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Mercury centres in caesium halide crystals

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Electronic absorption spectrum of CsBr crystals doped with Hg^{2+} showed three bands at 340, 250 and 217.5 nm at 300 K, which disappeared on ageing and reappeared on quenching the crystals from 700 K. Radiation damage studies indicated the formation of Hg^{+} centres and on prolonged irradiation Hg^{0} centres. Similar results have also been obtained in the case of $CsI:Hg^{2+}$.

1. Introduction

Small concentrations of aliovalent impurities incorporated into ionic crystals form localized energy levels between the valence band and the conduction band. Such impurity centres act as probes for the study of electronic and ionic processes in these crystals. Many experiments have established the models for the various defect centres in NaCl-type lattices, but comparatively less attention has been given to defect centres in caesium halides. In particular, it was found difficult to incorporate divalent cationic impurities in such crystals [1].

Among the Group II B elements, mercury is unique in having both mono- and divalent ions in aqueous solutions. Very few studies on mercury centres in fcc crystalline matrices have been carried out [2–5]. Not much work has been reported on caesium halide (simple cubic) lattices. Hence the present work is undertaken in order to observe the possible changes due to the changes in the structure of the host lattice and also to study the defect properties in these matrices.

2. Experimental details

Crystals of CsBr and CsI doped with Hg^{2+} ions were grown by the Stockbarger method from the melt using evacuated quartz ampoules which were sealed off at a pressure of 10^{-5} torr. The concentration of the impurity was around 200 p.p.m. All the materials used for the crystal growth were of Analar grade. Optical absorption measurements were made on a CARY-14 spectrophotometer. The low temperture spectra were recorded using a metal bath-type cryostat. A cobalt source was used for γ-irradiating the crystals.

3. Results and discussion

3.1. Mercury in CsBr

As-grown single crystals of CsBr doped with Hg^{2+} show prominent bands at 340, 250 and a shoulder at 217.5 nm at 300 K as shown in Fig. 1. The characteristic feature of the mercury centres is that on ageing (48 h at 300 K) all the above bands disappear as indicated by curve 3 (Fig. 1). On quenching the crystal from 700 K, all the above bands reappear. Similar results have been obtained in the case of $KCl:HgCl_2$ [4], where on ageing, mercury precipitates as $HgCl_2$ in the crystal and on quenching the mercury ions are dispersed back into the lattice and the characteristic spectrum of Hg^{2+} ions was obtained. The optical absorption spectrum of $CsBr:Hg^{2+}$ recorded at 80 K is shown by curve 2 of Fig. 1. At 80 K all the bands are well defined.

In order to identify the species giving rise to the observed spectrum and to understand the formation of new defects on irradiation, the $CsBr:Hg^{2+}$ crystals were subjected to various dosages of γ radiation and the recorded spectrum is shown in Fig. 2. It can be seen that the two bands peaking at 340 and 217.5 nm in the as-grown unirradiated sample vanish on irradiation. On the other hand, the band at 250 nm is reduced in intensity and its half-width increases. In additon, a well-defined F-band is observed at 685 nm which grows in intensity as the radiation dosage increases. On irradiating $CsBr:Hg^{2+}$ crystal, Hg^{2+} centre traps an electron and is converted into Hg^{+}. Hence the bands at 340 and 217.5 nm which vanish on irradiation are due to Hg^{+} centres. The complex nature of the band at 250 nm indicates that apart from Hg^{2+} centres, some other species which is formed on irradiation is also responsible for the absorption, since the half-width increases as the radiation dosage increases, though there is a reduction in intensity. Tentatively the species which are giving rise to this band can be assigned to Hg^{2+} and Hg^{+}. Another possibility is that the band at 250 nm may be due to paired aggregates ($Hg^{+}–Hg^{+}$). It is known that while doping with Hg^{2+}, some Hg^{+} is also formed by decomposition, as in the case of potassium halide crystals doped with mercury [3]. It is also known that monovalent mercury dimerizes by the formation of metal–metal bonds, i.e. $Hg^{+}–Hg^{+}$. On quenching the crystal, the original shape of the band is restored since the aggregates are broken. Therefore, from the above studies, it is clear that the band at 250 nm is due to more than one centre and the most probable species giving rise to the absorption in this region are Hg^{2+} and irradiation product Hg^{+}. The assignments for the various bands are given in Table I.

