

Optical properties of rare earth-doped ZBLAN glasses

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An investigation has been made of the radiative and non-radiative properties of the well known ZBLAN glass composition doped with individual rare earth elements (Pr^{3+} , Nd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Tm^{3+}) at levels between 0.1 and 4 mol%. The optical absorption and fluorescence spectra of the samples were measured and also the lifetimes for some transitions. Using the Judd–Ofelt model, the radiative decay rates between the different levels, the lifetimes and the branching ratios were calculated. These results and comparison of calculated and measured lifetimes are discussed with respect to radiative and non-radiative rates and quantum efficiencies. The multiphonon rates below 3200 cm^{-1} are found to be less in ZBLAN than in other host materials (ZBLA, SiO_2 , YAG).

1. Introduction

The favourable physical properties of ZBLAN vis-à-vis other fluoride glasses have already led to the production of low-loss fibres for short-haul applications [1]. This glass has interesting properties as host material for active laser devices, e.g., fibre lasers, upconversion fibre lasers, and fibre amplifiers [2–4], due to its IR transparency and the possibility of doping with up to 6 mol% rare earth ions. Application of the Judd–Ofelt theory to the absorption and fluorescence spectra allows complete characterization of the spectroscopic properties of the rare earth ions in ZBLAN glasses and their suitability for active laser devices. Thus, radiative properties of the rare earths can be theoretically calculated from the absorption spectra, and predictions of excited state absorption (ESA) effects between the ions can be made. Further, non-radiative, e.g., multiphonon, and other energy transfer transitions which can bear significant influence on the lasing properties can be included.

The objective of this work is to collect together and discuss the most significant theoretical and

experimental optical measurements of the rare earths which, to date, have not been comprehensively published for ZBLAN glasses. Particular emphasis has been laid on the results for Ho^{3+} and Er^{3+} .

2. Experimental

2.1. Glass preparation

A series of glasses was prepared of the mol% composition $52\text{ZrF}_4\text{--}19\text{BaF}_2\text{--}4\text{AlF}_3\text{--}20\text{NaF}\text{--}(5-x)\text{LaF}_3$, with x mol% of the rare earth ion fluoride. The values of x were: 3 mol% $\text{Pr}^{3+}/\text{Dy}^{3+}$; 4 mol% Tm^{3+} ; 0.1, 0.5 and 4 mol% Nd^{3+} and 0.1, 0.5, 1, 3 and 4 mol% $\text{Er}^{3+}/\text{Ho}^{3+}$. Only highly pure, dried fluorides were used for preparation of the glasses which were melted in platinum crucibles under dry nitrogen. After casting, the samples were annealed at T_g and subsequently polished with commercial media and a water-free lubricant.

2.2. Measurements

Absorption spectra were measured with a Cary 2300 double beam spectrometer over the range 0.2 to $3\text{ }\mu\text{m}$. The measured spectral absorptions,

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D , were corrected for reflection losses and normalized using the sample thickness, d (cm), and the dopant concentration, C (mol%), to give values of $\alpha = 10D/(dC)$ in dB/cm/mol%. The thus modified spectra were used for calculation of the Judd–Ofelt parameters, spontaneous emission transition probabilities, lifetimes and branching ratios, using the Judd–Ofelt theory as described previously [5].

Fluorescence lifetimes and intensity spectra, over the range 0.5–3 μm , were measured with a spectral radiometer consisting of a computer-controlled monochromator with exchangeable reflec-

tion-grating, a Si/PbS-detector, lock-in amplifier (also computer-controlled) and a digital storage oscilloscope. All the lines of an argon-ion laser were used to obtain fluorescence spectra by optical excitation of the rare earth ion absorption bands. The fluorescence spectra were corrected for the spectral characteristics of the spectrometer by calibration with a tungsten lamp. Lifetime measurements were made with the 488 nm argon ion line, in order to avoid parasitic ESA of the pump. The accuracy of the measured lifetimes is better than $\pm 3\%$. All measurements were carried out at room temperature.

