

THE INFLUENCE OF DISTORTION OF THE Te(IV) COORDINATION OCTAHEDRON ON ITS LUMINESCENCE

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The luminescence of the following compounds is reported: Cs_2TeCl_6 and Rb_2TeBr_6 , both with undistorted TeX_6^{2-} octahedra ($X = \text{Cl}, \text{Br}$), and $(\text{PDA})\text{TeCl}_6$ and $\text{Ca}(\text{H}_2\text{O})_7\text{TeBr}_6$, both with distorted TeX_6^{2-} octahedra. In agreement with results obtained earlier for other ions with the s^2 configuration, the distortion results in an increase of the Stokes shift and a decrease of the thermal quenching temperature.

1. Introduction

The luminescence of ions with s^2 configuration has been studied for many years, but nevertheless the way in which the crystal structure of the host lattice influences this type of luminescence is not well understood [1,2]. For Bi^{3+} ($6s^2$) it has been observed that tight octahedral coordination results in emission of the Bi^{3+} ion with small Stokes shift and vibrational structure. However, if the Bi^{3+} ion shows its characteristic asymmetric coordination with short and long Bi^{3+} -anion distances on different sides of the central ion, the luminescence shows a surprisingly large Stokes shift [1-3]. This has been ascribed to the tendency of the Bi^{3+} ion to return to a more symmetrical coordination in the excited state. These observations suggest that the Stokes shift of the emission is determined by the distortion of the coordination octahedron of the s^2 ion in the ground state. For the Sb^{3+} ion ($5s^2$) we also found evidence for this statement [4].

It is difficult to prove in a direct way that this relation between Stokes shift and distortion really holds. The main reason for this is that the concentration of

s^2 ions in a luminescent material is usually only a few percent, so that it is hard to measure its coordination characteristics. The spectra often do not yield much information, since they are of the broad-band type, with only a few exceptions. Recently we have performed EXAFS measurements on $\text{LaPO}_4\text{-Bi}$, the luminescence of which shows a very large Stokes shift [5]. This study yields evidence that the coordination of the Bi^{3+} ion is distorted from that of the La^{3+} ion.

This paper approaches this problem from a different point of view. A few years ago several investigators reported independently on the luminescence of the TeCl_6^{2-} octahedron where the central metal ion has $5s^2$ configuration [6-8]. The host lattices used were those with K_2PtCl_6 structure, viz. Rb_2TeBr_6 , Cs_2TeCl_6 and Cs_2TeBr_6 , $\text{Cs}_2\text{HfCl}_6\text{:Te}$, $\text{Cs}_2\text{HfBr}_6\text{:Te}$ and $\text{Rb}_2\text{SnBr}_6\text{:Te}$. These lattices contain statically undistorted TeCl_6^{2-} and TeBr_6^{2-} octahedra. X-ray diffraction experiments on Rb_2TeBr_6 at temperatures down to 12 K confirmed this coordination [9]. These compositions show a luminescence which is characteristic for Te(IV) in the $5s^2$ state.

Abriel and co-workers [10] have shown that the TeX_6^{2-} ($X = \text{Cl}, \text{Br}, \text{I}$) octahedron is strongly dis-

torted in crystals with an acentric point symmetry for the Te site (strong pseudo-Jahn–Teller effect, ref. [11]). With a center of symmetry for this position a dynamically distorted anion with mean symmetry $m\bar{3}m$ results. This high-symmetry crystal field is given for the simple alkali hexahalotellurates(IV) with an antiferro-type arrangement of cations and anions, for example. But this dynamical distortion (weak pseudo-Jahn–Teller effect, ref. [11]) is evident from spectroscopic measurements only (FTIR experiments, e.g. ref. [12]). Here we use for simplicity the terms distorted and undistorted polyhedra.

