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Investigation of the growth and optical properties of a Co$^{2+}$-doped Na$_5$Lu$_9$F$_{32}$ single crystal

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A 0.1 mol.% CoF$_2$-doped Na$_5$Lu$_9$F$_{32}$ single crystal with high quality in the size of $\sim$$\phi$10 mm×100 mm was grown by the Bridgman method. Three peaks located at 504, 544, and 688 nm and a broad band in the range of 1200–1600 nm were observed in the absorption spectra. The absorption peak position suggests cobalt ions in the divalent state in the grown crystal. Moreover, the cobalt ions are confirmed to locate in the distorted cubic crystal structure. Upon excitation of 500 nm light, a sharp emission peak at 747 nm ascribed to the $^{2}T_{2}(H_1) \rightarrow ^{4}A_{2}(F)$ transition was observed for the crystal. The Co$^{2+}$-doped Na$_5$Lu$_9$F$_{32}$ single crystal shows a potentially promising material for the application of a passively $Q$-switched laser operating in the near-infrared range.

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Rare earth ions and transition metal ions are known as two mainly luminous centers. Unlike rare earth ions, transition metal ions show broad luminescence characteristics due to the exposure of 5d outer orbital to the crystal field. Interest in crystals doped with transition metal ions is related to their potential application in the design of tunable solid-state lasers. The reported laser operation in a Ni$^{2+}$-doped MgF$_2$ single crystal leads to intense research efforts to explore new crystals containing transition metal ions. Cobalt (Co) with two valence states (+2, +3) is well recognized as an important transitional active luminescent ion and is a luminescent center for solid materials capable of producing visible (VIS) and infrared fluorescence emission. Materials doped with Co$^{2+}$ ions are used for tunable laser applications in the VIS and near-infrared (NIR) regions due to their intense and broad luminescence. Recently, passive $Q$-switch material operating in the NIR eye-safe spectral range gains particular interest, as it can be employed in the fabrication of a compact and low-cost laser generating nanosecond pulses for various applications. A Co$^{2+}$ ion exhibiting a broad absorption band in the range of 1200–1600 nm when doped into different host materials makes Co$^{2+}$-doped materials promising candidates for passive $Q$-switched lasers, for instance, Co$^{2+}$-doped yttrium aluminum garnet (Co$^{2+}$:YAG), Co$^{2+}$-doped yttrium scandium gallium garnet (Co$^{2+}$:YSGG), and transparent glass-ceramics.

Glass, glass-ceramic, and single crystals are the main solid hosts for active transition metal ions. Single crystals display superior optical performance and physical-chemical properties in general. A single crystal with a rigid cyclic symmetric structure shows higher luminous efficiency when doped with transition metal ions compared to glass hosts. Meanwhile, glass-ceramics tend to exhibit lower transmission that is ascribed to the scattering of nanoparticles inside. Moreover, many single crystals are thermally, mechanically, and chemically stable.

Very recently, rare-earth-doped Na$_5$Lu$_9$F$_{32}$ single crystals as promising laser and up-conversion materials have received enormous research attention. The excellent properties, such as broad range transparency and low minimum phonon energy, make Na$_5$Lu$_9$F$_{32}$ crystal a potential solid-state luminescent material for wide band tunable laser applications. Moreover, the comparable ion radius between Co$^{2+}$ (74 pm) and Lu$^{3+}$ (85 pm) opens the possibility of the substitution of Lu$^{3+}$ ions by the Co$^{2+}$ ion.

In this work, we report the growth of a Co-ion-doped Na$_5$Lu$_9$F$_{32}$ single crystal by the Bridgman method. Our result suggests that the Co ion in the single crystal is in a divalent state. The spectroscopic properties of the grown crystal were investigated by absorption and emission spectra measurements. We also discussed the possible crystal sites for Co$^{2+}$ ions from the structure of the Na$_5$Lu$_9$F$_{32}$ single crystal and measured spectra.

A single crystal of Co-doped Na$_5$Lu$_9$F$_{32}$ (99.99% purity) was grown by an improved Bridgman technique. The crystal was grown from 99.99% pure raw materials of NaF, LuF$_3$, and CoF$_2$. The molar composition of the mixed ingredients was NaF:$\text{LuF}_3$:$\text{CoF}_2 = 40:59.9:0.1$. The mixture of the weighted raw materials was thoroughly ground in a mortar for about 0.5 h. Following that, the mixture was heated by the ventilation of anhydrous HF at 750–800°C for 8–10 h to completely remove the residual moisture. A seed of pure Na$_5$Lu$_9$F$_{32}$ single crystal with...
the <001> direction was placed at the bottom of the homemade platinum (Pt) crucible with a cylinder shape before loading the prepared mixture into the crucible. The crucible was sealed completely to avoid contamination from water and oxygen in the air and to prevent the volatilization of the melt during crystal growth. The detailed growing process by the Bridgman approach has been reported.[13]

The crystal was obtained by removing the Pt crucibles, and the obtained crystal was transparent with a purple color. The crystal grown by the Bridgman approach was about 100 mm in length and 10 mm in diameter, as shown in Fig. 1(a). The opaque part a few centimeters long at the top of the crystal could be the excess NaF in the starting material. The crystal was cut into slices with a thickness of 2 mm along the growth direction for optical characterizations and polished.