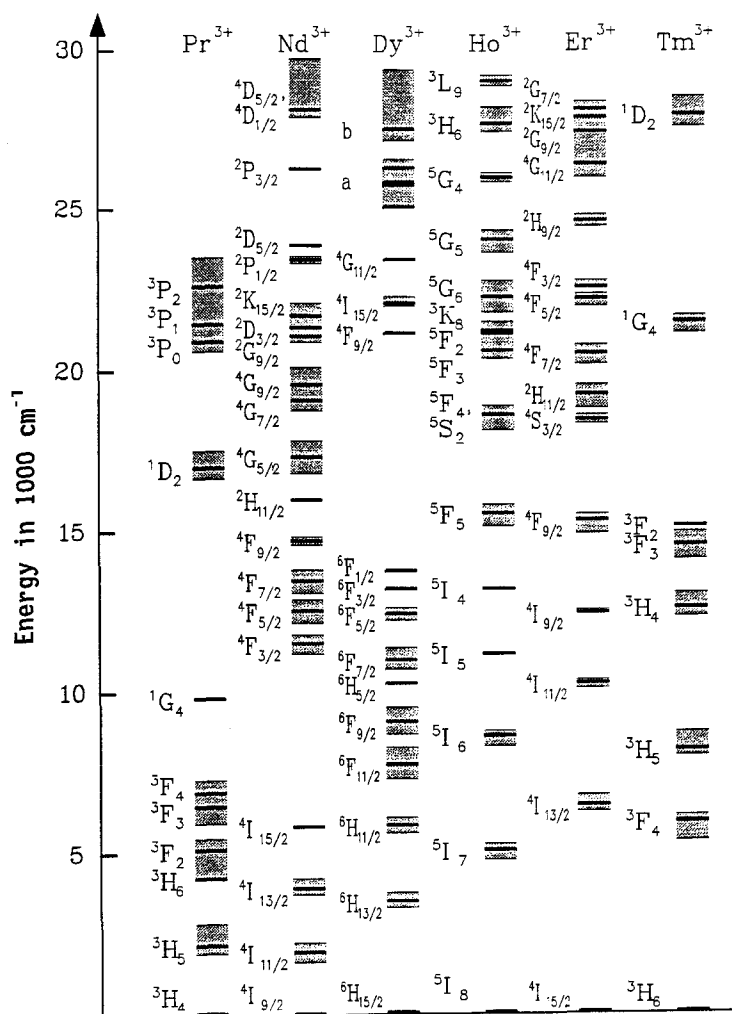


Fig. 1. Energy level diagram of selected rare earth ions in ZBLAN glasses.

Table 1
Judd–Ofelt parameters of selected rare earth ions in fluorozirconate glasses

Rare earth ions	Glass	Ref.	$\Omega_2 \times 10^{-22} \text{ cm}^2$	$\Omega_4 \times 10^{-22} \text{ cm}^2$	$\Omega_6 \times 10^{-22} \text{ cm}^2$	$\delta \times 10^{-8}$
Pr^{3+}	ZBLAN	here	84	479	913	9
	ZBLA	[9]	6	505	692	221
Nd^{3+}	ZBLAN	here	210	371	462	3.5
	ZBN	[10]	195	365	417	1.5
	ZBLA	[11]	110	380	553	–
Dy^{3+}	ZBLAN	here	186	142	237	2
	ZBLA	[12]	322	135	238	8
	ZBLALi	[13]	270	180	200	11
Ho^{3+}	ZBLAN	here	230	230	171	5
	ZBLA	[14]	228	208	173	23
Er^{3+}	ZBLAN	here	291	178	100	3
	ZBLAN	[15]	297	123	117	–
	ZBLA	[5]	254	139	96	14
Tm^{3+}	ZBLAN	here	270	159	109	5
	ZBLA	[16]	280	190	100	30

Table 2
Optical emission properties of selected transitions in Nd^{3+} -, Ho^{3+} -, Er^{3+} - and Tm^{3+} -doped ZBLAN glasses

