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Scandium Borate ($ScBO_3$) as a Host Lattice for Luminescent Lanthanide and Transition Metal Ions

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Abstract

The luminescence of the following ions in $ScBO_3$ is reported: Ce^{3+}, Gd^{3+}, Eu^{3+} and Cr^{3+}. The lanthanide ions show luminescence spectra which reveal the influence of the fact that these ions occupy a small site (Sc^{3+}). The vibronic lines are relatively strong. The 4f → 5d bands are characterized by small Stokes shifts. The Cr^{3+} ion, however, shows the influence of occupying a large site: the crystal field is weak and the emission is of the broad-band type ($^4T_2 \rightarrow {}^4A_2$). The vibrational structure in this band is analyzed.

Introduction

Scandium borate ($ScBO_3$) has the calcite structure with a six-coordinated site for the Sc^{3+} ion with S_6 site symmetry [1]. For trivalent lanthanide ions this site is small. Compare, for example, the radii for six coordination of Sc^{3+} ($r = 0.76$ Å) and Gd^{3+} ($r = 0.94$ Å). On the other hand, this site is too large for trivalent transition metal ions. The Cr^{3+} ion, for example, has $r = 0.61$ Å.

In order to investigate the influence of site space on the luminescence properties, we investigated the following ions in $ScBO_3$: Ce^{3+}, Gd^{3+}, Eu^{3+} and Cr^{3+}. In the evaluation we used earlier results on Ce^{3+} and Tb^{3+} in $ScBO_3$ [2]. It turns out that the lanthanide ions in $ScBO_3$ behave as being more strongly covalently bonded than usual, whereas Cr^{3+} is more weakly covalently bonded.

Experimental

Samples were prepared from high purity Sc_2O_3, boric acid and the oxides of the dopants, using methods described elsewhere [2, 3]. Dopant concentrations varied from 0.3 to 1.0 atomic percent. The samples were checked by X-ray powder diffraction.

The optical measurements were performed as described before [4].

Results and Discussion

$ScBO_3$–Gd^{3+}

The emission spectrum of $ScBO_3$–Gd is given in Fig. 1. This spectrum does not vary much with temperature. The intensity is weak because the absorption strength of 1% Gd^{3+} in $ScBO_3$ in the $^8S \rightarrow {}^6I$ transition is low. In the spectrum the pure electronic $^6P_{7/2} \rightarrow {}^8S$ emission dominates (314.2 nm). This position is at relatively low energy, indicating a reduction of the interelectronic interaction parameters by covalency. We assume that this is the consequence of the short Gd–O distances, the Gd^{3+} ion occupying too small a site.

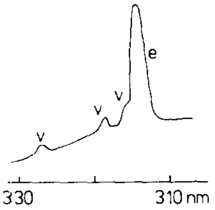

Fig. 1. Emission spectrum of $ScBO_3$–Gd^{3+} at 4.2 K. The electronic $^6P_{7/2} \rightarrow {}^8S$ transition is indicated by e, the vibronic transitions by v. Excitation is into the $^8S \rightarrow {}^6I$ transition.

At the lower energy side of this emission transition, we observed three vibronic features. Their energy difference with the main line are ~200, 425 and 1320 cm^{-1}. The intensity of each line is about 5% of the main line. This is a rather high value [5–7]. This effect is also ascribed to a relatively high covalency.

The energy differences correspond to the three most intense bands in the infrared spectrum of $ScBO_3$ [8], as is to be expected from theory [5]. The 1320 cm^{-1} line corresponds to a cooperative vibronic transition due to coupling of the electronic transition with the asymmetric stretching frequency of the borate group (BO_3^{3-}). The 425 cm^{-1} line corresponds to coupling with a vibrational mode which is a combination of BO_3^{3-} libration and Sc–O stretching, and the 200 cm^{-1} line to coupling with a mode which may be Sc–O bending.

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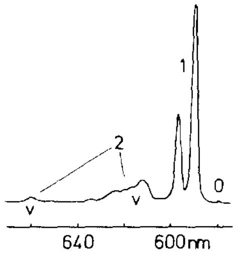

Fig. 2a. Emission spectrum of $ScBO_3$–Eu^{3+} at 4.2 K. The notation 0, 1, 2 indicates the transitions $^5D_0$–$^7F_{0,1,2}$. Vibronic transitions are indicated by v (for more details see Table I). Excitation wavelength was 395 nm.

