser excitation (**Figure 9**). When the fluorescence was analyzed with a spectrometer it revealed a weaker peak at 426 nm and more intense peaks in the blue, green, orange and red regions, respectively at 492 ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 549 ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 580 ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 631 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_3$). Because the emission spectrum is a superposition of blue, green and red colors, sample emission appears to

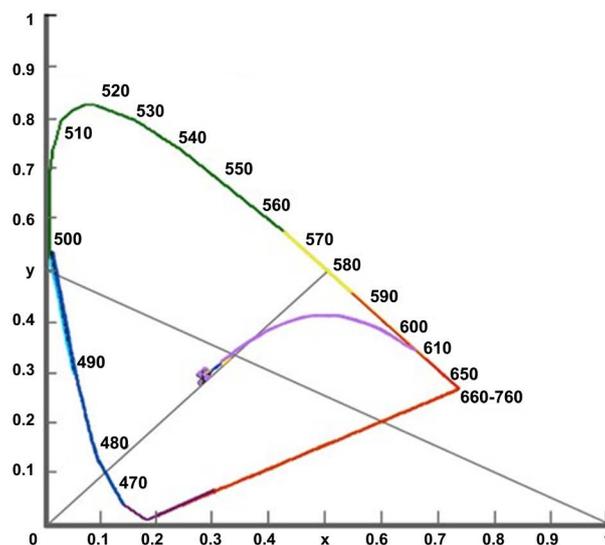


Figure 7. Chromaticity diagram of $\text{LaF}_3: \text{Eu}^{3+}$ measured with 405 nm diode laser excitation. Color coordinates are $x = 0.273$ and $y = 0.282$ and CCT is 9557 K.

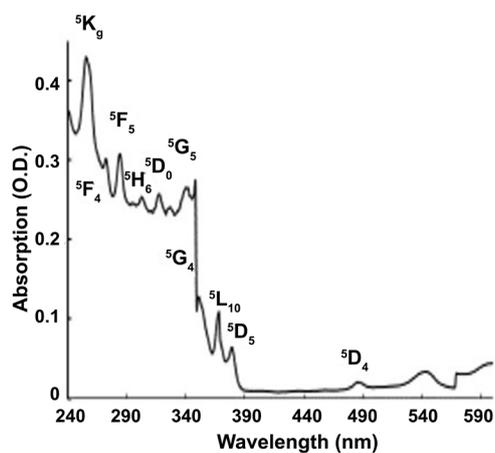


Figure 8. Absorption spectrum of Tb^{3+} -doped CaF_2 .

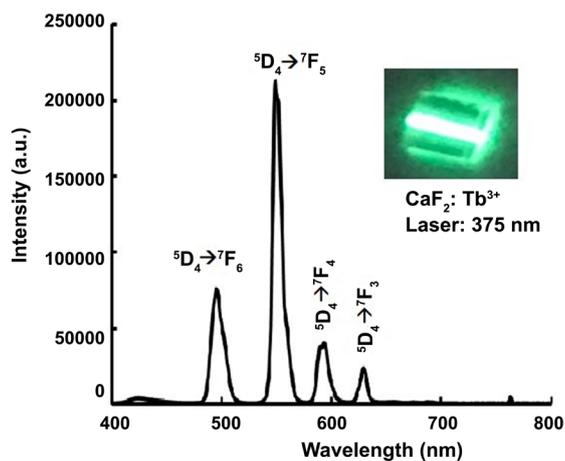


Figure 9. Fluorescence spectrum of $\text{CaF}_2: \text{Tb}^{3+}$ generated with 375 nm laser excitation. Inset is the sample photograph under laser illumination.

be white as shown in the inset of **Figure 9**. The emission intensity of the green peak is relatively more intense. Moreover, the responsivity of human eye is maximum for the green color emission. Hence, the sample scattering is greenish in appearance. The 375 nm laser ($26,666\text{ cm}^{-1}$) resonantly excites 5G_6 level ($26,547\text{ cm}^{-1}$) as shown in **Figure 10**, which relaxes in cascade to the lower levels causing 5D_4 levels to emit. When lifetimes were measured by monitoring different emission wavelengths they all revealed the same value $4.4 \pm 0.3\text{ ms}$, which confirms that all these wavelengths arise from the same upper level, 5D_4 . The uncertainty in lifetime is large when monitored at different emission wavelengths, because of the spectral overlap arising from different sites.

