

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

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Received March 2, 2018; accepted April 3, 2018; posted online May 25, 2018

A 0.1 mol.% CoF_2 -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal with high quality in the size of $\sim\phi 10\text{ mm}\times 100\text{ mm}$ 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 centered at 1472 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 ${}^2\text{T}_2(\text{H}_1)\rightarrow{}^4\text{A}_2(\text{F})$ transition was observed for the crystal. The Co^{2+} -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal shows a potentially promising material for the application of a passively Q -switched laser operating in the near-infrared range.

OCIS codes: 160.4670, 140.3380, 160.4760.

doi: 10.3788/COL201816.061601.

Rare earth ions and transition metal ions are known as two mainly luminous centers^[1,2]. 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^[3,4]. 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^[5]. 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^[6,7]. Materials doped with Co^{2+} ions are used for tunable laser applications^[8] 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 ($\text{Co}^{2+}:\text{YAG}$), Co^{2+} -doped yttrium scandium gallium garnet ($\text{Co}^{2+}:\text{YSGG}$), and transparent glass-ceramics^[9,10].

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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystals as promising laser and up-conversion materials have received enormous research attention^[11,12]. The excellent properties, such as broad range transparency and low minimum phonon energy, make $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal a potential solid-state luminous 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal and measured spectra.

A single crystal of Co-doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ (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 $\text{NaF}:\text{LuF}_3:\text{CoF}_2 = 40:59.9:0.1$. 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal with

the $\langle 001 \rangle$ 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 $2^\circ/\text{min}$. 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$. It is obvious that the diffraction peaks of the as-grown crystal match perfectly with those of the standard $\text{Na}_5\text{Lu}_9\text{F}_{32}$ (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

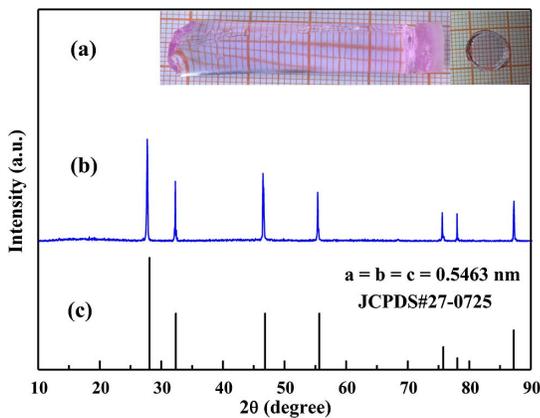


Fig. 1. (a) Photograph of Co^{2+} -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal. Left: the boule of the crystal; right: polished slice. (b) XRD pattern of the $\text{Co}^{2+}:\text{Na}_5\text{Lu}_9\text{F}_{32}$. (c) Standard line pattern of the $\text{Na}_5\text{Lu}_9\text{F}_{32}$ (No. 27-0725).

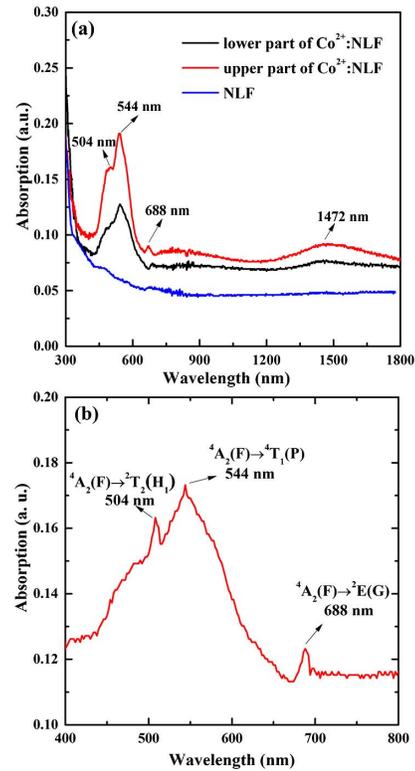


Fig. 2. (a) Absorption spectra of Co doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystals. (b) Enlarged absorption spectra from 400 to 800 nm.

$\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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 growing 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 $\text{Na}_5\text{Lu}_9\text{F}_{32}$ is smaller than 1.

The Co ion has two stable valence states of Co^{2+} and Co^{3+} in different hosts. Co^{2+} and Co^{3+} are both possible when Co ions are doped into the $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal.

The valence of the Co ion is dependent on the coordination environment it locates^[14]. 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^[15,16].

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+} ^[17]. Moreover, the 504, 544, 688, and 1472 nm bands in Fig. 2 can be attributed to ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{T}_2(\text{H}_1)$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{E}(\text{G})$, and ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$ transitions, respectively, which are very similar to the absorption characteristics of Co^{2+} in other hosts^[18]. This experimental result suggests the Co ion in the $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal is in a divalent state.

