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The growth, structure and optical properties of CsI-PbI$_2$ co-evaporated thin films

F. Somma
INFM&Dept. of Physics, University Roma Tre, via V. Navale 84, 00146 Rome, Italy

M. Nikl, K. Nitsch
Institute of Physics AS CR, Cukrovarnicka 10, 162 53 Prague, Czech Republic

C. Giampaolo
Dept. of Geology, University Roma Tre, Largo San L. Murialdo 1, 00146 Rome, Italy

A.R. Phani, S. Santucci
INFM&Dept. of Physics, University of L’Aquila, via Vetoio 10, 67010 Aquila, Italy

The structure and optical properties of thin films grown by vacuum co-evaporation of CsI and PbI$_2$ powders from two independent crucibles were studied. Typical thickness of the grown films was about 0.5 micrometer. X-ray diffraction spectroscopy using different grazing angles (0.1°-2°) revealed the formation of ternary phases, namely CsPbI$_2$, and CsPbI$_4$ and gave us an estimate of their percentage in volume. The sizes of the aggregates were estimated by the Warren- Aberbach method in around 20-40 nm. A direct observation of the thin film surface by atomic force microscopy was performed. Absorption and luminescence spectroscopies were employed to characterize the optical properties of these ternary nano-aggregate phases in the 4.2 - 300 K temperature ranges.

1. Introduction

The phase diagrams of Cs-X-PbX$_2$ (X=Cl,Br,I) allows the formation of CsPbX$_3$, Cs$_4$PbX$_6$ and in some cases also CsPbCl$_3$ and CsPbBr$_3$ single crystals has been reported in the literature, their optical properties were investigated [1-4] and their band structure was calculated [5]. Recently, the creation of nanoaggregates was reported in Pb-doped single crystal CsX (X=Cl, Br) hosts, [6,7] quantum size effects associated with decreasing crystallite size was invoked to explain a high temperature shift in their luminescence and broadening in the absorption and emission spectra. Similar processes were noted in co-evaporated CsBr-PbBr$_2$ films [8], where X-ray diffraction spectroscopy revealed evidence for the creation of CsPbI$_3$ and Cs$_3$PbBr$_6$ nanoaggregates. The bulk Cs$_3$PbBr$_6$ (X=Cl,Br) crystals were grown in recent years despite of the problems due to the unavoidable incongruent growth process [9] their luminescence properties were reported in Refs. [10] and [11], including the comparison with the nanocrystalline Cs$_3$PbX$_6$ phase in a thin film system with X=Br [11]. The formation and optical properties of the Cs-Pb-X ternary nanoaggregates were reviewed recently in Ref. [12]. Up to our knowledge there is only one study related to the luminescence and reflection spectra of CsPbI$_3$ single crystals in the literature [13]. Nothing is known about the optical and structural properties of the Cs$_3$PbI$_6$ compound, even its existence has not been proved in the Cs-I-PbI$_3$ phase diagram study [14]. Cs$_3$PbX$_6$ compounds offer an interesting comparison with the classical KX:Pb$^{2+}$ (X=Cl, Br, I) model systems because their luminescence and decay kinetics properties are due to the same local structure of the emission centers (octahedron (PbX$_6$)$_{3+}$), while their crystal structures are generally different. Recent results related to the emission of Pb-based aggregated phases in CsI:Pb single crystals have shown a rather complex behavior of the observed emission spectra, but the X-ray diffraction spectroscopy failed in finding any Cs-Pb-I ternary structures even after extended annealing procedures [15]. The presence of ternary Cs-Pb-X microphases seem to be more easily evidenced in co-evaporated CsX-PbX$_2$ thin films as compared to Pb-doped single crystals due to the higher percentage of the PbX$_2$ component allowed in thin film samples, this has been shown for X= Br [8,12].

To complete the study of the optical and structural properties of these heavy alkali metal-lead-halides, CsPbI$_3$ and CsI-PbI$_2$ co-evaporated films were prepared and subject to structural and spectroscopic characterizations.

2. Experimental details

The studied samples were prepared by evaporation of CsPbI$_3$ powder (obtained by milling of CsPbI$_3$ crystals previously grown using Bridgman technique) under vacuum employing quartz and glass substrates using a single crucible (CP13 sample series). Alternatively, the co-evaporation of CsI and PbI$_2$ powders (99.9+% purity) from two independently driven molybdenum crucibles was used to achieve a well-defined mixing of the components already in a vapour phase (CPM3 sample series). The typical growth rate was about 1 nm/s, the thickness of the films was around 300 - 600 nm. Each evaporation procedure yielded eight samples, the dimensions of the sample support were 10x10 mm. The samples were firstly measured by absorption spectroscopy to check homogeneity throughout the series, afterwards were characterized employing the X-ray diffraction, atomic force microscopy and other measurements.