The F-centre growth rate was studied using pure and Hg^{2+}-doped CsBr crystals for the same dosages of irradiation. Irradiated $CsBr:Hg^{2+}$ crystal shows that Hg^{2+} suppresses the growth rate of F-centres and that

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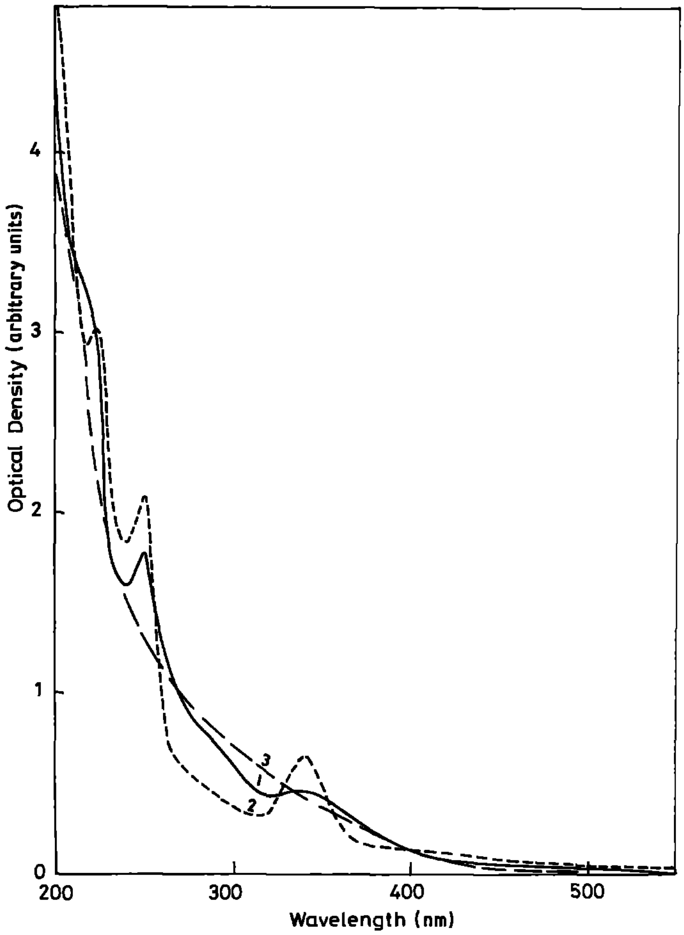

Figure 1 Optical absorption spectra of CsBr : Hg^{2+}, (——) at 300 K (curve 1); (– – –) at 80 K (curve 2); (— —) effect of ageing (curve 3).

Hg^{2+} is converted to Hg^{+}. Here Hg^{+} is the primary product. These Hg^{+} ions further trap electrons to form Hg^0 centres, which is a secondary product and its concentration is very low as compared to the other centre. There is some evidence of Hg^0 centres, which are formed on higher dosage of irradiation, giving rise to a band at 290 nm which shows no temperature dependence.

Fig. 3 shows the optical absorption spectrum of CsBr : Hg^{2+} crystal irradiated with gamma rays for 30 min at room temperature and the spectrum recorded both at room temperature and 80 K. The spectrum at 80 K shows the bands due to Hg^{2+} at 340 nm along with bands due to Hg^{+} centres at 250 nm and that due to Hg^0 centres at 290 nm. The band due to Hg^{+} becomes more prominent at 80 K and that due to Hg^0 does not show any significant temperture dependence. Another notable change in the spectrum recorded at 80 K as compared with that of room temperature is the shift in the position of the F-band towards lower wavelength. In the case of alkali halides, the band due to Hg^0 occurs around 275 nm [3]. The band due to Hg^0 is not strongly temperature dependent as the centres form isolated coagulated groups.

3.2. Mercury in CsI

The optical absorption spectra of CsI : Hg^{2+} recorded at room temperature and 80 K are shown in Fig. 4 along with the spectrum of the sample irradiated by

TABLE I Optical absorption data of mercury in CsBr and CsI crystals

Crystal	Band position (nm)		Assignments
	300 K	80 K	
CsBr : Hg^{2+} unirradiated	340	340	Hg^{2+}
	250	250	Hg^{+}-paired aggregates
	217.5	217.5	Hg^{2+}
CsBr : Hg^{2+} gamma-irradiated	290	290	Hg^0
	250	250	Hg^{+}
CsI : Hg^{2+} unirradiated	390	390	Hg^{2+}
	340	340	Hg^{+}
	285	285	Hg^{2+}
		250	Hg^{+}
		225 215	Exciton bands
CsI : Hg^{2+} gamma-irradiated	340	–	Hg^{+}
	250	–	Hg^{+}

