Optical Studies on Sol-Gel Derived Lead Chloride Crystals

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ABSTRACT
Optical characterization of lead chloride crystals prepared by sol-gel method is reported. The relevant sol-gel technique is used for the preparation of PbCl₂ samples with five different types. In this paper, we report the absorption and fluorescence behaviour of pure, UV & IR irradiated and electric & magnetic field applied lead chloride crystal samples in solution phase at two different concentrations. Optical bandgap and emission studies of these crystals are also done.
KEYWORDS: Lead chloride, absorption, fluorescence, gel method, spectroscopy

Introduction
Fluorescence spectroscopy is of overwhelming importance in the field of photo physics. Lead chloride is a well known photosensitive material possessing ionic crystalline nature belonging to orthorhombic system [1]. PbCl₂ is the model material from heavy element halogenide group since it satisfies high birefringence, low attenuation coefficient and wide transparency range [2]. Many of the researchers reported the luminescence property of PbCl₂ [3]. Under excitation in the fundamental absorption region, PbCl₂ crystals exhibit two types of intrinsic luminescence [4]. W.C.DE Gruijter had done emission studies on PbCl₂ [5]. The top of the valence band is composed of Pb²⁺-6s with considerable admixing of chlorine-np, while the bottom of the conduction band is made up of Pb²⁺-6p [6]. PbCl₂ is classified as a normal class I crystal and its transmission range is wide [7-8]. PbCl₂ finds importance in experimental field due to their large band gap and exhibiting interesting features from the stand point of electron-lattice interaction [9-18]. Lead halide based materials can be used as laser hosts with low phonon energies. The Pb²⁺ in the PbCl₂ crystal is known to be emissive in aqueous solution [19-22].

Experimental Technique
In our spectroscopic studies the PbCl₂ crystal samples used were prepared by using a stock solution of sodium meta silicate (SMS). A quantity of 25 ml. of SMS solution of specific gravity 1.03, whose pH was adjusted to be 6.5, 7.0, 7.5, 8.0 and 8.5 by titration with 1M tartaric acid, and was allowed to gel in five various boiling test tubes without any disturbances. Growth experiments were conducted for different densities of the gel ranging from 1.02 to 1.06. It was found that for the same concentration of HCl, tartaric acid and lead nitrate solution, the rate of growth of the needles is conspicuously larger and the needles are larger for lesser densities of the gel. This is due to the increased rate of diffusion of HCl in the gel and increased mobility of the molecules of the crystals at lower densities of the gel. PbCl₂ crystals were obtained by the reactions of lead nitrate, tartaric acid and HCl (99.9% Sigma-Aldrich). Two
different PbCl₂ crystal samples were obtained by irradiating pure PbCl₂ crystals with ultra violet (UV lamp (insect Killer)) and Infrared radiations (HL4311 (PHILIPS) 230V~50Hz~150w). The other two samples were prepared by subjecting the crystal to an electric field of 20 V using parallel plate arrangement and subjecting the crystal to a magnetic field using two bar magnets kept on either side of the experimental test tube perpendicular to the length of the test-tube. Thus five PbCl₂ samples were obtained for our studies viz pure, UV and IR irradiated, samples subjected to electric and magnetic fields. The sol-gel derived PbCl₂ samples were subjected to X-ray diffraction studies (XPERT-PRO using K-Alpha 1.54060 A₀ (XRDML)). The crystal structure of PbCl₂ is confirmed to be orthorhombic dipyramidal with each Pb having a coordination under 9. Observations under petrological microscope reveal that PbCl₂ crystals grown under all the five conditions show inclined extinction. The prepared crystal samples were powdered using mortar and pestle, weighed about 0.15g and dissolved in 15 ml of single distilled water (SDW) to obtain a concentration c₁=0.01 gm/ml. Another concentration c₂=0.02 gm/ml was obtained by dissolving 0.32g in 20 ml of SDW. For the dissolution a magnetic stirrer was used and the solvent evaporation was prevented by using a sealed glass container. Linear absorption of the crystal samples in solution phase was recorded using Jasco V-570 UV/VIS/IR Spectrophotometer. Optical band gap of these samples were obtained from linear absorption measurements. The emission and excitation studies were carried out by taking the room temperature fluorescence spectra of these PbCl₂ samples using a Cary Eclipse fluorescence spectrophotometer (Varian).

**Result And Discussion**

Observations under petrological microscope reveal that PbCl₂ crystals grown under all the four conditions show inclined extinction. The dendrites grown under the four conditions show variations from one another. Those grown under infrared radiation are radiating type while those in visible light are fibrolitic. Large massive dendritic growth was observed under ultra violet radiation. The tendency for radiating along the axis of the crystal was found when grown in all the conditions. A study of external morphology shows that the crystals grown in the presence of radiation are needle shaped good quality acicular aggregates with shinning edges. Each individual in the aggregate is highly brittle, tubular needles. The habit of lead chloride crystals that is least affected morphologically by external factors can be described as elongated along the c axis with (100), (010) as main forms and (110), (120) and (210) as smaller faces, while at the top (011) is the dominant form. From the external observations of four sets of lead chloride dihydrate crystals, it is clear that there is no change in the external morphology by naked eye.

1. **Absorption Studies**

Optical absorption spectra of PbCl₂ samples at two different concentrations c₁ and c₂ are shown in the figure 1.

