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Spectral analysis of single-crystal $\text{LiKGdF}_5:\text{Er}^{3+}$, Tb^{3+}

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Abstract

Single-crystal $\text{LiKGdF}_5:\text{Er}^{3+}$, Tb^{3+} was synthesized by using hydrothermal techniques. After measuring luminescence and excitation spectra, we observed the up-converted green ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) emissions, as well as the weak blue emissions from Er^{3+} ions in the crystal. Analysis indicates that the blue up-conversion occurs via a sequential absorption of three photons. By assuming the ion is in a C_{2v} instead of the actual C_2 site, a crystal-field (cf) calculation has been performed on the reduced $^7\text{F}_J$ basis of the ground ^7F term of the Tb^{3+} ion. Excellent correlation was obtained between the experimental transition energies and the computed level structures. The cf parameter obtained is very well transferable to the Er^{3+} energy levels in LiKGdF_5 .

1. Introduction

Anisotropic fluoride crystals are favourable hosts for the doping of some rare earth (RE) ions. Such doped fluoride crystals often exhibit interesting optical properties. Nevertheless, spectroscopic reports on RE doped LiKGdF_5 are scarce. Some comparison studies of the crystal structure and optical properties between the two crystals LiKYF_5 and LiKGdF_5 [1–3] doped with lanthanide ions are conducted. The results show that the crystal structure is unchanged (except for lattice constants) and suggest that the fluoride LiKGdF_5 is characterized as a single-site crystal, with RE^{3+} ions at the Gd^{3+} site in C_2 symmetry. Due to the growing interest in vacuum ultraviolet (VUV: $E > 50\,000\text{ cm}^{-1}$, $\lambda < 200\text{ nm}$) spectroscopy, Makhov *et al* [4]

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reported the luminescence properties of LiKGdF₅: Er³⁺, Tm³⁺ crystals and showed that they are promising materials for VUV-excited phosphors; Wegh [5] studied the visible quantum cutting via down-conversion in LiGdF₄: Er³⁺, Tb³⁺ upon Er³⁺4f¹¹ → 4f¹⁰5d excitation. However, in the case of LiKGdF₅: Er³⁺, Tb³⁺, to the best of our knowledge, no report of any spectroscopic results can be found.

In the present work, spectroscopic studies of LiKGdF₅: Er³⁺, Tb³⁺ are presented. A detailed energy level scheme of the ground ⁷F term of the Tb³⁺ ion has been obtained through measurements of low temperature emission and excitation spectra. With infrared laser excitation, the up-conversion spectra of Er³⁺ ions in the crystal were obtained. Our results demonstrate that the up-converted green ²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2} and red ⁴F_{9/2} → ⁴I_{15/2} emissions essentially originate from excited state absorption (ESA) and up-converted blue emissions ²P_{3/2} → ⁴I_{11/2} and ²P_{3/2} → ⁴I_{13/2} from a sequential absorption of three photons. Semiempirical calculations are performed on the Tb³⁺ ion in LiKGdF₅ and the crystal-field (cf) parameters obtained are used to reproduce the ground energy levels of Er³⁺ as a test of their validity.

2. Experiment

The LiKGdF₅ single crystal co-doped with Er³⁺ (2%) and Tb³⁺ (0.4%) was prepared by using hydrothermal techniques. The synthesis process was similar to that given in [6]. The sample was placed in a circulating liquid helium optical cryostat (OXFORD International) with a temperature-regulated gas system, allowing the temperature to be varied between 10 and 300 K. The excitation spectra were recorded using radiation from a coumarin 480 dye laser pumped by the third harmonics of YAG:Nd³⁺ (λ = 1.06 μm, pulse duration 10 ns with a repetition rate of 30 Hz) and the emission spectra were probed using a Jobin-Yvon HR-1000 monochromator equipped with a Hamamatsu R374 photomultiplier. The output was analysed by a Stanford SR-510 lock-in amplifier and stored in the computer memory. The up-conversion spectra of Er³⁺ ions were measured and analysed by using a Jobin-Yvon LABRAM-HR confocal laser Raman spectrometer system with a 785 nm semiconductor laser.