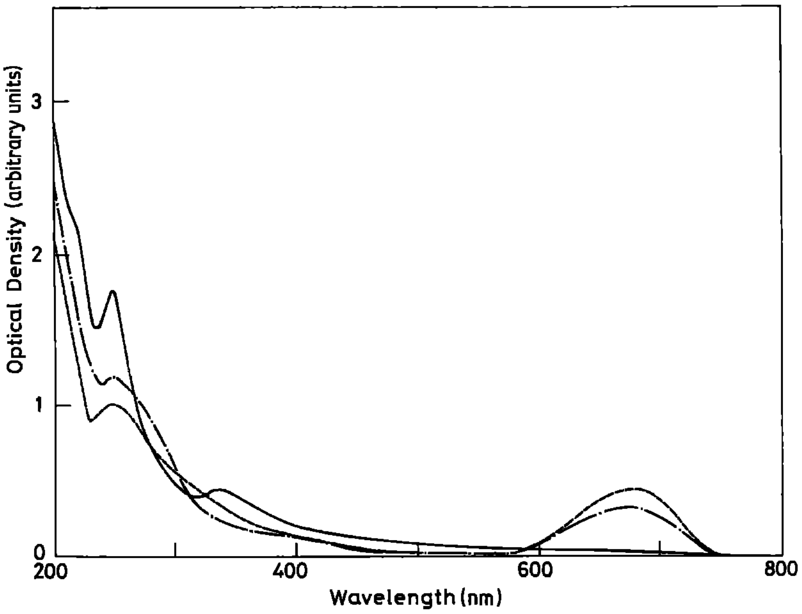

Figure 2 Optical absorption spectra of γ-irradiated CsBr : Hg^{2+} at different dosages of irradiation. (——) Unirradiated, (–·–) irradiated 10 min, (– – –) irradiated 30 min.

γ-rays at 300 K. The spectrum recorded at room temperature shows three bands at 390, 340 and 285 nm. At 80 K, all the above bands become well defined and a weak band at 250 nm appears along with two intense and sharp bands at 225 and 215 nm which are the exciton bands [6]. These are due to the transitions from the components of the spin orbit split halide valance band to an s-like electron orbital.

On irradiation, the bands at 390 and 285 nm disappear indicating that they are due to Hg^{2+} centres, whereas the bands at 340 and 250 nm, which become prominent on irradiation, are due to Hg^{+} (Fig. 4). The band positions and the assignments are given in Table I.

Hg^{2+} is isoelectronic with Au^{+} and has the same outer electronic structure as Cu^{+} and Ag^{+}. The ground state of Hg^{2+} which is a $5d^{10}$ system is $^1S_0$ and the excited states are $5d^96s$ and $5d^96p$. Lushchik and Lushchik [7] have assigned the bands observed in the spectrum of KCl doped with Cu^{+}, Ag^{+} and Au^{+} ions to $nd^{10} \rightarrow nd^9(n+1)p$ on the basis of band gap compressions which is expected when a metal ion is placed in a strong crystal field. The transitions nd^{10} to $nd^9(n+1)s$, are phonon-induced which

