P: ISSN NO.: 2394-0344 RNI No.UPBIL/2016/67980 VOL-3* ISSUE-11*(Part-1) February 2019
E: ISSN NO.: 2455-0817 *Remarking An Analisation*

Spectral and Thermal Properties of Tb^{3+} Doped ZBLAN Glasses

Abstract

ZBLAN glasses containing Tb^{3+} in (40- x): ZrF_4: $10BaF_2$: $10LaF_3$: $15AlF_2$: 25NaF: xTb_2O_3 (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption spectra were recorded at room temperature for all glass samples. The experimental oscillator strengths were calculated from the area under the absorption bands. Slater-Condon parameter (F_2), Lande's parameter (ξ_{4f}), Nephlauxetic ratio (β') and Bonding parameter ($b^{1/2}$) have been computed. Using these parameters energies and intensities of these bands has been calculated. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated.

Keywords: ZBLAN Glasses, Optical Properties, Judd-Ofelt Theory, Rare Earth Ions.

S.L.Meena
Ceremic Laboratory,
Dept. of Physics,
Jai Narain Vyas University,
Jodhpur, Rajasthan, India

Introduction

ZBLAN glasses find a wide range of technological applications as electro-chemical devices as ionic conductors, optoelectronic devices, environmental sensing and infrared spectroscopy [1-4].ZBLAN is a heavy metal fluoride glass, which shows a wide transmission range of 0.3-5μm and high emission efficiency for rare earth ions[5-7].Among RE^{3+} ions, Tb^{3+} is an interesting ion for spectroscopic studies, because it exhibits several electronic transitions in the UV and VIS. Glasses containing heavy metal oxides exhibits good non-linear optical properties and good chemical durability. The past literature shows that the rare earth ions find more important application in the preparation of the laser materials [8-12].

Aim of the Study

In this work, we have studied on the absorption and emission properties of Tb^{3+} doped ZBLAN glasses. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6), which are sensitive to the environment of rare earth ion. From these parameters, important optical properties such as radiative transition probability for spontaneous emission, radiative lifetime of the excited states and branching ratio can be estimated.

Experimental Techniques

Preparation of glasses

The following Tb^{3+} doped ZBLAN glasses containing Tb^{3+} in (40-x): ZrF_4: $10BaF_2$: $10LaF_3$: $15AlF_2$: 25NaF: xTb_2O_3 (where x=1, 1.5, 2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of ZrF_4, BaF_2, LaF_3, AlF_2, NaF and Tb_2O_3. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1020^0C, for preparation of ZBLAN glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to150^0C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 250^0C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

Table 1 Chemical composition of the glasses

Sample	Glass composition (mol %)
ZBLAN (UD)	40 ZrF_4: 10 BaF_2: 10 LaF_3: 15 AlF_2: 25 NaF
ZBLAN (TB1)	39ZrF_4: 10 BaF_2: 10 LaF_3: 15 AlF_2: 25 NaF: 1 Tb_2O_3
ZBLAN (TB 1.5)	38.5 ZrF_4: 10 BaF_2: 10 LaF_3: 15 AlF_2: 25 NaF: 1.5 Tb_2O_3
ZBLAN (TB 2)	38 ZrF_4: 10 BaF_2: 10 LaF_3: 15 AlF_2: 25 NaF: 2 Tb_2O_3

ZBLAN (UD) - Represents undoped ZBLAN glass specimens
ZBLAN (TB) - Represents Tb^{3+} doped ZBLAN glass specimens

Theory

Oscillator Strength

The intensity of spectral lines is expressed in terms of oscillator strengths using the relation [13].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon (v)\, d v \quad (1)$$

Where, ε (*v*) is molar absorption coefficient at a given energy *v* (cm^{-1}), to be evaluated from Beer–Lambert law.

Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated, using the modified relation [14].

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \quad (2)$$

Where, c is the molar concentration of the absorbing ion per unit volume, l is the optical path length, $\log I_0/I$ is absorbtivity or optical density and $\Delta\upsilon_{1/2}$ is half band width.

