Spectra of Zirconium Barium Fluoride Glass Containing Octahedrally Coordinated Chromium(III) and Nickel(II), or Mixtures of Manganese(II) and Neodymium(III)**

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Abstract: The absorption spectra of chromium(III) and nickel(II) on octahedral sites in a zirconium barium fluoride glass are analyzed, and compared with vitreous and crystalline mixed oxides, suggesting slightly longer Cr–F and Ni–F distances than in crystalline fluorides. Luminescence and energy transfer between manganese(II) and neodymium(III) in ZBLA glass are studied, indicating the potential for new laser materials.

Conventional glasses are usually mixed oxides of boron(III), silicon(IV), or phosphorus(V) together with oxides of several metallic elements. When spectroscopic properties of lanthanoide narrow-line absorption and luminescence became of interest for lasers[1,2] the glasses containing germanium(IV) or tellurium(IV) oxides were shown to be more favorable from the point of view of less extensive non-radiative de-excitation. Nevertheless, terawatt lasers (intended for inducing thermonuclear fusion of deuterium and tritium) such as SHIVA operating since 1979, and NOVA since 1984, at Livermore, California[3,4] are based on silicate glasses doped with neodymium(III).

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Mixed fluorides are experimentally more difficult to prepare and handle, and there are known only a few cases of composition ranges which remain vitreous. They tend to be much narrower than those typical for mixed oxides. The first successful category of fluoride glasses was revealed[5,6] at the Université de Rennes, 1975, essentially consisting of zirconium(IV) and barium(II) fluoride, together with smaller amounts of fluorides of trivalent elements (colloquially called ZBLA glass). Another important category of fluoride glasses containing zinc(II) (or manganese), gallium(III), and lead(II) fluorides was first prepared[7] at the Université du Maine, Le Mans. The absorption spectra and luminescence of $4f^{11}$ erbium(III) and $3d^5$ manganese(II), and the mutual energy transfer between excited states of these two species, were studied[8]. In ZBLA glass, the luminescence of $4f^2$ praseodymium(III)[9], $4f^6$ europium(III)[10], $4f^{10}$ holmium(III)[11,12], and erbium(III)[13] occurs from several more excited J-levels than usual, because the lower limit (still allowing perceptible luminescence) for the energy gap between the emitting J-level and the closest lower-lying J-level is 2000 cm^{-1} (0.24 eV), some 2 to 4 times smaller than in nearly all other glasses and crystals. It may be noted that this rich emission spectrum (proceeding to several low J-levels besides the ground state) is also observed at room temperature, without need for cryogenic conditions.

The purpose of this note is to report on an investigation of $3d^3$ chromium(III) and $3d^8$ nickel(II) in ZBLA glass, and the energy transfer between $3d^5$ manganese(II) and $4f^3$ neodymium(III). It has been demonstrated[7] from the absorption spectra of Cr^{III} and Ni^{II} in zinc gallium lead fluoride glass that nearly all (or all) of the colored species is very close to (cubic) octahedral symmetry, since small amounts on sites with lower symmetry would have relatively much stronger absorption bands. In view of the feasible substitution for Zn^{II} and Ga^{III} with comparable ionic radii, this result was not surprising, as one would also extrapolate from the fact that almost all Cr^{III}, and the large majority of all paramagnetic Ni^{II}, complexes in solution, as well as solid compounds, show the coordination number $N = 6$ with octahedral symmetry. However, it is not perfectly trivial that Cr^{III} and Ni^{II} in ZBLA glass (known from Raman spectra[14] to have more complicated coordination behavior) should be octahedral to a high approximation. On the other hand, there is some evidence from the atypical absorption spectrum[8] of Mn^{II} in manganese gallium lead fluoride glass that a mixture of N values, say 6 and 7, may occur. The sextet ground state of Mn^{II} does not exhibit preference for any site symmetry, as do the quartet ground state of Cr^{III} and the triplet ground state of Ni^{II} which both minimize the anti-bonding character of the 3d electrons[15,16]. In 24 different phosphate glasses containing varying amounts of Mn^{II}, long lifetimes (8 to 13 ms) of the lowest quartet state were observed [17]. Though most of the emission probably originates in octahedral sites, a gradual red-shift as a function of increasing manganese concentration may correspond to strong effects of antiferromagnetic coupling and/or to energy transfer (trapping) to minority sites of lower energy of their lowest quartet state. A previous report by *Ohishi* et al.[18] on absorption spectra of octahedrally coordinated V^{III}, Cr^{III}, Co^{II}, Ni^{II} as well as of Fe^{II}, Cu^{II}, and several lanthanoides in ZBLA-type glasses (intended for optical fibers) can be compared to our findings. Their Cr^{III} was dissolved in 61 ZrF_4:32 BaF_2:4 GdF_3:3 AlF_3 but a precipitation of colloid grey particles when NiF_2 had been added, could only be prevented by simultaneous addition of NaF to the molten glass.

