

Fluorine and Heavy Metal Oxide Effects on Spectral Properties of Tm^{3+} in Silicate Glasses

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ABSTRACT

The fluorine doping along with heavy metal oxides remarkably raised the 3H_4 lifetime and the quantum efficiency in Tm^{3+} -doped silicate glasses. 29 mol% of fluorine substitution for oxygen in $70SiO_2-15PbO-12ZnO-3KO_{1/2}$ glass raised 3H_4 lifetime to 193 μs . Refractive indices were raised by heavy metal oxide substitution, but hardly changed by fluorine substitution. The fluorine doping changed the local structure around Tm^{3+} ions, then low energy vibrations related to fluorine are considered to largely reduce the multi-phonon relaxation rates in the oxyfluoride silicate glasses. The 3H_4 lifetimes and absorption and emission spectra of Tm^{3+} -doped silicate and oxyfluoride silicate glasses are reported, and Judd-Ofelt calculation results are discussed in this paper.

Key words : Tm, Silicate glass, Fluorine

1. Introduction

The increasing demand for high capacity Wavelength Division Multiplexing (WDM) transmission systems has stimulated the development of wide band optical fiber amplifier to extend bandwidth of WDM systems. The C-band and L-band based on erbium-doped fiber amplifier have been actively developed, but they account for less than 25% of the usable low-loss telecommunication window of silicate fiber (approximately 1.4~1.7 μm).¹⁾ Thulium-Doped Fiber Amplifier (TDFA) has been developed for S-band (1.45~1.52 μm) amplifications, since Komukai *et al.* first demonstrated the TDFA with thulium-doped fluoride fiber.²⁾ Kasamatsu *et al.* introduced gain-shifted TDFA using dual pumping scheme.³⁾ And many studies of highly efficient TDFA using multi wavelength pumping scheme have been actively reported.^{4,5)} Despite of recent progress of TDFA using Tm^{3+} -doped fluoride fiber, it is considered to have serious disadvantages at splicing and long-term stability.

For highly efficient amplification based on $Tm^{3+} : ^3H_4 \rightarrow ^3F_4$ transition, the host glass must have low phonon energy because the amplification is difficult on a high phonon energy glass due to the fast non-radiative transition of $^3H_4 \rightarrow ^3H_5$ through multi-phonon relaxation.^{6,7)} This is the reason why the TDFA using silicate fiber was scarcely developed. Recently, S-band fiber amplifier has been reported with a Tm-doped silicate fiber.^{8,9)} However, the gain was small for the Tm-doped silicate fiber to be used in S-band fiber ampli-

fier, and the compositional study of Tm^{3+} -doped silicate glasses on spectral properties has not been done yet. Therefore, the study of optical property dependence on host glass composition in Tm^{3+} -doped silicate glasses is needed. We have studied the effects of heavy metal oxide and fluorine substitution on spectral properties of Tm^{3+} ion in silicate glasses.

2. Experiment

Glass samples were prepared by a conventional melting and quenching method. Starting materials were oxide, fluoride and carbonate powders with more than 99.9% purity. Melting was carried out in air by using an electric furnace. Mixed powder was melted in a platinum crucible at 1450~1500°C for 60 min, and the glass and crucible was quenched in water, then annealed at 600°C for 60 min. Then the glass samples were cut and optical polished. A 795 nm Ti : sapphire laser excited by Ar ion laser was used to pump the sample, and a monochromator and an InSb detector were used to measure the fluorescence spectrum. The fluorescence lifetimes for the 3H_4 and 3F_4 levels were measured with a Ti : sapphire laser, a chopper wheel, band-pass filters and the InSb detector coupled with a HP 500 MHz digital oscilloscope. The wavelength of the excitation laser was tuned to 795 nm for the lifetime measurements. Absorption spectra were measured with a UV-Visible-NIR spectrophotometer.

