

THE LUMINESCENCE OF $\text{Cs}_2\text{NaSbCl}_6$ AND $\text{Cs}_2\text{NaSbBr}_6$: A TRANSITION FROM A LOCALIZED TO A DELOCALIZED EXCITED STATE

E.W.J.L. OOMEN, W.M.A. SMIT and G. BLASSE

Physical Laboratory, State University of Utrecht, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

Received 11 March 1987; in final form 21 April 1987

The luminescences of $\text{Cs}_2\text{NaSbCl}_6$ and $\text{Cs}_2\text{NaSbBr}_6$ are reported. For $\text{Cs}_2\text{NaSbBr}_6$ the luminescence properties are described in terms of a band model. For $\text{Cs}_2\text{NaSbCl}_6$ the luminescence is interpreted in terms of isolated Sb^{3+} centres, comparable with $\text{Cs}_2\text{NaMCl}_6\text{-Sb}^{3+}$ ($M = \text{Sc, Y, La}$). The radius of the Sb^{3+} ion is larger in the chloro- than in the bromo-elpasolite.

1. Introduction

Recently we reported on the luminescence of Sb^{3+} ions in elpasolite host lattices Cs_2NaMX_6 ($M = \text{Cs, Y, La; X = Cl, Br}$) [1-3]. In these systems the Sb^{3+} ion ($5s^2$ configuration) is octahedrally coordinated by halide ions. The luminescence properties of Sb^{3+} in Cs_2NaMX_6 were similar to those of monovalent s^2 ions in alkali halides. These alkali halide systems have been studied extensively and theoretical models have been worked out for these systems [4-6].

The compound $\text{Cs}_2\text{NaSbCl}_6$ has the cubic elpasolite structure [7]. We found that $\text{Cs}_2\text{NaSbBr}_6$ also possesses this structure. It seemed interesting to study the luminescence in order to compare it with that of the diluted systems $\text{Cs}_2\text{NaMX}_6\text{-Sb}^{3+}$.

The luminescence of the Bi^{3+} ion ($6s^2$) in the elpasolites $\text{Cs}_2\text{NaYCl}_6$, $\text{Cs}_2\text{NaYBr}_6$ and $\text{Cs}_2\text{NaLaCl}_6$ was investigated earlier, and could be ascribed to transitions on the isolated Bi^{3+} ion [8,9]. Pelle et al. [10] studied the luminescence of $\text{Cs}_2\text{NaBiCl}_6$, which has the same crystal structure. The excitation spectra of $\text{Cs}_2\text{NaBiCl}_6$ are similar to those of Bi^{3+} in $\text{Cs}_2\text{NaYCl}_6$ and $\text{Cs}_2\text{NaLaCl}_6$. The emission spectra of the concentrated Bi^{3+} compound, however, were different from those of the diluted systems. This has been ascribed to migration of the excitation energy among the Bi^{3+} ions [11].

In view of the large Stokes shift [1-3] no energy migration is expected for Sb^{3+} ions. Surprisingly, the results for $\text{Cs}_2\text{NaSbBr}_6$ do not fit this expectation.

2. Experimental.

2.1. Sample preparation

Powdered samples of $\text{Cs}_2\text{NaSbX}_6$ ($X = \text{Cl, Br}$) were prepared from the following starting materials: CsX (Merck, optipur), NaX (Merck, optipur), Sb_2O_3 (Merck, p.a.) and HX (Baker A.R.). Stoichiometric quantities of CsX , NaX and Sb_2O_3 are dissolved in concentrated HX . The solvent is evaporated by heating, and some methanol acidified with HX is added. Again the solvent is evaporated, some methanol is added and is evaporated under a dry nitrogen atmosphere at 150°C . After repeating the last step, the powder is fired for one week at 300°C under a dry nitrogen atmosphere to remove all methanol and/or methanolate. In this way $\text{Cs}_2\text{NaSbCl}_6$ is obtained as a white powder and $\text{Cs}_2\text{NaSbBr}_6$ as a dark-yellow powder. Because of the hygroscopic nature of the samples, they were handled in a glove box under a dry nitrogen atmosphere.