3. Spectroscopic studies

3.1. Emission and site-selective excitation spectra of LiKGdF₅: Er³⁺, Tb³⁺

The Tb³⁺ and Er³⁺ ions possess 4f⁸ and 4f¹¹ ground configurations, respectively. For the C₂ site symmetry of RE ions in a LiKGdF₅ matrix, ^{2S+1}L_J levels of the Tb³⁺ ion are split into 2J + 1 cf levels due to the cf effect and no electric dipole transitions are forbidden between two cf levels. Also for Er³⁺ ions (Kramers' ions) in LiKGdF₅, the degenerate free ion ^{2S+1}L_J state is split into J + 1/2 Stark levels for any symmetry lower than cubic and all the electric dipole transitions between two cf levels are also allowed [7].

A typical emission spectrum of LiKGdF₅: Er³⁺, Tb³⁺ under 355 nm excitation at 12 K is shown in figure 1(a), where only emissions from the Er³⁺ ions were observed because the Tb³⁺ ions cannot be excited at this wavelength. Our findings are that the stronger emission lines around 550 nm stem from the transition of ⁴S_{3/2} → ⁴I_{15/2}, while the weaker ones around 650 nm are from the ⁴F_{9/2} → ⁴I_{15/2}. Due to the low temperature and the large energy span between the two Stark levels of ⁴S_{3/2} [8], only the lower Stark level of ⁴S_{3/2} emits photons at 12 K. According to the selection rules, the transition ⁴S_{3/2} → ⁴I_{15/2} should appear as eight peaks, as shown in figure 1(a). Thus, the Stark levels of ⁴I_{15/2} can be deduced.

Figure 1(b) presents the emission spectrum of Tb³⁺ ions in LiKGdF₅: Er³⁺, Tb³⁺ at 12 K. The observed emissions correspond to transitions from the excitation state ⁵D₄ to the ground

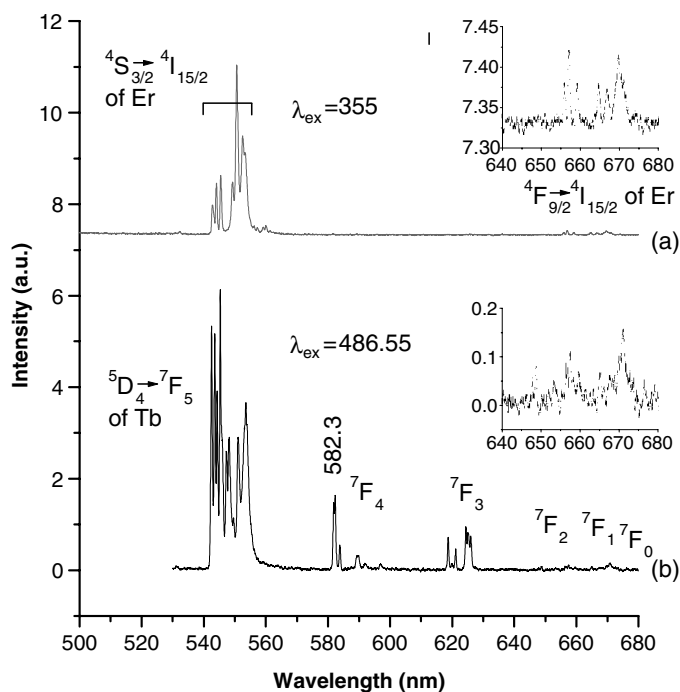


Figure 1. Emission spectra of LiKGdF₅:Er³⁺ (2%), Tb³⁺ (0.4%) at 12 K. (a) $\lambda_{\text{ex}} = 355$ nm; (b) excitation of the ⁵D₄ level of Tb³⁺ with $\lambda_{\text{ex}} = 486.55$ nm.

