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Optical properties of Nd^{3+}-doped fluorophosphate glasses

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Abstract

Optical absorption spectra of Nd^{3+}-doped fluorophosphate glasses of the type $75NaPO_3$–24AF–$1NdF_3$ (A=Li, Na, K) and of the type $75NaPO_3$–$24AF_2$–$1NdF_3$ (A=Ca, Sr, Ba, Zn, Cd) have been recorded. The dipole strengths are parameterised in terms of three phenomenological Judd–Ofelt intensity parameters Ω_λ (λ=2, 4 and 6). With the knowledge of these intensity parameters, the probability for spontaneous emission, the branching ratios and the radiative lifetime are calculated. The relation between the spectral intensities and the glass composition is discussed. The optical properties of the fluorophosphate glasses are compared with those of phosphate and fluoride glasses. It is shown that the choice of the cation only has a minor influence on the spectral intensities. The spectral behaviour of the fluorophosphate glasses is intermediate between the spectral behaviour of pure phosphate and fluoride glasses.

Keywords: Rare earths; Lanthanides; Neodymium; Optical spectroscopy; Judd–Ofelt theory; Intensities

1. Introduction

Fluorophosphate glasses have been the subject of several spectroscopic investigations, due to their potential as laser host matrixes [1–4]. Characteristic properties of these glasses are a low refractive index and a low dispersion [5]. The majority of these glasses contain $Al(PO_3)_3$ or $Ba(PO_3)_2$ as the phosphate component. These compounds are more stable to moisture than other metaphosphates. Phosphate glasses based on the alkali metaphosphates are hygroscopic, but addition of fluorides increases the resistance to water [6]. Numerous $NaPO_3$–BaF_2 based fluorophosphate glasses are known, either with a high content of transition metal ions [6] or rare-earth ions [7,8].

In this paper, we report a spectroscopic study of trivalent neodymium ions in fluorophosphate glasses of the type $75NaPO_3$–24AF–$1NdF_3$ (A=Li, Na, K) and of the type $75NaPO_3$–$24AF_2$–$1NdF_3$ (A=Ca, Sr, Ba, Zn, Cd). The aim of the study was to investigate the influence of the chemical composition on the spectral intensities in the fluorophosphate glass matrix. The spectral properties are compared with those of phosphate and fluoride glasses.

2. Experimental details

Sodium metaphosphate ($NaPO_3$), CaF_2 and SrF_2 were purchased from Prolabo, BaF_2 and MgF_2 from Aldrich, LiF, NaF and KF from Merck, CdF_2 from Fluka and ZnF_2 from Riedel-de-Haën. Neodymium fluoride was synthesised from the corresponding oxide. Neodymium oxide (3N) was obtained from Rhône–Poulenc. The transformation of the oxide into the fluoride is done by mixing the neodymium oxide with an excess (2× the stoichiometric amount) of ammonium bifluoride (NH_4F,HF) and heating the mixture in a vitreous carbon crucible for 3 h. During this fluorination step a complex fluoride $(NH_4)_3NdF_6$ is formed [9]. This complex fluoride is subsequently decomposed at 450°C. The decomposition step lasts for 4 h.

The glass samples were prepared by melting the required amounts of sodium metaphosphate and the fluoride compounds in a platinum tube at a temperature of ca. 900°C. After melting, heating was continued for 15 min to homogenise the melt. Then, the melt was cast in a brass mould (preheated to 250–300°C). In order to remove strain, the glass samples were annealed for 4 h in an oven at 270°C. Finally, the glass samples were cut and polished. The glasses show the typical blue–violet color of the Nd^{3+} ion [10]. The fluorophosphate glasses containing the alkali fluorides and to a lesser extent those containing ZnF_2 and

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CdF_2 are hygroscopic. They give a sticky feeling when touched.

The density of the glass samples were determined by Archimedes' method, using CCl_4 as the immersion liquid. The refraction index n_D was measured on an Abbé refractometer (ATAGO 3T). The optical path length was measured to the nearest 0.01 cm. Absorption spectra were recorded at room temperature on a Shimadzu UV-3100 spectrophotometer.

