

Alternative Method for Studying Color Centers in CsCl Thin Films

Kuldeep Kumar, & P.Arun,¹ R.Kumar,² N.C.Mehra,³ L.Makinistian,^{4,5} and E.A.Albanesi^{4,5}

¹*Department of Physics & Electronics, S.G.T.B. Khalsa College,
University of Delhi, Delhi-110 007, India**

²*Department of Physics. Ch. Charan Singh University, Meerut, Uttar Pradesh, India*

³*University Science & Instrumentation Center,
University of Delhi, Delhi-110 007, India*

⁴*Facultad de Ingeniería, Universidad Nacional de Entre Ríos, 3101 Oro Verde (ER), Argentina*

⁵*Grupo de Materiales Computacionales, INTEC-CONICET,
Guemes 3450- 3000 Sante Fe, Argentina*

The optical properties of cesium chloride (CsCl) are changed with presence of vacancies in the crystal structure giving rise to what is called as "color centers". We have unconventionally adopted Tauc's method to determine the characteristic color centers and have modeled the correlation among the film optical properties and lattice size, highlighting the interrelation between the structural and optical properties of alkali halide films.

I. INTRODUCTION

Excess alkali atoms or vacancies due to lack of halogen atoms in Alkali Halides (AH) compounds are known to give color in otherwise transparent crystals. In the literature such "color centers" are manufactured by X-ray irradiating AH crystals.^{1,2} This results in characteristic peaks with large absorption in the UV-visible spectra. Usual characterization of color centers are done by analysing the peak positions whose intensity ofcourse depends on the number of vacancies manufactured. In this present article we report our study of color centers in CsCl thin films. The color-centers are formed due to the thermal evaporation method used in fabricating these thin films, where some AH molecules might have dissociated on heating. However, since the number would have been small, the vacancies developed in turn would be minimum resulting in the absorption spectra having no distinct peaks. We have used the slope of the

gradually increasing absorption with decreasing wavelength to comment on the nature of color centers. This method though is routinely used to compute the optical band edge, has not been used in studying color centers.

To relate our experimental findings, we have then theoretically modeled the CsCl system. For our calculations we have used the FP-LAPW method within the density functional theory (DFT), in the form implemented by the WIEN2k code,³ a very accurate first-principles scheme used in modeling properties of materials. We have used the so called generalized gradient approximation (GGA),^{4,5} in the formal parametrization scheme of Perdew-Burke-Ernzerhof (PBE).⁶ This corrected functional is semi-local and thus more sensitive to non-spherical components of the density, resulting in a better performance than the local density approximation (LDA) when applied in a full potential scheme like the WIEN2k. It is to be emphasized, though, that both LDA and GGA always yield underestimated band gaps. An usual, empirical correction of this is done by using the scissors operator,⁷ which basically consists of adjusting the band gap with a constant potential to reproduce the experimental energy band gaps. This operator is often used, particularly in the determination of the band gap offsets^{8,9} which appear when considering interfaces between different semiconductors, in optical transitions¹⁰, and also when bulk properties under pressure are studied.¹¹ We have applied it, with a constant value of 2.45 eV, to our results of densities of states by shifting up the regions above the Fermi energy.

II. EXPERIMENTAL

Thin films of Cesium Chloride were grown by thermal evaporation using 99.98% pure starting material obtained from Loba Chemie Pvt Ltd, Mumbai. The films were grown on microscopic glass substrates kept at room temperature at distance of 12-15cm above the boat. Thin films were grown at vacuum better than 10^{-6} - 10^{-7} Torr. Films grown by this method were found to be transparent or slightly translucent with a bluish or bluish-green tinge depending on the films thickness. The films were removed from the chamber and immediately kept in a desiccator. All our studies were completed within five days of sample fabrication.

III. RESULTS AND DISCUSSION

A. Structural Studies

Structural studies of the films were done using X-ray diffractometer (Philips PW 3020). The as grown films of CsCl were found to be polycrystalline in nature without exception. Characterizing peaks were found between $2\theta = 20 - 50^\circ$ (fig 1). The peak positions match those listed in ASTM Card No.05-0607 confirming the chemical composition of the thin films to be that of CsCl. Cesium Chloride exists in simple cubic state with a chlorine atom at the center of the cube and one cesium atom at every corner of the unit cell.¹² The first peak is located around 21.5° is Miller indexed as (100). Hence, the inter-planar spacing or the ' d ' value of this peak is the lattice constant of unit cell itself.