3. Results and Discussion

The 3H_4 lifetime of Tm^{3+} ion in silica glass is less than 20 μs and the quantum efficiency of the $Tm^{3+} : ^3H_4 \rightarrow ^3F_4$ transition is several % as reported early.⁹⁾ This is predominantly

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Table 1. Lifetimes for ${}^3\text{H}_4$ of Tm^{3+} in Silicate Glasses

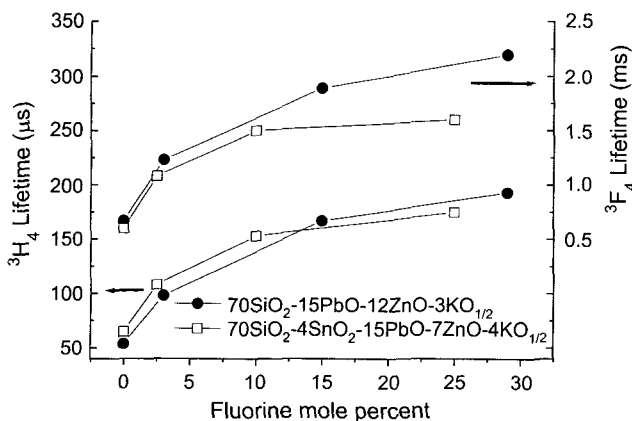
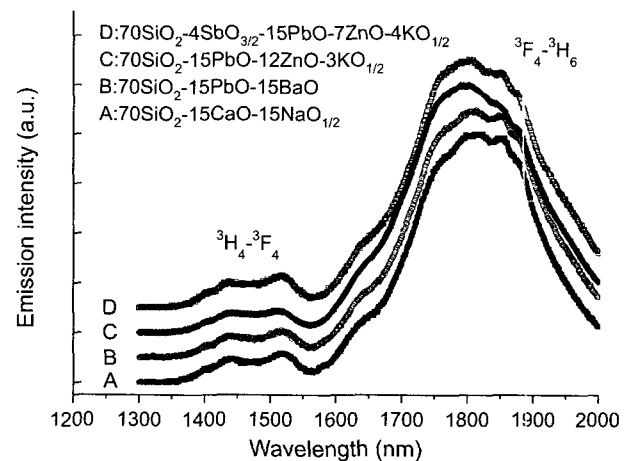
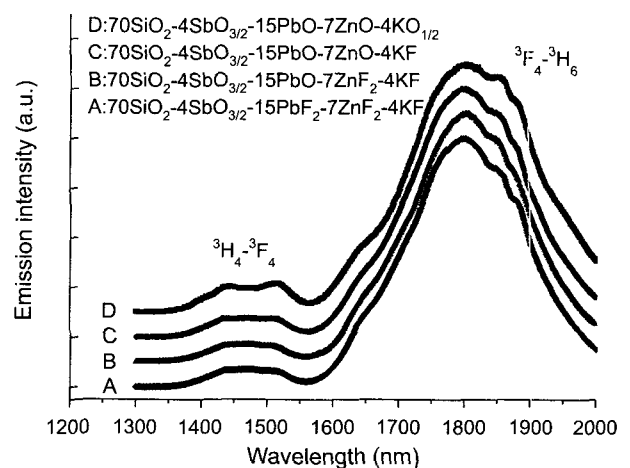
Host glass composition	Lifetime of $\text{Tm}^{3+} : {}^3\text{H}_4$
$70\text{SiO}_2\text{-}15\text{CaO}\text{-}15\text{NaO}_{1/2}$	34 μs
$70\text{SiO}_2\text{-}15\text{ZnO}\text{-}15\text{KO}_{1/2}$	34 μs
$70\text{SiO}_2\text{-}15\text{PbO}\text{-}15\text{BaO}$	43 μs
$70\text{SiO}_2\text{-}15\text{PbO}\text{-}12\text{ZnO}\text{-}3\text{KO}_{1/2}$	54 μs
$70\text{SiO}_2\text{-}4\text{SnO}_2\text{-}15\text{PbO}\text{-}7\text{ZnO}\text{-}4\text{KO}_{1/2}$	62 μs
$70\text{SiO}_2\text{-}4\text{SbO}_{3/2}\text{-}15\text{PbO}\text{-}7\text{ZnO}\text{-}4\text{KO}_{1/2}$	65 μs
$70\text{SiO}_2\text{-}4\text{InO}_{3/2}\text{-}15\text{PbO}\text{-}7\text{ZnO}\text{-}4\text{KO}_{1/2}$	65 μs
$70\text{SiO}_2\text{-}4\text{TiO}_2\text{-}15\text{PbO}\text{-}7\text{ZnO}\text{-}4\text{KO}_{1/2}$	64 μs

caused by multi-phonon relaxations because the energy gap between ${}^3\text{H}_4$ and ${}^3\text{H}_5$ is about 3600 cm^{-1} while the highest phonon energy of silicate glasses is around 1100 cm^{-1} .¹⁰⁾ In order to comparison, the ${}^3\text{H}_4$ lifetime of Tm^{3+} in a conventional soda-lime silicate glass was measured. It was 34 μs as shown in Table 1.