Transition	λ (nm)	A (s^{-1})	β	$\Delta\lambda$ (nm)	$\sigma_p \times 10^{-20} \text{ cm}^2$	τ_c (ms)	τ_m (ms)	$\beta \cdot \eta$ (%)
<i>Neodymium</i> ³⁺								
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$	1320	227	0.10	56	0.74	0.44	0.46	10
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$	1050	1135	0.50	32	2.64	0.44	0.46	50
$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$	885	915	0.40	44	0.78	0.44	0.46	40
<i>Holmium</i> ³⁺								
$^5\text{I}_7 \rightarrow ^5\text{I}_8$	2030	79	1.00	145	0.56	12.65	12.01	95
$^5\text{I}_6 \rightarrow ^5\text{I}_7$	2850	21	0.09	88	0.96	5.87	3.50	6
$^5\text{I}_6 \rightarrow ^5\text{I}_8$	1149	150	0.91	48	0.47	5.87	3.50	5
$^5\text{F}_5 \rightarrow ^5\text{I}_8$	650	1536	0.78	34	0.86	0.50	0.29	45
$^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_5$	1355	59	0.02	42	0.28	0.34	0.30	2
$^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_6$	1010	189	0.06	29	0.40	0.34	0.30	5
$^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_7$	740	892	0.34	21	0.75	0.34	0.30	27
$^5\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8$	545	1794	0.61	24	0.39	0.34	0.30	54
<i>Erbium</i> ³⁺								
$^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$	1540	100	1.00	82	0.42	9.52	8.69	91
$^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$	2720	21	0.13	123	0.57	8.69	6.71	10
$^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$	980	86	0.87	38	0.13	8.69	6.71	67
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{9/2}$	1660	46	0.04	–	–	0.70	0.57	–
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{11/2}$	1131	25	0.02	–	–	0.70	0.57	–
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$	850	316	0.27	31	0.31	0.70	0.57	22
$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	540	770	0.67	–	–	0.70	0.57	–
<i>Thulium</i> ³⁺								
$^3\text{F}_4 \rightarrow ^3\text{H}_6$	1660	152	1.00	177	0.57	6.56	5.64	86
$^3\text{H}_4 \rightarrow ^3\text{H}_5$	2270	16	0.02	–	–	1.32	–	–
$^3\text{H}_4 \rightarrow ^3\text{F}_4$	1500	55	0.08	–	–	1.32	–	–
$^3\text{H}_4 \rightarrow ^3\text{H}_6$	805	665	0.90	36	0.46	1.32	–	–

3. Results

The measured absorption and fluorescence spectra are to be seen in ref. [6] and agree with the results in ref. [7]. An energy diagram for the trivalent rare earth ions, as calculated from the absorption spectra in ZBLAN glass, is shown in fig. 1. The shaded areas, representing absorptions greater than 0.5 dB/cm/mol%, indicate inhomogeneous broadening of the absorption bands. Beyond this arbitrary boundary, the absorption properties of the various bands are sufficiently broad that, in most cases, no exact correspondence of the pump wavelength and that of maximum absorption in the fibre laser/amplifier is necessary. This fact is particularly significant for the use of pump-ESA. The shaded areas are also helpful in the search for viable energy transfers between rare earth ions with equal or similar energy levels [8].

The Judd–Ofelt parameters calculated from the absorption spectra are given in table 1 for all the rare earth ions. The least-square fits agree well with the values found for similar zirconium fluoride glasses. The accuracy of the fit, and thus the accuracy of the Judd–Ofelt parameters obtained, is illustrated by the very small values of the rms deviation, δ , as defined in ref. [5]. The optical emission properties of the rare earth ions such as spontaneous emission probabilities, A , radiative lifetimes, τ , and branching ratios, β , can then be calculated from the Judd–Ofelt parameters. These data, along with the normalized fluorescence half-height widths, $\delta\lambda$, induced emission cross-sections, σ_p , measured lifetimes, τ_m , and the product $\beta \cdot \eta$ ($\eta = \tau_m/\tau_c$) are given in table 2 for selected Nd^{3+} , Ho^{3+} , Er^{3+} and Tm^{3+} transitions.