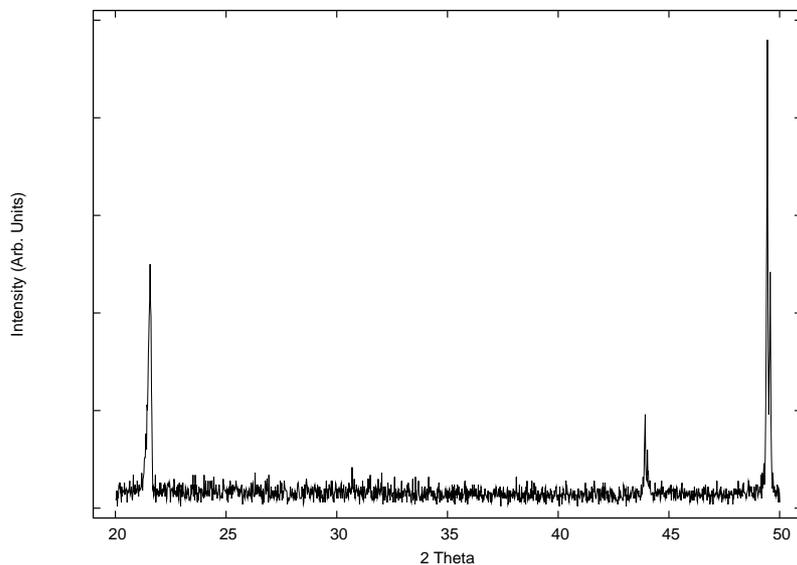


FIG. 1: X-Ray diffraction pattern of a CsCl thin film studied.

B. Optical Studies in Visible Region

We now detail the results of our optical studies carried out using the UV-visible spectroscope (Shimadzu's UV 2501-PC). The refractive index of the thin films are usually calculated by employing Swanepoel's method.¹⁴ This involves drawing two envelopes connecting the maxims

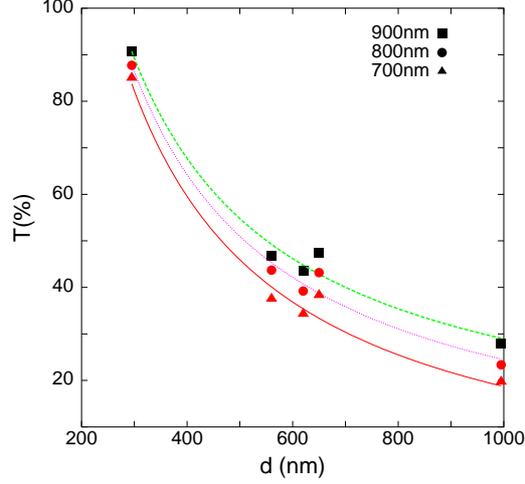


FIG. 2: The figure shows the variation in transmission value with increasing film thickness at different wavelengths. The nature of variation is same for all wavelengths with the best fit taking the form $d = A + \frac{B}{d}$.

and the minima are seen in the fringes of the transmission spectra. The interference fringes seen in the transmission spectra is the result of multiple reflection from air-film and film-substrate interface. However, the transmission spectra of CsCl films without exception did not show multiple and sharp fringes. This inevitably made estimation of the refractive index difficult. The lack of multiple and sharp fringes in films may be due to the thickness of the thin film being very large or the refractive index of single layer films being of the same order (nearly same values) as the substrate. Since the first possibility of all our films being too thick is ruled out, it can safely be assumed that the refractive index of CsCl films is similar to the refractive index of our glass substrate. The refractive index of single crystalline CsCl is reported to be 1.6.¹⁵ Pinholes with water vapor trapped in it would reduce the refractive index in the case of thin films. This would result in the refractive index of the thin film to lie between 1.5 and 1.6, which is very near to the refractive index of the glass (i.e. ~ 1.5). Since the distinguishability of film and substrate diminishes the lack of interference fringes is explained. However, the data of transmission spectra data for various samples reveal a dependence on film thickness (fig 2).