(This figure is in colour only in the electronic version)

term ⁷F_{*J*} (*J* = 0–5) with ⁵D₄ → ⁷F₅ transitions dominant. It can be seen that the transitions ⁵D₄ → ⁷F₅ of Tb³⁺ and ⁴S_{3/2} → ⁴I_{15/2} of Er³⁺ occur just in the same spectral frequency range. The overlap of the two spectra increases the difficulty of measuring the excitation spectrum of Tb³⁺ ions. To avoid the interference from the emission from Er³⁺ ions, we use the 582.3 nm spectral line (⁵D₄ → ⁷F₄) as the monitoring wavelength. Figure 2 shows the excitation spectrum of Tb³⁺ ions in the range of the ⁷F₆ → ⁵D₄ transition at 12 K. There are nine peaks observed in the figure, which is in full accord with the selection rules of C₂ symmetry. Similarly, in order to separate the emissions of Tb³⁺ ions, the second strongest excitation peak, 486.55 nm, instead of the strongest one that has some overlap with the ⁴I_{15/2} → ⁴F_{7/2} transition of Er³⁺ ions, was chosen to resonantly excite the Tb³⁺ ions. In fact, figure 1(b) is obtained using this consideration. Therefore, transitions of ⁵D₄ → ⁷F_{*J*} (*J* = 0–5) can be clearly assigned. Accordingly, with the aid of the energy value for the lowest Stark level of ⁵D₄ found from the excitation spectrum in figure 2, almost all sublevel energies of ⁷F_{*J*} (*J* = 0–5) can be deduced, as summarized in table 1.

3.2. Up-conversion upon excitation into the ⁴I_{9/2} manifold of Er³⁺

Figure 3 shows the up-conversion spectra of LiKGdF₅: Er³⁺, Tb³⁺ under 785 nm excitation at room temperature. The observed emissions only originate in the transitions of Er³⁺ ions because the laser used here cannot excite Tb³⁺ ions. Intense green and red emission bands located around 522, 542 and 665 nm wavelength are attributed to ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively. It is worth noticing that almost no spectral lines around 522 nm could be observed in figure 1(a). This behaviour is related to the Boltzmann

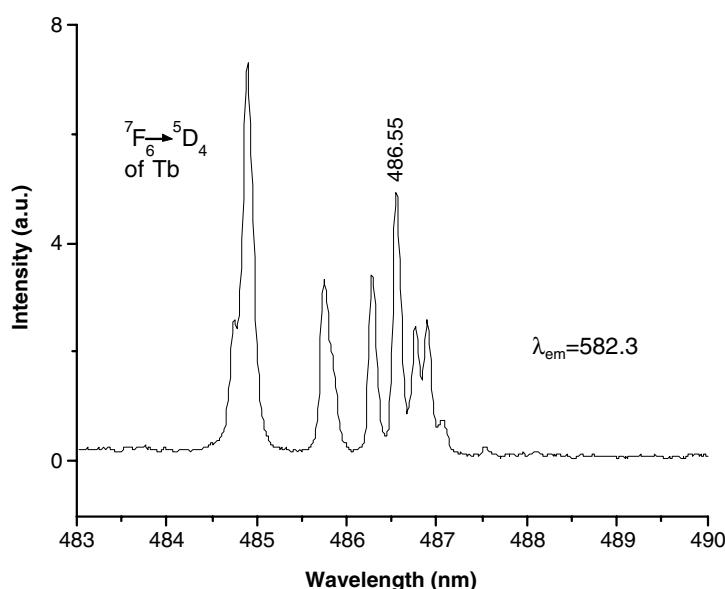


Figure 2. Excitation spectrum of LiKGdF₅: Er³⁺ (2%), Tb³⁺ (0.4%) at 12 K for 582.3 nm emission (⁵D₄ → ⁷F₄) of Tb³⁺ in ⁷F₆ → ⁵D₄ transition region.

distribution of ions in ²H_{11/2} and ⁴S_{3/2} levels, which are separated by an energy gap of about 710 cm⁻¹. At low temperature, only the lower-lying ⁴S_{3/2} level is occupied, as shown in figure 1(a), while at room temperature thermalization leads to some population of the ²H_{11/2} level and emission from there, as reported for the Er³⁺ ion in various hosts [9–12].