The samples were checked by X-ray powder diffraction ($\text{CuK}\alpha$ radiation) using a Philips PW 170 diffractometer. The diffraction patterns of $\text{Cs}_2\text{NaSbCl}_6$ and $\text{Cs}_2\text{NaSbBr}_6$ were similar to those of Cs_2NaMX_6 ($M = \text{Sc, Y, La; X = Cl, Br}$). The values obtained for the lattice parameters are gathered in table 1. Apart from the diffraction lines of $\text{Cs}_2\text{NaSbX}_6$, some weak lines arising from impurities were observed. These impurities could be ascribed to

Table 1
Elpasolite lattice parameter values

Lattice	a_0 (Å)	Ref.
Cs ₂ NaScCl ₆	10.4875	[7]
Cs ₂ NaYCl ₆	10.7315	[7]
Cs ₂ NaSbCl ₆	10.7780	[7]
Cs ₂ NaLaCl ₆	10.9923	[7]
Cs ₂ NaScBr ₆	11.070	[12]
Cs ₂ NaSbBr ₆	11.21 ± 0.01	this work
Cs ₂ NaYBr ₆	11.301	[12]
cs ₂ NaLaBr ₆	11.50 ± 0.02	this work

CsX, NaX and reaction products of Cs₂NaSbX₆ with air (section 3).

2.2. Optical instrumentation

Luminescence and decay time measurements were performed with the same instrumentation as described in ref. [2].

3. Results and discussion

3.1. Cs₂NaSbCl₆

The Cs₂NaSbCl₆ sample shows an intense white luminescence under UV excitation. The emission and

excitation spectra of our sample reveal two luminescent centres. Fig. 1 shows the emission and excitation spectra taken at 5 K. There are two emission bands with maxima at 21200 cm⁻¹ (centre 1) and 18300 cm⁻¹ (centre 2). Each centre has a different excitation spectrum: centre 1 is excited in the energy region from 28500 to 40000 cm⁻¹, centre 2 in the region 26000–40000 cm⁻¹. The excitation spectrum of centre 1 always overlaps with that of centre 2, so that excitation in centre 1 leads to both emission bands.

The emission of centre 2 increases when the Cs₂NaSbCl₆ sample is exposed to air. A similar luminescence was observed for samples of Cs₃Sb₂Cl₉, and was ascribed to Sb³⁺ in a decomposition product [13]. Accordingly, the centre 2 luminescence is assumed to originate from a decomposition product formed by exposure of Cs₂NaSbCl₆ to air. This is confirmed by the X-ray diffraction results. The impurity peaks in the diffraction pattern of Cs₂NaSbCl₆ increased when Cs₂NaSbCl₆ was kept in air.

The luminescence of centre 1 is ascribed to the intrinsic Sb³⁺ ion in Cs₂NaSbCl₆. Decay measurements were performed on this luminescence. All decay curves were exponential. The decay time is plotted versus temperature in fig. 2. At low temperature the emission originates from the ³P₀ level, leading to a radiative decay time τ_0 of 1420 ± 20 μ s,