Judd-Ofelt Intensity Parameters

According to Judd [15] and Ofelt [16] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold │$4f^N$ (S, L) J> level and the terminal J' manifold │$4f^N$ (S', L') J'> is given by:

$$\frac{8\Pi^2 mc\, \bar{\upsilon}}{3h(2J+1)} \frac{1}{n} \left[\frac{\left(n^2+2\right)^2}{9} \right] \times S\left(J, J'\right) \quad (3)$$

Where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum \Omega_\lambda \langle 4f^N (S, L) J \| U^{(\lambda)} \| 4f^N (S', L') J' \rangle^2 \quad (4)$$

λ =2, 4, 6

In the above equation m is the mass of an electron, c is the velocity of light, *v* is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, Ω_λ (λ = 2, 4, 6) are known as Judd-Ofelt intensity parameters

Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R), and laser parameters like fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p).

The spontaneous emission probability from initial manifold │$4f^N$ (S', L') J'> to a final manifold │$4f^N$ (*S, L) J* >**|** is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2 v^3}{3h(2J'+1)} \left[\frac{n(n^2+2)^2}{9} \right] \times S(J', \bar{J}) \quad (5)$$

Where,

$$S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$$

The fluorescence branching ratio for the transitions originating from a specific initial manifold │$4f^N$ (S', L') J'> to a final many fold│$4f^N$ (S, L) J > is given by

$$\beta [(S', L') J'; (S, L) J] = \sum_{SLJ} \frac{A[(S' L)]}{A[(S' L') J' (\bar{S} L)]} \quad (6)$$

Where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{SLJ} A[(S', L') J'; (S,L)] = A_{\text{Total}}^{-1} \quad (7)$$

Where, the sum is over all possible terminal manifolds. The stimulated emission cross - section for a transition from an initial manifold │$4f^N$ (S', L') J'> to a final manifold│$4f^N$ (S, L) J >| is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S', L') J'; (\bar{S}, \bar{L}) \bar{J}] \quad (8)$$

Where, λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$)

The nature of the R-O bond is known by the Nephelauxetic Ratio (β') and Bonding Parameter ($b^{1/2}$), which are computed by using following formulae [17, 18]. The Nephelauxetic Ratio is given by

$$\beta' = \frac{v_g}{v_a} \quad (9)$$

Where, v_g and v_a refer to the energies of the corresponding transition in the glass and free ion, respectively. The values of bonding parameter ($b^{1/2}$) is given by

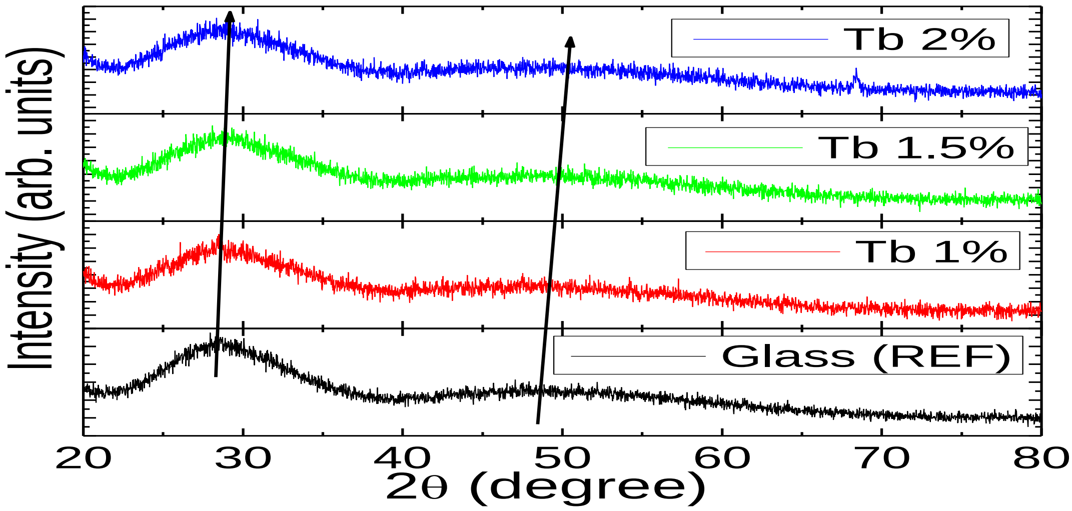
$$b^{1/2} = \left[\frac{1-\beta'}{2}\right]^{1/2} \quad (10)$$