3. Theoretical background

The transitions observed in the absorption spectra of trivalent lanthanide ions are intraconfigurational f–f transitions. The majority of these transitions are induced electric dipole transitions, although a few magnetic dipole transitions are known. The intensities of the transitions can be characterised by the dipole strength D:

$$D = \frac{1}{108.9 \times C \times d} \int \frac{A(\bar{\nu})}{\bar{\nu}} \mathrm{d}\bar{\nu}, \tag{1}$$

where C is the concentration of the neodymium ion (mol l^{-1}), d is the optical path length (cm), A is the absorbance and $\bar{\nu}$ is the wavenumber (cm^{-1}). The dipole strength is expressed in D^2 (Debye^2). According to the Judd–Ofelt theory [11,12], the intensity of induced electric dipole transitions can be described in terms of three phenomenological intensity parameters Ω_λ ($\lambda = 2$, 4 and 6):

$$D = \frac{10^{36}}{2J+1} \frac{(n^2+2)^2}{9n} e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \left\langle J \| U^{(\lambda)} \| J' \right\rangle \right|^2. \tag{2}$$

The factor 10^{36} converts D^2 units into esu cm. The elementary charge e is 4.803×10^{-10} esu. The degeneracy of the ground state is equal to $2J+1$ (i.e. 10 for Nd^{3+}). The factor $\frac{(n^2+2)^2}{9n}$ takes into account that the neodymium ion is not in a vacuum, but in a dielectric medium (n is the refractive index of the glass). Finally, the $\left\langle J \| U^{(\lambda)} \| J' \right\rangle$ are reduced matrix elements. The Ω_λ parameters can be determined by a standard-least squares fitting method.

The Judd–Ofelt intensity parameters can be used to calculate several radiative properties of the lanthanide ions. The spontaneous emission coefficient (also called probability for spontaneous emission or the Einstein coefficient for spontaneous emission) $A(\Psi J, \Psi' J')$ is given by the expression:

$$A(\Psi J, \Psi' J') = \frac{64\pi^4 \bar{\nu}^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} D^{\mathrm{ED}}_{\mathrm{calc}} + n^3 D^{\mathrm{MD}}_{\mathrm{calc}} \right]. \tag{3}$$

As for absorption spectra, it is assumed implicitly that all the crystal-field components of the initial state are equally populated. If the lifetime of the state is long compared to the rate at which it is populated in the excitation process, thermal equilibrium at the temperature of the system can be achieved before emission takes place. Because an excited state ΨJ is relaxed to several lower lying states $\Psi' J'$, the radiative branching ratio β_R is defined:

$$\beta_R(\Psi J, \Psi' J') = \frac{A(\Psi J, \Psi' J')}{\sum_{\Psi' J'} A(\Psi J, \Psi' J')}. \tag{4}$$

The branching ratios can be used to predict the relative intensities of all emission lines originating from a given excited state. The experimental branching ratios can be found from the relative areas of the emission lines. Once all emission probabilities that depopulate an initial level $^{2S+1}L_J$ have been calculated, they can be used to determine how fast that level is depopulated. This rate is given by the radiative lifetime $\tau_R(\Psi J)$:

$$\tau_R(\Psi J) = \frac{1}{\sum_{\Psi' J'} A(\Psi J, \Psi' J')}. \tag{5}$$

Stronger emission probabilities and more transitions from a level lead to faster decay and shorter lifetimes.

4. Results and discussion

The absorption spectra for the different glass compositions were recorded at room temperature. Room temperature spectra are necessary for application of the Judd–Ofelt theory, because this theoretical model assumes that all crystal-field levels of the ground state are equally populated. This condition is fairly well fulfilled at room temperature, if the crystal-field splitting is not too large (a few hundred cm^{-1}). The transitions in the absorption spectrum were assigned by comparing with the values reported by Carnall et al. for LaF_3:Nd^{3+} [13]. From the spectra, the experimental dipole strengths were derived and these were used to determine the Judd–Ofelt intensity parameters Ω_λ ($\lambda = 2$, 4 and 6). The matrix elements in the fitting procedure were those given by Carnall et al. for Nd^{3+} in aqueous solution [14]. In the case of overlapping transitions, the matrix elements of the corresponding transitions were summed (see Table 1). All the transitions observed in the spectrum are induced electric dipole transitions. No magnetic dipole contributions were taken into account. The spectral assignments, the experimental and calculated dipole strengths for Nd^{3+} in the glass matrix $75NaPO_3$–$24CaF_2$–$1NdF_3$, are given in Table 2. The intensity results for the other glasses are analogous, so that we restrict ourselves to report only the Ω_λ parameters (Table 3). For the sake of comparison, not only the intensity parameters for fluorophosphate glasses are given in Table 3, but also parameter sets for two phosphate