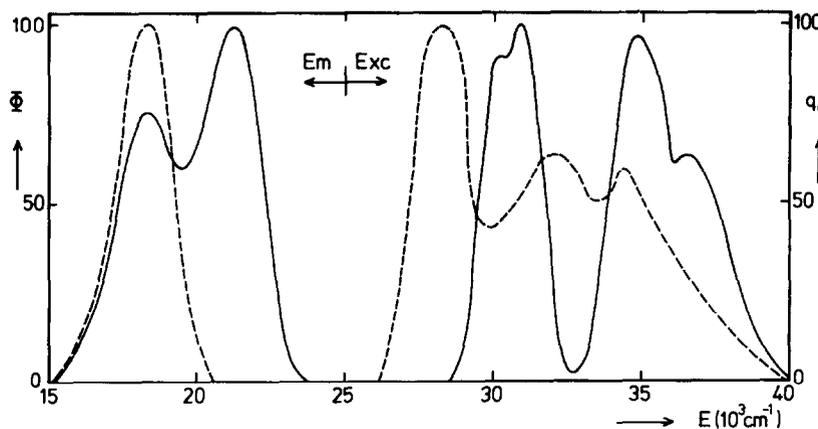


Fig. 1. Emission and excitation spectra of Cs₂NaSbCl₆ at 5 K. Emission spectra are recorded for excitation energies of 27600 cm⁻¹ (broken line) and 30300 cm⁻¹ (full line). Excitation spectra are recorded for emission at 22200 cm⁻¹ (centre 1, full line) and at 18200 cm⁻¹ (centre 2, broken line). See also text. Φ denotes the radiant power per constant energy interval in arbitrary units. q_r gives the relative quantum output in arbitrary units. All spectra are normalized.

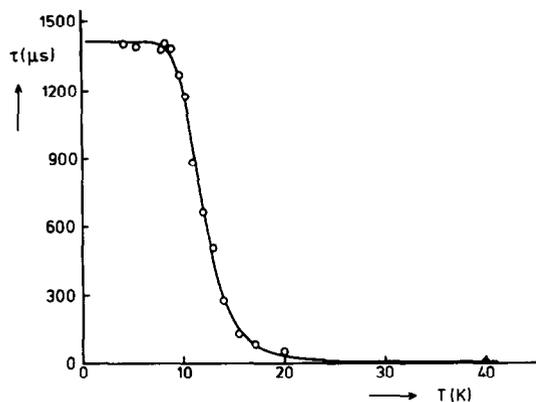


Fig. 2. Decay time versus temperature for $\text{Cs}_2\text{NaSbCl}_6$. Emission is at 21200 cm^{-1} . The drawn line represents the best fit to a three-level scheme. See also text.

reflecting the forbidden character of the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition. At higher temperatures the $^3\text{P}_1$ level becomes occupied leading to shorter decay times. Using a three-level scheme [14,15], values for the trap depth $\Delta E (=E(^3\text{P}_1) - E(^3\text{P}_0))$ and the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ radiative decay time τ_1 can be obtained, viz. $\Delta E = 76 \pm 4\text{ cm}^{-1}$ and $\tau_1 = 0.15 \pm 0.07\text{ }\mu\text{s}$.

The spectral data and the trap depth ΔE of $\text{Cs}_2\text{NaSbCl}_6$ can be compared with the corresponding values for Sb^{3+} in $\text{Cs}_2\text{NaMCl}_6$ [2] (table 2). This reveals clearly that the luminescence of $\text{Cs}_2\text{NaSbCl}_6$ is similar to the luminescence of dopant Sb^{3+} ions in $\text{Cs}_2\text{NaMCl}_6$, indicating that the Sb^{3+} ions in $\text{Cs}_2\text{NaSbCl}_6$ behave as isolated centres with the characteristic s^2 ion transitions. This is supported by the results of the decay time measurements.

It is well known that the Stokes shift of a dopant Sb^{3+} ion increases when the space available in the

host lattice for the Sb^{3+} ion increases [2,3,17]. This is ascribed to the preference of the Sb^{3+} ion for asymmetric coordination [18,19]. Table 2 shows that the Stokes shift indeed increases with increasing lattice parameter. Furthermore, table 2 shows that ΔE decreases when the Stokes shift increases. This is a quite common situation for isolated s^2 ions [3,17,20], and has been explained in terms of quenching of the spin-orbit interaction by the Jahn-Teller effect [21].

The only difference between the diluted and the concentrated system is the temperature quenching, which for $\text{Cs}_2\text{NaSbCl}_6$ starts at about 200 K, while for $\text{Cs}_2\text{NaMCl}_6\text{-Sb}^{3+}$ no temperature quenching is observed up to room temperature. This might be due to thermally activated energy transfer. For Cs_2TeCl_6 similar observations have been made [22].

3.2. $\text{Cs}_2\text{NaSbBr}_6$

The emission and excitation spectra of $\text{Cs}_2\text{NaSbBr}_6$ at 4.2 K are given in fig. 3. The luminescence intensity of the sample is weak compared to that of $\text{Cs}_2\text{NaSbCl}_6$. The emission consists of a broad band with a maximum at 12800 cm^{-1} and two very weak lines with maxima at 20800 and 21000 cm^{-1} . Temperature quenching of these two sharp emission lines starts already below 2 K. At 20 K they are completely quenched. The quenching of the broad emission band around 12800 cm^{-1} starts around 8 K (fig. 4). A fast quenching leaves only 10% of the original intensity at about 16 K. A much slower quenching occurs above 16 K, until at about 50 K the emission has completely vanished.