The intensity of the up-converted luminescence I_0 is proportional to the n th power of the pump intensity I_i ($I_0 \propto I_i^n$) [13] where n is the order of the up-conversion process, i.e. the number of pump photons required to populate the emitting state. The intensity of the up-converted green and red emission has been measured as a function of the pump power. From a fit of the curve $\ln(I_i)$ versus $\ln(I_0)$ we have obtained a slope of 1.6, which indicates a two-photon up-conversion process.

Very interestingly, we have also observed the up-converted emission bands in the blue region (400–500 nm) under the same 785 nm excitation as shown in figure 3(a). Weak bands centred at 411, 470 and 490 nm could be assigned to the ²P_{3/2} → ⁴I_{13/2}, ²P_{3/2} → ⁴I_{11/2} and ⁴F_{7/2} → ⁴I_{15/2} transitions, respectively. The intensity dependence of the ²P_{3/2} emission leads to a slope of 2.6, which strongly suggests the occurrence of a three-photon up-conversion process.

The possible mechanism resulting in green and red up-conversion spectra has been proposed in several papers [14–17]. It was suggested that the dominant mechanism is ESA under near-infrared laser excitation in a sample with low (2%) Er³⁺ concentration. Similar to what has been proposed in [14], the observed green and red up-conversion phenomena in LiKGdF₅ may happen via the following ESA process: with 785 nm pumping, Er³⁺ ion is excited initially from ⁴I_{15/2} to the ⁴I_{9/2} state, and then reaches the lower ⁴I_{11/2} level, undergoing non-radiative relaxation. Then the same ion absorbs the second photon and is promoted to the ⁴F_{3/2} level. Finally, the Er³⁺ ion decays to the emitting levels (²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2}) by multiphonon relaxation and gives rise to emission there. In addition, a possible energy transfer up-conversion process cannot be rejected. Other different competitive mechanisms occurring

Table 1. Experimental and calculated level energies for Tb³⁺ in LiKGdF₅.

^{2S+1} L _J level	<i>E</i> (exp) (cm ⁻¹)	<i>E</i> (calc) (cm ⁻¹)	^{2S+1} L _J level	<i>E</i> (exp) (cm ⁻¹)	<i>E</i> (calc) (cm ⁻¹)
⁷ F ₆	0	-16	⁷ F ₃	4350	4363
	—	—		4379	4393
				4413	4425
⁷ F ₅	2081	2103		4498	4481
	2115	2121		4517	4490
	2141	2130		—	4568
	2174	2146		4538	4569
	2195	2198	⁷ F ₂	—	4965
	—	2275		5172	5184
	2271	2284		5210	5229
	2367	2357		5303	5286
	—	2375		—	5383
		2442			
		2452			
⁷ F ₄	3326	3316	⁷ F ₁	5606	5615
	3340	3341		5665	5650
	3384	3376		5723	5726
	3418	3408	⁷ F ₀	5865	5876
	3491	3500			
	3560	3578			
	3618	3621			
	—	3678			
	3760	3751			

simultaneously could be invoked to generate the up-converted green and red luminescence (for more details refer to [18, 19]).

As stated before, the power dependence of up-converted ${}^2P_{3/2} \rightarrow {}^4I_{13/2}$ and ${}^2P_{3/2} \rightarrow {}^4I_{11/2}$ transitions indicates that a three-photon process is involved, which is seldom reported in the fluoride matrix. The mechanism may occur via a sequential absorption of photons (figure 4), as reported in other system [14, 19]. First, the 785 nm light excites the Er³⁺ ion to the ${}^4I_{9/2}$ multiplet. The Er³⁺ ion then immediately relaxes to the ${}^4I_{11/2}$ level by a non-radiative process. A second and third photon excites the Er³⁺ ion to the ${}^4G_{7/2}$ level. Again, non-radiative decay results in population of the ${}^2P_{3/2}$ level and gives emissions of ${}^2P_{3/2} \rightarrow {}^4I_{13/2}$ and ${}^2P_{3/2} \rightarrow {}^4I_{11/2}$.