In this paper we report on the luminescence of these statically distorted octahedra. For this purpose we selected $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{TeCl}_6 \equiv (\text{PDA})\text{TeCl}_6$, where the TeCl_6^{2-} octahedron has Te–Cl distances 2.43 (2 \times), 2.49, 2.56 and 2.67 Å (2 \times) [13], and $\text{Ca}(\text{H}_2\text{O})_7\text{TeBr}_6$, where the TeBr_6^{2-} octahedron has Te–Br distances 2.58 (2 \times), 2.68 (2 \times) and 2.84 Å (2 \times) [14]. It was observed that upon distortion the luminescence of the Te(IV) octahedron shows a larger Stokes shift and a lower thermal quenching temperature.

2. Experimental

The preparation of the hexabromo- and hexachloro-tellurates(IV) was described elsewhere [9,10,13,14]. The way in which the optical measurements were performed has been reported [3,8].

3. Results and discussion

3.1. Cs_2TeCl_6

The emission spectrum of Cs_2TeCl_6 has been analyzed in detail by Schmidtke and co-workers [6]. This spectrum shows an extensive vibrational progression in the e_g mode (240 cm^{-1}) of the TeCl_6^{2-} octahedron, indicating a tetragonal Jahn–Teller distortion in the excited state. From their calculation of the potential energy surfaces it is possible to estimate the energy barrier between equivalent minima. This value is at least 2000 cm^{-1} , which suggests the Jahn–Teller effect in the excited state to be static.

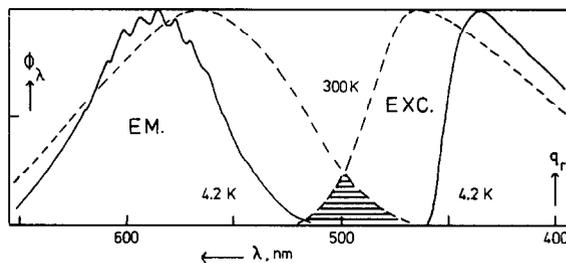


Fig. 1. Emission spectra (EM) and excitation spectra (EXC) of the luminescence of Cs_2TeCl_6 at 4.2 K (full lines) and 300 K (broken lines). The relative quantum output (q_r) and the spectral radiant power per constant wavelength interval (Φ_λ) are given in arbitrary units. The spectral overlap (see text) is hatched. The spectra are independent of excitation wavelength and monitored emission wavelength, respectively.

Our spectra at 4.2 K reproduce the vibrational structure in the emission band. The frequency involved is $230 \pm 15 \text{ cm}^{-1}$ in good agreement with ref. [6]. The vibrational structure broadens at higher temperatures and disappears at about 60 K. Thermal quenching of the luminescence starts above 200 K.

It is interesting to note that the emission maximum shifts to higher energies upon increasing the temperature. Whereas this maximum is at about 585 nm at 4.2 K, it is at 565 nm at 300 K (fig. 1). This thermal shift appears at about 100 K. The emission band broadens considerably at higher temperatures. By fitting the spectral half-width δ to $\delta(T) = \delta(0) [\tanh(h\nu/2kT)]^{-1/2}$ [15], we arrive at $\nu \approx 180 \text{ cm}^{-1}$ (fig. 2). This value relates to the excited state, whereas the value $230 \pm 15 \text{ cm}^{-1}$ relates to the ground state. Since ν is an effective frequency, it is questionable whether the two values may be compared.

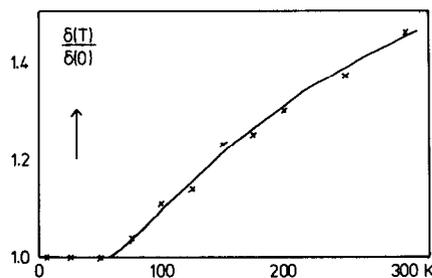


Fig. 2. The relative emission bandwidth as a function of temperature. Crosses indicate experimental points, the full line is the fit for $\nu = 180 \text{ cm}^{-1}$ (see text).

Schmidtke and co-workers [6] expect the excited-state frequency to be the higher one; the effective frequency may well contain a contribution from lower-frequency modes.