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

Figure 3 suggests $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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

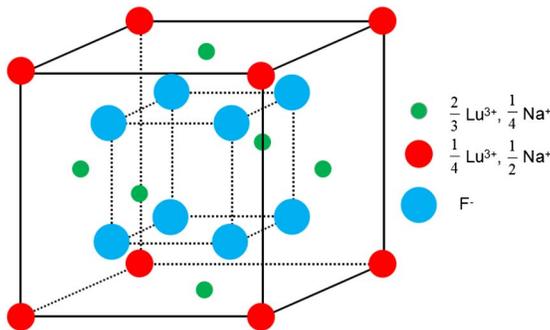


Fig. 3. Schematic cell structure of cubic $\text{Na}_5\text{Lu}_9\text{F}_{32}$ single crystal.

ionic crystal structure is determined by the ratio of the radius between the positive ion and negative ion^[20]. The ratio in the range of 0.732–1.000 is suitable to form a stable cubic crystal structure. The ionic ratio between Co^{2+} and F^- is 0.687 in the $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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^[21–23]. However, studies focused on the lattice parameters of the Co^{2+} 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^{2+} 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^{2+} -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal can be calculated by the following equations^[24]:

$$D_1 = 10D_q, \quad (1)$$

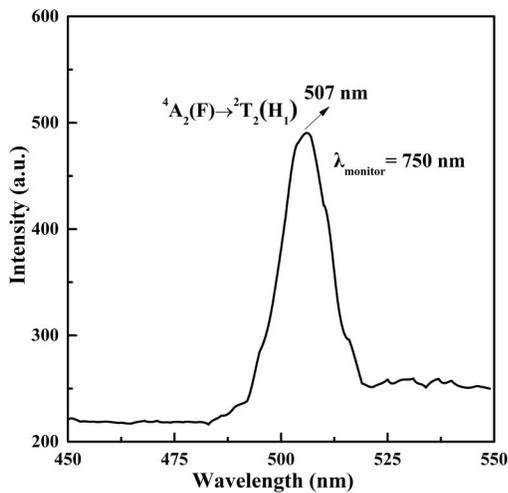
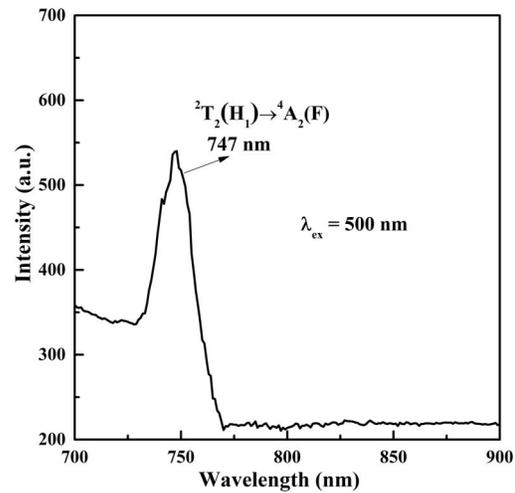
$$D_3 = 9B + 3C + 10D_q, \quad (2)$$

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 ${}^4\text{A}_2(\text{F}) \rightarrow {}^2\text{E}(\text{G})$ 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 ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_2(\text{F})$ transition. Therefore, the D_1 value was estimated to be 3906 cm^{-1} . The C/B ratio is the same for the Co^{2+} 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: $D_q = 309.6 \text{ cm}^{-1}$, and $B = 473.7 \text{ cm}^{-1}$. The ratio between D_q and B is equal to $309.6/473.7 = 0.825 < 1$, which indicates the Co^{2+} -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal belongs to the weak field site crystal. The similarity of the lattice field intensity for the Co^{2+} -doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ 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^{2+} -doped crystals are listed in Table 1.

Figure 4 illustrates the excitation spectra of Co-doped $\text{Na}_5\text{Lu}_9\text{F}_{32}$ monitored at the wavelength of 750 nm. An excitation peak centered at 507 nm implies that the

Table 1. D_q , B , D_q/B Parameters of Co^{2+} -doped Crystals

Crystals	Coordination Number	D_q (cm^{-1})	B (cm^{-1})	D_q/B	References
MgAl_2O_4	4	499	470	0.548	[16]
ZnO	4	390	700	0.557	[21]
KMgF_3	6	740	920	0.80	[22]
MgF_2	6	730	920	0.79	[22]
MgO	6	880	780	1.13	[22]
$\text{Mg}_3\text{B}_2\text{O}_6$	6	943.3	821.6	1.15	[23]
CdF_2	8	412	452	0.912	[24]
CaF_2	8	388	463.9	0.836	[24]
$\text{Na}_5\text{Lu}_9\text{F}_{32}$	8	390.6	473.7	0.825	This work

Fig. 4. Excitation spectra of $\text{Co}^{2+}:\text{Na}_5\text{Lu}_9\text{F}_{32}$ measured at 750 nm.Fig. 5. Emission spectra of $\text{Co}^{2+}:\text{Na}_5\text{Lu}_9\text{F}_{32}$ crystal excited by 500 nm light.