4. Simulation of the energy level scheme and discussions

The total Hamiltonian H describing the interactions within the $4f^N$ electron configuration is composed of two parts: one accounting for the free ion energy level structure (H_f) and the other (H_{cf}) for the energy level splitting caused by the cf [20]. Usually, to fit the energy levels of a given RE ion embedded in a crystalline medium we treat the two-part interactions simultaneously. The basic theoretical feature of the procedure is given by Judd [21] and Wybourne [20]. In this work, we consider mainly the cf contribution that is expressed as a sum of tensorial operators:

$$H_{cf} = \sum_{k,q,i} B_q^k C_q^k(i), \quad (1)$$

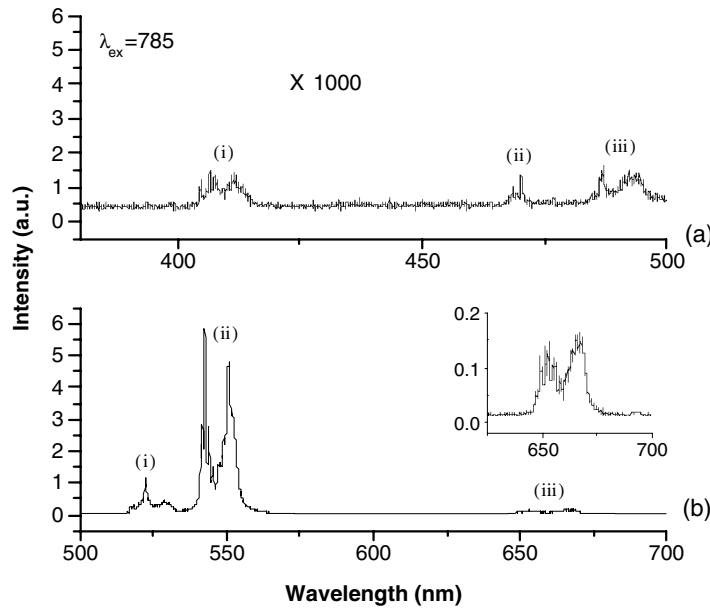


Figure 3. Room temperature up-conversion spectra of LiKGdF₅: Er³⁺ (2%), Tb³⁺ (0.4%) upon excitation at 785 nm. (a) This shows (i) $^2P_{3/2} \rightarrow ^4I_{13/2}$, (ii) $^2P_{3/2} \rightarrow ^4I_{11/2}$, (iii) $^4F_{7/2} \rightarrow ^4I_{15/2}$. (b) This shows (i) $^2H_{11/2} \rightarrow ^4I_{15/2}$, (ii) $^4S_{3/2} \rightarrow ^4I_{15/2}$, (iii) $^4F_{9/2} \rightarrow ^4I_{15/2}$.

where B_q^k are the cf parameters and their number depends on the local point symmetry of the RE ion.

The site symmetry of Tb³⁺ in LiKGdF₅ is C₂. However, to simplify the calculation it could be approximated as C_{2v} higher than C₂ [22]. In our approach, for the first time, C_{2v} instead of C₂ symmetry was applied to the cf energy level simulations of RE ions in a LiKGdF₅ matrix. As we know, there are nine cf parameters ($B_0^2, B_2^2, B_0^4, B_2^4, B_4^4, B_0^6, B_2^6, B_4^6$ and B_6^6) associated with the C_{2v} symmetry. The complete 4f⁸ configuration of the Tb³⁺ ion consists of 3003 Stark levels. In order to simplify the computational process, only the 31 experimentally observed Stark levels of the isolated ⁷F ground term were included in the simulation. This is considered reasonable due to the fact that the cf operator acts only within the ⁷F multiplet [23].

The cf parameter values shown in table 2 were obtained by a fitting procedure between the experimental and calculated energy levels. The mean square deviation σ is employed to evaluate the fitting results, as expressed below:

$$\sigma = \left(\frac{\sum (E_{\text{exp}} - E_{\text{calc}})^2}{n - p} \right)^{1/2} \quad (2)$$

where E_{exp} and E_{calc} are, respectively, the experimental and calculated level energies. n is the number of experimental energy levels and p is the number of cf parameters [24]. Experimental and calculated energy level schemes for the Tb³⁺ ion in the C_{2v} symmetry site are given in table 1 and the cf parameters obtained are listed in table 2.

