Non-Linear Optical Studies on Sol-Gel Derived Lead Chloride Crystals Using Z-Scan Technique

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Abstract
In this paper we report the preparation, optical characterization and non linear optical behavior of pure lead chloride crystals. Lead chloride samples subjected to UV and IR irradiation and electric and magnetic fields have also been investigated. Optical nonlinearity in these lead chloride samples was determined using single beam and high sensitive Z-scan technique. Non linear optical studies of these materials in single distilled water show reverse saturable absorption which makes them suitable for optical limiting applications.

Keywords: Sol gel method; UV irradiation; linear absorption; optical band gap; nonlinear absorption; optical limiting.

Introduction
Lead Chloride is known as a model material for the group of heavy element halogenides since it possesses high bire fringe, low attenuation coefficient, wide transparency range and good mechanical properties [1]. PbCl$_2$ has drawn attention of many workers because they exhibit interesting features from the stand point of the electron-lattice interaction [2-15]. These materials are important for their luminescent properties. Two types of luminescence are observed in PbCl$_2$, the excitonic luminescence and the recombinational luminescence [7]. The acousto optic figure of merit of PbCl$_2$ crystals is high and their transmission range is wide. The band gap of PbCl$_2$ is also large [16]. A large set of 15 optical functions contains the most complete information on the optical properties and electronic structure of PbCl$_2$ [17-18]. V.V.Sobolev et al reported the electronic structure and anisotropic optical properties of PbCl$_2$ crystals. PbCl$_2$ is an ionic crystal with orthorhombic structure with four molecules in the unit cell [19]. A.Kaldor and G.A.Somraj reported the photodecomposition in PbCl$_2$ [20]. Photonic materials with optical limiting properties find applications in devices for protecting eyes and sensors from intense optical radiations. A nonlinear optical crystal like PbCl$_2$ can be employed for applications depending on their band gap and nonlinearities PbCl$_2$ exists in nature in crystalline form as large needles. Deviated from the normal way of crystal growth in gels in which two nutrient solutions were allowed to interact in the gel medium, in the method reported here, a two stage reaction is made use of. In the first stage one of the reactants is incorporated in the gel as a colloidal precipitate and the other nutrient is allowed to diffuse into the gel and to produce the crystal in the second stage. Experiments on the growth of Lead chloride confirm the utility of this method for growth of lead chloride crystals under the influence of ultraviolet and infrared radiations. Lead halide based materials have recently emerged as laser hosts with low phonon energies. In this paper we report for the first time, to the best of our knowledge, the linear and nonlinear optical behavior of PbCl$_2$ samples in solution phase and their optical limiting properties using open aperture z-scan technique.

Experimental Technique
PbCl$_2$ crystals were prepared by sol-gel technique using sodium meta silicate as stock solution. Lead nitrate, tartaric acid and HCl (99.9% Sigma –Aldrich) were used for the preparation. Samples were prepared for various concentrations of HCl. It was found that for the same density of the gel and at the same concentration of tartaric acid and lead nitrate solution, the rate of growth of the needle-like crystals is higher and is longer for higher concentration of HCl. However, for high concentration of HCl the needle-like crystals are thin and are in large number. The effect is a result of the increase in nucleation due to the high rate of reaction. A compromise between the density of the gel and the concentration of the acid it is possible to establish, in the gel, a conducive environment for the needles and single crystals of lead chloride to be grown in silica gel of specific gravity 1.03 using 2NHCl. Two different PbCl$_2$ crystal samples were obtained by irradiating pure PbCl$_2$ 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 PbCl$_2$ 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 Å (XRDML)). The crystal structure of PbCl₂ is confirmed to be orthorhombic dipyramidal with each Pb having coordination under 9. Observations under petrological microscope reveal that PbCl₂ crystals grown under all the five conditions show inclined extinction. A study of external morphology shows the crystals grown in the presence of radiations are needle shaped good quality acicular aggregates with shining edges.