Due to the high concentration of TeCl_6^{2-} octahedra, the optical absorption of the samples is very strong (all compounds are strongly coloured). This makes not only diffuse reflection spectra unreliable to estimate the position of the absorption transitions, but even more so the excitation spectra. The absorption maximum is expected to correspond to excitation minima. To derive the Stokes shift from our excitation spectra, we used the experimentally observed excitation maxima. These do not necessarily correspond to the absorption maxima. However, as long as we compare only these "apparent Stokes shifts" with each other, the error involved will be small. Due to the broadening and shifts of the spectral bands, and in view of thermal quenching in a few cases, all Stokes shifts are taken at 4.2 K.

The excitation maximum of the Cs_2TeCl_6 luminescence is at 435 nm at 4.2 K (fig. 1) resulting in a value for the Stokes shift of 5000 cm^{-1} . At higher temperatures this band broadens considerably and shifts to lower energy.

It is interesting to consider the question of the reason for the thermal quenching of the luminescence of Cs_2TeCl_6 which takes place in the region 200–300 K. Since Ackerman has shown that the isomorphous and diluted composition $\text{Cs}_2\text{Hf}_{0.99}\text{Te}_{0.01}\text{Cl}_6$ emits efficiently at 300 K [7], we can assume that the quenching in the case of Cs_2TeCl_6 is due to concentration quenching by a process based upon migration of the excitation energy through the lattice to quenching sites [1,2]. Since the shortest Te–Te distance amounts to 7.3 \AA , the primary transfer step has to overcome a large distance.

The critical distance for energy transfer (R_c) was calculated for $\text{TeCl}_6^{2-} - \text{TeCl}_6^{2-}$ transfer at 300 K from the formula [16]

$$R_c^6 = (0.6 \times 10^{28})(4.8 \times 10^{-16} f/E^4) \text{ SO}.$$

The oscillator strength f of the relevant $^1\text{S}_0 - ^3\text{P}_1$ transition was taken to be 10^{-2} [17]; E , the energy of maximum spectral overlap, is 2.5 eV according to our spectra; SO, the spectral overlap of emission and absorption, amounts to 0.1 eV^{-1} as derived from our

spectral data. This yields $R_c \approx 21 \text{ \AA}$, nearly three times the shortest Te–Te distance.

Energy migration is therefore, possible. In fact the transfer probability at 300 K is $3^6 \approx 700$ times the radiant probability. The average excited state makes 700 transfers during its lifetime. The corresponding diffusion length is about $700^{1/2} \times 7.3 \approx 200 \text{ \AA}$. This is far enough to reach possible quenching sites. Below 300 K the emission and excitation bands start to narrow. This makes the factor SO drastically smaller, so that soon the temperature is reached where migration is hampered. Actually SO vanishes at 4.2 K (fig. 1).

Finally one might wonder what the reason is for this temperature dependence of the emission and excitation bands. The broadening will be related to the low vibrational frequencies involved. The effects are considerably more pronounced than in, for example, oxides. The large thermal shift, however, seems to have another origin. Schmidtke and co-workers [6] have shown that the energy surface of the excited state contains equivalent X minima separated by an energy barrier mentioned above. This implies that the minimum cannot be considered as a paraboloid, but is probably fairly asymmetrical. In that case occupation of the higher vibrational levels results in a shift of the emission band to higher energies [18]. Actually the system will approach the transition from a static to a dynamic Jahn–Teller effect.

The shift of the excitation band is probably related to the increasing Jahn–Teller splitting of the corresponding absorption band [19]. However, as argued above, such a splitting is hard to deduce from our excitation spectra. It has been observed by Stufkens [20] for the TeCl_6^{2-} octahedron in solution.

Therefore we have to conclude that the Jahn–Teller effect in the excited state of the cubic TeCl_6^{2-} octahedron determines the luminescence properties of the TeCl_6^{2-} octahedron for an important part. By applying a method proposed by Magnai et al. [21], and using the $^3\text{P}_1 - ^3\text{P}_0$ energy difference for Te(IV) as derived in ref. [8], and the absorption maxima as given in ref. [20], we arrive at a value for the effective Jahn–Teller coupling constant (I) $I^2 \approx 1.6 \text{ eV}$, a rather high value.