Table 1
Matrix elements used for the Judd–Ofelt parameterisation of the spectral intensities in the absorption spectra of Nd^{3+} doped fluorophosphate glasses

Transition $\leftarrow {}^4I_{9/2}$	$\lvert\langle J\lVert U^{(2)}\rVert J'\rangle\rvert^2$	$\lvert\langle J\lVert U^{(4)}\rVert J'\rangle\rvert^2$	$\lvert\langle J\lVert U^{(6)}\rVert J'\rangle\rvert^2$
${}^4F_{3/2}$	0	0.2293	0.0549
${}^2H_{9/2}$,${}^4F_{5/2}$	0.0102	0.2451	0.5124
${}^4F_{7/2}$,${}^4S_{3/2}$	0.0010	0.0449	0.6597
${}^4F_{9/2}$	0.0009	0.0092	0.0417
${}^2H_{11/2}$	0.001	0.0027	0.0104
${}^4G_{5/2}$,${}^2G_{7/2}$	0.9736	0.5941	0.0673
${}^4G_{7/2}$,${}^2K_{13/2}$,${}^4G_{9/2}$	0.0664	0.2180	0.1271
${}^2K_{15/2}$,${}^4G_{11/2}$,${}^2D_{3/2}$,${}^2G_{9/2}$	0.0010	0.0441	0.0364
${}^2P_{1/2}$	0	0.0367	0
${}^2I_{11/2}$,${}^4D_{1/2}$,${}^4D_{3/2}$,${}^4D_{5/2}$	0.0050	0.5257	0.0479

glasses and two fluoride glasses. With the aid of the parameter sets in Table 3, the radiative properties (Einstein coefficients A, branching ratios β_R and radiative lifetimes τ_R) for the glasses have been calculated. These results are summarised in Table 4. The absorption spectrum of Nd^{3+} in the $75NaPO_3$–$24CaF_2$–$1NdF_3$ glass is given in Fig. 1.

From Table 2 it is clear that the Judd–Ofelt theory can provide a fairly good description for the spectral transitions of Nd^{3+} in the glass matrices. The largest deviations between theory and experiment are found for the weak transitions. This is partially due to the larger uncertainty on the determination of the experimental dipole strength.

If we compare the Judd–Ofelt parameters for the different Nd^{3+} doped fluorophosphate glasses, no large variations are found. Moreover, if we take the errors on the parameters into account, it is acceptable to say that the Ω_4 and the Ω_6 parameters are the same for all fluorophosphate glasses. The choice of the cation (Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+} or Cd^{2+}) has virtually no influence on these parameters. Even the more sensitive Ω_2 parameter varies only relatively slightly. The Ω_2 parameter is larger in glasses containing alkali metal fluorides than in glasses containing fluorides of the earth alkaline metals. The ZnF_2- and CdF_2-containing glasses have a Ω_2 parameter that is closer to the values for the alkaline metals than for the earth alkaline metals, although one would expect that the reverse were true. The values of Ω_4 and the Ω_6 parameters of the fluorophosphate glasses are close to the value for the phosphate glass $99NaPO_3$–$1NdF_3$. Only the Ω_2 parameter is significantly larger for the phosphate glass than for the

Table 2
Measured and calculated dipole strengths for the transitions in the absorption spectrum of the glass matrix $75NaPO_3$–$24CaF_2$–$1NdF_3$[a]