PbCl₂ crystal samples in solution phase were used for linear and nonlinear optical studies. For these studies the crystals were grinded by mortar and pestle and the powder form was dissolved in 20 ml of single distilled water to prepare a solution of 2.8x10⁻³ M concentration. A magnetic stirrer was used for the dissolution process and the solvent evaporation was prevented by using a sealed glass container. Linear absorption of the samples was recorded using Jasco V-570 UV/VIS/IR Spectrophotometer. Optical band gap of these samples were obtained from linear absorption measurements. High sensitive single beam z-scan experiment based on spatial beam distortion was used for optical nonlinear studies [21]. A Q-switched Nd:YAG laser (Spectra physics Lab-1760, 532 nm, 7ns, 10 Hz) was used as the source. The PbCl₂ sample solutions were taken in a 1 mm thick cell and moved along the z-axis through the focal point of a lens of focal length 20 cm. The experimental set up was explained in detail in refer [22-23]. The radius of the beam waist w₀ was calculated as 42.6µm and Rayleigh length z₀=πw₀²/λ is estimated to be 10.7 mm which is much greater than the thickness of the sample cell (1 mm). Thus Raleigh length satisfies the basic criteria of taking z-scan. By using an energy ratiometer (Rj 7620 Laser Probe Corp) having two identical pyro electric detector heads (Rjp 735), the transmitted beam energy, reference beam energy and their ratios were simultaneously measured. We used CS₂ as the standard for the initial calibration of z-scan set up.

Result and Discussion
The linear stability of steady-state needle shaped crystals in dendritic growth was studied in the presence of anisotropies in both surface tension and interfacial kinetics. The needle shaped crystals were linearly unstable for certain range of values of the surface tension and kinetic coefficients. This instability results in complex tipsplitting and side-branching events that lead to morphological transitions. Needle crystals have been observed to be faceted at low velocities of growth. This can be explained by the theory of diffusion-limited growth with the addition of a supplementary condition fixing the shape of the facet depending on the average temperature on it. Linear absorption spectrum of lead chloride samples is as shown in figure1. The absorption edge of PbCl₂ is located in the uv region. The band gap of the samples was estimated from the graph of hν verses (αhν)² where α is linear absorption coefficient which is related to the band gap (hv)²α as (αhν)²=k (hv-Eg), where hv is the incident light energy, k is a constant and Eg is the optical band gap of lead chloride. Figure 2 represents the band gap plot of PbCl₂.

![Figure 1. Linear absorption spectra of PbCl₂.](image1)

![Figure 2. Direct band gap plot of PbCl₂.](image2)

Figure 3 shows the open aperture z-scan plot of PbCl₂ samples. The solid curves are theoretical fit to the open aperture z-scan experimental data. The nonlinear absorption coefficient β can be obtained from this open aperture z-scan data by fitting the normalized transmittance data to the open aperture formula given as [21]

\[
T(Z, S = 1) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \left[ q_0(z) \right]^{m+n} \left[ \frac{m+1}{m+1/2} \right] |q_0(z)| < 1
\]
where:

$$Z_0 = \frac{kw_o^2}{2}$$ is the diffraction length of the beam

$$k = \frac{2\pi}{\lambda}$$ is the wave vector, \(w_o\) = the beam waist radius at the focal point, \(L_{\text{eff}} = (1-\text{exp}(-\alpha L))/\alpha\) is the effective thickness of the sample, \(I_0\) is the laser intensity at the focal plane.

$$q_0(z) = \frac{[I_0/\beta L_{\text{eff}}]}{1 + (Z^2/Z_0^2)}$$

Open aperture z-scan studies were carried out by focusing the input beam on to the sample at 532 nm using a Q-switched Nd: YAG laser. In order to estimate the limits to which the molecules would be showing RSA behavior, z-scan curves were recorded at different fluences in the ns regime. The symmetrical traces indicate that no other processes such as scattering or damage occur. We measured the transmittance of PbCl$_2$ samples as a function of the sample position \(z\) measured with respect to the focal plane. Using a single Gaussian laser beam, we measured the transmittance of the samples at two different input fluences (100 and 125 MW/cm$^2$) as shown in figure 3. From figure 3 it is clear that the nonlinear absorption coefficient is positive due to the transmission minimum at the focal point. For our samples, there is no depletion of ground state population because the transmission curves exhibit RSA.

The wavelength used in our experiment is 532 m, which corresponds to two photon absorption (TPA). The photon energy is within the range \(2hv>E_g>hv\), where \(hv=2.33\text{eV}\) and \(E_g\) is the optical band gap of PbCl$_2$ varying from 4.4 eV to 4.6 eV as shown in Table 1. Lead chloride solutions suppress the peak and enhances valley to show RSA in the transmittance curve. Nonlinear absorption coefficient \(\beta\) for two input fluence values are given in table 1.