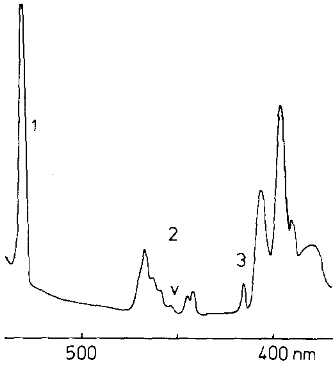

Fig. 2b. Excitation spectrum of the emission of $ScBO_3$–Eu^{3+} at 4.2 K. The notation 1, 2, 3 indicates the transitions $^7F_0$–$^5D_{1,2,3}$. Vibronic transitions are indicated by v (for more details see Table II). Emission wavelength was monitored at 595 nm.

$ScBO_3$–Eu^{3+}

The luminescence of $ScBO_3$–Eu^{3+} has been reported superficially long ago [9]. Figure 2 presents the emission and excitation spectrum of the Eu^{3+} emission. In the ultraviolet part of the excitation spectrum there is a broad band with a maximum at about 250 nm, which is due to the charge-transfer transition. This is the position to be expected for six-coordinated Eu^{3+} [10].

The emission spectrum (Fig. 2a) shows only two pure electronic transitions, *viz.* the magnetic-dipole $^5D_0$–$^7F_1$ transition which is split into two as expected for the S_6 site symmetry. The electric-dipole transitions occur only as vibronic transitions in accordance with the inversion site symmetry at the Sc^{3+} ion.

Table I presents an analysis of the vibronic transitions coupled to the $^5D_0$–$^7F_2$ emission transition. The zero-phonon line involved is not observed, but its position was derived by comparing the low- and high-temperature emission spectra. The latter shows also vibronic lines on the higher-energy side. The vibronic structure forced us to assume the presence of another zero-phonon line at 300 cm^{-1} lower energy which is also not observed. This puts the cubic $^7F_2$ crystal-field splitting at 300 cm^{-1}.

The vibrations involved are all observed in the infrared spectrum [8] as is to be expected for a parity-forbidden electric-dipole transition. They are the Eu–O bending mode, the Eu–O stretching/BO_3^{3-} libration mode, and the ν_2 and ν_3 modes of the BO_3^{3-} group. It is interesting to note that the splitting of the ν_3 mode in the cooperative vibronic emission transition is much larger than in the IR spectrum of $ScBO_3$. We assume that this presents an asymmetry in the crystalline field at the borate group next to a dopant Eu^{3+} ion, because it is surrounded by five Sc^{3+} ions and one Eu^{3+} ion. We did not observe this splitting in the emission spectrum of $ScBO_3$–Gd^{3+}. This is due to the weak emission intensities in that case, which makes it necessary to open the slits of the monochromator, so that the resolving power is low.

Table II shows the vibrational structure in the $^7F_0 \rightarrow {^5D_2}$ transition in the excitation spectrum of the Eu^{3+} emission of $ScBO_3$–Eu^{3+} at 4.2 K. The position of the origin was determined as described above. The splitting of the ν_3 (BO_3^{3-}) vibration is the same as in the emission spectrum. The ν_4 (BO_3^{3-}) mode is also observed. Since the splitting of the $^5D_2$ level is usually smaller than that of the $^7F_2$ level, it is not surprising that, under the resolving

TABLE I. Vibrational Structure in the $^5D_0$–$^7F_2$ Emission Transition of Eu^{3+} in $ScBO_3$ at 4.2 K

Position	Assignment		From IR spectrum of $ScBO_3$ [8]
16600[a]	(0–0)(i)		
16340	(0–0)(i) – 260	Eu^{3+}–O^{2-}	285, 262
16300[a]	(0–0)(ii)		
16155	(0–0)(i) – 455	Eu^{3+}–O^{2-}/BO_3^{3-}	422
16030	(0–0)(ii) – 270	Eu^{3+}–O^{2-}	285, 262
15790	(0–0)(i) – 810	ν_2 (BO_3^{3-})	764, 740
15330	(0–0)(i) – 1270	ν_3 (BO_3^{3-})	1260, 1240
15160	(0–0)(i) – 1440	ν_3 (BO_3^{3-})	1220, 1200
14915	(0–0)(ii) – 1385	ν_3 (BO_3^{3-})	

[a] Not observed, see text. All values in cm^{-1}.