Transition $\leftarrow {}^4I_{9/2}$	$\bar{\nu}$ (cm^{-1})	D_{exp} (10^{-6} Debye^2)	D_{calc} (10^{-6} Debye^2)	$D_{exp}-D_{calc}$ (10^{-6} Debye^2)	D_{calc}/D_{exp}
${}^4F_{3/2}$	11578	375	383	−8	1.02
${}^2H_{9/2}$,${}^4F_{5/2}$	12486	1250	1186	64	0.95
${}^4F_{7/2}$,${}^4S_{3/2}$	13406	1108	1173	−64	1.06
${}^4F_{9/2}$	14636	73	82	−9	1.12
${}^2H_{11/2}$	15863	45	21	24	0.47
${}^4G_{5/2}$,${}^2G_{7/2}$	17209	1681	1687	−6	1.00
${}^4G_{7/2}$,${}^2K_{13/2}$,${}^4G_{9/2}$	19033	660	547	113	0.83
${}^2K_{15/2}$,${}^4G_{11/2}$,${}^2D_{3/2}$,${}^2G_{9/2}$	21255	179	118	61	0.66
${}^2P_{1/2}$	23333	35	46	−11	1.31
${}^2I_{11/2}$,${}^4D_{1/2}$,${}^4D_{3/2}$,${}^4D_{5/2}$	28543	691	751	−60	1.09

[a] The Judd–Ofelt parameters used for the intensity calculation are: $\Omega_2=(2.78\pm0.31)\cdot10^{-20}$ cm^2, $\Omega_4=(4.16\pm0.36)\cdot10^{-20}$ cm^2 and $\Omega_6=(5.56\pm0.24)\cdot10^{-20}$ cm^2. The r.m.s. value is $65\cdot10^{-6}$ Debye^2.

Table 3
Judd–Ofelt intensity parameters of neodymium-doped fluorophosphate, phosphate and fluoride glasses

Glass composition	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 ($10^{-20}$$cm^2$)
$75NaPO_3$–$24LiF$–$1NdF_3$	3.44±0.36	4.14±0.42	6.28±0.32
$75NaPO_3$–$24NaF$–$1NdF_3$	3.19±0.29	3.73±0.34	5.55±0.26
$75NaPO_3$–$24KF$–$1NdF_3$	3.61±0.30	3.81±0.35	5.83±0.27
$75NaPO_3$–$24CaF_2$–$1NdF_3$	2.78±0.31	4.16±0.36	5.56±0.24
$75NaPO_3$–$24SrF_2$–$1NdF_3$	2.39±0.34	4.02±0.40	6.10±0.30
$75NaPO_3$–$24BaF_2$–$1NdF_3$	2.41±0.28	3.27±0.32	5.19±0.25
$75NaPO_3$–$24ZnF_2$–$1NdF_3$	3.75±0.40	4.05±0.47	5.99±0.36
$75NaPO_3$–$24CdF_2$–$1NdF_3$	3.19±0.27	3.88±0.31	5.73±0.24
$99NaPO_3$–$1NdF_3$	4.52±0.39	3.94±0.45	5.93±0.34
$75NaPO_3$–$24.5ZnO$–$0.5Nd_2O_3$	3.76±0.25	3.27±0.29	5.23±0.22
$53ZrF_4$–$30BaF_2$–$3LaF_3$–$3AlF_3$–$10NaF$–$1NdF_3$ (ZBLAN:Nd^{3+})	1.95±0.25	2.54±0.29	3.92±0.22
$23ZrF_4$–$15AlF_3$–$9YF_3$–$12SrF_2$–$15BaF_2$–$25ZnF_2$–$1NdF_3$	1.38±0.22	2.58±0.25	3.86±0.19

Table 4
Calculated radiative properties of Nd^{3+} in fluorophosphate, phosphate and fluoride glasses[a]