Tb^{3+} -doped materials revealed emission from 5D_3 level under Ar^+ laser excitation [27] [28], due to stepwise two-photon excitation mechanism. However, in Tb^{3+} -doped CaF_2 , no emission was detected from 5D_3 level under 375 nm laser excitation. When the 375 nm laser beam passed through $LaF_3: Tb^{3+}$ (1%) the sample glow was much brighter. The laser light was absorbed by the sample within a millimeter length of the sample. However, the emission spectrum revealed numerous peaks (**Figure 11**). An analysis of the energy levels [12]-[17] indicates that the 375 nm laser light resonantly excites one of the crystal fields components of Tb^{3+} in LaF_3 host. Tb^{3+} occupies a single type of site in this material. Selection rules permit absorption and emission transitions among different energy levels of terbium ion. Intensity parameters predict emission transitions from 5D_3 and 5D_4 levels to several lower manifolds. Hence, the emission spectrum of $LaF_3: Tb^{3+}$ revealed many more emission peaks (**Figure 11**) than those observed in $CaF_2: Tb^{3+}$ (**Figure 9**). 5D_3 level emission transitions occur from 380 to 480 nm (5D_3 to 7F_J ($J = 6$ to 0)). The spectral peaks from 480 to 700 nm region correspond to 5D_4 to 7F_J ($J = 6$ to 0) transitions. Lifetime measurements confirmed these assignments. The lifetime of 5D_3 level is 1.18 ms whereas

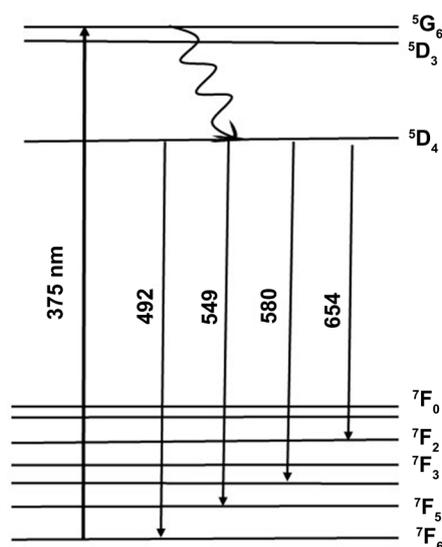


Figure 10. Partial energy level diagram of Tb^{3+} showing the excitation and emission transitions.

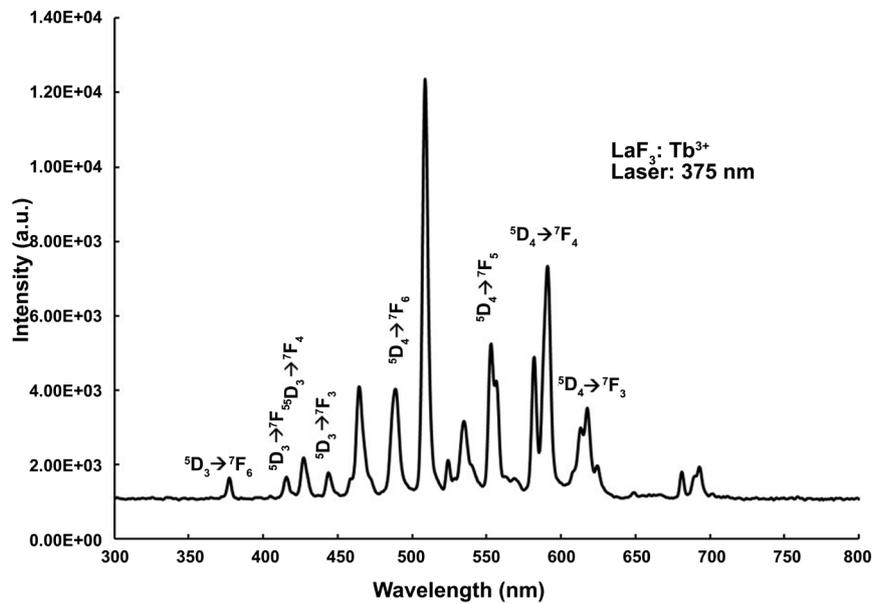


Figure 11. Fluorescence spectrum of $\text{LaF}_3:\text{Tb}^{3+}$ induced by 375 nm laser.