We have examined the effect of heavy metal oxide in silicate glasses by substitutions of the network modifying ions with heavy metal ions while SiO_2 content was fixed as 70 mol%. The ${}^3\text{H}_4$ lifetime was not changed with the substitution of barium and potassium ions. However, the substitutions of lead and zinc ions raised the ${}^3\text{H}_4$ lifetime. Additions of tin or indium, antimony, titanium ion further increased the ${}^3\text{H}_4$ lifetime. The heavy metal oxides can increase the ${}^3\text{H}_4$ lifetimes of Tm^{3+} in silicate glasses, but the increasing increments were small.

Fluorine substitutions also extended the ${}^3\text{H}_4$ lifetime of Tm^{3+} in silicate glasses. When 3 mol% and 29 mol% of fluorine substituted for oxygen in $70\text{SiO}_2\text{-}15\text{PbO}\text{-}12\text{ZnO}\text{-}3\text{KO}_{1/2}$ glass, ${}^3\text{H}_4$ lifetime was measured to be 98 μs and 193 μs , respectively. As shown in Fig. 1 the ${}^3\text{H}_4$ lifetime largely increased by a relatively small substitution of fluorine and it increased with the substitution content of fluorine.

Figs. 2 and 3 show fluorescence spectra for ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transitions of Tm^{3+} in the silicate and oxyfluoride silicate glasses. The shape of spectrum hardly changed by the substitution of heavy metal oxides as shown in Fig. 2.

**Fig. 1.** The dependence of ${}^3\text{H}_4$ and ${}^3\text{F}_4$ lifetimes on fluorine content in heavy metal oxide silicate glasses.**Fig. 2.** Emission spectra for Tm^{3+} -doped silicate glasses.**Fig. 3.** Emission spectra for Tm^{3+} -doped oxyfluoride silicate glasses.

However, the substitution of fluorine changed the spectrum shape obviously. The spectrum for ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition in silicate glasses represented double peaks, while the double peaks for spectrum of ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$ transition were merged into single peak by a relatively small substitution of fluorine. This means that the ligand field around Tm^{3+} ions is obviously changed by the fluorine substitution.

Fig. 4 shows absorption cross-section spectra of $70\text{SiO}_2\text{-}15\text{CaO}\text{-}15\text{NaO}_{1/2}$, $70\text{SiO}_2\text{-}15\text{PbO}\text{-}12\text{ZnO}\text{-}3\text{KO}_{1/2}$, and $70\text{SiO}_2\text{-}15\text{PbF}_2\text{-}12\text{ZnF}_2\text{-}3\text{KF}$ glasses. The absorption cross-section of the silicate glass containing heavy metal oxides was larger than that of the soda-lime glass. The absorption cross-section further increased with the substitution of fluorine.

Refractive indices, densities, results of Judd-Ofelt calculations, quantum efficiencies, and multi-phonon relaxation rates of the silicate and oxyfluoride silicate glasses are shown in Table 2. The substitution of heavy metal oxides raised the refractive index, but it was hardly changed by the substitution of fluorine. The substitution of heavy metal oxides in the silicate glass raised the density of glass, and the fluorine substitution further

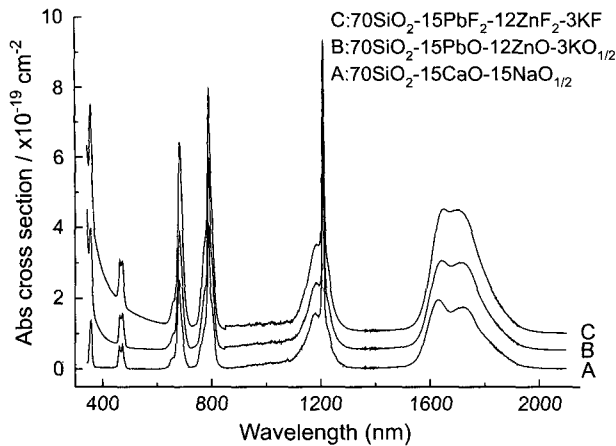


Fig. 4. Absorption cross-section spectra for Tm³⁺-doped silicate glasses.