The X-ray diffraction (XRD) measurements to identify the phase composition of the crystal were recorded by a Bruker D8 Advance (Germany). The XRD data were collected within 2θ range of 10°–90° at a scan speed of 2°/min. The absorption spectra measurements for the samples were measured 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). All of the measurements were performed at room temperature and in atmospheric conditions.

Figure 1(b) shows the XRD pattern of the as-grown single crystal, and Fig. 1(c) shows a standard card of Na₅Lu₉F₃₂. It is obvious that the diffraction peaks of the as-grown crystal match perfectly with those of the standard Na₅Lu₉F₃₂ (JCPDS card No. 27-0725), and no diffraction peaks due to other crystalline phases were detected, indicating that they have the same crystal structure. It implies that the introduction of a small amount of Co ions did not transform the phase structure of the matrix crystals. The lattice parameters of the as-grown cubic Na₅Lu₉F₃₂ crystals could be calculated according to the XRD pattern data as follows: a = b = c = 0.5463 nm.

Figure 2(a) displays the absorption spectra of the Co-ion-doped and undoped Na₅Lu₉F₃₂ crystals in the wavelength range from 300 to 1800 nm, measured at room temperature. Figure 2(b) is an enlarged absorption spectrum of Co-doped Na₅Lu₉F₃₂ crystal in the range of 400 to 800 nm. Three absorption peaks at 504, 544, and 688 nm in the VIS range and a broad absorption band centered at 1472 nm from the wavelength of 1200 to 1600 nm can be observed in Fig. 2(a). Meanwhile, no characteristic absorption peaks of Co ions were observed for the undoped crystal sample. The transmittance of the undoped polished slice with 2 mm thickness in the VIS range was about 89%.

It was also found that the absorption intensities increase gradually from the lower part of the crystal, corresponding to the initial growing stage to the upper part of the final growing stage. Considering that the thickness of the sample is identical, the increase of absorption indicates more Co ions were doped into the crystal on the initial growth stage. The observation of color in Fig. 1(a) is consistent with this assumption, where the single crystal becomes purpler in the lower part. Hence, the effective segregation coefficient of Co ions in Na₅Lu₉F₃₂ is smaller than 1.

The Co ion has two stable valence states of Co²⁺ and Co³⁺ in different hosts. Co²⁺ and Co³⁺ are both possible when Co ions are doped into the Na₅Lu₉F₃₂ crystal.
The valence of the Co ion is dependent on the coordination environment it locates. The investigation of the absorption features for the Co\(^{2+}\) and Co\(^{3+}\) ions indicates Co ions in the trivalent state show two distinct absorption peaks centered at 714 and 435 nm, respectively.

No observation of such peaks can be found in the absorption spectra in this work (Fig. 2). Hence, one may ascribe the measured absorption peaks to Co\(^{2+}\) ions. Additionally, the entire process of crystal growth was accomplished in a closed environment, which is helpful for Co ions to form Co\(^{2+}\). Moreover, the 504, 544, 688, and 1472 nm bands in Fig. 2 can be attributed to \(^4\)A\(_2\)(F) → \(^2\)T\(_2\)(H\(_1\)), \(^4\)A\(_2\)(F) → \(^4\)T\(_1\)(P), \(^4\)A\(_2\)(F) → \(^2\)E(G), and \(^4\)A\(_2\)(F) → \(^4\)T\(_1\)(F) transitions, respectively, which are very similar to the absorption characteristics of Co\(^{2+}\) in other hosts. This experimental result suggests the Co ion in the Na\(_5\)Lu\(_9\)F\(_{32}\) crystal is in a divalent state.

Co cations can substitute Na\(^+\) and Lu\(^{3+}\) crystal sites when doped into the Na\(_5\)Lu\(_9\)F\(_{32}\) crystal. To clearly illustrate the crystal site of the Co ion, the schematic of the cell structure of cubic Na\(_5\)Lu\(_9\)F\(_{32}\) single crystal is displayed in Fig. 3, inferred from Ref. [19]. The Na\(_5\)Lu\(_9\)F\(_{32}\) compound in the microscopic condition has a cubic cell with the unit cell parameter \(a = b = c = 0.5463\) nm (space group Fm\(_3\)m).

