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Abstract. CsCl crystals grown from water solution give a broad fluorescence emission between 340 nm and 500 nm due to the OH^- ions embedded in the lattice, which are also responsible for the 267 nm absorption band observed in these crystals. Eu doped CsCl crystals give a prominent emission with maximum at 440 nm, due to the divalent Eu ions. The emission due to OH^- ions is also observed in CsCl:Eu crystals.

1. Introduction

Divalent rare-earth ions have been found to be suitable candidates for the active media of broadly tunable solid state lasers in the visible region [1]. In addition, Eu doped alkali halides have been found to be suitable for dosimetric applications [2] and useful as selective UV dosimeter materials in the actinic region [3] and as x-ray imaging screens [4]. Such versatile applications call for a better understanding of the basic processes involved in the luminescence phenomena in these materials. This work presents and discusses the results of photoluminescence investigations carried out on undoped and Eu doped CsCl crystals.

2. Experimental details

A saturated solution of CsCl (Analar, BDH, Poole, UK) was allowed to evaporate at room temperature in a closed chamber. Pure CsCl crystallizes from its water solution as dendrites. Doping with Eu impurity ($EuCl_2$, Indian Rare-Earths Ltd, Udyogamandal, India) gives rise to cubic crystals. The dendritic CsCl needles, the transparent plates from the tip portions of dendrites and the cubic Eu doped crystals were collected, and were heated at 400 °C for 4 h followed by a quench to room temperature. The optical absorption of the samples in the region 185–800 nm was measured with a Hitachi-3000 UV–visible spectrophotometer. The fluorescence spectra was recorded in a Hitachi 650-10S fluorescence spectrophotometer with a Himamatzu R928F photomultiplier tube. The optical absorption and the fluorescence spectra were measured at room temperature.

3. Results

Figure 1 shows the absorption spectrum of a CsCl crystal in the UV–visible region. It has a virtually flat visible region and a slowly increasing absorption edge in the UV region. Over the absorption edge, a sharp band at 267 nm and a shoulder at 220 nm are observed (a
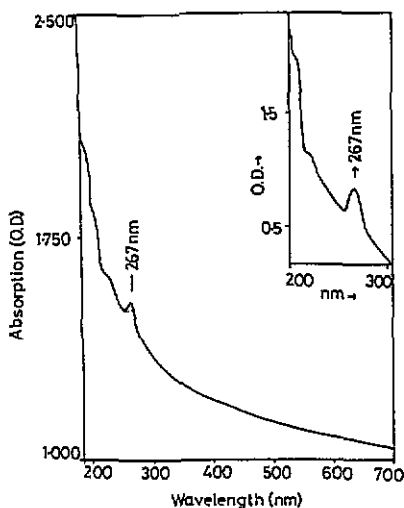
Figure 1. The optical absorption spectrum of a pure CsCl crystal. Inset, a typical absorption spectrum of CsCl crystals in the region 200–300 nm.
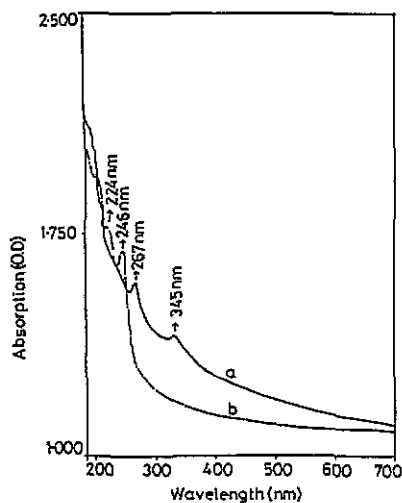

Figure 2. The optical absorption spectra of (a) CsCl:Eu and (b) CsCl:Ni crystals.

typical absorption spectrum of CsCl crystals in the UV region between 200 and 300 nm is shown in the inset).

Figure 2 exhibits the absorption spectrum of a CsCl:Eu crystal. Also shown is a typical absorption spectrum of CsCl:Ni crystals. In CsCl:Eu crystals, besides the sharp absorption band at 267 nm and the shoulder at 220 nm (both of which are present in pure CsCl also), the presence of a band at 345 nm could be detected. As could be observed from the absorption spectrum of the CsCl:Ni crystal, doping with Ni impurity results in the disappearance of the 267 nm absorption band, but gives rise to two new bands at 246 nm and 224 nm.