Glass	Transition ${}^4F_{3/2}\rightarrow$	A (s^{-1})	β_R	ΣA (s^{-1})	τ_R (μs)
$75NaPO_3$–24LiF–$1NdF_3$	${}^4I_{15/2}$	15	0.005	2711	369
	${}^4I_{13/2}$	291	0.107		
	${}^4I_{11/2}$	1410	0.520		
	${}^4I_{9/2}$	994	0.366		
$75NaPO_3$–24NaF–$1NdF_3$	${}^4I_{15/2}$	16	0.005	2890	346
	${}^4I_{13/2}$	308	0.107		
	${}^4I_{11/2}$	1499	0.518		
	${}^4I_{9/2}$	1067	0.369		
$75NaPO_3$–24KF–$1NdF_3$	${}^4I_{15/2}$	16	0.005	2819	355
	${}^4I_{13/2}$	304	0.108		
	${}^4I_{11/2}$	1469	0.521		
	${}^4I_{9/2}$	1030	0.365		
$75NaPO_3$–$24CaF_2$–$1NdF_3$	${}^4I_{15/2}$	13	0.005	2552	392
	${}^4I_{13/2}$	261	0.102		
	${}^4I_{11/2}$	1298	0.508		
	${}^4I_{9/2}$	980	0.384		
$75NaPO_3$–$24ZnF_2$–$1NdF_3$	${}^4I_{15/2}$	16	0.005	2905	344
	${}^4I_{13/2}$	309	0.106		
	${}^4I_{11/2}$	1505	0.518		
	${}^4I_{9/2}$	1075	0.370		
$75NaPO_3$–$24SrF_2$–$1NdF_3$	${}^4I_{15/2}$	15	0.005	2699	370
	${}^4I_{13/2}$	290	0.107		
	${}^4I_{11/2}$	1405	0.520		
	${}^4I_{9/2}$	989	0.366		
$75NaPO_3$–$24CdF_2$–$1NdF_3$	${}^4I_{15/2}$	15	0.005	2701	370
	${}^4I_{13/2}$	287	0.106		
	${}^4I_{11/2}$	1399	0.518		
	${}^4I_{9/2}$	1000	0.370		
$75NaPO_3$–$24BaF_2$–$1NdF_3$	${}^4I_{15/2}$	13	0.005	2353	425
	${}^4I_{13/2}$	257	0.109		
	${}^4I_{11/2}$	1234	0.524		
	${}^4I_{9/2}$	848	0.360		
$99NaPO_3$–$1NdF_3$	${}^4I_{15/2}$	16	0.005	2893	346
	${}^4I_{13/2}$	310	0.107		
	${}^4I_{11/2}$	1503	0.520		
	${}^4I_{9/2}$	1063	0.368		
$75NaPO_3$–24.5ZnO–$0.5Nd_2O_3$	${}^4I_{15/2}$	14	0.005	2437	410
	${}^4I_{13/2}$	267	0.110		
	${}^4I_{11/2}$	1280	0.525		
	${}^4I_{9/2}$	876	0.360		
$53ZrF_4$–$30BaF_2$–$3LaF_3$–$3AlF_3$–10NaF–$1NdF_3$ (ZBLAN:Nd^{3+})	${}^4I_{15/2}$	9.9	0.005	1781	562
	${}^4I_{13/2}$	193	0.108		
	${}^4I_{11/2}$	930	0.522		
	${}^4I_{9/2}$	649	0.364		
$23ZrF_4$–$15AlF_3$–$9YF_3$–$12SrF_2$–$15BaF_2$–$25ZnF_2$–$1NdF_3$	${}^4I_{15/2}$	9.6	0.005	1737	576
	${}^4I_{13/2}$	186	0.106		
	${}^4I_{11/2}$	902	0.519		
	${}^4I_{9/2}$	640	0.368		

[a] Calculation was performed with the parameter sets given in Table 3.