TABLE II. Vibrational Structure in the $^7F_0$–$^5D_2$ Excitation Transition of the Eu^{3+} Ion in $ScBO_3$ at 4.2 K

Position	Assignment	
21240[a]	(0–0)	
21440	(0–0) + 200	Eu^{3+}–O^{2-}
21640	(0–0) + 400	Eu^{3+}–O^{2-}/(BO_3^{3-})
21810	(0–0) + 570	ν_4 (BO_3^{3-})
22050	(0–0) + 810	ν_2 (BO_3^{3-})
22520	(0–0) + 1280	ν_3 (BO_3^{3-})
22680	(0–0) + 1440	

[a] Not observed, see text. All values in cm^{-1}.

power used, we now only need one electronic origin to explain the vibrational structure.

The $^7F_0 \leftrightarrow {}^5D_0$ transition is completely forbidden under the present site symmetry. It is nevertheless observed in the emission spectrum as a very weak peak at 579.8 nm with an intensity equal to 1% of that of the $^5D_0$–$^7F_1$ emission lines. As an electronic transition it could not be observed in the excitation spectrum. However, the excitation spectrum shows very weak features which are at 800, 1270 and 1440 cm^{-1} higher energy than the $^5D_0 \rightarrow {}^7F_0$ transition. These are ascribed to cooperative vibronic transitions involving the $^5D_0 \rightarrow {}^7F_0$ transition and ν_2 (BO_3^{3-}) and ν_3 (BO_3^{3-}), respectively.

It is possible to compare the vibronic intensity in the spectra of different compounds by assuming that the magnetic-dipole $^5D_0$–$^7F_1$ transition has the same intensity in all compounds. Since this transition is not forbidden by site-dependent selection rules, this is a good approximation. In this way the vibronic intensity in the case of $ScBO_3$–Eu^{3+} is found to be relatively high. Compare, for example, $ScBO_3$–Eu^{3+} where the intensity ratio ($^5D_0$–$^7F_2$)/($^5D_0$–$^7F_1$) is 0.65 with $Eu_2Mg_3(NO_3)_{12} \cdot 24H_2O$ where this ratio amounts to 0.35 [11]. In the latter compound the Eu^{3+} ion occupies also an inversion-symmetry site, but this time with twelve coordination, so that the Eu–O distances will be longer and the covalency weaker. The vibronic intensity seems to increase with increasing degree of covalency which is not unexpected. The $^7F_1$ splitting in the case of $ScBO_3$–Eu^{3+} (200 cm^{-1}) is also much larger than in $Eu_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (50 cm^{-1}), pointing to a much stronger crystalline field. In both compounds the Eu^{3+} ion has the same site symmetry, *viz.* S_6.

In Cs_2NaYCl_6–Eu^{3+} the Eu^{3+} ion occupies an octahedral site. The ($^5D_0$–$^7F_2$)/($^5D_0$–$^7F_1$) intensity ratio is given here as 0.40 [12], which is also lower than for $ScBO_3$–Eu^{3+}.

We now turn to lanthanide ions which show d → f broad-band transitions.

$ScBO_3$–Ce^{3+}

The Ce^{3+} ion is even larger than the Gd^{3+} and Eu^{3+} ions (r(VI)Ce^{3+} = 1.01 Å). The Ce^{3+} ion in $ScBO_3$ may well present this ion in one of the smallest possible sites. The luminescence of $ScBO_3$–Ce^{3+} has been reported long ago [13], and investigated in more detail later [2]. The emission spectrum shows the broad-band 5d → 4f emission band with two maxima due to the splitting of the $4f^1$ ground state. The excitation spectrum consists of several broad bands corresponding to the crystal-field split 4f → 5d transition.

In view of the lack of space at the Ce^{3+} site, it should be expected that the relaxation in the excited state is strongly restricted, *i.e.* the broad bands are expected to show vibrational structure and the Stokes shift should be small. This is what has been observed [2, 13]. In ref. 2 only the zero-phonon transitions have been reported. Here we present a more elaborate analysis which leads to clear conclusions.

The spectra obtained are similar to those in the literature. Tables III and IV present the vibrational structure in the lower-energy side of the excitation spectrum and the higher-energy side of the emission spectrum. Because the electronic transition involved (4f–5d) is completely allowed, the analysis should differ essentially from that given before for the 4f–4f transitions of the Gd^{3+} and Eu^{3+} ions. This is indeed the case.