Result and Discussion

XRD Measurement

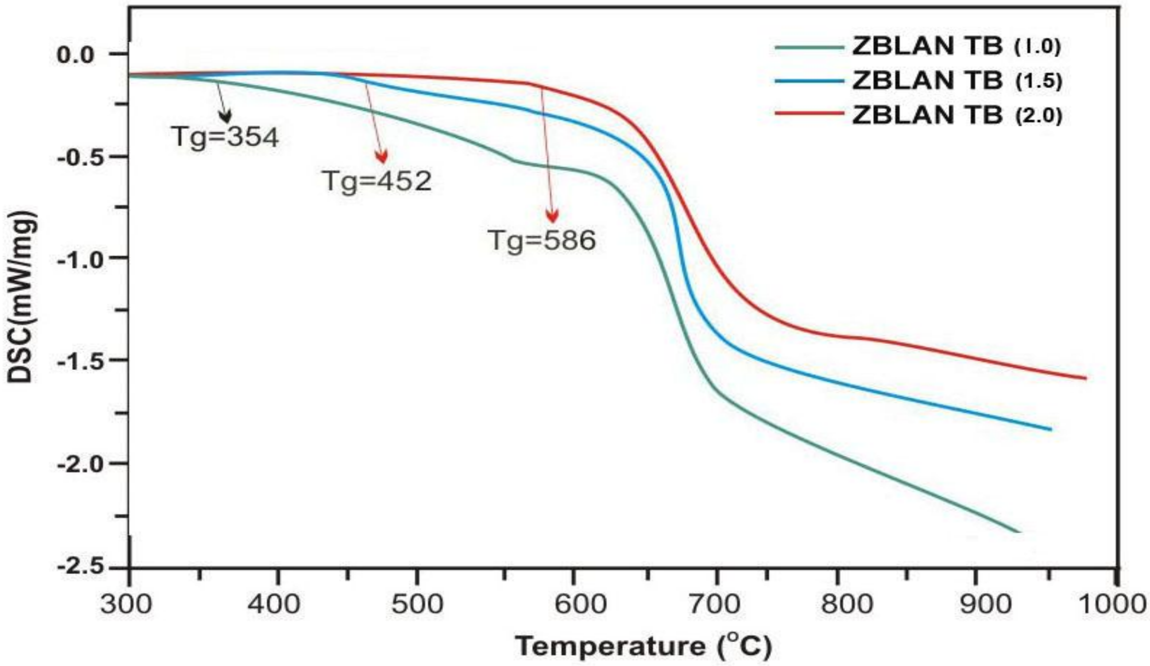
Figure 1 presents the XRD pattern of the samples containing show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

Fig.1: X-ray Diffraction Pattern of ZBLAN (TB) Glasses



Thermal Properties

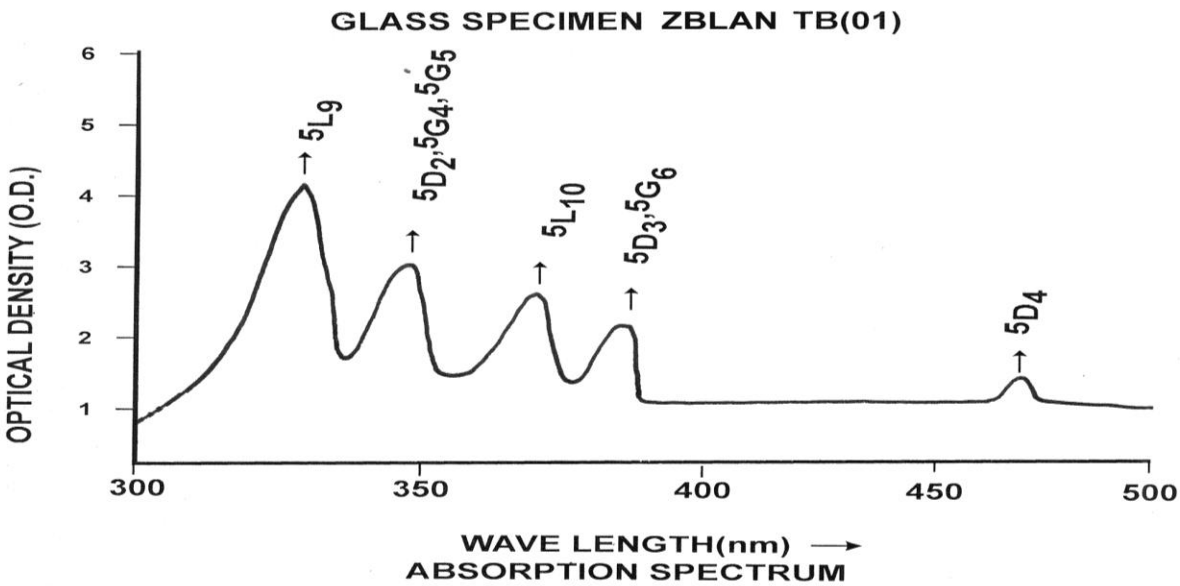
Figure 2 shows the thermal properties of ZBLAN glass from 300^{0}C to 1000^{0}C. From the DSC curve of present glasses system, we can find out that no crystallization peak is apparent and the glass transition temperature T_g are 354^{0}C, 452^{0}C and 586^{0}C respectively. The T_g increase with the contents of Tb_2O_3 increase. We could conclude that thermal properties of the ZBLAN glass are good for fiber drawing from the analysis of DSC curve.