Absorption spectra of CsCl shows a increasing absorption as one proceeds from $\lambda = 900\text{nm}$ to 300nm . Such trend have been reported by Rabin et al¹ and Avakian et al² in CsCl single

crystals. On these sloped backgrounds they reported the appearance of peaks which represented color-centers created by excess of alkali atoms, which in turn generate halogen vacancies, or by halogen vacancies created by X-irradiation. These vacancies give rise to energy levels within the forbidden band explaining peaks in absorption spectra and a color to the usually transparent crystal. In the referred works^{1,2} color-centers were created by irradiating the single crystals with X-rays. In unirradiated samples, the peaks due to color-centers are too faint. Even for irradiated samples, the peaks may be faint and usually become prominent only when the pre-irradiated absorption spectra is used as the baseline and subtracted from the spectra.¹ However, these works do not comment on the sloped absorption background which also shows variation on X-ray irradiation.

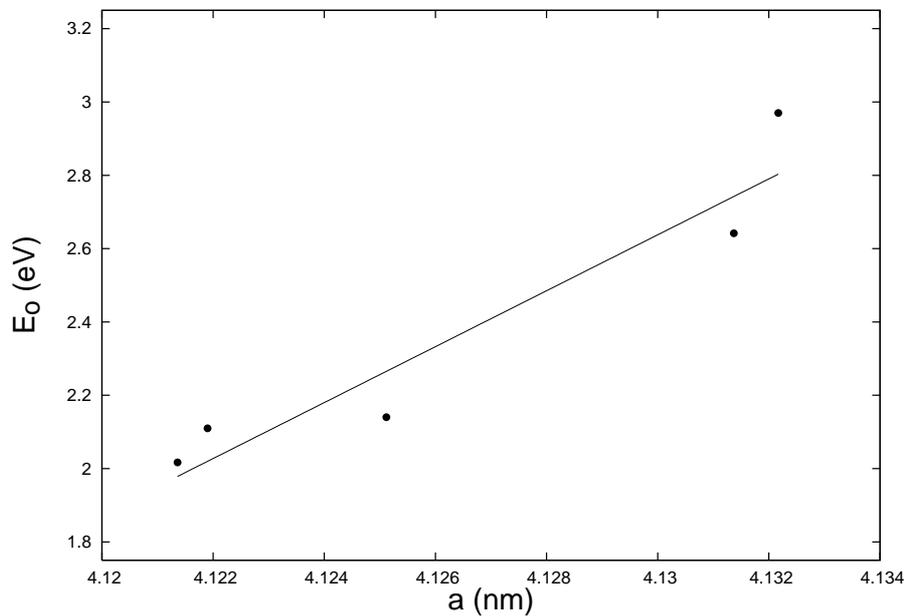


FIG. 3: *The variation of the optical energy gap with lattice constants.*

A slope in the absorption spectra is usually associated with multiple energy levels coming together forming bands. Assuming, color centers to form narrow bands within the forbidden band, we have used Tauc's¹⁶ for estimating band gap from the absorption spectra near band edges to determine the difference in energy level edge's (E_o) from the valence band to that of the narrow bands coming in existence due to color-centers.

We plot E_o as a function of lattice constants of the unit cells in fig 3. E_o associated with the color center film thickness. Films of thickness around 300nm has energy of 3eV associated with

it's color-center while the 1000nm thick film has $E_0 \sim 2\text{eV}$, explaining the bluish to bluish-green tinge seen for the films with increasing film thickness. To analyze these results, we have modeled the point defects in our poly-crystalline films, with a cubic super-cell of 53 atoms with a Cl vacancy in its center. Because of the presence of Cs in the compound, we have included in our study the spin-orbit interaction. While this interaction splits up some energy bands, the main effects occur mainly in the intermediate valence band region (between -5.3 and -7.6 eV), which is far from the top of the valence band. Thus, it is not relevant in the energy region that determines the band gap.