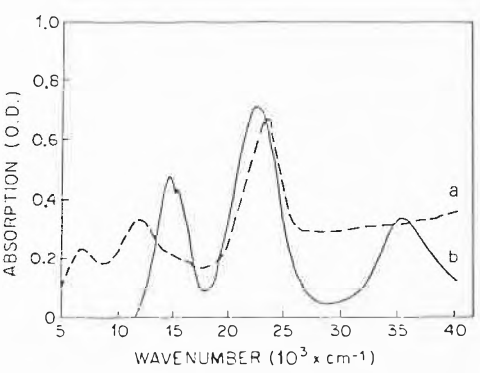

Fig. 1. Absorption spectra of Ni^{II} (curve a) and Cr^{III} (curve b) in ZBLA glass at room temperature.

Table 1. Wave-lengths λ (in nm) and wave-numbers σ (in cm^{-1}) of the three spin-allowed absorption bands of chromium(III) and nickel(II) in ZBLA glass (cf. Fig. 1) and corresponding «ligand field» parameters.

	Cr^{III}		Ni^{II}	
	λ_n	σ_n	λ_n	σ_n
n = 1	676	14800	1450	6900
n = 2	445	22500	834	12000
n = 3	288	34700	429	23300
B	850		970	
β	0.93		0.935	

Fig. 1 shows the absorption spectra of Cr^{III} and Ni^{II} in ZBLA glass. Table 1 gives the wave-lengths λ_n (n = 1, 2, 3) and the wave-numbers σ_n of the maxima of the three spin-allowed transitions. The subshell energy difference Δ (previously called 10Dq) corresponds to the maximum (or strictly to the centre of gravity) of the first spin-allowed transition. The Racah parameter[15, 16] of interelectronic repulsion B is derived from the diagonal sum rule

$$B = (\sigma_2 + \sigma_3 - 3\,\sigma_1)/15 \qquad (1)$$

Such a derivation is rarely possible in Cr^{III} because the third spin-allowed transition is usually hidden by electron transfer bands or other intense absorption. In such Cr^{III} cases, B can be derived[19] from σ_1 and σ_2 alone, providing $B = 875$ cm^{-1} for our sample. The nephelauxetic ratio β is the ratio between B from equation (1) and B_0 for the gaseous ion, 918 cm^{-1} for $Cr^{3\oplus}$ and 1041 cm^{-1} for $Ni^{2\oplus}$. It is interesting to compare the parameters of Table 1 with related materials (vitreous and crystalline oxides) which were compiled for 36 Cr^{III} cases[20] where Δ varies from 16200 to 18200 cm^{-1} in crystalline materials (and is determined mainly by the Cr–O distance dependent on the other cations present) and can be as high as 18350 cm^{-1} in micro-crystallites of $ZnAl_{2-x}Cr_xO_4$ in a limpid glass-ceramic.