Absorption spectra

The absorption spectra of Tb^{3+} doped ZBLAN (TB 01) glass specimen has been presented in Figure 3 in terms of optical density versus wavelength (nm). Five absorption bands have been observed from the ground state $^7F_6$ to excited states $^5D_4$, $^5D_3$, $^5L_{10}$, $^5D_2$, and $^5L_9$ for Tb^{3+}doped ZBLAN glasses.

Fig.2: UV-VIS absorption spectra of ZBLAN (TB) glasses.



The experimental and calculated oscillator strengths for Tb^{3+} ions in ZBLAN glasses are given in Table 2

Table 2. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Tb^{3+} ions in ZBLAN glasses.

Energy level	Glass ZBLAN (TB01)		Glass ZBLAN (TB1.5)		Glass ZBLAN (TB02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^5D_4$	0.0495	0.65	0.0488	0.63	0.0555	0.61
$^5D_3$	0.3465	0.97	0.3528	0.95	0.3577	0.92
$^5L_{10}$	1.1376	1.72	1.135	1.69	1.1506	1.67
$^5D_2$	0.5414	1.95	0.5416	1.93	0.5560	1.91
$^5L_9$	0.9891	2.24	0.9918	2.22	0.9976	2.19
R.m.s.deviation	0.9631		0.9422		0.910901	

Computed values of (F_2), Lande's parameter (ξ_{4f}), Nephlauxetic ratio (β') and bonding parameter ($b^{½}$) for Tb^{3+} doped ZBLAN glass specimen are given in Table 3

Table 3. F_2, ξ_{4f}, β' and $b^{½}$ parameters for Terbium doped glass specimen.

Glass Specimen	F_2	ξ_{4f}	β'	$b^{½}$
Tb^{3+}	400.26	1820.87	0.9703	0.1219

Judd-Ofelt intensity parameters Ω_λ (λ = 2, 4, 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions. In the present case the three Ω_λ parameters follow the trend $\Omega_4 < \Omega_6 < \Omega_2$. The values of Judd-Ofelt intensity parameters are given in Table 4.

Table 4. Judd-Ofelt intensity parameters for Tb^{3+} doped ZBLAN glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZBLAN(TB 01)	4.009	1.217	2.418	0.5033
ZBLAN (TB 1.5)	3.640	1.542	2.408	0.6404
ZBLAN (TB 02)	5.088	1.046	2.443	0.4282

Fluorescence Spectrum

The fluorescence spectrum of Tb^{3+}doped in ZBLAN glass is shown in Figure4. There are four bands observed in the Fluorescence spectrum of Tb^{3+}doped ZBLAN glass. The wavelengths of these bands along with their assignments are given in Table 5. Fig. (4).Shows the fluorescence spectrum with four peaks ($^5D_4 \rightarrow {}^7F_6$), ($^5D_4 \rightarrow {}^7F_5$), ($^5D_4 \rightarrow {}^7F_4$) and ($^5D_4 \rightarrow {}^7F_3$), respectively for glass specimens.