3.2. Rb_2TeBr_6

The spectral data for Rb_2TeBr_6 are taken from ref. [8] to make comparisons more reliable. This host lattice also contains undistorted $TeBr_6^{2-}$ octahedra [9]. At 4.2 K the maximum of the emission band is at 680 nm, that of the excitation band at 485 nm. This implies a Stokes shift of 6000 cm^{-1} . The lower-energy position of the spectral bands is due to a reduction of the interelectron repulsion energy parameters going from the chloride to the bromide [17].

This luminescence is quenched between 100 and 200 K. The lower-energy position of the spectral bands is probably responsible for this intracentre quenching [22]. The diluted composition $Cs_2(Hf,Te)Br_6$ also quenches below room temperature [7]. Let us now turn to the results for the distorted $Te(IV)$ octahedra.

3.3. (PDA) $TeCl_6$

At 4.2 K (PDA) $TeCl_6$ shows an efficient yellow emission. The maximum of the single emission band is situated at 625 nm, that of the lowest excitation band at 415 nm. This yields a Stokes shift of 8000 cm^{-1} . The emission spectrum does not show any vibrational structure, as observed for Cs_2TeCl_6 .

Temperature quenching of the luminescence starts at about 60 K and is practically complete at 125 K. The spectral positions at 125 K are not strikingly different from those at 4.2 K (maxima at 625 and 420 nm). The same holds for the line broadening. Therefore the quenching is due to an intracentre quenching process, and not to energy migration to quenching centres. Note that in the case of Cs_2TeCl_6 (with

smaller Stokes shift) the latter process only becomes apparent above 200 K.

To summarize, the emission of the distorted $TeCl_6^{2-}$ octahedron shows a larger Stokes shift and a lower quenching temperature than that of the undistorted octahedron. We shall now see that the same is true for the $TeBr_6^{2-}$ octahedron.

3.4. $Ca(H_2O)_7TeBr_6$

This compound shows a deep-red luminescence. The maximum of the single emission band is at 4.2 K at 710 nm, that of the excitation band at 470 nm, so that the Stokes shift is 7500 cm^{-1} . Thermal quenching starts at 50 K and is practically complete at 110 K.

The efficiency of this luminescence at 4.2 K is considerably lower than that of Rb_2TeBr_6 (about one order of magnitude). Such a large difference is not observed upon comparing Cs_2TeCl_6 and (PDA) $TeCl_6$. This may be ascribed to one or both of the following reasons:

(i) It is well known that the efficiency of broadband red emission is sensitive to the value of the Stokes shift and the position of the excited state [22].

(ii) The water molecules in the lattice offer high-frequency vibrations which may facilitate the non-radiative transitions.

3.5. Comparison of the results on individual compounds

Table 1 shows convincingly that distortion of the TeX_6^{2-} octahedron results in a larger Stokes shift, and consequently in a lower thermal quenching temperature of the emission. The case of the chlorides is the

Table 1

Comparison of structural and luminescence properties of some compounds with $TeCl_6^{2-}$ or $TeBr_6^{2-}$ octahedra

Compound	TeX_6^{2-} octahedron	Emission maximum ^{a)} (nm)	Excitation maximum ^{a)} (nm)	Stokes shift ^{a)} (cm^{-1})	Quenching region (K)
Cs_2TeCl_6	undistorted	585	435	5000	200–300
(PDA) $TeCl_6$	distorted	625	415	8000	60–125
Rb_2TeBr_6	undistorted	680	485	6000	100–200
$Ca(H_2O)_7TeBr_6$	distorted	710	470	7500	50–110

^{a)} Values at 4.2 K.

most convincing, since the actual intracentre quenching in the case of Cs_2TeCl_6 starts above 300 K, as becomes clear from the diluted system (see section 3.1).