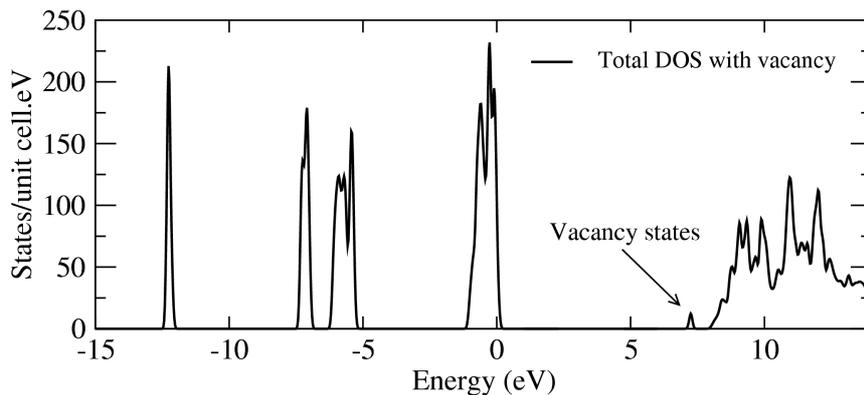


FIG. 4: *Calculated density of states of the CsCl lattice with a Cl vacancy.*

Fig 4 shows the calculated density of states (DOS), where a flat band of localized states appears in the band gap, close to the bottom of the conduction band. Many of these vacancy states are filled with trapped electrons, turning the films active in the visible region. The minimum energy differences E_0 between these localized states to the first significant conduction band states are about 1.5 eV, and to the subsequent close first shoulders are about 1.6 eV, and 2.1 eV, in close agreement with the experimental F-centers energy of about 2.0 eV for bulk¹² CsCl. We have also calculated the energy position of the F-centers for different lattice parameter into the range at which our films were formed. The data points in fig 5 show theoretically calculated E_0 for different lattice parameters, which occur at about 1.5 eV. In all cases, there are also close subsequent peaks up to about 2.0 eV (not shown in fig).

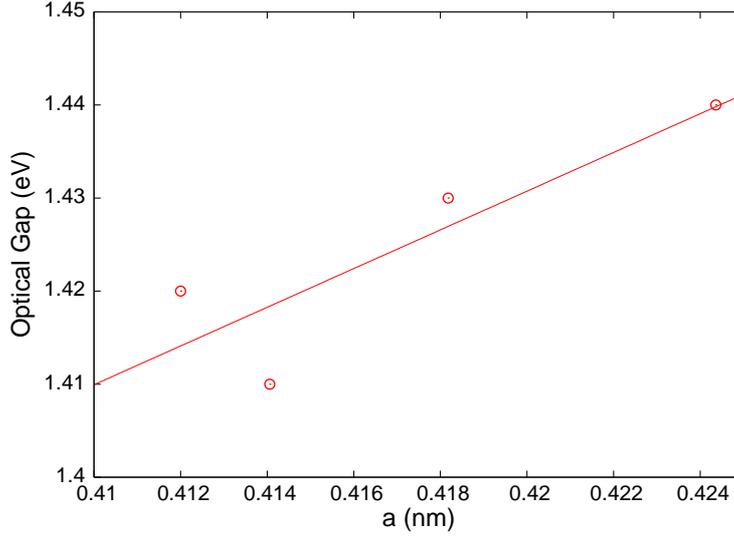


FIG. 5: *Calculated optical energy gaps at different lattice parameters.*

IV. CONCLUSIONS

Thin films of cesium chloride were fabricated on glass substrates held at room temperature. Due to CsCl's wide bandgap, these films should have been transparent, however, our film's had blue (very-light) to bluish green tinge which suggests existence of color centers created by either excess Cs atoms or vacancies due to absence of Cl atoms. These lead to variation in the unit cell's lattice size, resulting in variation in the inter-atomic distances between neighboring Cs-Cl, Cs-Cs and Cl-Cl atoms. The band structure is also expected to change giving rise to altered optical properties of the films. We believe our theoretical and experimental results highlight these material behavior.

Acknowledgment

The discussions with Dr. Bob Angelnier is gratefully acknowledged. The help in completing the spectroscopic and diffraction analysis by Mr. Dinesh Rishi (USIC), Mr. Padmakshan and Mr. Rohtash (Department of Geology, Delhi University) is also acknowledged. L.M. and E.A.A. acknowledge financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Universidad Nacional de Entre Ríos (UNER), and the Agencia

Nacional de Promoción Científica y Tecnológica (ANPCyT), Argentina.

- * Electronic address: arunp92@physics.du.ac.in
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