increased the glass density. In the material having no absorption, the refractive index (n) can be represented with dielectric constant as

$$n = \sqrt{\frac{\epsilon'}{\epsilon_0}} \quad (1)$$

where ϵ' is the dielectric constant of the material and ϵ_0 is the permittivity of vacuum. Generally fluorine substitutions lower the refractive index and the dielectric constant because a fluorine has a lower electric dipole moment than an oxygen. However, the fluorine substitution in the heavy metal oxide silicate glass did not change the refractive index. It is considered that the packing effect on increasing refractive indices compensates the dipole moment effect on decreasing refractive indices.

Judd-Ofelt (J-O) approach for determining radiative and nonradiative transition rates of rare earth ion in glass has been widely used.¹¹⁻¹³⁾ In the J-O analysis, the line strength for an electric dipole transition (S_{ed}) is given by

$$S_{ed}(aJ; bJ') = e^2 \sum_{t=2,4,6} \Omega_t |f^N[\alpha SL]J |U^{(t)}| f^N[\alpha' S'L']J'|^2 \quad (2)$$

where e is the electronic charge, Ω_t the J-O parameter and $\langle U^{(t)} \rangle$ is doubly reduced matrix element. The J-O param-

eters are determined from absorption spectra and refractive indices. We calculated the values of Ω_2 , Ω_4 , and Ω_6 for our glass samples by using the procedure provided in Ref. 13. In these calculations, the doubly reduced matrix elements from Ref. 7 were used. The values of J-O parameters for the silicate and oxyfluoride silicate glasses are listed in Table 2. After obtaining J-O parameters, the radiative transition rate ($W_r = 1/\tau_r$) can be determined by

$$W_r(aJ; bJ') = \frac{16\pi^3 n^2}{3h\epsilon_0 \lambda^3 (2J+1)} (\chi_{ed} S_{ed} + \chi_{md} S_{md}) \quad (3)$$

where h is Planck constant, ϵ_0 the permittivity of vacuum, λ the central wavelength of the transition, J is the total angular quantum number, and the χ terms account for a local field correction and are given by $\chi_{ed} = (n^2 + 2)^2/9n$ and $\chi_{md} = n$.^{14,15)}

Measured decay rate (W_m) from the excited state energy level can be expressed as

$$W_m = W_r + W_{mp} + W_{et} + W_{cr} \quad (4)$$

where W_r is the radiative transition rate calculated from J-O analysis and W_{mp} , W_{ep} and W_{cr} are the rates of non-radiative transitions due to multi-phonon relaxation, energy transfer, and cross relaxation, respectively.¹⁶⁾ Because the concentration of the Er³⁺ ion was kept low enough, W_{et} and W_{cr} can be neglected in our cases. Thus, W_m can be written as following equation.

$$W_m = \frac{1}{\tau_m} = W_r + W_{mp} \quad (5)$$

Thus, the multi-phonon relaxation rates can be determined by using the equation (3) and (5) after the lifetime is measured experimentally and the radiative transition rate is calculated.

As shown in Table 2, the ³H₄ intrinsic lifetime calculated from J-O analysis was reduced by the heavy metal oxide substitution and further decreased with the fluorine substitution. On the other hand, the measured ³H₄ lifetime was extended by the heavy metal oxide substitution and further increased with the fluorine substitution. Therefore, the quantum efficiency was extensively raised to attain to 30% in the Tm³⁺-doped 70SiO₂-15PbF₂-12ZnF₂-3KF glass.