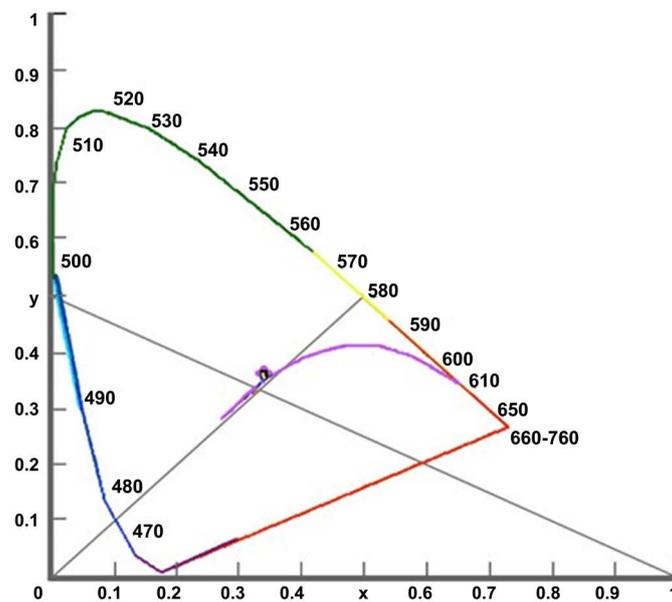


Figure 12. Chromaticity diagram of $\text{LaF}_3:\text{Tb}^{3+}$ measured with 375 nm diode laser excitation. The color coordinates are $x = 0.342$ and $y = 0.365$.

the lifetime of $^5\text{D}_4$ is longer. Human beings are used to sunlight. How pleasant the sample emission is dependent on the number of spectral wavelengths present in the visible regions. It is customary to characterize the white light in terms of color coordinates. For this purpose, a chromaticity diagram was constructed from the spectral measurements. The color coordinates for $\text{LaF}_3:\text{Tb}^{3+}$ are $x = 0.342$ and $y = 0.365$ (Figure 12). These values are close to those of sunlight values, $x = 0.33$ and $y = 0.33$. It is not surprising because the spectrum of Tb^{3+} -doped LaF_3 revealed more peaks in the visible region. The measured coor-

ordinates of Tb³⁺-doped CaF₂ are $x = 0.329$ and $y = 0.558$ (not shown). The y coordinate deviated from that of sunlight value, $y = 0.33$ because of the intense green light emitted by CaF₂: Tb³⁺ (**Figure 9**). In a fluoride host the energy gap between the ⁵D₃ and ⁵D₄ multiplets is approximately 6000 cm⁻¹. Hence, emission occurs from both ⁵D₃ and ⁵D₄ states to lower manifolds.

4. Conclusions

Our studies indicate that the color coordinates of Dy³⁺-doped CaF₂, Eu³⁺-doped LaF₃ and Tb³⁺-doped LaF₃ are close to that of sunlight and hence these materials are ideal for the development of diode pumped solid state white light emitters. Only low concentrations of the dopant ions are needed as higher concentrations of the dopant will lead to concentration quenching. Though we demonstrated this effect in fluoride single crystals, other low phonon glasses will also work for this purpose. Our investigations indicate that rare-earth ion doped phosphors have potential applications for solid state lighting. Oxyfluoride glasses retain the crystalline emission properties and maintain bulk properties of oxide glasses [29]. Hence, oxide glasses embedded with rare-earth fluoride nanocrystals may exhibit white-light emission.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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