Multiphonon rates, W_{MP} , have been established as a function of the energy gap to the next lowest energy level, ΔE , by lifetime measurement of certain energy levels in both 0.1 mol% Ho^{3+} -doped and in 0.1 mol% Er^{3+} -doped ZBLAN fibres. Extraneous effects being no longer significant at these low dopant concentrations, using the values in table 2, multiphonon rates are given by $W_{\text{MP}} = \tau_m^{-1} - \tau_c^{-1}$.

Figure 2 shows a regression of the calculated

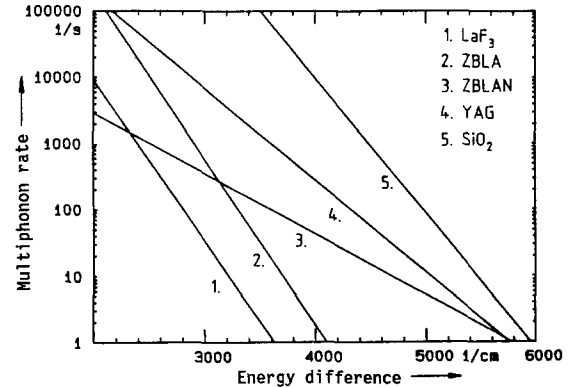


Fig. 2. Measured multiphonon rates as a function of ΔE for ZBLAN glass.

W_{MP} values to the empirical expression $W_{\text{MP}} = C \exp(-\alpha \Delta E)$ [5] confirming their exponential dependence on the energy gap, ΔE . Values for C and α were $1.99 \times 10^5 \text{ s}^{-1}$ and 0.0021 cm, respectively.

4. Discussion

It is not intended to consider the ions Nd^{3+} , Pr^{3+} and Dy^{3+} in great detail here. The results for Nd^{3+} are comparable to those in refs. [10] and [11] as was to be expected. For Pr^{3+} and Dy^{3+} , the radiative transitions in the IR of greatest interest are very strongly influenced by multiphonon transitions due to the large number of closely neighbouring energy levels. For Pr^{3+} , calculations show that transitions to lower lying levels are conceivable from the $^1\text{G}_4$ level at 3.4, 2.9, 2.1, 1.7 and 1.3 μm , and from the $^3\text{F}_3$ and $^3\text{H}_6$ levels at 2.3 μm , although they would be difficult to realise. The $^1\text{G}_4$ level is only weakly absorbing and is at present inaccessible to semiconductor lasers while the latter two levels are considerably weakened by multiphonon transitions, due to the energy gaps of less than 2500 cm^{-1} to the nearest lower levels. Although the $\text{Dy}^{3+6}\text{F}_{5/2}$ level is suitable for semiconductor-diode pumping at 800 nm, transitions between the lower levels are largely characterized by multiphonon transitions, such that only the three-level transitions from the

levels ${}^6\text{H}_{11}$ and ${}^6\text{H}_{13/2}$ at 1.7 and 2.8 μm may be of use.