The excitation spectrum of the emission band at 12800 cm^{-1} consists of a broad band, starting at

Table 2

Spectral data at 80 K and $\Delta E(^3\text{P}_1 \rightarrow ^3\text{P}_0)$ values for Sb^{3+} luminescence in elpasolite lattices. All values in cm^{-1} . Additionally, the lattice parameters a_0 and the radii of the trivalent host lattice cations are given (both in Å). See also text

Composition	Lower excitation maximum of the A band	Emission maximum	Stokes shift	ΔE	Lattice parameter ^{a)}	Radius host lattice cation ^{b)}
$\text{Cs}_2\text{NaScCl}_6\text{-Sb}^{3+}$	30300	22700	7600	110	10.4875	0.745
$\text{Cs}_2\text{NaYCl}_6\text{-Sb}^{3+}$	30300	21400	8900	78	10.7315	0.900
$\text{Cs}_2\text{NaSbCl}_6$	30200	21200	9000	76	10.7780	0.76
$\text{Ca}_2\text{NaLaCl}_6\text{-Sb}^{3+}$	30300	20300	10000	67	10.9923	1.032

^{a)} Ref. [7]. ^{b)} Ref. [16].

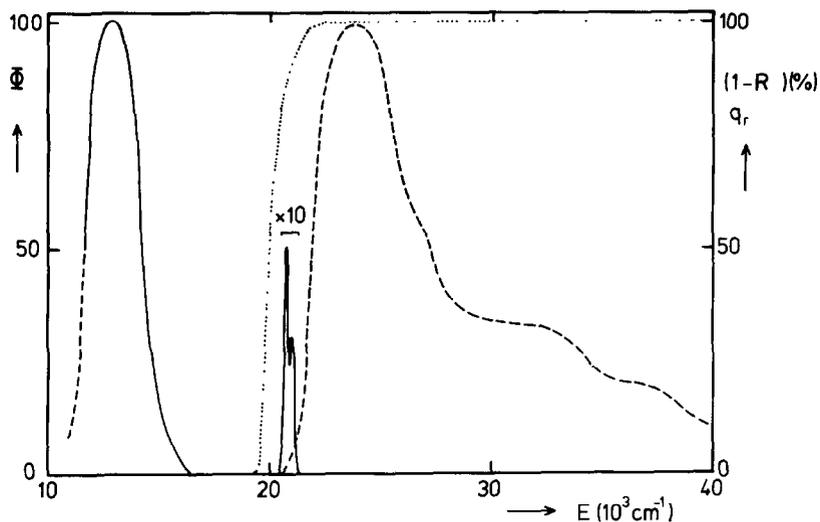


Fig. 3. Emission (full line) and excitation (broken line) spectra of $\text{Cs}_2\text{NaSbBr}_6$ at 4.2 K. The emission lines around 21000 cm^{-1} are ten times magnified for clarity. The dotted line represents the diffuse reflectance spectrum at room temperature. All spectra are normalized.

20500 cm^{-1} (fig. 3). Because of the weakness of the emission lines around 21000 cm^{-1} it was not possible to obtain a reliable excitation spectrum of this emission. However, excitation at any energy in the region from 20500 to 40000 cm^{-1} leads to this emission. In addition, fig. 3 shows the diffuse reflectance spectrum of $\text{Cs}_2\text{NaSbBr}_6$ at room temperature.