Fig.4: Fluorescence spectrum of ZBLAN glasses doped with Tb^{3+}

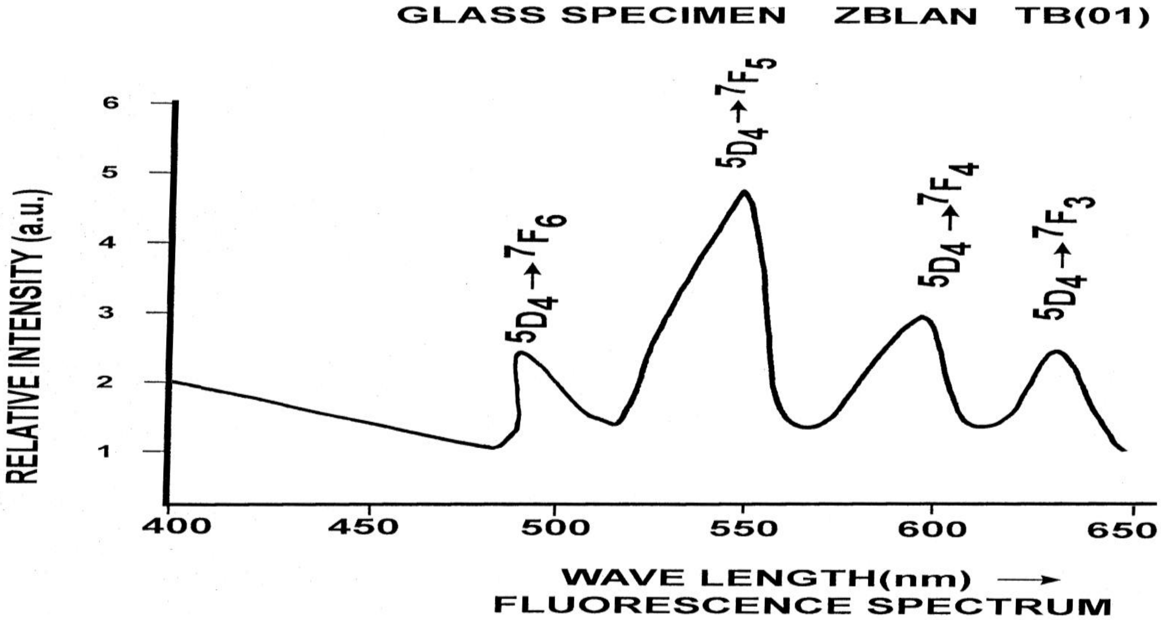


Table5. Emission peak wave lengths (λ_p), radiative transition probability (A_{rad}), branching ratio (β_R), stimulated emission crosssection (σ_p), and radiative life time (τ_R) for various transitions in Tb^{3+}doped ZBLAN glasses.

		ZBLAN (TB 01)				ZBLAN (TB 1.5)				ZBLAN (TB 02)			
Transition	**λ_p(nm)**	**A_{rad}(s^{-1})**	**β_R**	**σ_p ($10^{-20}cm^2$)**	**τ_R(μs)**	**A_{rad}(s^{-1})**	**β_R**	**σ_p ($10^{-20}cm^2$)**	**τ_R(μs)**	**A_{rad}(s^{-1})**	**β_R**	**σ_p ($10^{-20}cm^2$)**	**τ_R(μs)**
$^5D_4 \rightarrow ^7F_6$	488	2094.77	0.1068	0.2735		2072.64	0.1116	0.2662		2341.72	0.0990	0.2991	
$^5D_4 \rightarrow ^7F_5$	550	13445.90	0.6854	2.0578		12447.10	0.6702	1.8894		16675.30	0.7053	2.5106	
$^5D_4 \rightarrow ^7F_4$	582	1518.62	0.0774	0.6585	50.973	1645.00	0.0886	0.5191	53.844	1512.66	0.0639	0.4710	42.297
$^5D_4 \rightarrow ^7F_3$	625	2559.01	0.1304	0.3908		2407.31	0.1296	0.5451		3112.65	0.1317	0.7021	

Conclusion

In the present study, the glass samples of composition (40- x): ZrF_4: $10BaF_2$: $10LaF_3$: $15AlF_2$: 25NaF: xTb_2O_3. (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^5D_4$)→$^7F_5$) for glass ZBLAN (TB 01), suggesting that glass ZBLAN (TB 01) is better compared to the other two glass systems ZBLAN (TB 1.5) and ZBLAN (TB 02).