The cf parameter set obtained is then used to calculate the Er³⁺ ion energy level in the LiKGdF₅ matrix as a test of its reliability. We would like to point out that, though only the eight experimental levels of the ground $^4I_{15/2}$ in Er³⁺ ion are used in the fitting procedure, measurement of the cf parameters could be done. It is because the strongly reduced ground manifold $^4I_{15/2}$ is the term most affected by the cf parameters [25]. The free ion parameters

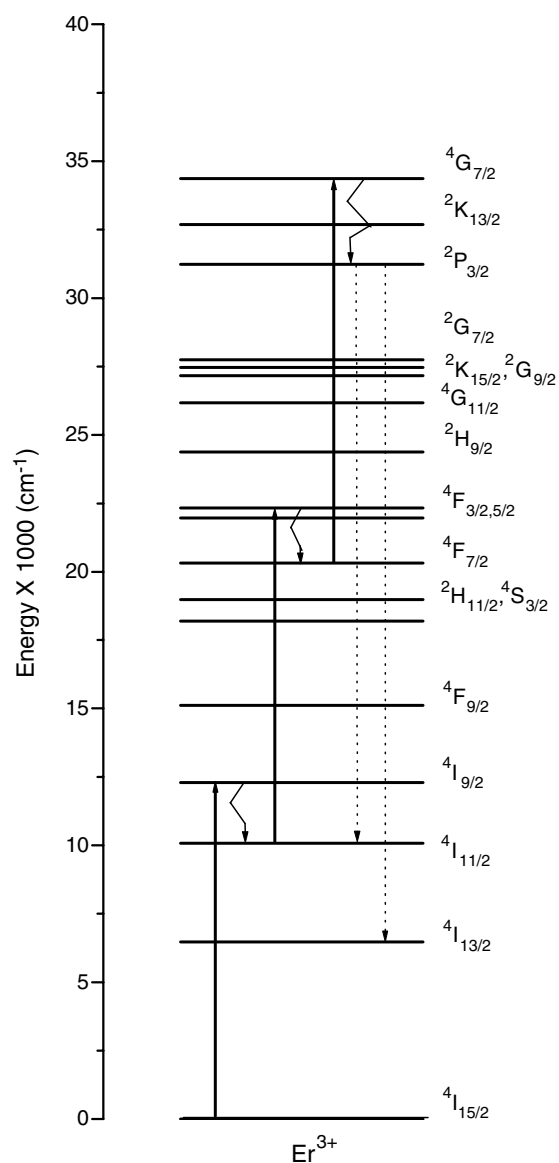


Figure 4. Energy level diagram of Er³⁺ ions in LiKGdF₅ showing the up-conversion process responsible for the blue emission with $\lambda_{\text{ex}} = 785$ nm.

used here are from LiYF₄ data [26]. The fitting result is quite good, giving some consistency to the parameter set (see table 3).

5. Conclusion

The luminescent properties of single-crystal LiKGdF₅: Er³⁺, Tb³⁺ were studied. The detailed assignments of the ground ⁷F term of the Tb³⁺ ion were obtained on the basis of the selective excitation and emission spectra at low temperature. Our experimental observation revealed

Table 2. CF parameters for Tb³⁺ in LiKGdF₅. All values are in units of cm⁻¹, except for *n* which is the number of levels simulated.

Parameter	Value (cm ⁻¹)
B_0^2	-396
B_2^2	188
B_0^4	1924
B_2^4	-599
B_4^4	-126
B_0^6	186
B_2^6	-224
B_4^6	-310
B_6^6	110
<i>n</i>	31
σ	17.5

Table 3. Experimental and calculated level energies for Er³⁺ in LiKGdF₅.