The value for Δ of Cr^{III} in ZBLA glass is distinctly lower than 16100 cm^{-1} reported[21] for the cubic elpasolites $K_2NaGa_{0.95}Cr_{0.05}F_6$ and K_2NaCrF_6 suggesting 1.5 percent (0.03 Å) longer average Cr–F distances in the glass than in the crystal, as discussed below for some analogous Ni^{II} cases. Our Cr^{III} band positions in Table 1 are virtually identical with 14750, 22470, and 34500 cm^{-1} reported by *Ohishi* et al.[18] also finding ^2E at 15390 cm^{-1}. The parameters in Table 1 are closer to $CrF_6^{3\ominus}$ in solution having $\Delta = 15200$ cm^{-1} and $B = 820$ cm^{-1} (according to personal communication from *Claus Schäffer*, cf. ref[15]). They fall inside the intervals $\Delta = 14500$ to 16400 cm^{-1} and $B = 620$ to 850 cm^{-1} as given[22] for Cr^{III} in 14 highly different mixed-oxide glasses, and may also be compared with $\Delta = 17450$ cm^{-1} and $B = 725$ cm^{-1} for $Cr(OH_2)_6^{3\oplus}$. The first absorption band of the fluorides, and many oxide cases, shows a complicated structure, because the two first doublet levels ^2E and $^2T_1$ almost coincide with $^4T_2$ providing additional complications of spin-orbit coupling. The most prominent narrow peak occurs at 654 nm (15300 cm^{-1}) in our ZBLA glass, to be compared with 15430 cm^{-1} in a zirconium barium thorium fluoride glass[22], which should represent the position of ^2E to a good approximation. Since $^4T_2$ is distinctly stretching well below ^2E, one expects any luminescence to be a broad-band transition between the two lowest quartet levels. No luminescence could be detected[22] in the latter glass, whereas our sample showed a weak microsecond emission in the near infra-red. This forms a striking contrast, not only to the cubic elpasolites[21] with temperature-dependent lifetimes in the range 0.2 to 0.6 ms, but also to Cr^{III} in a lithium lanthanum phosphate glass[23] with lifetimes around 0.02 ms (0.025 ms at the same low Cr^{III} concentration as in the ZBLA glass) and a quantum yield up to 0.23. Much higher quantum yields are observed in glass-ceramics containing crystallites (much smaller than 400 nm) of spinel-type $MgAl_{2-x}Cr_xO_4$ and the isotypic gahnite $ZnAl_{2-x}Cr_xO_4$[24] and of other types[20, 25, 26]. Such glass-ceramics may be useful as laser materials, conceivably replacing the crystalline alexandrite $Al_{2-x}Cr_xBeO_4$.