Comparison of the luminescence of $\text{Cs}_2\text{NaSbBr}_6$ with that of $\text{Cs}_2\text{NaMBr}_6\text{-Sb}^{3+}$ ($M=\text{Sc, Y, La}$) [3] makes clear that the luminescence of the concentrated compound differs strongly from that of the diluted systems. This leads to the conclusion that the luminescence of $\text{Cs}_2\text{NaSbBr}_6$ does not originate from isolated Sb^{3+} ions. The edge emission of this com-

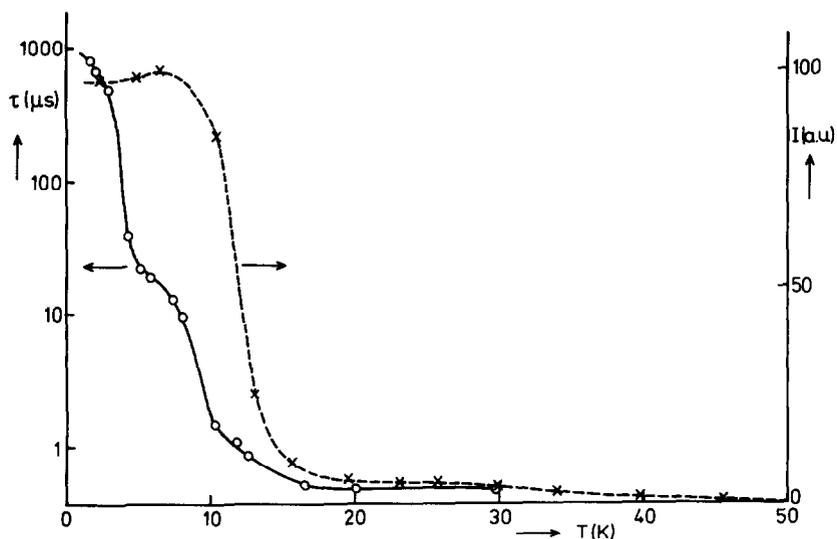


Fig. 4. Decay time (O) and intensity (X) of the 12800 cm^{-1} emission of $\text{Cs}_2\text{NaSbBr}_6$ versus temperature. The lines are drawn by hand.

pond suggests strongly that we are dealing with a semiconductor-type emission. The possibility that the luminescence originates from the intervalence charge-transfer transition $\text{Sb}^{3+} \rightarrow \text{Sb}^{5+}$ is unlikely, since Sb^{5+} ions are known as killer centres [13]. Moreover, the edge emission becomes difficult to explain.

It is of interest, therefore, to compare the luminescence of $\text{Cs}_2\text{NaSbBr}_6$ with that of compounds such as $\text{Cs}_3\text{Bi}_2\text{Br}_9$, $\text{Cs}_3\text{Bi}_2\text{Cl}_9$ and $\alpha\text{-Cs}_3\text{Sb}_2\text{Cl}_9$, the luminescence of which is explained using a semiconductor model [13,23]. The excitation spectrum of $\text{Cs}_2\text{NaSbBr}_6$ is then ascribed to band-band transitions. The valence band is made up mainly of 5s wavefunctions and the conduction band of the 5p functions of the Sb^{3+} ions, both mixed to a certain extent with the 4s and 4p functions on the bromine atoms. This model has to be confirmed by photoconductivity measurements on single crystals. However, we were not able to grow single crystals from the solution. Growing single crystals of $\text{Cs}_2\text{NaSbBr}_6$ in another way seems to be a very hard task in view of the high volatility of antimony in this compound.

The two weak emission peaks near the band edge are due to free and/or bound exciton recombination. When the temperature is raised, detrapping occurs. From the temperature dependence of the emission intensity an activation energy for detrapping can be obtained [23], viz. about 10 cm^{-1} . The emission band around 12800 cm^{-1} is ascribed to deep centre recombination. Similar assignments were made for $\text{Cs}_3\text{Bi}_2\text{Cl}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$ and $\alpha\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ [13,23].