The even spread of Ho^{3+} energy levels out to 20000 cm^{-1} produces a wealth of radiative transitions up to wavelengths of 3 μm . The most interesting transitions are those from the ${}^5\text{I}_7$ level at 2.02 μm , the ${}^5\text{I}_6$ level at 1.15 and 2.85 μm and the neighbouring, thermally coupled ${}^5\text{S}_2$ and ${}^5\text{F}_4$ levels at 0.55, 0.74, 1.0 and 1.35 μm . Since lifetimes decrease with increasing energy, all Ho^{3+} 4-level laser transitions will in principle exhibit self-saturation during laser operation. Despite the considerably longer lifetime (11 ms) of the ${}^5\text{I}_7$ level in comparison to the higher levels, CW operation of Ho^{3+} -doped fibre-lasers can be rendered possible by efficient pump-ESA at 530, 640 and 740 nm [4], whereby the lower level for the laser transition is the ${}^5\text{I}_7$ level. Excitation at 530 nm gives rise to very strong coupling between the ${}^5\text{I}_7$ and ${}^5\text{G}_5$ levels, with an oscillator strength $f_{\text{esa}} = 280 \times 10^{-8}$, which is quite as strong as the GSA to the ${}^5\text{F}_4$ level with $f_{\text{gsa}} = 300 \times 10^{-8}$. At 640 nm, the absorptions from the excited level are equally as significant up to the ${}^5\text{F}_3$ level with $f_{\text{esa}} = 153 \times 10^{-8}$ and to the ${}^5\text{F}_5$ level with $f_{\text{gsa}} = 275 \times 10^{-8}$. Since ESA and GSA are equally as strong at both wavelengths, they should be particularly suitable for CW operation of fibre lasers, with a laser transition to the ${}^5\text{I}_7$ level. At a wavelength of 750 nm, however, with very weak absorption from the ${}^5\text{I}_7$ ground state to the ${}^5\text{F}_4$ level and $f_{\text{gsa}} = 2 \times 10^{-8}$, coupling between the excited state and the ${}^5\text{F}_4$ level with $f_{\text{esa}} = 70 \times 10^{-8}$ is considerably less.

Results showed no particular change in the lifetimes of the ${}^5\text{I}_6$ and ${}^5\text{I}_7$ levels with Ho^{3+} concentration up to 4 mol% in ZBLAN glasses. However, for the coupled ${}^5\text{F}_4/{}^5\text{S}_2$ levels, a drastic decrease can already be seen at 0.5 mol%. This decrease is caused by two conceivable cross-relaxation processes between neighbouring Ho^{3+} ions, due to two simultaneous non-radiative transitions: ${}^5\text{F}_4/{}^5\text{S}_2 \rightarrow {}^5\text{I}_4$ and ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$ or ${}^5\text{F}_4/{}^5\text{S}_2 \rightarrow {}^5\text{I}_7$ and ${}^5\text{I}_8 \rightarrow {}^5\text{I}_4$.

The few, equally distributed Er^{3+} energy levels allow a series of fluorescence to be seen. The most important of these are from the ${}^4\text{I}_{13/2}$ at 1.5 μm , from the ${}^4\text{I}_{11/2}$ at 1.0 and 2.7 μm and from

the ${}^4\text{S}_{3/2}$ (which is thermally coupled to the ${}^2\text{H}_{11}$) at 0.54, 0.85, 1.01 and 1.35 μm . For all of these 4-level transitions, the lifetimes of the destination levels are greater than those of the initial levels as for Ho^{3+} , leading, in principle, to self-saturation. Continuous operation can be realised for the ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ transition at 2.7 μm by ESA of the pump at 640/800 nm [4]. At 640 nm there is very strong coupling between the ${}^4\text{I}_{13/2}$ and ${}^4\text{F}_{5/2}$ levels with an oscillator strength $f_{\text{esa}} = 108 \times 10^{-8}$, and weaker coupling to the ${}^2\text{H}_{11}$ level at 790 nm ($f_{\text{esa}} = 30 \times 10^{-8}$) and to the ${}^4\text{S}_{3/2}$ at 836 nm ($f_{\text{esa}} = 42 \times 10^{-8}$). The latter pump wavelengths should also be equally suitable for optical amplification in the range 2.65–2.8 μm due to ESA of the pump. Amplification using the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition at 1.55 μm can only realistically be achieved with direct excitation of the initial level, since there is no effective ESA of the pump at around 1.5 μm .

No particular change in the lifetime of the ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$ levels was observed with Er^{3+} concentration up to 4 mol% in the ZBLAN glasses whereas a drastic decrease could already be seen for the ${}^4\text{S}_{3/2}$ level at 0.5 mol%. This decrease is caused by two conceivable cross-relaxation processes between neighbouring Er^{3+} ions, due to two simultaneous non-radiative transitions: ${}^4\text{S}_{3/2} \rightarrow {}^5\text{I}_{9/2}$ and ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{13/2}$ or ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ and ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{9/2}$.