The Δ value for Ni^{II} in ZBLA glass is unusually small, when compared with 8800 for NiO; 8650 for $Ni_xMg_{1-x}O$; 8500 for $Ni(OH_2)_6^{2\oplus}$; 7400 for $NiTiO_3$; and 7300 for $Ni_xMg_{1-x}TiO_3$ (all values[15] in cm^{-1}). It is particularly interesting to compare with the values for Ni^{II} in crystalline fluorides[15, 27] such as 7800 for spinel-type Li_2NiF_4; 7700 for rutile-type NiF_2; 7500 for perovskite-type $KNiF_3$ ($B = 950$ and 960 cm^{-1} in the two latter compounds, to be compared with 940 cm^{-1} in $Ni(OH_2)_6^{2\oplus}$ and 840 cm^{-1} in $Ni_xMg_{1-x}TiO_3$). *Rüdorff* et al.[27] pointed out that such variations can be ascribed to slightly varying internuclear distances R. At face value, one might consider a proportionality to R^{-5} as confirming the earlier electrostatic model based on the tiny non-spherical part of the huge Madelung potential (this explanation is already beyond rescue because of the higher Δ of water than of many oxygen-ligated anions) but *Smith*[28] pointed out that an exponential variation $\exp(-kR)$ of the squares of the overlap integrals[29–32] entering the angular overlap model[16, 32, 33] agrees with 5% increase of the anti-bonding effect for each percent decrease of R. In this perspective, ZBLA glass seems to have Ni–F distances on the average 1.6% (0.03 Å) longer than crystalline $KNiF_3$. *Ohishi* et al[18] report the three σ_n from Table 1 in their fluoride glass at 6540, 11360, and 22940 cm^{-1}. These values would give $B = 979$ cm^{-1} in equation (1) but *Ohishi* et al. prefer another set of parameters $\Delta = 6630$ and $B = 956$ cm^{-1}. The variation of the observed σ_n from Table 1 suggests even longer Ni–F distances, some 2.4% longer in their glass than in $KNiF_3$. This difference might be related to their NaF addition. In mixed oxides, more dramatic effects can occur, Δ of Ni^{II} being decreased to 6000 cm^{-1} in ilmenite-type $Ni_xCd_{1-x}TiO_3$ (isotypic with $NiTiO_3$ and $MgTiO_3$) and, as shown by *Reinen*, to only 4800 cm^{-1} in the perovskite (elpasolite superstructure?) $Ba_2Ca_{1-x}TeNi_xO_6$[15]. However, in such substituted crystals (like in the classical case of ruby $Cr_xAl_{2-x}O_3$) a doubt always remains whether the distance M–X between metal atoms M carrying a partly filled shell and the closest neighbor atoms X fully adapts to the internuclear distances in the closed-shell host lattice. More convincing evidence comes from hydrostatic high pressure spectra (especially for atoms[28] on special positions) but substituted crystals remain the only technique of significantly increasing R. A direct determination of R (with a precision of about 0.02 Å) is accessible to EXAFS using the X-ray absorption edge of the substituting M, even in low concentration[34–36].

The only possibility of luminescence of Ni^{II} in ZBLA glass would be at the foot (some 6000 cm^{-1}) of the first absorption band, but we did not detect any. The spin-forbidden absorption band due to the lowest singlet level ^1E corresponds to the rather broad shoulder at 15000 cm^{-1} (see Fig. 1) comparable to the peak[27] of crystalline Ni^{II} fluorides between 15000 and 15400 cm^{-1}; and a weak shoulder at 14920 cm^{-1} in the fluoride glass of *Ohishi* et al.[18].

As described in the experimental section, we also studied Nd^{III} in ZBLA glass, together with Mn^{II} or Cr^{III}. The well-known luminescence[1] from $^4F_{3/2}$ situated 11400 cm^{-1} above the ground state was seen to have a lifetime 0.34 ms, when excited in the yellow to $^4G_{5/2}$ of Nd^{III}. Further on, a short-lived (0.02 ms) emission is detected from $^2P_{3/2}$ (26100 cm^{-1} above the ground state and 2400 cm^{-1} above the closest lower J-level $^2D_{5/2}$) and another with a lifetime 1.5 µs from $^4D_{3/2}$ at 28100 cm^{-1} (2000 cm^{-1} above $^2P_{3/2}$).

In ZBLA glass simultaneously containing Nd^{III} and Cr^{III}, energy transfer from Cr^{III} by excitation in the strong absorption at 450 nm is quite efficient, since the $^4F_{3/2}$ emission (to the Nd^{III} ground state) at 876 nm has the same lifetime 0.4 ms as by excitation at 579 nm. This may be compared with the mutual influence[23] between Cr^{III} and Nd^{III} in lithium lanthanum phosphate glass, where the lifetimes of one component alone in low concentration are in the 0.02 ms and 0.2 ms range, respectively.