The decay time of the broad emission band at 12800 cm^{-1} is measured as a function of temperature. All decay curves were exponential. The luminescence intensities of the emission lines at 21000 cm^{-1} are too weak to perform decay time measurements. The decay time behaviour of the red emission band suggests that isolated Sb^{3+} is involved in the deep centre. Since oxygen is an obvious choice for an impurity in the sample, we assume that the Sb^{3+} ion of the deep centres is associated with oxygen (see also $\alpha\text{-Cs}_3\text{Sb}_2\text{Cl}_9$, $\text{Cs}_3\text{Bi}_2\text{Cl}_9$, $\text{Cs}_3\text{Bi}_2\text{Br}_9$ [13,23]). The longest decay time measured for the red emission amounts to $775 \mu\text{s}$ at 1.5 K. Assuming a value for the radiative decay at 0 K of about $800 \mu\text{s}$, ΔE could be obtained from a three-level fit in the temperature region 1.5–6 K and amounts to $15 \pm 3 \text{ cm}^{-1}$. The decrease of the decay time for temperatures above 6

K represents a thermally activated non-radiative process (fig. 4). The activation energy can be obtained from the temperature dependence of the decay time above 6 K and from the temperature dependence of the emission intensity [23]. In both cases ΔE amounts to about 40 cm^{-1} .

3.3. General discussion

From the above discussion it is clear that the luminescence in $\text{Cs}_2\text{NaSbCl}_6$ and $\text{Cs}_2\text{NaSbBr}_6$ has a completely different origin. The difference is most easily described in terms of localized, self-trapped exciton states (S state) and delocalized, nearly free exciton states (F state) as discussed by Toyozawa [24]. The occurrence of S or F states is balanced by the ratio $g = E_{1r}/B$, where E_{1r} denotes the lattice relaxation energy of the S state and B the energy lowering resulting from coherent propagation through the lattice of the F state. Rather abrupt changes from F to S states may occur when the balancing ratio exceeds a critical value ($g \approx 1$) [24,25].

The emission of $\text{Cs}_2\text{NaSbCl}_6$ is clearly S state emission, viz. a Stokes-shifted, broad-band emission. In contrast with this, the narrow edge emission of $\text{Cs}_2\text{NaSbBr}_6$ reveals the occurrence of F states. For this compound the value of B is rather large, as becomes evident by comparing the band edge of $\text{Cs}_2\text{NaSbBr}_6$ with the lower-energy excitation band of the diluted system $\text{Cs}_2\text{NaMBr}_6\text{-Sb}^{3+}$ [3]. The two present concentrated systems form a nice example of the change from localized excitons, captured at a particular site after lattice relaxation, to free or loosely bound mobile excitons moving from one site to another.

It is well known that (trivalent) ns^2 ions in concentrated compounds are often asymmetrically coordinated by their ligands. This is ascribed to the influence of the lone pair of the metal ion, which points in the direction of the more distant ligands [26–28]. As a result the a_0 value for $\text{Cs}_2\text{NaSbCl}_6$ will be considerably larger than expected from Shannon's value of 0.76 \AA [16]. As Shannon discussed for the case of the Bi^{3+} ion ($6s^2$), the radius of the s^2 ion increases in structures where the lone-pair character becomes dominant. The asymmetric distortion in $\text{Cs}_2\text{NaSbCl}_6$ cannot be static, because X-ray diffrac-

tion shows that $\text{Cs}_2\text{NaSbCl}_6$ possesses the cubic elpasolite structure.

In view of the high symmetry of the Sb^{3+} position in $\text{Cs}_2\text{NaSbCl}_6$ a dynamic distortion of the SbCl_6^{2-} octahedra should be taken into account. Vibronic coupling between the ground state (a_{1g}^2) and the first excited states ($a_{1g}t_{1u}$) may lead to a fluctuating structural deformation of the ground state, stabilized by the high-symmetry crystal field [29,30]. Such dynamic distortions were recently reported for the compounds A_2TeX_6 ($\text{A}=\text{Rb}, \text{Cs}$; $\text{X}=\text{Cl}, \text{Br}$) in which the tetravalent $5s^2$ ion Te^{4+} occupies a high-symmetry position [29,30]. As in $\text{Cs}_2\text{NaSbCl}_6$, the luminescence in these systems is ascribed to isolated $5s^2$ centres (Te^{4+}) [31,32], indicating that the lone pair is the driving force for these distortions.

In the case of $\text{Cs}_2\text{NaSbBr}_6$ the $5s^2$ electrons of the Sb^{3+} ion are delocalized to form a valence band. This will reduce the radius of the Sb^{3+} ion in comparison with $\text{Cs}_2\text{NaSbCl}_6$. This is confirmed by the a_0 value (see table 1), which is now in line with the ionic radii (table 2).

