

LUMINESCENCE OF A HIGHLY CHARGED MERCURY-LIKE ION: TELLURIUM(IV)

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The luminescence of Rb_2TeBr_6 is reported and interpreted in terms of the $5s^2$ configuration of the Te^{4+} ion.

The luminescence of mercury-like ions is well known and has been studied in detail [1]. Especially the alkali halides doped with mercury-like ions have been investigated thoroughly [2]. These studies are restricted to ions with valencies 1, 2 and 3. Here we wish to report the observation of luminescence from a more highly charged ion, viz. $\text{Te}^{4+}(5s^2)$.

For our investigation we selected the compound Rb_2TeBr_6 . Recently its crystal structure has been determined down to liquid-helium temperatures [3]. At room temperature the structure is of the K_2PtCl_6 type, i.e. the TeBr_6^{2-} octahedra have perfect octahedral symmetry and do not share anions. At 45 K a phase transition occurs, but the TeBr_6^{2-} group remains undistorted. They only show a ferrotorotative displacement with tilt angle 4.7° . This compound seems therefore to be ideal as a model compound for investigation of the luminescence of the Te^{4+} ion.

Samples were prepared as described in ref. [3]. They were checked by X-ray diffraction. They have a brilliant red colour. The way in which the optical measurements were performed has been described before [4].

Below 200 K Rb_2TeBr_6 shows a strong deep-red luminescence under ultraviolet and visible excitation. The emission spectrum consists of a single band with a maximum at about 680 nm. The emission intensity is temperature independent from liquid-helium temperature to 100 K. The thermal quenching region extends from about 100 to 180 K.

The excitation spectrum of this emission contains three bands, viz. an asymmetric one with a maximum at about 485 nm (A), another one at 410 nm and a

broad one at about 350 nm (C). Their intensities are about equal. This implies a Stokes shift of 0.75 eV. The energy difference between the A and C band is about 1.1 eV. When this work was finished, we became aware of similar emission spectra at 77 K for Cs_2TeCl_6 and Cs_2TeBr_6 (ref. [5]).

All decay curves of the emission were exponential. Fig. 1 shows the temperature dependence of the decay time of the luminescence of Rb_2TeBr_6 . Between 10 and 20 K there is a drop in decay time from the millisecond to the microsecond region. Note that the luminescence intensity is constant in this temperature range. This shows that the decay times have to be analysed with a three-level scheme [6]. If the level sequence is $0 < 1 < 2$, the fit procedure yields $\Delta E = 90 \pm 4 \text{ cm}^{-1}$, $\tau_1 = 2215 \pm 25 \mu\text{s}$ and $\tau_2 = 600 \pm 250 \text{ ns}$. Here ΔE is

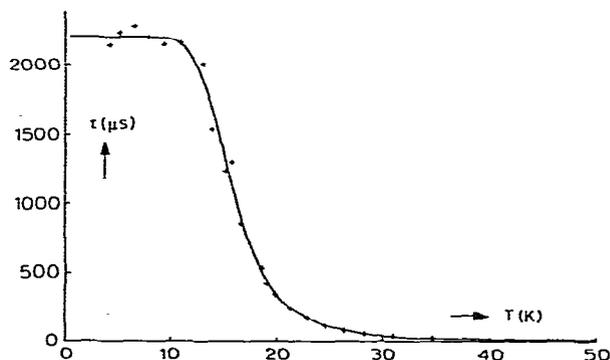


Fig. 1. Decay times of the emission of Rb_2TeBr_6 as a function of temperature. Excitation wavelength 380 nm, emission wavelength 680 nm.

the energy difference between levels 1 and 2, and τ_i the purely radiative decay time of level i .

The same luminescence was observed for isomorphous $\text{Rb}_2\text{SnBr}_6 : \text{Te}$. The emission band was slightly shifted to higher energy as observed also for the analogous cesium compounds [5]. This shows that the luminescence is due to the TeBr_6^{2-} octahedron.

An analysis of the present observations in terms of the $5s^2$ configuration of Te^{4+} is obvious. Stufkens [7] has reported the absorption spectrum of $(\text{Bu}_4\text{N})_2\text{TeBr}_6$ in CH_2Cl_2 and found the A band ($^1\text{S}_0 - ^3\text{P}_1$) at about 460 nm and the C band ($^1\text{S}_0 - ^1\text{P}_1$) at about 330 nm. In Rb_2TeBr_6 we find these transitions at 485 and 350 nm. The asymmetry observed in the A excitation band is ascribed to the dynamical Jahn-Teller effect [2,7].

The emission is due to the $^3\text{P}_{1,0} \rightarrow ^1\text{S}_0$ transition, i.e. level 0 in the three-level scheme is the ground state $^1\text{S}_0$, level 1 is $^3\text{P}_0$, level 2 is $^3\text{P}_1$. The energy difference $^3\text{P}_1 - ^3\text{P}_0$ is 90 cm^{-1} . At liquid-helium temperature the emission is from $^3\text{P}_0$ as shown by the long decay time (2.2 ms) resulting from the $J=0 \rightarrow J=0$ selection rule. Above 10 K the $^3\text{P}_1$ level is also occupied and the decay time decreases. The value of τ_2 ($\approx 0.6 \mu\text{s}$) reflects the spin selection rule.

One observation does not fit in this general scheme, viz. the presence of a strong band in the excitation spectrum between the A and the C band. It is far too strong to be assigned to the B band which was observed by Stufkens as a weak shoulder. We ascribe this band to the D band [2], i.e. to a charge-transfer transition from the Br^- ions to the central Te^{4+} ion.

For the lower-charged mercury-like ions the D band

is usually found at energies higher than that of the C band [2]. However, the high positive charge of the Te^{4+} ion will shift the D band to lower energies. A similar observation has been made before for Bi^{3+} in bromides [8].

Finally we note that energy migration among the TeBr_6^{2-} octahedra is not possible in view of the considerable Stokes shift [9]. As a consequence no concentration quenching of the luminescence is observed.

In conclusion we have characterized the luminescence of one of the higher charged mercury-like ions, viz. $\text{Te}^{4+}(5s^2)$.

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