This result confirms, therefore, our earlier statement that a distortion of the s^2 ion polyhedron leads to a larger Stokes shift. In this connection it is interesting to note that the Stokes shift of the Te(IV) ion luminescence in oxidic anti-glasses is larger than in the present compounds, viz. 10000–15000 cm^{-1} [23]. In these compositions the Te(IV) ion occupies strongly distorted oxygen polyhedra.

Finally we note that the actual situation in these Te(IV) octahedra is not easy to describe exactly. Obviously there is a strong pseudo-Jahn–Teller effect active in the excited state which is stabilized in the low-symmetry crystal fields of the PDA- and $\text{Ca}(\text{H}_2\text{O})_7$ -compounds. The distortion of the ground-state octahedron is due to a mixing of 5s and 5p orbitals (vibronic coupling, weak pseudo-Jahn–Teller effect). It is clear that the luminescence properties are sensitive to these effects.

References

- [1] G. Blasse, *Rev. Inorg. Chem.* 5 (1983) 319.
- [2] G. Blasse, *Mat. Chem. Phys.* 16 (1987), to be published.
- [3] C.W.M. Timmermans and G. Blasse, *J. Solid State Chem.* 52 (1984) 222.
- [4] E.W.J.L. Oomen, L.C.G. van Gorkem, W.M.A. Smit and G. Blasse, *J. Solid State Chem.* 65 (1986) 156; E.W.J.L. Oomen, W.M.A. Smit and G. Blasse, *J. Phys.* 19 (1986) 3263.
- [5] F.B.M. van Zon-Duivenvoorden, D.C. Koningsberger, E.W.J.L. Oomen and G. Blasse, to be published.
- [6] R. Wernicke, H. Kupka, W. Ensslin and H.H. Schmidtke, *Chem. Phys.* 47 (1980) 235; J. Degen, H.H. Schmidtke and C.A. Chatzidimitrou-Dreisemann, *Theoret. Chim. Acta* 67 (1985) 37.
- [7] J.F. Ackerman, *Mat. Res. Bull.* 19 (1984) 783.
- [8] G. Blasse, G.J. Dirksen and P.A.M. Berdowski, *Chem. Phys. Letters* 112 (1984) 313.
- [9] W. Abriel and J. Ihringer, *J. Solid State Chem.* 52 (1984) 274.
- [10] W. Abriel, *Acta Cryst.* B42 (1986) 449.
- [11] I.B. Bersuker, *The Jahn–Teller effect and vibronic interactions in modern chemistry* (Plenum Press, New York, 1984).
- [12] W. Abriel and E.J. Zehnder, *IIIrd European Conference on Solid State Chemistry, Book of Abstracts, Vol. 1* (1986) p. 155.
- [13] W. Abriel and C. Friedrich, *Z. Naturforsch.* 40b (1985) 1691.
- [14] W. Abriel and H. Ehrhardt, *Angew. Chem. Intern. Ed.* 23 (1984) 963.
- [15] D. Curie, in: *Optical properties of ions in solids*, ed. B. DiBartolo (Plenum Press, New York, 1975) p. 71.
- [16] G. Blasse, *Philips Res. Rept.* 24 (1969) 131.
- [17] C.K. Jørgensen, *Absorption spectra and chemical bonding* (Pergamon Press, Oxford, 1962) p. 186.
- [18] A. Fukuda, *Phys. Rev. B1* (1970) 4161.
- [19] Y. Toyozawa and M. Inoue, *J. Phys. Soc. Japan* 21 (1966) 1663.
- [20] D.J. Stufkens, *Rec. Trav. Chim.* 89 (1970) 1185; D.J. Stufkens and A. Schenk, *Rec. Trav. Chim.* 90 (1971) 190.
- [21] D. Mugnai, A. Ranfagni, O. Pilla, G. Viliani and M. Montagna, *Solid State Commun.* 35 (1980) 975.
- [22] K.C. Bleijenberg and G. Blasse, *J. Solid State Chem.* 28 (1979) 303.
- [23] G. Blasse, G.J. Dirksen, E.W.J.L. Oomen and M. Trömel, *J. Solid State Chem.* 63 (1986) 148.