



	Experiment title: Dopant incorporation in PbS quantum dots for solar cells	Experiment number: HC-1847
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Report:

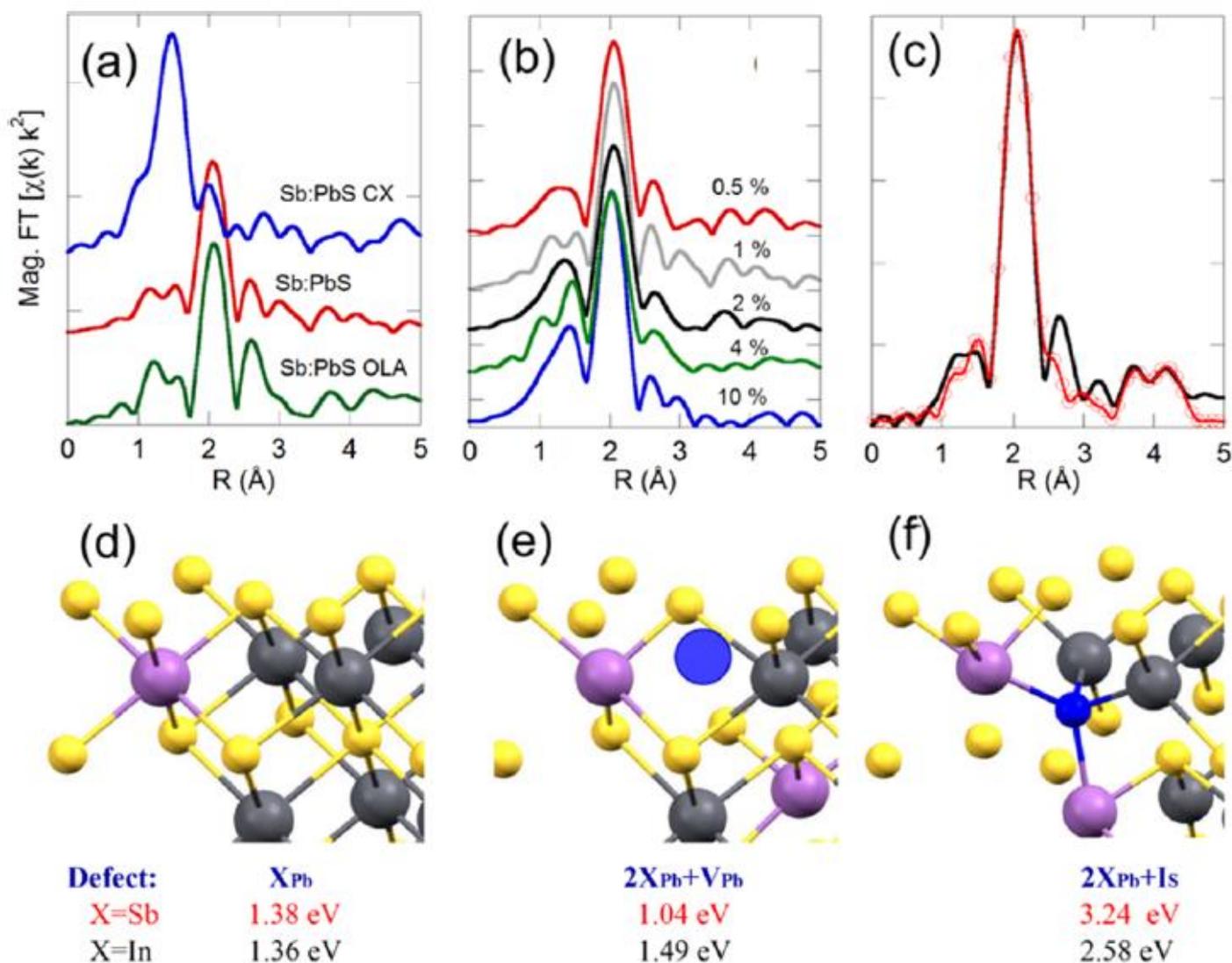
Colloidal quantum dots (CQDs) are a class of nanomaterials whose unique optical properties has created a revolution in solution-processed photovoltaics, light-emitting diodes, and photodetectors. These applications require photoactive semiconductor components with accurately controlled optical and electronic properties. The lack of control over the electronic properties of CQD solids, in particular their doping character, still acts as a roadblock toward more-advanced device architectures and functionalities. Doping CQDs with aliovalent elements that can act as electron donors or acceptors is a very promising approach. Although aliovalent doping has been the cornerstone in doping single crystalline semiconductors to control carrier type and density, very few prior works report electronic doping with aliovalent cations for CQD solids and a complete understanding of the mechanisms at play has yet to be developed. Several semiconducting CQDs (CdSe, InAs, PbS) have been doped with a range of elements either during the synthesis, post-synthetically in solution, or via solid-state surface treatments. Yet, a complete picture of the factors that determine the efficacy and mechanism of dopant incorporation in the host, as well as the corresponding optoelectronic effects that doping causes, still remain elusive.

Dopant incorporation, the primary prerequisite step in doping, is governed by both kinetics and thermodynamics. A relevant kinetic factor is whether the dopant precursor reacts fast enough during CQD growth, compared to the precursors providing the elements of the host CQD. Dopant incorporation is further determined by whether the dopant stays long enough on the surface of the as-grown CQD to react with the host lattice and be overcoated by the latter. On the other hand, thermodynamics dictate the energy required for the formation of a specific dopant complex within the host lattice and, thus, its occurrence likelihood. Following aliovalent dopant incorporation, a question that still remains is what determines the location of a dopant in the host material. The dopant site, e.g., whether the dopant is located on the surface or the core and whether it is substitutional or interstitial, will affect its optoelectronic impact on the CQD solid.

In order to elucidate the above points we have performed XAFS measurements at the high energy In and Sb K – edges on In and Sb doped PbS CQD thick films drop – cast on glass substrates.

We have studied three kinds of samples: 1) Dopant added as a metal acetate precursor; 2) similar to the first series but with the addition of oleylamine (OLA) precursor acting as a regulator of the growth process; 3) samples in which the dopant incorporation was attempted using a cation exchange (CX) process. For all series the dopant concentration ranged from 0.5 to 10%. The objective of the XAFS measurements was to determine if the dopants were effectively incorporated in the bulk of the CQD and, if so, to determine the incorporation site; ab – initio DFT simulations of the local structure of various candidate dopant incorporation sites was also performed.

In the figure we show the Magnitude of the Fourier Transforms for Sb doped samples. A brief comment follows and we refer to the publication for a full discussion. Panel (a) compares spectra for various 1% doped samples and shows that in the CX sample Sb is found only on the surface of the CQD in a fully oxidized form (main peak at 1.5 Å) while in the other two samples it is mostly incorporated in the bulk (main peak at 2.5 Å). All In doped samples were found to be oxidized. Panel (b) compares the FT for the first series of samples. Panel (c) reports the comparison between the experimental data and the best fit with a neutrally charged vacancy complex composed by 2 Sb atoms substitutional to Pb plus a Pb vacancy, showing good agreement; a simple substitutional site gave poor agreement. Panels (d), (e) and (f) report the local structure of the simulated dopant structures.



These results have been published in Chemistry of Materials **28**, 5384 – 5393 (2016), DOI: 10.1021/acs.chemmater.6b01445