Due to the widely spread energy level structure of Tm^{3+} , and the consequently low multiphonon transition losses, virtually all of the transitions are radiative and have already given rise to fibre lasers [17,18]. Transitions from the ${}^3\text{H}_4$ level at 0.8, 1.5 and 2.3 μm , and from the ${}^3\text{F}_4$ level at 1.8 μm are particularly interesting for practical applications since they can be brought about by excitation of the ${}^3\text{H}_4$ level by semiconductor laser diode at 790 nm. Further, due to the close proximity of the long-lived ${}^3\text{F}_4$ level, self-saturation of the ${}^3\text{H}_4 \rightarrow {}^3\text{H}_5$ transition at 2.3 μm should be avoidable by decreasing the pump-wavelength, since there is very strong coupling between the ${}^3\text{H}_5$ and ${}^1\text{G}_4$ levels with an oscillator strength of $f_{\text{esa}} = 134 \times 10^{-8}$ and therefore efficient ESA of the pump at 750 nm. An optimum wavelength for the GSA and ESA must exist in

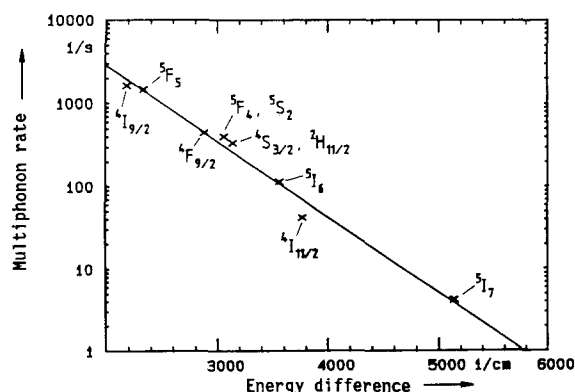


Fig. 3. Multiphonon emission rates of ZBLAN glass and other host materials as a function of the energy gap to the next lower level.

the range 750 to 790 nm. Similarly, by pumping at this optimum wavelength, use of the $^1G_4 \rightarrow ^3F_4$ (644 nm) and $^1G_4 \rightarrow ^3H_6$ (480 nm) transitions must be possible for upconversion lasers which have been realised to date by pumping at 647 nm, starting from the Tm^{3+} 1G_4 and 1D_2 levels [18].

Figure 3 gives a comparison of the multiphonon rates for ZBLAN glasses (300 K) and other host materials as a function of the energy gap. In ZBLAN glasses (300 K) the multiphonon rates for energy gaps below 3200 cm^{-1} (fig. 2) are less than those in ZBLA glasses (77 K). These results confirm the suitability of ZBLAN glasses, with respect to multiphonon losses with the rare earth ions, as host material for lasers operating in the infrared.

It should be emphasized that the use of very low concentrations is necessary for the measurement of multiphonon rates since, particularly in the case of the Er^{3+} $^4S_{3/2}$ and $^4F_{9/2}$ and the Ho^{3+} 5S_2 , 5F_4 and 5F_5 levels, lifetimes can be reduced by up to 20% by extraneous energy transfer mechanisms.

5. Conclusions

The radiative and non-radiative properties were investigated for the well known ZBLAN glass composition doped with the rare earth elements Pr^{3+} , Nd^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Tm^{3+}

at levels between 0.1 and 4 mol%. The optical absorption and fluorescence spectra of the samples and also the lifetimes for some transitions were measured. The calculated Judd-Ofelt parameters agree well with previous work and show a high degree of accuracy in their rms deviation from the fit to results. The Judd-Ofelt parameters were used in calculation of all the significant optical emission and ESA properties of the ions of greatest interest. The multiphonon rates below 3200 cm^{-1} are found to be less in ZBLAN than in other host materials (ZBLA, SiO_2 YAG).

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