Table 2. Refractive Indices and Judd-Ofelt Parameters, Calculated and Measured Lifetimes, Quantum Efficiencies, and Multi-phonon Relaxation Rates of Tm³⁺ in Silicate Glasses

Glass	70SiO ₂ -15CaO-15NaO _{1/2}	70SiO ₂ -15PbO-12ZnO-3KO _{1/2}	70SiO ₂ -15PbF ₂ -12ZnF ₂ -3KF
Index	1.52	1.66	1.65
Density (g/cm ³)	2.758	4.050	4.122
S _{ed} (for ³ F ₄ ← ³ H ₆)	6.84 × 10 ⁻⁶²	8.21 × 10 ⁻⁶²	1.08 × 10 ⁻⁶¹
Ω ₂	4.37 × 10 ⁻²⁴	5.37 × 10 ⁻²⁴	7.12 × 10 ⁻²⁴
Ω ₄	6.25 × 10 ⁻²⁶	3.35 × 10 ⁻²⁶	1.24 × 10 ⁻²⁶
Ω ₆	9.34 × 10 ⁻²⁵	9.59 × 10 ⁻²⁵	1.32 × 10 ⁻²⁴
τ _c for ³ H ₄ (μs)	1280	832	634
τ _m for ³ H ₄ (μs)	34	54	193
η (%)	2.6	6.5	30
MPR (sec ⁻¹)	2.95 × 10 ⁴	1.67 × 10 ⁴	3.98 × 10 ³

An empirical rule for the multi-phonon relaxation rate is written as

$$W_{mp} = W_0 \exp(-\alpha \Delta E) \quad (6)$$

where W_0 is a positive constant depending on host glasses, ΔE is an energy gap between the excited state energy level of interest and immediately lower level.¹⁷⁾ It can be seen from equation (6) that the multi-phonon relaxation rate is exponentially increased with decreasing ΔE . And α is given by

$$\alpha = \frac{1}{h\nu} \left[\ln\left(\frac{P}{g}\right) - 1 \right] \quad (7)$$

where $h\nu$ is the phonon energy coupled to rare earth ions, p is the effective number of phonons participating in the multi-phonon relaxation and g is electron-phonon coupling strength.¹⁸⁾ Therefore, it is considered from the above equations (6) and (7) that the multi-phonon relaxation rate was reduced and the measured lifetime is raised by decreasing the host glass phonon energy coupled to Tm^{3+} ions.

In general, dominant contribution to multi-phonon relaxation process involves the highest phonon energy vibration. The high energy stretching modes of network forming polyhedra are responsible for the multi-phonon relaxation process in glasses. It is considered that the heavy metal oxide substitutions partially reduce the phonon energy of host glass while the phonon energy of the major network formers of SiO_2 contribute dominantly to the multi-phonon relaxation process. However, the case of the fluorine substitution is different. A relatively small doping of fluorine obviously enhanced the lifetime and the quantum efficiency as shown in Tables 1 and 2. These results represent that the fluorine ions are not randomly dispersed in the host glass but predominantly gather around Tm^{3+} ions. The local structure around Tm^{3+} ions is different from the structure of the host glass matrix in the Tm^{3+} -doped oxyfluoride silicate glasses. The fluorescence spectra shown in Fig. 3 demonstrate these explanations. Therefore, the low energy vibrations related to fluorine are considered to largely affect the multi-phonon relaxation process in the oxyfluoride silicate glasses.

4. Conclusions

We have described the spectral properties of Tm^{3+} -doped silicate and oxyfluoride silicate glasses. The heavy metal oxides can increase the ${}^3\text{H}_4$ lifetimes of Tm^{3+} in silicate glasses, but the increasing increments were small. However, the fluorine doping along with heavy metal oxides was remarkably raised the ${}^3\text{H}_4$ lifetime and the quantum efficiency in silicate glasses. ${}^3\text{H}_4$ lifetime of the Tm^{3+} -doped $70\text{SiO}_2\text{-}15\text{PbF}_2\text{-}12\text{ZnF}_2\text{-}3\text{KF}$ glass was measured to be 193 μs and the quantum efficiency was 30%. The fluorine doping is supposed to change the local structure around the Tm^{3+} ions, and the low energy vibrations related to fluorine are considered to largely reduce the multi-phonon relaxation rate in the oxyfluoride silicate glasses. The fiber made of the

heavy metal oxides and fluorine co-doped silicate glass might have excellent stability and apply fusion splicing. The Tm^{3+} -doped silicate glasses containing heavy metal oxides and fluorine appear to be excellent candidate materials for TDFA.

