Structural Transformations in Cs_2SnI_6 Defect Perovskite under High Pressure

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Cs_2SnI_6 crystallizes into the vacancy-ordered double perovskite structure (space group $Fm\overline{3}m$) [1]. It can be regarded as a 0D defect variant of the simple 3D perovskite $CsSnI_3$ structure with isolated $[SnI_6]^{2-}$ octahedra. Despite the absence of 3D covalency via Sn−I−Sn connectivity, the close-packed anionic lattice forms dispersive frontier electronic bands with mobile carriers which are activated by intrinsic defects in the structure, most probably iodine vacancies and presents a short band gap of 1.26 eV. Combined with the advantage of the non-toxicity of Sn and their very high stability in oxygen and moisture [1], the defect perovskites are very interesting materials in photovoltaics, both as light absorbers [2] and as hole-transporting materials (HTMs) [3].

Pressure on the giga-pascal scale can be used as an external stimulus to investigate the behavior of perovskite absorbers in a controllable and predictable way, since it is known to trigger a wide variety of structural transformations in organic and inorganic solids [4]. Up to now very few high pressure studies have been performed on purely inorganic defect halide perovskites with the Sn^{2+} cation [5], [6].

The Cs_2SnI_6 material was prepared from its binary precursors, as previously described [3]. A symmetric diamond anvil cell was employed to generate high pressure. Monochromatic X-ray beam with the wavelength of $\lambda=0.4859(3)$ Å was used for the sychnotron diffraction experiments (SXRD) carried out at the B1 station, Cornell High Energy Synchrotron Source (CHESS). A Renishaw inVia Reflex spectrometer was employed for the micro-Raman experiments in combination with excitation at 785 nm using a high power near-infrared (NIR) diode laser.

As shown by the SXRD patterns in Figure 1, Cs_2SnI_6 undergoes a continuous structural phase transition starting at ~8 GPa and completing at ~10 GPa, with both the original cubic phase and the transformed monoclinic phase being present between 8-10 GPa. According to the Rietveld analysis at high pressure, the material adopts a nearly orthogonal monoclinic *I2/m* structure which occurs through tilting of the SnI_6 octahedra about the monoclinic b-axis, accompanied by their axial expansion along the c-axis. Furthermore, upon pressure release the reverse phase transition to the ambient pressure *FCC* structure is completed only below 4 GPa. In fact, *I2/m* is amongst the candidate structures often encountered in high-pressure distorted perovskites [7].
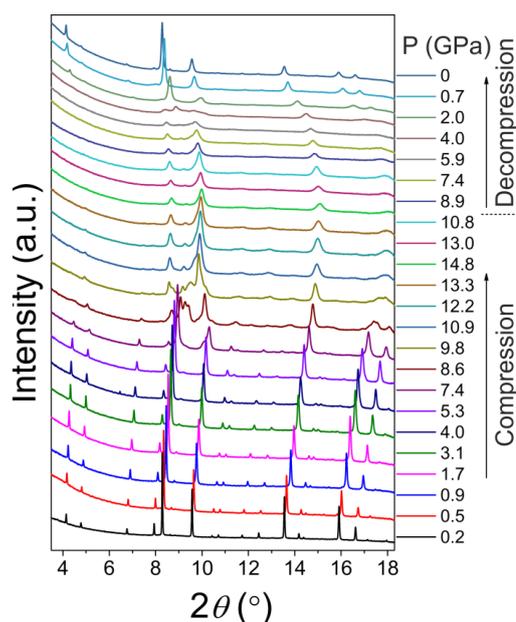

Figure 1. Phase transformation of Cs_2SnI_6 from the FCC cubic lattice to the monoclinic *I2/m*, upon compression above ~8-10 GPa. The tranformation is reversible with hysteresis; the compound returns to its original FCC structure upon decompression below 4 GPa.