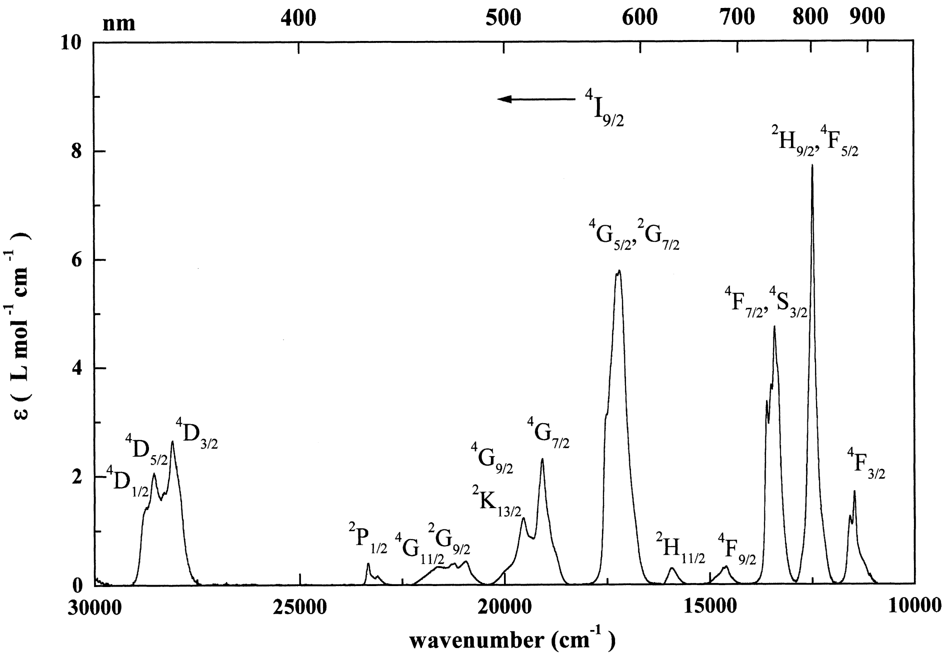

Fig. 1. Absorption spectrum and spectral assignments of Nd^{3+} in $75NaPO_3$–$24CaF_2$–$1NdF_3$ glass at room temperature.

fluorophosphate glasses. On the other hand, fluoride glasses show intensity parameters which are smaller than for fluorophosphate and phosphate glasses. The resemblance of the absorption spectra of the different glass compositions is illustrated in Fig. 2. It can be expected that the spectroscopic properties of the fluorophosphate glasses are intermediate between the spectroscopic properties of phosphate and fluoride glasses. Since both PO_4^{3-} and F^- ions are hard bases and can coordinate the hard acid Nd^{3+}, a mixed anion coordination is expected for Nd^{3+} in fluoro-