The structural properties of the films were investigated by grazing incidence X-ray diffraction (XRD) performed using the Cu K$_{α}$ radiation ($λ$= 1.5406 Å) with a ω-
diffractometer SIEMENS D5000. In order to obtain higher resolution, an improved full width at half maximum (FWHM) and intensity, the measurements were performed employing the Bragg Brentano method using fixed slits. Small grazing incidence angles were used (0.1° - 2°) in the measurements of diffraction spectra.

The morphology of the thin films was studied by atomic force microscopy (AFM). AFM measurements were performed in the contact mode with a Park Scientific Instruments CP microscope equipped with high aspect ratio conical tip (PSI Ultralever™ with 80° sidewall angle and 5 nm minimum radius).

The absorption spectra of the thin films were measured in the UV/VIS spectral range using a Perkin-Elmer λ900 spectrophotometer equipped with a Leybold cryo-cooler for low temperature measurements. Luminescence spectra were measured by Spectrofluorometer 199S (Edinburgh Instrument) equipped with the hydrogen steady-state and coaxial ns pulsed flashlamps, for its further description see e.g. Ref. 3,6,10.

3. Results and discussion

The XRD spectra (Fig. 1) of the co-evaporated sample CPM3 give evidence of the formation of CsPbI₃ and Cs₄PbI₆ nanoaggregates in the samples studied. The aggregate (crystallite) sizes were determined by the Warren-Aberbach method [16] and the medium sizes obtained for the four phases present are as follows: CsI ... 43 nm, Cs₄PbI₆ ...36 nm, CsPbI₃ ...24 nm and PbI₂ ...34 nm. The interpretation of the XRD spectra is based on the JCPDS database of the structures. In the case of Cs₄PbI₆ structure a good agreement with the observed experimental diffraction spectrum was obtained only after simulation of its diffraction pattern based on Cs₄PbBr₆ reflections. Their change after Br → I exchange was derived taking into account the diffraction pattern change coming from CsPbBr₃ to CsPbI₃ structures.

The AFM technique was used to study the surface morphology of the insulating films prepared. In Fig. 2 the two-dimensional image of the CPM3 sample surface is given. It shows that the grain size of a crystallite is between 100 and 300 nm, which is a higher than the values obtained from the XRD measurements.

The disagreement between the grain size determination from XRD and AFM measurements can be explained taking into account the fact that the XRD determination is based on the size of defect-free volume, while the AFM measurement directly visualizes the grains without consider the degree of structural imperfection. Taking into account the grain (crystallite) sizes obtained from both experiments, it is reasonable to conclude that an average grain observed by the AFM contains other smaller size crystallites belonging to different orientations, as observed in the XRD. The absorption spectra of CPM3 sample were measured at different temperatures and are shown in Fig. 3. The peak around 410 nm can be ascribed to the CsPbI₃ nanocrystal xcitonic absorption, based on its close position to the exciton peak found in the reflection spectrum of bulk CsPbI₃ [13]. Furthermore, excitation in this spectral region leads to a broad-band emission around 535 nm, which was also observed in ref. 13 and ascribed to the auto-localized exciton luminescence in the CsPbI₃ structure. In the spectrum of the CPI3 thin film (higher relative content of Pb ions in the evaporated substance with respect to the CPM3 sample) an increased amplitude of the 410 nm absorption is obtained and another peak at around 490 nm is visible. The latter absorption can be ascribed to the PbI₂ exciton absorption based on the literature data [17].

The excitation within the absorption peak at 365 nm gives rise to an intense emission band around 430 nm. This absorption peak can be ascribed to the Cs₄PbI₆ exciton transition based on (PbI₆)⁴⁻ octahedron, which is

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FIG. 1. X-ray diffraction patterns of the co-evaporated Cs-PbI₂ thin film (CPM3) at different grazing incidence angles.

FIG. 2. AFM picture of the co-evaporated Cs-PbI₂ sample (2x2µm² area) showing the grain morphology of the thin films grown.
supported by: (i) similarity in the position of the absorption, excitation and emission peaks with those of Cs\textsubscript{4}PbI\textsubscript{6} powder, we have apparently obtained a mixture of the CsPbI\textsubscript{3} molecules in the vapor phase and the tendency of the CsI-PbI\textsubscript{2} system to create both ternary compounds, allowed by the phase diagram [14].

4. Conclusion

Ternary CsPbI\textsubscript{3} and Cs\textsubscript{4}PbI\textsubscript{6} nanophases were evidenced in the co-evaporated CsI-PbI\textsubscript{2} thin film system. In agreement with the literature data, the CsPbI\textsubscript{3} nanocrystals showed the excitonic absorption around 410 nm and a broad-band emission around 535 nm. The absorption at 365 nm was ascribed to the auto-localized exciton transition based on the (Pb\textsubscript{6})\textsuperscript{4+} octahedron in the Cs\textsubscript{4}PbI\textsubscript{6} nanocrystals.

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References

[16]. Warren E. and Averbach B. L., J. Appl. Phys. 21, 595,(1953)