References

1. *Androz, G., Bernier, M. , Faucher,D. and Vallee,R.(2008). "2.3W single transverse mode thulium-doped ZBLAN fiber laser at 1480 nm," Optics Express, vol. 16, no. 20, pp. 16019–16031.*
2. *Golding, P. S. , Jackson, S. D. , King, T. A. and Pollnau, M. (2000). "Energy transfer processes in Er^{3+}-doped and Er^{3+}, Pr^{3+}- co doped ZBLAN glasses," Physical Review B, vol. 62, no. 2, pp. 856–864.*
3. *Qin, G. , Huang, S. , Feng, Y. , Shirakawa, A. and Ueda,K.-I. (2005). "Multiple-wavelength up-conversion laser in Tm^{3+}-doped ZBLAN glass fiber," IEEE Photonics Technology Letters, vol. 17, no. 9, pp. 1818–1820.*
4. *Méjean,G., Kasparian,J. , Salmon, E. , Yu, J. , Wolf, J.-P. , Bourayou, R., Sauerbrey, R. Rodriguez, M., Wöste, L. and Lehmann, H.(2003)"Towards a supercontinuum-based infrared lidar," Appl. Phys. B 77, 357–359.*
5. *Mukherjee, S., Porten, V. and Patel, C. K. N. (2010). "Standoff detection of explosive substances at distances of up to 150 m," Appl. Opt. 49, 2072–2078*
6. *Lancaster, D.G., Gross,S. , Ebendorff-Heidepriem,H., Kuan,K. , Monro,T.M. Ams,M., Fuerbach,A. Withford,M.J. (2011)."Fifty percent internal slope efficiency femtosecond direct-written Tm^{3+}ZBLAN waveguide laser", Optics Letters 36, (9), 1587-1589.*
7. *Qin, G. , Huang, S. , Feng,Y. , Shirakawa,A. , Musha, M. and Ueda,K.-I. (2006)."Power scaling of Tm^{3+} doped ZBLAN blue upconversion fiber lasers: modeling and experiments," Applied Physics B, vol. 82, no. 1, pp. 65–70.*
8. *Schneide,J. , Carbonnier, C. and Unrau,U. B. (1997)."Characterization of a Ho^{3+}-doped fluoride fiber laser with a 3.9-μm emission wavelength," Appl. Opt. 36, 8595–8600.*

9. *Liu,K. , Liu,J. , Shi,H. , Tan,F. and Wang,P. (2014)"High power mid-infrared supercontinuum generation in a single-mode ZBLAN fiber with up to 21.8Waverage output power," Opt. Express 22, 24384–24391.*
10. *Ohsawa K. and Shibata,T. (1984)."preparation and characterization of ZrF_4 BaF_2-LaF_3-NaF-AlF_3 glass optical fibers," Journal of Light wave Technology, vol. 2, no. 5, pp. 602–606, 1984.*
11. *Parker,J. M. (1989)."Fluoride glasses, Annual Review of Materials Science, vol. 19, pp. 21–41.*
12. *Chen, Z., Taylor, A. J. and Efimov, A. (2009)."Coherent mid-infrared broadband continuum generation in non-uniform ZBLAN fiber taper," Optics Express, vol. 17, no. 7, pp. 5852–5860.*
13. *Gorller-Walrand, C. and Binnemans, K. (1988). Spectral Intensities of f-f Transition. In: Gshneidner Jr., K.A. and Eyring,L., Eds., Handbook on the Physics and Chemistry of Rare Earths, Vol. 25, Chap. 167, North-Holland, Amsterdam, 101.*
14. *Sharma, Y.K., Surana, S.S.L. and Singh, R.K. (2009). Spectroscopic Investigations and Luminescence Spectra of Sm^{3+} Doped Soda Lime Silicate Glasses. J.Rare Earths, 27, 773.*
15. *Judd, B.R. (1962). Optical Absorption Intensities of Rare Earth Ions. Physical Review, 127, 750.*
16. *Ofelt, G.S. (1962) Intensities of Crystal Spectra of Rare Earth Ions. J.Chemical Physics, 37, 511.*
17. *Sinha, S.P. (1983).Systematics and properties of lanthanides, Reidel, Dordrecht.*
18. *Krupke, W.F. (1974). IEEE J.Quantum Electron QE, 10,450.*