References

- [1] E.W.J.L. Oomen and G.J. Dirksen, *Mat. Res. Bull.* 20 (1985) 453.
- [2] E.W.J.L. Oomen, W.M.A. Smit and G. Blasse, *J. Phys. C* 19 (1986) 3263.
- [3] E.W.J.L. Oomen, G.J. Dirksen, W.M.A. Smit and G. Blasse, *J. Phys. C*, to be published.
- [4] A. Fukuda, *Sci. Light (Tokyo)* 13 (1964) 64.
- [5] A. Fukuda, *Phys. Rev. B* 1 (1970) 4161.
- [6] A. Ranfagni, D. Mugnai, M. Bacci, G. Vilianni and M.P. Fontana, *Advan. Phys.* 32 (1983) 823.
- [7] L.R. Morss, M. Siegal, L. Stenger and N. Edelstein, *Inorg. Chem.* 9 (1970) 1771.
- [8] A.C. van der Steen, *Phys. Stat. Sol.* 100b (1980) 603.
- [9] A. Wolfert and G. Blasse, *J. Solid State Chem.* 59 (1985) 133.
- [10] F. Pelle, B. Jacquier, J.P. Denis and B. Blanzat, *J. Luminescence* 17 (1978) 61.
- [11] R.C. Powell and G. Blasse, *Struct. Bonding* 42 (1980) 43.
- [12] G. Meyer and H.C. Gaebell, *Z. Naturforsch.* 33b (1978) 1476.
- [13] C.W.M. Timmermans, S.O. Cholakh and G. Blasse, *J. Solid State Chem.* 46 (1983) 222.
- [14] A.E. Hughes and G.P. Pells, *Phys. Stat. Sol.* 71b (1975) 707.
- [15] G. Boulon, C. Pedrini, M. Guidoni and Ch. Pannel, *J. Phys. (Paris)* 36 (1975) 267.
- [16] R.D. Shannon, *Acta Cryst.* A32 (1976) 751.
- [17] E.W.J.L. Oomen, L.C.G. van Gorkom, W.M.A. Smit and G. Blasse, *J. Solid State Chem.* 65 (1986) 156.
- [18] C.W.M. Timmermans and G. Blasse, *J. Solid State Chem.* 52 (1982) 222.
- [19] W.M.A. Smit and E.W.J.L. Oomen, Fall meeting of the Electrochemical Society, San Diego, USA (1986), Extended abstracts, Vol. 86-2, No. 699.
- [20] G. Blasse and A.C. van der Steen, *Solid State Commun.* 31 (1979) 993.
- [21] D. Mugnai, A. Ranfagni, O. Pilla, G. Vilianni and M. Montagna, *Solid State Commun.* 35 (1980) 975.
- [22] G. Blasse, G.J. Dirksen and W. Abriel, *Chem. Phys. Letters* 136 (1987) 460.
- [23] C.W.M. Timmermans and G. Blasse, *Phys. State. Sol.* 106b (1981) 647.
- [24] Y. Toyozawa, *J. Luminescence* 12/13 (1976) 13.
- [25] G. Blasse, *Rev. Inorg. Chem.* 5 (1983) 319.
- [26] R.J. Gillespie, *Molekülgeometrie* (Verlag Chemie, Weinheim, 1975).
- [27] J.F. Sawyer and R.J. Gillespie, *Progr. Inorg. Chem.* 34 (1986) 65.
- [28] J. Galy and R. Enjalbert, *J. Solid State Chem.* 44 (1982) 1.
- [29] W. Abriel, *Acta Cryst.* B42 (1986) 449.
- [30] W. Abriel and E.J. Zehnder, IIIrd European Conference on Solid State Chemistry, Regensburg, West Germany (1986), Book of Abstracts, Vol. 1, p. 155.
- [31] R. Wernicke, H. Kupka, W. Ensslin and H.H. Schmittke, *Chem. Phys.* 47 (1980) 235.
- [32] G. Blasse, G.J. Dirksen and P.A.M. Berdowski, *Chem. Phys. Letters* 112 (1984) 313.