Figure 3 suggests Na\(_5\)Lu\(_9\)F\(_{32}\) and CaF\(_2\) have a similar structure. The blue balls located at the centers of eight small cubes represent F\(^-\) ions, while the green and red balls located at the surface and vertex of the crystal cell are Na\(^+\) and Lu\(^{3+}\) ions, respectively. The probability of Na\(^+\) and Lu\(^{3+}\) ions occupying the surface of the crystal cell is 1/4 and 2/3, respectively, while the possibility for a vertex is 1/2 and 1/4, respectively. The coordination number for both Na\(^+\) and Lu\(^{3+}\) is eight surrounded by F\(^-\) ions. Lu\(^{3+}\) ions located at the surface and vertex can have different crystal fields regardless if it possesses the same coordination number. Substitution is more likely to occur if the cation has a similar radius and valence to Co ions. The radii for Lu\(^{3+}\), Na\(^+\), Co\(^{2+}\), Co\(^{3+}\), and F\(^-\) are 97.7, 118, 90, 54.5, and 131 pm, respectively. It is evident that the size of Co\(^{2+}\) is the nearest to that of Lu\(^{3+}\), suggesting that the possible crystal site for substitution is a Lu\(^{3+}\) ion. The coordination number of the cation in the ionic crystal structure is determined by the ratio of the radius between the positive ion and negative ion. The ratio in the range of 0.732–1.000 is suitable to form a stable cubic crystal structure. The ionic ratio between Co\(^{3+}\) and F\(^-\) is 0.687 in the Na\(_5\)Lu\(_9\)F\(_{32}\) single crystal, which slightly deviates from the recommended range. When the Co ion replaces the Lu sites, the mismatch in charge and ion radius can lead to a distorted cubic shape, resulting in miraculous transformations in the absorption spectra. It may also explain the obtained crystal in a purple color instead of the commonly observed pink.

The crystal field theory mainly discusses the energy level splitting of the d orbit of the transition elements under the influence of the electric field arising from the ligand charge and the effect on the crystal structure and properties. Numerous research efforts have been devoted to investigating the lattice parameters of Co\(^{2+}\)-doped octahedral and tetrahedral crystals centered at an oxygen ion. However, studies focused on the lattice parameters of the Co\(^{3+}\) ion in the coordination center of F\(^-\) ions are limited. Moreover, there is even less research on the parameters of the lattice field in the cubic structure, in which Co\(^{3+}\) is doped into the coordination center with eight F\(^-\) ions.

The parameter of the octahedral crystal field \(D_q\) and the Racah parameter \(B\) for a Co\(^{3+}\)-doped Na\(_5\)Lu\(_9\)F\(_{32}\) crystal can be calculated by the following equations:

\[
D_1 = 10D_q, \quad (1)
\]

\[
D_3 = 9B + 3C + 10D_q, \quad (2)
\]

where \(D_1\) and \(D_3\) are the energy difference of the first and third excited states compared to the ground state, respectively. It can be confirmed from Fig. 2 that the absorption peak at 688 nm is attributed to the \(^4\)A\(_2\)(F) → \(^2\)E(G) transition. Hence, \(D_3\) can be determined to be 14534.9 cm\(^{-1}\)(688 nm). The Fourier transform infrared (FTIR) spectrum from 400 to 4000 cm\(^{-1}\) was measured to determine the \(D_1\) value. A weak absorption band at 3906 cm\(^{-1}\)(2560 nm) was observed due to the \(^4\)A\(_2\)(F) → \(^4\)T\(_3\)(F) transition. Therefore, the \(D_1\) value was estimated to be 3906 cm\(^{-1}\). The \(C/B\) ratio is the same for the Co\(^{3+}\) in CaF\(_2\) lattices as for the free ion \((C/B = 4.48)\). By solving Eqs. (1) and (2), the crystal field and Racah parameters were obtained: \(D_q = 309.6\) cm\(^{-1}\), and \(B = 473.7\) cm\(^{-1}\). The ratio between \(D_q\) and \(B\) is equal to 309.6/473.7 = 0.825 < 1, which indicates the Co\(^{3+}\)-doped Na\(_5\)Lu\(_9\)F\(_{32}\) crystal belongs to the weak field site crystal. The similarity of the lattice field intensity for the Co\(^{3+}\)-doped Na\(_5\)Lu\(_9\)F\(_{32}\) and CaF\(_2\) is another indication of comparable structure for these crystals. Parameters of \(D_q, B\), and \(D_q/B\) of some other Co\(^{3+}\)-doped crystals are listed in Table 1.

Figure 4 illustrates the excitation spectra of Co-doped Na\(_5\)Lu\(_9\)F\(_{32}\) monitored at the wavelength of 750 nm. An excitation peak centered at 507 nm implies that the
sample can be excited most efficiently by the excitation light at the 507 nm wavelength.

Figure 5 shows the photoluminescence intensity of the crystal excited at 500 nm. An emission peak due to the $^2T_2(H_1) \rightarrow ^4A_2(F)$ transition in the range of 728 to 770 nm is observed. The direct exposure of the 5d orbital to the crystal field makes Co ions sensitive to the surrounding environment. Strong coupling between photons and electrons is expected under excitation, which can lead to the broadening of emission and absorption spectra[25].

A Co-ion-doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal was prepared by the Bridgman method under suitable growth conditions. The Co ions in the divalent state are confirmed to locate in the distorted cubic crystal structure surrounded by eight F$^-$ ions. The estimation of the lattice field parameter and Racah parameter validates that the $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal belongs to the weak field site crystal. The excellent spectroscopic properties suggest that the grown crystal may be a potential passive Q-switch material in the NIR range.

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