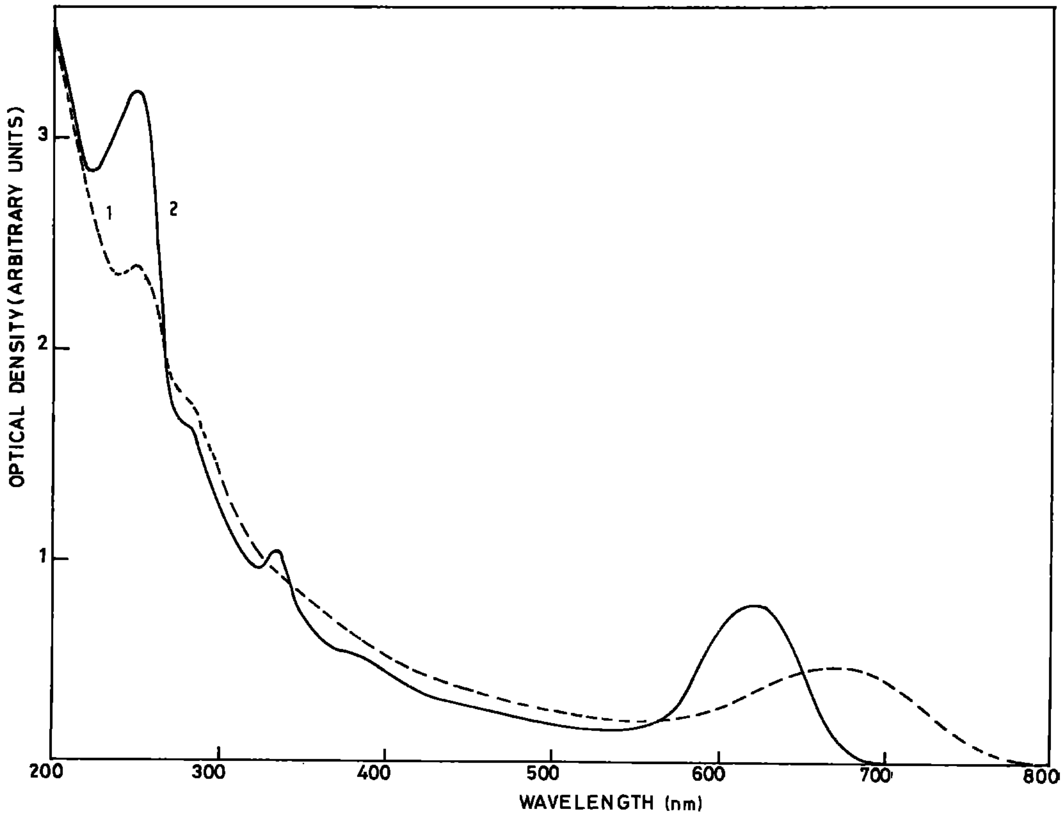

Figure 3 Optical absorption spectra of irradiated CsBr : Hg^{2+} crystals at 300 K (curve 1) and 80 K (curve 2).

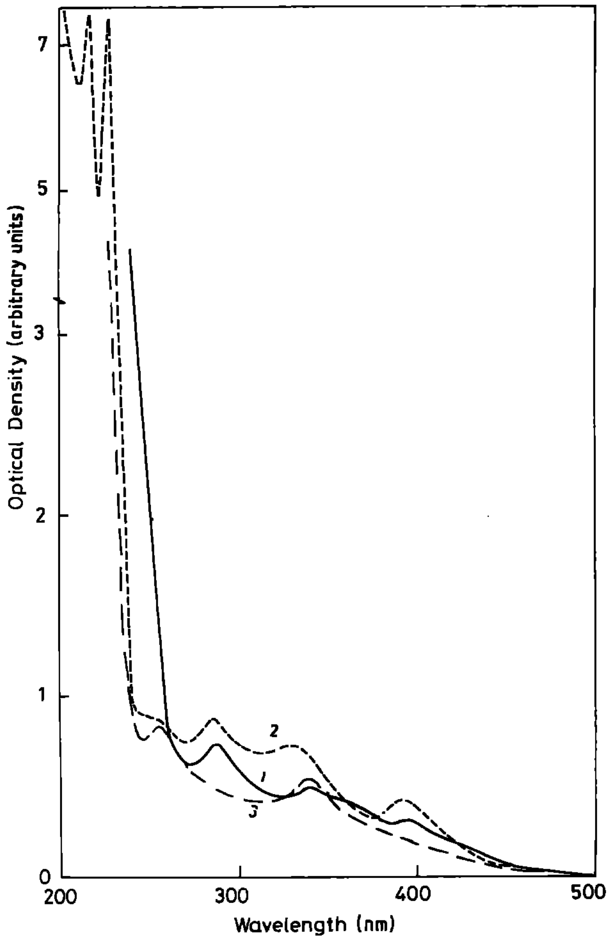

Figure 4 Optical absorption spectra of CsI : Hg^{2+} (——) at 300 K (curve 1), (– – –) at 80 K (curve 2) and (— — —) irradiated at 300 K (curve 3).

increases in intensity as the temperature increases. On the other hand, most of the spin forbidden d^{10} to d^9p transitions are likely to be only slightly intensified at lower temperature [8]. In the present case, the bands observed and their temperature variation support that $5d^{10}$ to $5d^96p$ transitions are responsible for the spectrum observed as in the case of KCl : Hg^{2+} [4].

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