Figure 3 shows the luminescence emission and excitation spectra of the CsCl crystals. Exciting the CsCl crystal at 267 nm gives a broad emission band between 340 nm and
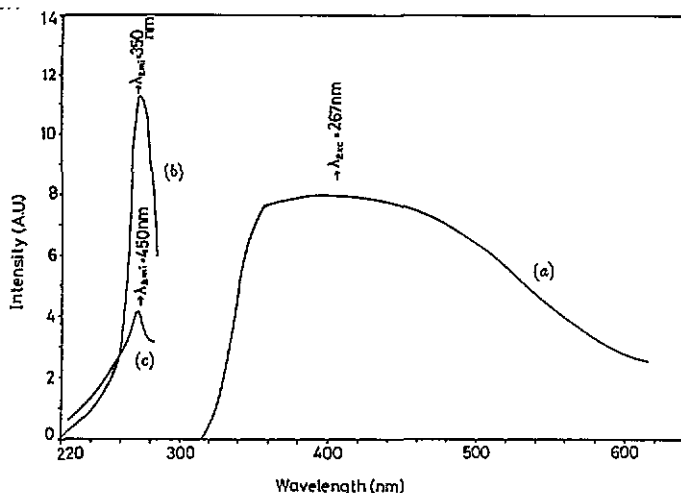
Figure 3. Luminescence emission (*a*) and excitation (*b*), (*c*) spectra of pure CsCl crystals.

500 nm. The excitation spectra corresponding to the emissions in the 340 nm and 450 nm regions show a narrow band at 267 nm. Exciting in other regions does not give any appreciable emission.

Figure 4 shows typical luminescence emission and excitation spectra of CsCl:Eu crystals. Exciting the crystal at 267 nm gives two emission bands, an intense band symmetric about 440 nm and a weak broad band starting at 340 nm, which is overlapped at higher wavelengths by the 440 nm emission band. Exciting the crystal at 345 nm gives a single intense emission band symmetrical about 440 nm. The intensity of the 440 nm emission band obtained with the 345 nm excitation is nearly double that under 267 nm excitation. The excitation spectrum corresponding to the emission at 440 nm shows an intense band with maximum at 345 nm, which has a structure on its higher-wavelength half, and a shallow broad band around 260 nm. The excitation spectrum corresponding to the emission at 360 nm shows a narrow band at 267 nm.

4. Discussion

4.1. CsCl

The absorption spectrum of the CsCl crystal (figure 1) is similar to that observed by Avakian and Smakula [5, 6] and Rabin and Schulman [7] in CsCl crystals grown from solution, except for the 244 nm band observed by them but absent in our crystals. It is to be noted that the crystals used by the above authors were prepared without any attempt at attaining crystal purity, but rather to study the promotion of crystallization of CsCl from its water solution using urea as an additive. The absorption band at 244 nm was observed by Avakian and Smakula [5] not only in the crystals grown from solution but also in those grown from the melt, and was associated with some unknown impurity present in the base material. Hence, it is reasonable to assume that this impurity is not present in the base material used by us.

The absorption band at 267 nm was observed by Avakian and Smakula [5, 6] in CsCl crystals grown from water solution, but then found it to be absent when the same crystals were grown from the melt [5, 7]. Avakian and Smakula [5] have attributed this 267 nm
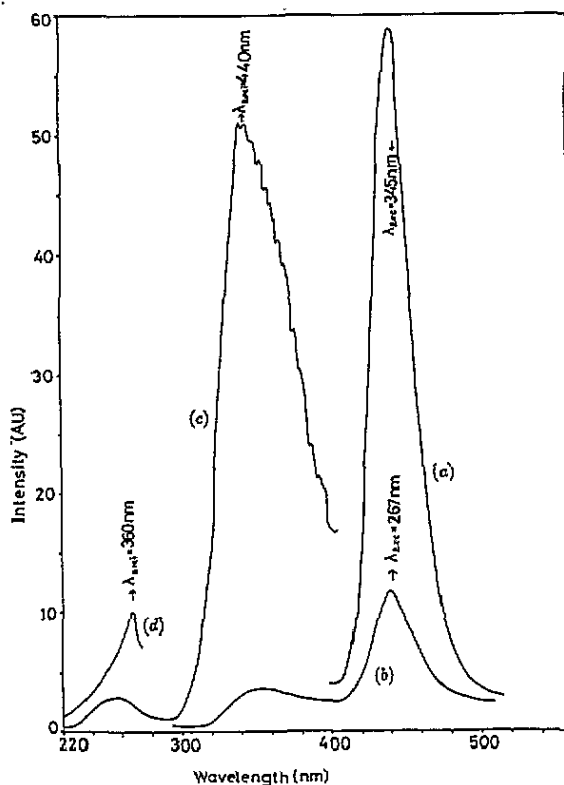
Figure 4. Luminescence emission (*a*), (*b*) and excitation (*c*), (*d*) spectra of CsCl:Eu crystals.

absorption band to the presence of NH_4^+ ions formed as a result of the hydrolysis of urea in solution, but the presence of this band in our undoped CsCl and as well as in CsCl:Eu (figure 2, curve a), CsCl:Ce and CsCl:Sm crystals, all of which have been grown from water solution without urea additive, and its absence in CsCl crystals when grown from the melt [5, 6], indicate that this band is due to some inherent stable impurity formed due to crystallization from water solution (it is to be noted that double-distilled water was used in growing the crystals). The possible stable impurities in crystals grown from water solution in open air are OH^- and O_2^- ions.