Energy transfer from simultaneously present Mn^{II} to Nd^{III} can be very efficient[37, 38]. Fig. 2 shows the approximately exponential decay with lifetime 0.34 ms by excitation in the neodymium band at 579 nm, the emission being measured at 876 nm, of the Mn^{II}/Nd^{III} ZBLA glass described in the experimental section. When the excitation is done at 404 nm, at the low-energy edge of the narrow ^6S–^4G absorption band of Mn^{II}, the same Nd^{III} emission at 876 nm shows a rise-time of about 0.1 ms followed by an exponential decay with the lifetime 1.45 ms. Such storage of energy in the lowest quartet of Mn^{II} was

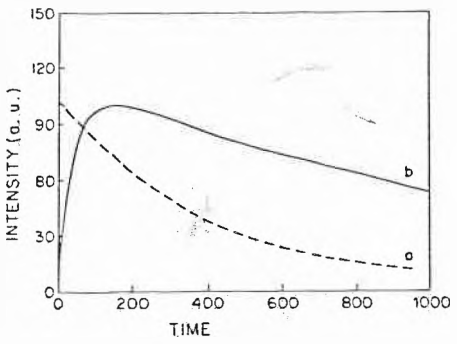

Fig. 2. Luminescence decay curve of ZBLA glass containing 1 mole percent each of Mn^{II} and Nd^{III}, showing Nd^{III} emission at $\lambda = 876$ nm. Curve a: direct excitation of Nd^{III} at $\lambda = 579$ nm, approximately exponential with lifetime 0.34 ms. Curve b: excitation of Mn^{II} at $\lambda = 404$ nm, subsequently transferring energy to Nd^{III}. The asymptotic exponential at the right-hand corresponds to the lifetime 1.45 ms.

previously observed[8] for Mn^{II} and Er^{III} in zinc gallium lead fluoride glass; related work on Mn^{II} and Nd^{III} in such a glass was recently published[39]. In the absence of neodymium, the luminescence of manganese(II) in ZBLA glass measured at 545 nm shows an approximately exponential decay curve with lifetime between 13 and 14 ms. The simplest rationalization for this decay being 9 times more rapid in the presence of 1 mole percent Nd^{III} is that the energy transfer is 8 times more rapid under these circumstances than luminescent decay of the Mn^{II} quartet state. This mechanism of energy storage has obvious potential applications in laser materials, since the effective lifetime of the lasing J-level of the trivalent lanthanoide can be dramatically enhanced, and the quasi-stationary concentration correspondingly increased.

Two recent reviews[2, 40] treat the luminescent properties of vitreous materials (with particular emphasis on fluoride glasses) containing trivalent lanthanoides.

Experimental

The samples were 2.5 × 0.5 × 0.5 cm parallelepipeds made from glasses prepared by Le Verre Fluoré S.A. (Z.I. du Champ Martin, F–35770 Vern-sur-Seiche) having the following mole percent composition:

Cr^{III} alone: 56.75 ZrF_4 : 34.25 BaF_2 : 4.5 LaF_3 : 4 AlF_3 : 0.5 CrF_3;

Ni^{II} alone: 56.75 ZrF_4 : 34.25 BaF_2 : 4.5 LaF_3 : 4 AlF_3 : 0.5 NiF_2;

Mn^{II}+Nd^{III}: 55.75 ZrF_4 : 33.75 BaF_2 : 4.5 LaF_3 : 4 AlF_3 : 1 MnF_2 : 1 NdF_3;

Cr^{III}+Nd^{III}: 56.5 ZrF_4 : 34 BaF_2 : 4.5 LaF_3 : 4 AlF_3 : 0.5 CrF_3 : 0.5 NdF_3.

The *absorption spectra* were measured on Cary 14 and/or Cary 219 Spectrophotometers, with undoped ZBLA glass as reference.

The *emission and excitation spectra* were measured on home-made fluorimeters based either on a Spex or a B&L monochromator.

The decay curves of *luminescence* were obtained by exciting the doped glasses either with a Molectron DL-200 tunable dye laser, pumped by a Molectron UV-400 pulsed nitrogen laser, or with the nitrogen laser directly. The transient signals were dispersed in a Jarrell-Ash monochromator (5 nm resolution) and detected in a R928 Hamamatsu photomultiplier. The amplified signals were captured at Biomation 8100 (10^{-8}s resolution), stored in a Nicolet Analyzer, and transferred to the computer memory for further processing.

In view of laser applications, it may be noted that all the spectroscopic measurements were performed at 300 K.

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