TABLE III. Vibrational Structure in the 5d → 4f Emission Transition of the Ce^{3+} Ion in $ScBO_3$ at 4.2 K

Position[a]	Assignment	
27585(s)	(0–0)	
27360(s)	(0–0) – 225	ν_b(Ce^{3+}–O^{2-})
27120(s)	(0–0) – 465	ν_s(Ce^{3+}–O^{2-})
26900(m)	(0–0) – 685	$\nu_s + \nu_b$
26630(s)	(0–0) – 955	$2\nu_s$
26525(s)	(0–0)′	
26315(m)	(0–0)′ – 210	ν_b'(Ce^{3+}–O^{2-})
26180(m)	(0–0) – 1405	$3\nu_s$
26070(m)	(0–0)′ – 455	ν_s'(Ce^{3+}–O^{2-})
25870(w)	(0–0)′ – 655	$\nu_s' + \nu_b'$

[a] s, strong; m, medium; w, weak. All values in cm^{-1}.

The excitation spectrum is the simpler of the two. There is a progression in a mode with frequency 450 cm^{-1} (see Table IV). This must be the Ce^{3+}–O^{2-} stretching vibration, which might have a certain borate character (see above). Further, we note a 190 cm^{-1} Ce^{3+}–O^{2-} bending vibration. There are no clear indications of coupling with the borate vibrations.

TABLE IV. Vibrational Structure in the 4f → 5d Excitation Transition of the Ce^{3+} Ion in $ScBO_3$ at 4.2 K

Position[a]	Assignment	
27460(s)	(0–0)	
27650(m)	(0–0) + 190	$\nu_b(Ce^{3+}–O^{2-})$
27920(s)	(0–0) + 460	$\nu_s(Ce^{3+}–O^{2-})$
28115(m)	(0–0) + 655	$\nu_s + \nu_b$
28380(m)	(0–0) + 920	$2\nu_s$
28550(w)	(0–0) + 1090	$2\nu_s + \nu_b$
28750(w)	(0–0) + 1290	$3\nu_s$

[a] s, strong; m, medium; w, weak. All values in cm^{-1}.

Table III shows that the emission spectrum starts in a similar way, however, the situation becomes complicated because another emission transition overlaps. Its origin is at 1060 cm^{-1} lower energy. There are no vibronics due to coupling with the borate vibrations.

At first sight the absence of borate vibronics seems to be surprising after their observation in the spectra of Eu^{3+} and Gd^{3+}. It should be realized that in the latter case the observation is much easier, the zero-phonon transitions being dominating and the vibronics very weak and relatively sharp. In the case of Ce^{3+} the vibrational structure can only be observed on top of a broad phonon side-band [2], which makes the observation of weak features impossible.

If we compare ν_s and ν_b for the excitation transition and the higher emission transition (which are the same electronic transition), it follows that the $Ce^{3+}–O^{2-}$ vibrations in the excited state are at lower frequencies than in the ground state, as is to be expected. The stretching frequency is lowered from 470 to 450 cm^{-1}. The decrease for the bending mode is similar, but rather inaccurate. This shows that the bond in the excited 5d state is weaker than in the 4f ground state. However, the difference is small, the small site restricting expansion.

In this connection we note that the first member of the progression has the highest intensity, which points also in this direction. Our analysis yields a Stokes shift of hardly more than 1000 cm^{-1}, the smallest one known for the Ce^{3+} ion. In $[Ce \subset 2.1.1]^{3+}$ cryptate with a rigid cage around the Ce^{3+} ion, it amounts to 2200 cm^{-1} [14].

The lower emission transition (with an accent in Table III) seems to show a slightly lower frequency for ν_s and ν_b than the higher one. However, the vibronics involved are weak and broad, and the difference is probably within experimental error. In ref. 2 the lower emission transition is assigned to a transition ending at a higher crystal-field component of the $^2F_{5/2}$ ground state. Recently, Aull and Jenssen [15] have reported on the Ce^{3+} luminescence of Ce^{3+}-activated elpasolites, for example Rb_2NaYF_6. It appears that in this host lattice the $Ce^{3+}(4f^1)$ ion is in a strong field, so that the 4f state does not split in the spin–orbit components $^2F_{5/2}$ and $^2F_{7/2}$, but in the crystal-field components, yielding a broad emission band.