The UV absorption band at 267 nm was found to be present in both the as grown crystals and the crystals thermally annealed at 400 °C for 4 h, but the thermal annealing treatment at 400 °C results in a small decrease in the intensity of this band (not shown in the figure). This goes against the possibility that the 267 nm absorption band is due to the O_2^- ions, as thermal treatment in open air always introduces more oxygen ions into the crystal. This favours the OH^- ions as the candidates responsible for the 267 nm absorption band.

If alkali halide single crystals are grown from the melt or solution in open air, they always contain hydroxide impurities, formed as a result of the decomposition of the salt by water present in air [8]. Optical investigations have shown that OH^- ions replace halogen ions in the alkali halide lattice. Alkali halide crystals containing OH^- ions are known to possess optical absorption bands characteristic of these impurities [9–11], one close to the fundamental absorption edge in the UV region due to its electronic transitions and other bands in the IR region due to vibrational excitations. The 267 nm absorption band is perhaps

the UV absorption band of the OH$^-$ ions in CsCl crystals.

This is supported by the fact that the 267 nm band is not present in Ni doped CsCl crystals (figure 2, curve b), but present in crystals doped with impurities such as Eu (figure 2, curve a). It is well known that the transition metal ions are incorporated into the body centred cubic Cs halides interstitially [12–14], with four Cl$^-$ ions at the corners of a face of the cube. In the case of divalent transition metal ions such as Ni [14], the charge compensation is achieved by the introduction of two Cs$^+$ vacancies along the axial positions (along the direction of the cubic axis). The absorption bands observed at 246 nm and 224 nm [15] in CsCl:Ni crystals grown from solution (figure 2, curve b), are not the characteristic absorptions of Ni [16], but probably due to charge transfer transitions, in which electrons are transferred from the adjacent anions (Cl$^-$ and OH$^-$ ions in this case). Rather, it is the charge transfer bands that have been observed in many Ni doped alkali halides [17, 18]. This may be the possible reason for the absence of the 267 nm band in Ni doped CsCl crystals. Thus in an interstitial site, the Ni^{2+} ion will be co-ordinated by four anions (Cl$^-$ and OH$^-$) at equatorial positions and two Cs$^+$ vacancies at axial positions. The exact structure of this MX$_4$L$_2$ coordination is outside the scope of the present work.

FTIR spectra of our CsCl crystals in a KBr pellet show the presence of OH$^-$ bands in these crystals at 3720 cm^{-1} and 3920 cm^{-1}, which have also been reported by Krantz and Luty [19]. The other characteristic of OH$^-$ IR bands, reported at 3575 cm^{-1} and 3625 cm^{-1} [19], are found to be strongly overlapped by the H$_2$O smear of the KBr pellet in our measurements. The thermal gravimetric analysis of the CsCl crystals does not show any weight loss related to the presence of H$_2$O. The only indicated weight loss occurs after the material melts around 645 °C and then starts decomposing until 830 °C. These results confirm again the presence of OH$^-$ ions in our CsCl crystals.

Alkali halide crystals are not known to give luminescence emission at and above room temperature, when pure. The characteristic intrinsic luminescence due to the recombination of the electrons and self-trapped holes is observable only at low temperatures ($<$ 180 K) [20]. However, impurities incorporated either in the manufacturing process or during the growth of the crystal and the accompanying thermal treatments may give their characteristic luminescence emission.

The emission spectrum of pure CsCl crystals (figure 3) is a broad band between 340 nm and 500 nm. The excitation corresponding to any emission in this region is a sharp band at 267 nm, which incidentally coincides with the observed OH$^-$ absorption band in the UV region.

Kostlin [21] and Patterson and Kabler [22] have studied the luminescence of KBr:OH$^-$ crystals at low temperatures. On irradiation into the OH$^-$ absorption in the UV region, they have observed a fluorescence band near 317 nm, with two more lower-intensity components towards longer wavelength, all of them 0.45 eV apart. The observed fluorescence was attributed to the radiative transitions of the excited OH$^-$ molecular ion. At higher temperatures the structure disappears and the emission broadens into a single band.