### Table 1. Measured values of nonlinear absorption coefficient and optical limiting threshold for PbCl$_2$ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_g) (eV)</th>
<th>(\beta) (cmGW$^{-1}$)</th>
<th>Optical limiting threshold (MWcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl$_2$ pure</td>
<td>4.6</td>
<td>122</td>
<td>65</td>
</tr>
<tr>
<td>PbCl$_2$ UV</td>
<td>4.5</td>
<td>135</td>
<td>42</td>
</tr>
<tr>
<td>PbCl$_2$ IR</td>
<td>4.4</td>
<td>98</td>
<td>70</td>
</tr>
<tr>
<td>PbCl$_2$ electric</td>
<td>4.6</td>
<td>36</td>
<td>27</td>
</tr>
<tr>
<td>PbCl$_2$ magnetic</td>
<td>4.5</td>
<td>83</td>
<td>14</td>
</tr>
</tbody>
</table>

Figure 3. Open aperture z-scan plot of PbCl$_2$ at different laser powers, (a).100 MW/cm$^2$ and (b). 125 MW/cm$^2$
The obtained nonlinearity is found to be of third order, as it fits to a TPA process. In general, induced absorption can occur due to a variety of processes [24]. The theory of TPA fitted well with the experimental curve infers that TPA is the basic mechanism. For 532 nm excitation, we can approximate the nonlinear absorption to an effective process and evaluate the nonlinear absorption coefficients [25-26].

Table 1 show that high nonlinearity is obtained for 100 MW/cm² and small value for 125 MW/cm². Thus when the incident intensity exceeds the saturation intensity, the nonlinear absorption coefficient of the medium decreases [27]. From these values of \( \beta \), it is clear that as the input laser intensity \( I_0 \) increases, the nonlinear behavior of lead chloride decreases, which is due to the removal of an appreciable fraction of photo carriers from the ground state. Here the TPA technique which is comparatively simpler than the single photon process is more indicative of bulk material characteristics.

Materials that exhibit RSA are currently of interest for use in optical limiting devices for protection of sensors and eyes from energetic light pulses. The maximum criteria identified for a material to act as an effective optical limiter are low limiting threshold, large dynamic range, and longer excited state life time to accumulate the population, high optical damage threshold, broadband response, fast response time and high linear transmittance [28].

Figure 4. optical limiting response of PbCl₂

In lead chloride samples optical limiting is due to TPA. PbCl₂ is a good optical limiter that transmits light at low input intensity while become opaque at high input fluences. PbCl₂ should have high transmittance for weak incident light and instantaneous response over a broad spectral range [29].

Figure 4 shows the optical limiting response of PbCl₂. The limiting threshold is an important factor which decides the efficiency of optical limiter. It is obvious that lower the optical limiting threshold, better the optical limiting material. The optical limiting property occurs mainly due to absorptive nonlinearity which corresponds to the imaginary part of the third order susceptibility [30]. The optical limiting threshold values at two different laser intensities are shown in table.1. From the table, it is observed that there is a small limiting threshold for low input fluence and limiting threshold increases with increase in \( I_0 \) values. From the values of fluence at the focus, the fluence values at other positions could be calculated using the standard equations for Gaussian beam waist [25].

Conclusion

Highly luminescent Lead Chloride crystals were prepared and characterized. Spectrophotometric studies were carried out to evaluate the band gap. Optical nonlinearity in five different PbCl₂ samples were investigated using z-scan technique. Observed nonlinearity is third order and two photon absorption coefficients were tabulated with different types of PbCl₂ samples in solution phase. The nonlinear curves exhibit valleys to show reverse saturable absorption indicating positive nonlinear absorption. RSA nature of the samples makes them suitable for optical limiting applications and the optical limiting threshold of these samples was evaluated. The nonlinear studies on these crystal solutions gave a clear picture that these materials are highly nonlinear due to their high values of nonlinear absorption coefficients. Thus these PbCl₂ crystals prepared by sol-gel technique are
well suited for applications in optoelectronic and nonlinear optical devices.

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References