^{2S+1} L _J level	<i>E</i> (exp) (cm ⁻¹)	<i>E</i> (calc) (cm ⁻¹)
⁴ I _{15/2}	0	-20
	16	11
	44	57
	92	104
	217	218
	264	272
	330	347
	349	376

the up-conversion emission of Er³⁺ in the crystal with infrared laser excitation. We proposed that this finding is just associated with the absorption of two and three photons. Moreover, the cf calculation was performed on the Tb³⁺ ions by using C_{2v} instead of the actual C₂ symmetry. We derived the set of cf parameters from our fitting. These parameters are found to be good for handling the ground levels of Er³⁺ ions too.

Acknowledgments

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References

- [1] Summers P L, Weidner H and Peale R E 1994 *J. Appl. Phys.* **75** 2184
- [2] Anderson F G, Weidner H, Summers P L, Peale R E, Zhang X X and Chai B H T 1994 *J. Lumin.* **60/61** 150
- [3] Nicholls J F H, Zhang X X, Bass M, Chai B H T and Henderson B 1997 *Opt. Commun.* **137** 281
- [4] Makhov V N, Khaidukov N M, Kirm M, Zimmerer G, Lam S K, Lo D and Suetin N V 2002 *Surf. Rev. Lett.* **9** 271
- [5] Wegh R T, van Loef E V D and Meijerink A 2000 *J. Lumin.* **90** 111

- [6] Balda R, Fernandez J, Ocariz I S, Voda M and Garcia A J 1999 *Phys. Rev. B* **59** 9972
- [7] Yin M, Li Y, Dong N, Makhov V N, Khaidukov N M and Krupa J C 2003 *J. Alloys Compounds* **352** 95
- [8] Couto dos Santos M A, Antic-Fidancev E, Gesland J Y, Krupa J C, Lemaitre-Blaise M and Porcher P 1998 *J. Alloys Compounds* **275–277** 435
- [9] Weber M J 1967 *Phys. Rev.* **157** 262
- [10] Reisfeld R and Eckstein Y 1974 *J. Non-Cryst. Solids* **15** 125
- [11] Shinn M D, Sibley W A, Drexhage M G and Brown R N 1983 *Phys. Rev. B* **27** 6635
- [12] Capobianco J A, Prevost G, Proulx P P, Kabro P and Bettinelli M 1996 *Opt. Mater.* **6** 175
- [13] Chamarro A and Cases R 1990 *J. Lumin.* **46** 59
- [14] Capobianco J A, Vetrone F, Boyer J C, Speghini A and Bettinelli M 2002 *Opt. Mater.* **19** 259
- [15] Shojiya M, Takahashi M, Kamno R, Kawamoto Y and Kadono K 1994 *Appl. Phys. Lett.* **65** 1874
- [16] Kojima K, Yoshida S, Shiraishi H and Maegawa A 1995 *Appl. Phys. Lett.* **67** 3423
- [17] Yamada N, Shionoya S and Kushida T 1972 *J. Phys. Soc. Japan* **32** 1577
- [18] Zhang H X, Kam C H, Zhou Y, Han X Q, Buddhudu S and Lam Y L 2000 *Opt. Mater.* **15** 47
- [19] Capobianco J A, Vetrone F and Boyer J C 2002 *J. Phys. Chem. B* **106** 1181
- [20] Wybourne B G 1965 *Spectroscopic Properties of Rare Earths* (New York: Interscience) p 163
- [21] Judd B R 1966 *Phys. Rev.* **141** 4
- [22] Carnall W T, Goodman G L, Rajnak K and Rana R S 1989 *J. Chem. Phys.* **90** 3443
- [23] Yin M, Krupa J C, Antic-Fidancev E and Lorriaux-Rubbens A 2000 *Phys. Rev. B* **61** 8073
- [24] Chen X Y and Luo Z D 1996 *J. Phys.: Condens. Matter* **8** 2571
- [25] Corbel G, Leblanc M, Antic-Fidancev E and Lemaitre-Blaise M 1999 *J. Solid State Chem.* **144** 35
- [26] Jayasankar C K, Reid M F and Richardson F S 1989 *Phys. Status Solidi b* **155** 559