



# Defect diffusion assisted formation of cesium metal clusters in cesium halide thin films

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## Abstract

This manuscript describes the evolution of grain structures in cesium halide films which leads to localized surface plasmon resonance (LSPR) peaks in UV–visible absorption spectra. Thin films of cesium halide age with time as grain boundaries recede making grains spherical in shape in order to minimize the free surface energy of the system. The process is also assisted by the presence of point defects/color centers in cesium halide films. The defects migrate outwards towards the grain surface, giving cesium metal clusters at the surface, resulting in core–shell structure. Along with volume diffusion, a surface diffusion of cesium takes place towards sites of facet grains boundaries resulting in a necking phenomenon, appearing like bridges between the daughter cesium halide grains (grains appearing due to the division of a single grain). Breaking away of the daughter cesium halide grains results in nano-rods that contribute to the SPR peak seen.

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**Keywords:** Nanostructures; Interfaces; Thin films; Color-centers; Diffusion

## 1. Introduction

The simple crystal structure of alkali halides made them popular candidates for study in crystallography, however, as crystallographic studies of alkali halides matured, research shifted towards theoretical evaluation of their band structures and effect of imperfections (defects) on it. Since the seventies, research, then shifted from the single crystal alkali halides to alkali halide thin

films. However, the hygroscopic nature of these compounds posed a hindrance. Yet, some applications have been developed with alkali halides in the thin film state. Tsuchiya et al. [1] took advantage of the high solubility of CsCl and used its thin films as steam etchable resists in IC fabrication. Progress in high energy physics and nuclear physics have stimulated research in materials science for better scintillation detectors for which there has been a new found interest in alkali halides [2]. Recently, alkali halide photo-cathode in particle detectors using the Ring Imaging Cherenkov Technique [3–6] have been investigated. Alkali halide thin films deposited on thin metal layers have also been found useful as a protective layer of the photo-cathode. An emerging field of research in alkali halides is studying their optical properties, especially the observation of localized surface plasmon resonances (LSPR). Scott et al. [7] observed

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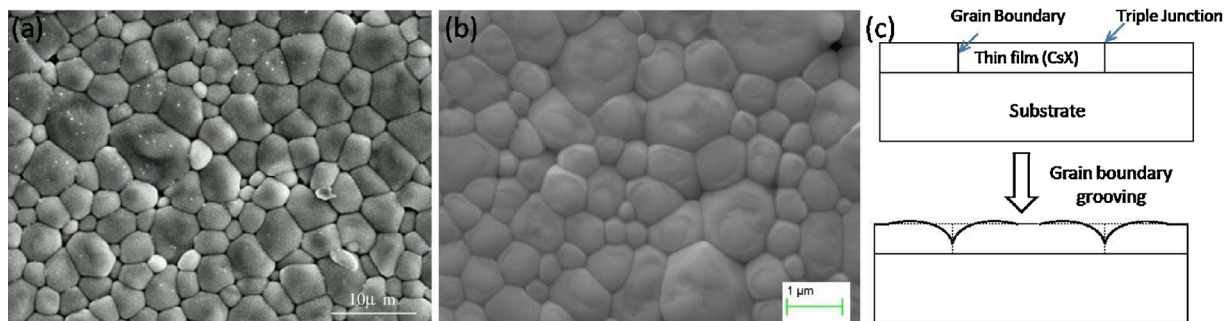


Fig. 1. SEM images show the surface morphology (polycrystalline nature) of thin films of cesium chloride (a) and cesium iodide (b). (c) Schematic showing the process of grain boundary grooving.

that heat-treatment of alkali halides led to the appearance of a strong narrow absorption peak. Similar to Scott, Orera et al. [8] also emphasized the role of heating on alkali halides, where the precipitation volume of metal cluster from alkali halides depended on the annealing time. Jensen [9] reported absorption band in CsBr spectra due to colloidal/metal clusters in cesium bromide at 1050 nm. This peak position was found to be insensitive to temperature. Also, Jensen [9] observed full width at half maxima (FWHM) decreases as the size of metal particles increases. Occurrence of LSPR in alkali halides has been extensively reported due to radiation, electron and heavy ion bombardment.

In our recent works we have reported optical properties of cesium halide thin films, namely, cesium chloride (CsCl) [10], cesium bromide (CsBr) [11] and cesium iodide (CsI) [12]. The optical properties of CsBr and CsI stood out due to the singular appearance of LSPR peaks in the visible region. As was the case in previous works, we too confirmed that the LSPR peaks arose due to formation of cesium metal clusters, however, two basic questions remain unanswered, “What mechanisms lead to the formation of cesium metal nano-clusters, especially the observed nano-rods?” and “Why does CsBr and CsI behave differently from CsCl?” Considering alkali halides have application as detector layers, these questions would also be of interest there. The direct experimental investigation into the formation of metal nano-clusters is difficult and not possible with our setup, hence, we logically speculate the sequence of events that lead to the formation of metal nano-clusters based on scanning electron microscopy (SEM) images of samples taken at regular intervals of evolution.

## 2. Results and discussion

Thin films of cesium halide were fabricated by thermal evaporation in vacuums lower than  $10^{-5}$  Torr.

The films were deposited on microscopy glass slides maintained at room temperature. All the films were fabricated under identical conditions. Looking at Fig. 1, an immediate observation is the striking similarity between morphology of CsCl, CsBr (not shown here) and CsI polycrystalline thin films. Large grains are tiled and tightly packed with sharp grain boundaries (Fig. 1a and b). For similar thick films ( $d \sim 150$  nm), the average grain size of CsI were found to be the largest ( $6500 \mu\text{m}$ ) while those of CsCl were the least ( $4300 \mu\text{m}$ ). The grains, however, do not have regular shapes. These SEM micrographs were taken within few hours of sample fabrication and thereafter at regular intervals to observe the “time” evolution of sample morphology.

### 2.1. Formation of spherical grains/surface diffusion

The morphologies gradually change with time as neighboring grains recede to become smaller and spherical in appearance (Fig. 2). The micrographs show the surface morphology of CsCl, CsBr and CsI films after ageing for 630 h since their fabrication. All the films showed an average grain size of  $1\text{--}1.5 \mu\text{m}$ . The grain density of the samples varied (CsCl being sparsely populated) hence different magnifications were maintained. The grain tends to take up spherical shape due to grain boundary grooving. “Grooving” [13–15] as the name suggests, is the phenomenon by which gaps appear between the grains of polycrystalline samples. The fissures develop from the film surface towards the substrate (Fig. 1c). Theoretical models show the grooving occurs due to atoms moving along the surface away from the grain boundary by surface diffusion [16].

The grains in these thin films are in fact forced to take up a spherical shape due to minimization of free energy ( $G$ ) of the system [17]. The equation used to model this behavior is given as

$$G = \gamma_s A_s + \gamma_b A_b \quad (1)$$

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