In $ScBO_3–Ce^{3+}$ the splitting observed in the emission spectrum is larger than the usually observed 2000 cm^{-1} ($^2F_{5/2}$–$^2F_{7/2}$), *viz.* about 3000 cm^{-1} [2, 13]. Also, the emission band is very broad, especially if the low value of the Stokes shift is taken into account. The level observed by us in emission is 1060 cm^{-1} above the ground level, which is too much for a crystal-field split $^2F_{5/2}$ level. Therefore, we propose that also in $ScBO_3–Ce^{3+}$ the strong-field scheme is appropriate for the $4f^1$ configuration. It is obvious to relate this to the short Ce–O distances in this host lattice. In connection with this, we note that the centre of gravity of the excited 5d configuration of Ce^{3+} in $ScBO_3$ is at relatively low energy, *viz.* 32 500 cm^{-1} [13]. All these observations indicate that the Ce^{3+} ion in $ScBO_3$ is more covalently bonded than is to be expected.

Finally we note that Hoshina and Kuboniwa [2] have reported the 4f–5d excitation spectra of the Tb^{3+} luminescence of $ScBO_3–Tb^{3+}$. The results are very similar to those for the f → d transition in the case of $ScBO_3$–Ce.

$ScBO_3–Cr^{3+}$

Following our arguments used above, the Cr^{3+} ion in $ScBO_3$ is expected to occupy a large site, *i.e.* to experience a low crystal field and to show $^4T_2 \rightarrow {}^4A_2$ broad-band emission.

The diffuse reflection spectrum of $ScBO_3$–Cr (0.3 at %) shows four broad bands, *viz.* at 635, 455, ~300 and ~220 nm. The first three are weak and are ascribed to the well-known d^3 crystal-field transitions $^4A_2 \rightarrow {}^4T_2$, $^4T_1(F)$, $^4T_1(P)$; the latter is intense and corresponds probably to the $Cr^{3+}–O^{2-}$ charge-transfer transition. What is of importance here is the position of the $^4A_2 \rightarrow {}^4T_2$ transition which yields immediately the value of the crystal-field splitting, *viz.* 15750 cm^{-1}. This is indeed a relatively weak crystal field for Cr^{3+} in a solid mixed-metal oxide.

At room temperature $ScBO_3–Cr^{3+}$ shows an efficient luminescence in the near infrared. The emission band is broad. Its maximum is at about 810 nm. Undoubtedly this is the $^4T_2 \rightarrow {}^4A_2$ emission band. Its excitation spectrum shows the same bands as the diffuse reflection spectrum, but the $^4A_2 \rightarrow {}^4T_1(P)$ and the charge-transfer transition are very weak. It is clear that excitation in these transitions results mainly in non-radiative losses.

The Stokes shift resulting from these data is 3500 cm^{-1}. This is three times the Stokes shift of the Ce^{3+} emission. It is clear that the Cr^{3+} ion has a better

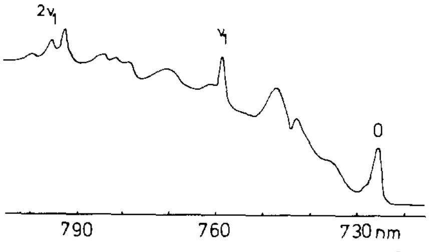

Fig. 3. Emission spectrum of $ScBO_3$–Cr^{3+} at 4.2 K. Correction would lift the longer wavelength side considerably. The zero-phonon transition is indicated by 0; its repetition in ν_1 is also shown. For a complete analysis see Table V. Excitation wavelength was 460 nm.

TABLE V. Vibrational Structure in the $^4T_2 \rightarrow {}^4A_2$ Emission Transition of Cr^{3+} in $ScBO_3$ at 4.2 K

Position[a]	Assignment[b]
13775(sh, s)	0–0
–40(w)	ν_r
– ~170(w)	ν_6
–320(m)	ν_4
–405(br, s)	ν_3, $\nu(Sc^{3+}–O^{2-})/\nu(BO_3^{3-})$
–610(sh, m)	ν_1
–645(w)	$\nu_1 + \nu_r$
–800(br, m)	$\nu_1 + \nu_6$
–940(m)	$\nu_1 + \nu_4$
–990(m)	$\nu_1 + \nu_3$
–1040(m)	
–1170(m)	$\nu_3\ (BO_3^{3-})$
–1215(m)	$2\nu_1$
–1280(w)	$2\nu_1 + \nu_r$
– ~1610(w)	$2\nu_1 + \nu_3$

[a] s, strong; m, medium; w, weak; sh, sharp; br, broad. [b] ν_r: lattice vibration; ν_i: octahedral CrO_6 modes. All values in cm^{-1}. The position of the origin is 13775 cm^{-1}.

opportunity to expand in the excited state than the Ce^{3+} ion. These room temperature characteristics of $ScBO_3$–Cr^{3+} are very similar to those for $SrAlF_5$–Cr^{3+} [16].