As shown in Figure 2, all Raman bands shift positively with pressure, as it is normally expected due to hardening of chemical bonding during compression. At ambient and very low pressure (0.22 GPa), only three first-order Raman bands are observed, all pertaining to Sn-I vibrations in the SnI_6 octahedra; the triply degenerate asymmetric bending X-Sn-X deformation, $\delta(F_{2g})$, at 78 cm^{-1} (mode #2), the doubly degenerate asymmetric Sn-X stretching $\nu(E_g)$, at 92 cm^{-1} (mode #3) and the non-degenerate Sn-X symmetric stretching vibration, $\nu(A_{1g})$, at 126 cm^{-1} (mode #4) [3]. The latter is very strong with intensity 15 times larger than #3, which is the second more intense mode. The spectrum further includes the second order $2\nu(A_{1g})$ mode at 250 cm^{-1} (mode #5). Above 0.62 GPa, the missing triply degenerate lattice mode $\nu_L(F_{2g})$ (mode #1), involving vibrations of the Cs atoms in the rigid $[SnI_6]$ lattice,

emerges at low frequency [3]. At 3.3 GPa the mode #3 vanishes and the strongest mode #4 appears just above the detection threshold (Figure 2) and this pattern continues up to 8 GPa. In this range (2 – 8 GPa) a new weak satellite band (we call it 4s) appears next to mode #4. The aforementioned changes in the spectral characteristics suggest an order-disorder phase transition in the range around 3.3 GPa range. This transition evolves gradually from 1.8 – 4.2 GPa. This is supported by a decrease in the slopes of the frequencies vs. pressure for all modes, at about 3.3 GPa, which probably stems from the considerable reduction in the compressibility of the crystal as evidenced by SXRD.
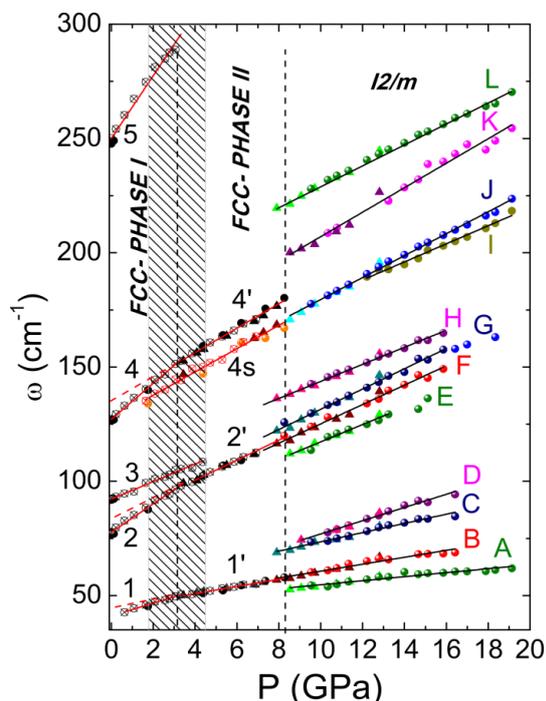

Figure 2. The pressure dependence of the Raman band frequencies upon compression in Cs_2SnI_6.

The transformation from FCC-Phase I to FCC-Phase II has the characteristics of breaking the long-range translational symmetry of the lattice, introducing local disorder, reducing the empty spaces in the lattice, and making, thus, the crystal less compressible. Raman spectroscopy is very sensitive to such changes; SXRD, on the other hand, does show the change in compressibility, but it cannot detect new motifs in the SXRD patterns or abrupt changes in the FWHM of the peaks because the average long range order apparently is hardly affected [8]. Thus, for SXRD, phase II is indistinguishable to the ambient pressure $Fm\overline{3}m$ one, while Raman data detect it as a new intermediate phase between 3 – 8 GPa. Such discrepancies in the phase identification between SXRD and Raman measurements close to order/disorder phase transitions often appear in the literature [9]. Above 8-10 GPa, an abrupt change, is observed in the Raman spectra Twelve modes well resolved in this region, named as A-L. This change is consistent with the phase transformation to the *I2/m* phase evidenced in the X-ray diffraction patterns.

Considering that introduction of local strains in the structure, e.g. by substitutional alloying, compensates for the imposed high pressure, our results provide key directions for modifying the local structure of the defect halide perovskites towards improving their optoelectronic properties and exploit their use in photovoltaic applications.

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