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 ${}^2\text{T}_2(\text{H}_1) \rightarrow {}^4\text{A}_2(\text{F})$ 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.

This work was supported by the National Natural Science Foundation of China (Nos. 51772159, 51472125, 11504188, and U1504626), the Natural Science Foundation of Zhejiang Province (No. LZ17E020001), and K. C. Wong Magna Fund in Ningbo University.

References

1. B. Yao, H. Li, S. Bai, Z. Cui, X. Li, X. Duan, Y. Shen, and T. Dai, *Chin. Opt. Lett.* **14**, 061401 (2016).
2. S. Y. Wu, G. D. Lu, Z. H. Zhang, L. H. Wei, and Y. X. Hu, *J. Alloys Compd.* **472**, 1 (2009).
3. W. Zou, J. L. Zhang, F. Chen, M. Anpo, and D. N. He, *Res. Chem. Intermed.* **35**, 717 (2009).
4. Z. Jia, Y. Yin, H. Yang, B. Zhang, J. He, M. Tonelli, and X. Tao, *Chin. Opt. Lett.* **14**, 021405 (2016).
5. J. Ferguson, H. J. Guggenheim, H. Kamimura, and Y. Tanabe, *J. Chem. Phys.* **42**, 775 (1965).
6. K. V. Yumashev, I. A. Denisov, N. N. Posnov, V. P. Mikhailov, R. Moncorgé, D. Vivien, B. Ferrand, and Y. Guyot, *J. Opt. Soc. Am. B.* **16**, 2189 (1999).
7. V. I. Burkov, L. N. Alyabyeva, Y. V. Denisov, and B. V. Mill', *Inorg. Mater.* **50**, 1119 (2014).

8. F. Yang, H. Wang, Y. Wei, and X. Lu, *J. Appl. Phys.* **83**, 163 (2006).
9. M. B. Camargo, R. D. Stultz, M. Birnbaum, and M. Kokta, *Opt. Lett.* **20**, 339 (1995).
10. M. B. Camargo, R. D. Stultz, M. Birnbaum, and M. Kokta, *Org. React. Mech.* **2**, 433 (1994).
11. Z. Feng, H. Xia, C. Wang, Z. Zhang, D. Jiang, J. Zhang, S. He, Q. Tang, Q. Sheng, and X. Gu, *Chem. Phys. Lett.* **652**, 68 (2016).
12. S. He, H. Xia, Q. Tang, Q. Sheng, J. Zhang, Y. Zhu, and B. Chen, *Cryst. Res. Technol.* **17**, 3136 (2018).
13. T. A. Campbell and J. N. Koster, *J. Cryst. Growth.* **147**, 408 (1995).
14. K. R. Kittilstved, D. A. Schwartz, A. C. Tuan, S. M. Heald, S. A. Chambers, and D. R. Gamelin, *Phys. Rev. Lett.* **97**, 037203 (2006).
15. J. F. Donegan, F. G. Anderson, F. J. Bergin, T. J. Glynn, and G. F. Imbusch, *Phys. Rev. B* **45**, 563 (1992).
16. D. L. Wood and J. P. Remeika, *J. Chem. Phys.* **46**, 3595 (1967).
17. D. A. Schwartz, N. S. Norberg, Q. P. Nguyen, J. M. P. And, and D. R. Gamelin, *JACS* **125**, 13205 (2003).
18. H. A. Weakliem, *J. Chem. Phys.* **36**, 2117 (1962).
19. P. J. Alonso and R. Alcalá, *Phys. Status Solidi* **81**, 333 (1977).
20. R. Hoppe, *Z. Kristallogr.* **150**, 23 (1979).
21. N. V. Kuleshov, V. P. Mikhailov, V. G. Scherbitsky, P. V. Prokoshin, and K. V. Yumashev, *J. Lumin.* **55**, 265 (1993).
22. H. Manaa, Y. Guyot, and R. Moncorge, *Phys. Rev. B* **48**, 3633 (1993).
23. H. G. Kim and W. T. Kim, *Phys. Rev. B* **41**, 8541 (1990).
24. Z. Li, *J. Appl. Polym. Sci.* **79**, 12 (1998).
25. C. A. Coulson and G. N. Robertson, *Proc. Roy. Soc. A* **337**, 167 (1974).