The similarity of our luminescence emission and excitation spectra from CsCl crystals (figure 3) to those of Kostlin [21] and Patterson and Kabler [22] from KBr:OH$^-$ crystals indicates that the 267 nm absorption band corresponds to OH$^-$ ions, and is responsible for the observed broad room temperature emission. It is to be noted that the above authors [21, 22] report the quenching of the OH$^-$ emission near room temperature, but our observations indicate otherwise.

The observed emission is not due to O$_2^-$ molecular ions, since the luminescence emission of these ions lies in the blue–green (450–550 nm) region [23].

4.2. CsCl:Eu

The rare-earth ion Eu is known to enter alkali halide lattices in the divalent state. In alkali metal halide crystals Eu substitutes for the host cations. Hernandez *et al* [24, 25] and Lopez *et al* [26, 27] performed rather extensive and systematic investigations on Eu doped Na, K and Rb halides. The absorption spectrum [24, 25] consisted of two broad bands in the UV region, which are due to the dipole allowed $4f^7$–$4f^65d$ transitions within the divalent Eu ions. Of these, the low-energy band (extending from about 320 nm to 400 nm) was found to possess a characteristic 'staircase' structure at room temperature, which resolves well at lower temperatures. Excitation at either of the two Eu^{2+} absorption bands was found to produce [26] a single emission band in the fast-quenched samples, which was attributed to the transition from the T_{2g} component of the $4f^65d$ configuration to the ground state ^8S. The excitation spectrum [26] of this emission consisted of two broad bands, which correlate quite well with those observed in absorption. Also it was noted [26] that in all alkali halide crystals, excitation with light lying in the higher-energy band of the absorption spectrum leads to a smaller amount of radiative emission than excitation in the low-energy band.

The absorption spectrum of a CsCl:Eu crystal (figure 2, curve a) shows a single band at 345 nm. The other higher-energy Eu^{2+} absorption band is not well resolved here. The excitation spectra come in handy here as they can be made use of not only in choosing the region of luminescence excitation, but also to determine the pattern of the ion's energy levels when its concentration is too small to be observed in the absorption spectra. It is observed that (figure 4) the excitation spectrum corresponding to the emission at 440 nm has two bands, an intense band with a maximum at 345 nm having the typical staircase structure of Eu^{2+} absorption, and a shallow broad band with maximum at 260 nm. This broad excitation band at 260 nm is in fact the other (higher-energy) Eu^{2+} absorption band, which is not resolved in the absorption spectrum (at room temperature). The staircase structure of the 345 nm band appears clearly in the excitation spectra.

As could be observed from the above discussions, the observations made by us on the CsCl:Eu crystals are similar to the observations of Hernandez *et al* [24, 25] and Lopez *et al* [26, 27]. These indicate that the 440 nm emission band is the characteristic emission of Eu^{2+} ions in CsCl lattice, and the 345 nm and 260 nm excitation bands are characteristic of Eu^{2+} ions, the 345 nm excitation band incidentally matching with the Eu^{2+} band observed in the absorption spectra. In fact Tewari *et al* [28] have studied the Suzuki phase in CsCl:Eu, Mn crystals through photoluminescence and observed the Eu^{2+} emission maximum around 445 nm.

The excitation spectrum corresponding to the 360 nm emission is a sharp band at 267 nm. The emission around 360 nm and the corresponding excitation at 267 nm have been observed in pure CsCl also, and have been attributed to OH^- ions embedded in the lattice.

The excitation at 345 nm (Eu^{2+} absorption) gives the characteristic Eu^{2+} emission, but excitation at 267 nm, which is OH^- absorption, gives emission due to both the OH^- ions (the 360 nm band) and the Eu^{2+} emission (the 440 nm band). This indicates that there is some energy transfer process from OH^- to Eu^{2+} ions active here. It is to be noted that the emission due to OH^- ions overlaps the lower-energy Eu^{2+} absorption band (at 345 nm), which will facilitate such an energy transfer. Energy transfer of the non-radiative type is also possible due to the close proximity of the OH^- absorption band (at 267 nm) and the higher-energy Eu^{2+} absorption band (260 nm).

5. Conclusions

The luminescence emission of CsCl crystals grown from water solution is due to the OH^- ions embedded in the lattice, which are also responsible for the 267 nm absorption band observed in these crystals.

Emission due to Eu^{2+} ions is the major luminescent emission in CsCl:Eu crystals. In addition, the emission due to the OH^- impurity ion is also observed. It appears that there is an energy transfer from OH^- to Eu^{2+} active in this system.

Acknowledgment

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