(a)

![Absorption Spectra](image)

(b)

![Absorption Spectra](image)

**Figure 1.** Room temperature absorption spectra of PbCl₂ at concentrations (a) c₁ and (b) c₂.

The absorption peak of PbCl₂ at the two concentrations c₁ and c₂ are located in the uv region at 266 nm corresponds to 4.6 eV. The peak at this particular wavelength is due to the electronic transition from the valence band to the PbCl₂ cation [23-24]. There is no valuable change in absorption peak for varying concentration. The above linear absorption spectra can be used for optical band gap studies on PbCl₂ in solution phase in single distilled water. The linear absorption coefficient α can be determined from absorption spectra, which is related to the band gap E_g as \( (\alpha hυ) = k (hυ-E_g) \), where \( hυ \) is the incident light energy, \( k \) is a constant.
and $E_g$ is the optical band gap of lead chloride. A graph of $E_g$ vs $hv$ gives the direct band gap of PbCl$_2$ for five different samples at two concentrations c1 and c2. The optical band gap of PbCl$_2$ for concentration c1 varies from 4.54 eV (pure) to 4.67 eV (magnetic). For irradiated and electric field applied PbCl$_2$ samples, $E_g$ is 4.54 eV and 4.55 eV respectively. When concentration is at c2, $E_g$ varies between 4.6 and 4.46 eV. The values of direct band gap at c1 and c2 are listed in the table1. Several types of chloride ion vacancies can exist in the lead chloride lattice which are electron traps in the energy range 4.2-4.4 eV above the valence band [24].

Figure 2. Optical band gap plot of Pure PbCl$_2$ sample at concentrations (a) c1 and (b) c2

Figure 2 shows the direct band gap behaviour of PbCl$_2$ samples at two different concentrations c1 and c2. The chloride ions at the largest distance are surrounded by four lead ions where as the closest chloride ions are surrounded by five lead ions [25]. It was suggested that the 4.6 eV absorption to be an exciton absorption, but on the other hand it might also be ascribed to a characteristic 6s$^2$-6s6p transition inside the lead ion.
2. Fluorescence Studies

Fluorescence spectra of PbCl$_2$ are taken at two different concentrations c1 and c2 for photoluminescence studies. Figure 3 represents the fluorescence emission spectra of five PbCl$_2$ samples in SDW. PbCl$_2$ sample solutions at concentrations c1 and c2 are excited at a wavelength of 270 nm gives three strong emissions at around 421 nm, 491 nm and 533 nm respectively.

Table 1. Measured values of optical band gap and emission peaks for PbCl$_2$ at concentrations c1 and c2 (gm/ml)

<table>
<thead>
<tr>
<th>PbCl$_2$ sample</th>
<th>Optical direct band gap at concentrations</th>
<th>Emission peak at</th>
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<tr>
<td></td>
<td>C1 (eV)</td>
<td>C2 (eV)</td>
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<tr>
<td>pure</td>
<td>4.54</td>
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<td>UV</td>
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<td>Magnetic</td>
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The excitonic transitions in lead chloride are partly explained by the 6s-6p transition in lead ions which gives the emission bands at three of the above transitions. Fluorescence in PbCl$_2$ is composed of broad guassian band with large stokes shift and it is indicative of strong exciton-acoustic phonon interaction [26]. The electric dipole transition from the 6p to 6s states also produces luminescence in PbCl$_2$. The excitons can relax into pairs of a self trapped electron (STEL) and a self trapped hole (STH) when both electrons and holes strongly interact with acoustic phonons. A repulsive correlation is ascribable to the origin of electron-hole separation. The repulsive correlation through acoustic phonons with the formation of cooper pairs mediated by these acoustic phonons cause the spontaneous breaking of excitons [27]. As concentration is increased, phonon vibration will induce more non radiative de excitations. Our PbCl$_2$ solutions show many peaks due to the stokes shift by the crystal field interactions resulting from
the strong interaction between phonon and Pb$^{2+}$ ions. From the fluorescence spectra given in the figure, it is evident that the emission peaks at 491 and 533 nm are assigned to the excitonic emissions. For pure PbCl$_2$ sample, the emission peak at 431 nm at concentration c2 is red shifted. The IR irradiated and electric field applied samples have almost same emission peak at 423, 492 and 533 nm for the two concentrations c1 and c2. The shifting of emission peaks at pure PbCl$_2$ sample is due to the band edge emission which are attributed to the quasi free recombination at the absorption band edge. Thus the spontaneous exciton dissociation has been revealed by the fluorescence emission in sol-gel derived PbCl$_2$ samples in solution phase.

Conclusions

High quality lead chloride crystals were prepared by sol-gel technique. The obtained PbCl$_2$ crystal samples of five different types in solution phase were subjected to spectrophotometric studies. The linear absorption spectra give the optical band gap details of these crystals. Photo luminescence studies on these lead chloride samples were done by fluorescence spectroscopy. The fluorescence emission of these crystals shows that PbCl$_2$ crystals have the band gap in connection with the 6s to 6p gap in lead ions and tend to become highly luminescent coming from the odd transition. Thus the high luminescence nature of lead chloride makes them suitable for applications in photography, acoustical-optical devices and radiation detectors.

Acknowledgements

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