REFERENCES

1. S. Sudo, "Optical Fiber Amplifiers: Materials, Devices, and Applications," 55-132, Artech House, Inc., Boston-London, 1997.
2. T. Komukai, T. Yamamoto, T. Sugawa, and Y. Miyajima, "1.47 μm Band Tm^{3+} Doped Fluoride Fiber Amplifier Using a 1.064 μm Upconversion Pumping Scheme," *Electron. Lett.*, **29** [1] 110-12 (1993).
3. T. Kasamatsu, Y. Yano, and H. Sekita, "1.50 μm -band Gain-shifted Thulium-doped Fiber Amplifier with 1.05 and 1.56 μm Dual-wavelength Pumping," *Opt. Lett.*, **24** [23] 1684-86 (1999).
4. F. Roy, A. L. Sauze, P. Baniel, and D. Bayart, "0.8- μm +1.4- μm Pumping for Gai-shifted TDFA with Power Conversion Efficiency Exceeding 50%," Technical Digest of Optical Amplifiers and their Applications 2001, PD4, Stresa, Italy.
5. F. Roy, "Recent Advances in Thulium-doped Fiber Amplifiers," Technical Digest of Optical Fiber Communication Conference 2002, ThZ1, Anaheim, CA, USA.
6. J. Sanz, R. Cases, and R. Alcalá, "Optical Properties of Tm^{3+} in Fluorozirconate Glass," *J. Non-cryst. Solids*, **93** [2-3] 377-86 (1987).
7. N. Spector, R. Reisfeld, and L. Boehm, "Eigenstates and Radiative Transition Probabilities for Tm^{3+} (${}^4\text{f}_{11}$) in Phosphate and Tellurite Glasses," *Chem. Phys. Lett.*, **49** [1] 49-54 (1977).
8. J. D. Minelly, "Applications of New Materials for Fibe Optic Amplifiers and Lasers," Proceedings of 27th European Conference on Optical Communication, 1 78, Amsterdam, Netherlands (2001).
9. B. Cole and M. L. Dennis, "S-band Amplification in a Thulium Doped Silicate Fiber," Technical Digest of Optical Fiber Communication Conference 2 TuQ3-1, Anaheim, CA, USA (2001).
10. J. S. Wang, E. M. Vogel, and E. Snitzer, "Tellurite Glass : A New Candidate for Fiber Devices," *Opt. Mater.*, **3** 187-203 (1994).
11. D. H. Cho, Y. G. Choi, and K. H. Kim, "Improvement of ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ Transition Rate and Thermal Stabilities in Er^{3+} -doped $\text{TeO}_2\text{-B}_2\text{O}_3\text{-(GeO}_2\text{)-ZnO-K}_2\text{O}$ Glasses," *ETRI J.*, **23** [4] 151-57 (2001).
12. L. R. Moorthy, T. S. Rao, K. Janardhnam, and A. Radhapaty, "Absorption and Emission Characteristics of Er^{3+} Ions in Alkali Chloroborophosphate Glasses," *Spectrochimica Acta Part A*, **56** 1759-71 (2000).
13. Z. Pan, S. H. Morgan, and J. Lumin, "Optical Transitions of Er^{3+} in Lead-tellurium-germanate Glasses," *J. Lumin.*, **75** [4] 301-08 (1997).
14. M. J. Weber, "Probabilities for Radiative and Nonradiative Decay of Er^{3+} in LaF_3 ," *Phys. Rev.*, **157** [2] 262-72 (1967).
15. M. D. Shinn, W. A. Silbley, M. G. Drexhage, and R. N. Brown, "Optical Transitions of Er^{3+} Ions in Fluorozir Con-

- ate Glass," *Phys. Rev. B-Condensed Matter*, **27** [11] 6635-48 (1983).
16. H. Toratani, T. Izumitani, and H. Kuroda, "Compositional Dependence of Nonradiative Decay Rate in Nd Laser Glasses," *J. Non-cryst. Solids*, **52** [1-3] 303-13 (1982).
17. M. J. Weber, "Multiphonon Relaxation of Rare-earth Ions in Yttrium Orthoaluminate," *Phys. Rev. B (Solid State)*, **8** [1] 54-64 (1973).
18. T. Miyakawa and D. L. Dexter, "Phonon Sidebands, Multiphonon Relaxation of Excited States and Phonon-assisted Energy Transfer Between Ions in Solids," *Phys. Rev. B (Solid State)*, **1** [7] 2961-69 (1970).