At 4.2 K the luminescence intensity increases by about a factor of two. Simultaneously a vibrational structure develops in the spectra. This is most obvious in the emission spectrum (see Fig. 3). In the excitation spectrum we observe the same zero-phonon line as in the emission spectrum. This facilitates the analysis, the results of which are given in Table V.

The zero-phonon transition must be a pure magnetic-dipole transition. These were also observed by Güdel *et al.* in Cr^{3+}-doped elpasolites [17]. This interpretation is confirmed by the large value of the radiative decay time (see below).

In the analysis the coupling with the ungerade octahedral Cr^{3+}–O^{2-} vibrations (ν_3, ν_4, ν_6) dominates, and there is a progression in the gerade ν_1 (Cr^{3+}–O^{2-}). The frequencies observed are considerably higher than for the lanthanide ions, as is to be expected. Furthermore, we find a lattice vibration and the two vibrations which correspond to the stronger bands in the infrared spectrum of $ScBO_3$. Unfortunately one of these overlaps the octahedral ν_3 mode (at 405 cm^{-1}), but the splitting of ν_3 can be found from $\nu_1 + \nu_3$. Since ν_3 is a three-fold degenerate stretching mode, it should split under S_6 symmetry.

The infrared-active borate vibrations are also observed in the vibrational structure in the $^4T_2 \rightarrow {}^4A_2$ emission band. Their presence is comparable to the cooperative vibronic bands in the spectra of Gd^{3+} and Eu^{3+}. There is no evidence for a Jahn–Teller distortion in the excited state of the Cr^{3+} ion, as observed by Güdel *et al.* [17] in the elpasolites from a progression in the octahedral ν_2 mode. The presence of the non-cubic crystal-field component in the case of $ScBO_3$ will probably prohibit such a distortion.

The value of the interelectronic parameter B can be calculated from the position of the $^4A_2 \rightarrow {}^4T_2$ and $^4T_1(F)$ absorption bands and has the value 630 cm^{-1}. This is the value usually found in fluorides and indicates a small amount of covalency. This is the opposite of the situation encountered with the lanthanide ions in $ScBO_3$.

The decay curve of the Cr^{3+} emission at 4.2 K is exponential. The decay time amounts to 280 μs. In view of the high efficiency of the emission, we assume this decay time to be a radiative decay time. Its value is very large. In $SrAlF_5$–Cr^{3+}, for example, its value is 105 μs. This long decay time is ascribed to the presence of inversion symmetry at the Cr^{3+} ion in $ScBO_3$. Our results indicate, therefore, that the small Cr^{3+} ion occupies the centre of the Sc^{3+} site.

Finally it is interesting to compare these results with those reported for $KZnF_3$–Cr^{3+} [18]. Here the host lattice has perovskite structure in which the Zn^{2+} ions occupy octahedral sites with cubic symmetry. About 90% of the Cr^{3+} ions occupy these sites, the other 10% occupy sites with lower symmetry, probably due to charge compensation. We have compared the results for the cubic Cr^{3+} sites with those for $ScBO_3$–Cr^{3+}. It turns out that the absorption spectra are very much alike. Also the emission spectra are similar, the band maximum at 300 K being 790 nm for $KZnF_3$–Cr^{3+}. At 80 K a weak vibrational structure was observed which was not analysed further. The decay time at 10 K amounts to 270 μs, which is in very good agreement with our results. In K_2NaScF_6–Cr^{3+} with cubic coordination for the Cr^{3+} ion, an even longer decay time has been reported, *viz.* 600 μs at 5 K [19].

Crystals of $KZnF_3$–Cr^{3+} show tunable laser operation in the near infrared spectral region [18]. In view of the analogy between the spectral characteristics of $KZnF_3$–Cr^{3+} and $ScBO_3$–Cr^{3+}, it may be expected that crystals of $ScBO_3$–Cr^{3+} will behave similarly.

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