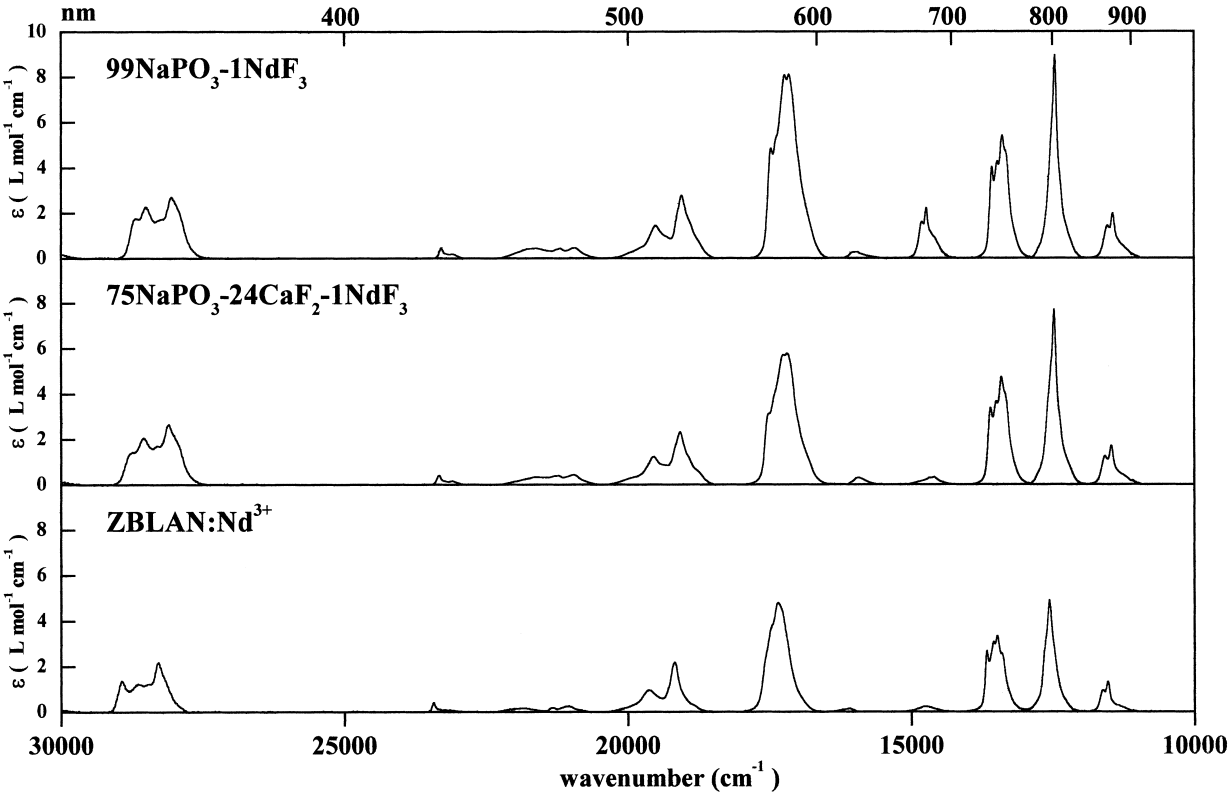

Fig. 2. Absorption spectra of $99NaPO_3$–$1NdF_3$, $75NaPO_3$–$24CaF_2$–$1NdF_3$ and ZBLAN:Nd^{3+} glasses at room temperature.

phosphate glasses [15,16]. Because of the larger molar fraction of phosphate ions in comparison with the fluoride ions, the spectroscopic properties tend to be closer to those of the phosphates. The trend of the parameter values is $\Omega_2 < \Omega_4 < \Omega_6$ for all the fluorophosphate glasses. The same trend is found for the fluoride glasses, whereas the trend is $\Omega_4 < \Omega_2 < \Omega_6$ for the phosphate glasses.

5. Conclusions

The optical absorption spectra and the Judd–Ofelt analysis of the spectral intensities of Nd^{3+}-doped fluorophosphate glasses of the type $75NaPO_3$–24AF–$1NdF_3$ (A = Li, Na, K) and of the type $75NaPO_3$–$24AF_2$–$1NdF_3$ (A = Ca, Sr, Ba, Zn, Cd) shows that the choice of the cation has only a minor influence on the spectral intensities. The spectral behaviour of the fluorophosphate glasses is intermediate between the spectral behaviour of pure phosphate and fluoride glasses. An increase of the intensity of the hypersensitive transition $^4G_{5/2},^2G_{7/2} \leftarrow ^4I_{9/2}$ is observed in the order, fluoride glasses < fluorophosphate glasses < phosphate glasses. For the other transitions, the intensities of Nd^{3+} in the fluorophosphate glass are close to that in the phosphate glass. The intensities in the fluoride glasses are considerably weaker.

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References

[1] S.E. Stokowski, R.A. Saroyan, M.J. Weber, Nd-Doped Laser Glass Spectroscopic and Physical Properties, M-095, Rev. 2, Vols. 1 and 2, Lawrence Livermore National Laboratory, Livermore CA, 1981.
[2] S.E. Stokowski, W.E. Martin, S.M. Yarema, J. Non-Cryst. Solids 40 (1980) 48.
[3] R. Balda, J. Fernandez, A. de Pablos, J.M. Fdez-Navarro, M.A. Arriandiaga, Phys. Rev. B 53 (1996) 5181.
[4] R. Balda, J. Fernandez, A. de Pablos, J. Phys. IV C4 (1994) 509.
[5] W. Jahn, Glasstechn. Ber. 34 (1961) 107.
[6] M. Matecki, M. Poulain, J. Non-Cryst. Solids 56 (1983) 111.
[7] M. Matecki, S. Jordery, J. Lucas, J. Mater. Sci. Lett. 11 (1992) 1431.
[8] M. Matecki, N. Duhamel, J. Lucas, J. Non-Cryst. Solids 184 (1995) 273.
[9] M. Poulain, in: I.D. Aggarwal, G. Lu (Eds.) Fluoride Glass Fiber Optics, Academic Press, San Diego, 1991.
[10] K. Binnemans, C. Görller-Walrand, Chem. Phys. Lett. 235 (1995) 163.
[11] B.R. Judd, Phys. Rev. 127 (1962) 750.
[12] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[13] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3, ANL-88-8 Report, Chemistry Division, Argonne National Laboratory, Argonne, IL, 1988.
[14] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4424.
[15] M.J. Weber, D.C. Ziegler, C.A. Angell, J. Appl. Phys. 53 (1982) 4344.
[16] R.C. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.