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The preparation and characterization of quasi-one-dimensional lead based perovskite $CsPbI_3$ crystals from HI aqueous solutions

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ABSTRACT

Quasi-one-dimensional lead based perovskite $CsPbI_3$ exhibits increasing interests in quantum dots, solar cells, *etc*. However, high quality large $CsPbI_3$ bulk crystals are still unexplored. Here we report $CsPbI_3$ crystal growth from HI aqueous solution by tailoring the solubility. The morphology and crystal structure of $CsPbI_3$ are characterized by SEM and XRD, which reveal the stick-like structure with the space group *Pnma* and lattice parameters $a = 10.46$ Å, $b = 4.80$ Å, and $c = 17.78$ Å. Ultra violet-visible transmission spectra substantiate $CsPbI_3$ being a direct-gap semiconductor with a band-gap ~2.69 eV. In addition, a broad emission at 550–580 nm with a large Stokes shift of 0.60 ~ 0.75 eV and the corresponding dissociation energy 7.58 meV was found using temperature and power dependent PL spectra. This emission was attributed to a strong electron–phonon coupling induced "self-trap excitons" in $CsPbI_3$. Our finding shields more light on the crystal growth, structure and optical properties of $CsPbI_3$.

1. Introduction

Lead based halide perovskites $APbX_3$ ($A^+ = Cs$, CH_3NH_3, $HC(NH_2)_2$; X = Cl, Br, I) have recently emerged in applications of solar cells [1,2], light emitting diode [3], laser [4], and nuclear detection [5–7], owing to their low material cost, impressive optical and electronic properties, such as the extremely low density of defects, excellent carrier transport, and surprisingly high defect tolerance [8–12]. As a kind of all-inorganic perovskite materials, $CsPbI_3$ exhibits much more superior chemical stability than those of the organic–inorganic hybrid perovskite counterparts by eliminating organic cation [13]. Besides, $CsPbI_3$ have also attracted intensive attention as a promoting candidate of quantum dots [14–17] and superior photodetectors [18], due to their high luminescent efficiency, ultrafast response and high stability.

Generally, $CsPbI_3$ crystals adopt as orthorhombic phase (*Pnma*) at ambient condition [19,20]. Different from the typical perovskite structure featured with three-dimensional network of corner-sharing octahedra, the crystal structure of $CsPbI_3$ includes double chains of edge-sharing $[PbI_6]^{4-}$ octahedra linked by Cs^+ cations (shown in Fig. 1). However, compared to plentiful reports about the crystal growth of three dimensional perovskite crystals from solution, the one dimensional crystal structure introduce many challenges for $CsPbI_3$ bulk crystals grown from a solution. Though large sized $CsPbI_3$ bulk crystals can be grown using high temperature Bridgeman method [20], only nanometer [18] or micron [19] sized $CsPbI_3$ crystals were reported previously. In this work, we would systematically study the growth of $CsPbI_3$ single crystals by the solution method. Based on the resulting samples, the crystal structure, morphology and optical-property characterizations of $CsPbI_3$ crystals have been investigated.

2. Experimental section

$CsPbI_3$ crystals were grown from hydroiodic acid (HI) aqueous solution in the temperature ranged of 75–64 °C. Fig. 2(a) illustrates the setup of crystal growth. The starting materials were CsI (99.99%, Sigma-Aldrich), PbI_2 (99.99%, Sigma-Aldrich) and HI aqueous solution (57 wt%). As shown in Fig. 2(b), the solubility curve demonstrates the positive temperature coefficient. According to the solubility curve, the starting components CsI + PbI_2 (mole ratio 1:1) and HI aqueous solution were set as 35 mg/ml. Before growth, the solution was stirred for 3 h at 80 °C, immediately then filtered using a 0.2 µm sized filter membrane for twice. The obtained pale yellow clear solution was used as the precursor. The precursor was held at 80 °C for 5 h, then slowly cooled down to 50 °C at a rate of 0.3 °C/h. As shown in Fig. 2(c), no crystals were generated from the solution at 75 °C. With the temperature decreasing, one stick-like yellow crystal firstly turned up at 69 °C

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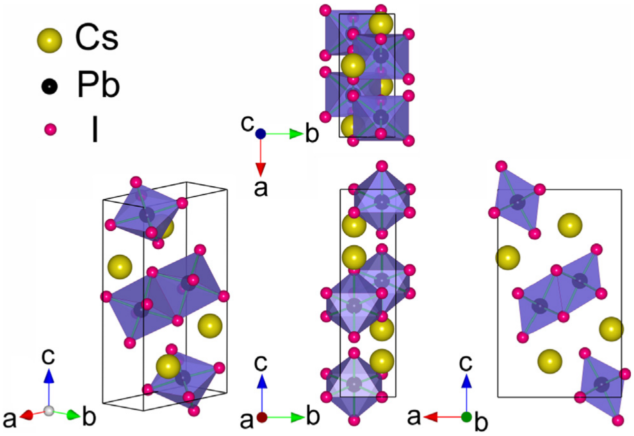

Fig. 1. Crystal structure of $CsPbI_3$ crystal.

(pointing by the arrow). Further decreasing the temperature to 64 °C, plenty of small crystals in the solution were formed and the growth was ended. After washing away the solution by the acetonitrile solution, many yellow stick-like crystals with millimeter-sizes can be obtained as shown in Fig. 2(d).

The compositions and morphologies of $CsPbI_3$ were carried out on Tescan MIRA3 XMU Field Emission Scanning Electron Microscope (SEM) with the energy-dispersive spectroscopy (EDS). Its crystal structure was determined by powder X-ray diffraction (XRD, Rigaku). The corresponding powder $CsPbI_3$ smaples were prepared by grinding as-grown single crystals for 1 h. These results were analyzed by Rietveld refinement (the general structure analysis software package GSAS-EXPGUI) [12]. 2 mm × 0.5 mm × 5 mm sized single crystal was used to measure the UV–vis spectra were recorded at room temperature by UV-3150 spectrometer (Shimadzu UV–Vis-NIR). The photoluminescence (PL) spectra were conducted based on a 1 mm × 0.5 mm × 7 mm sized $CsPbI_3$ crystal using a FLS-920 fluorescence spectroscopy with the excitation wavelength of 325 nm.

3. Results and discussions

3.1. Crystal morphology and structure

Fig. 3 shows two typical as-grown $CsPbI_3$ single crystals characterized by SEM. The planar-view SEM images show $CsPbI_3$ crystals have the stick-like shapes. The composition of as-grown $CsPbI_3$ crystals was determined by EDS, with the Cs, Pb and I ratio of 1:1.04:2.99, which is close to the stoichiometric ratio. The element mappings of Cs, Pb and I are also presented in Fig. 3. The uniform distribution of Cs, Pb and I suggests that the growth is homogeneous.

The crystal structure of stick-like $CsPbI_3$ was determined by powder XRD with the Rietveld refinement, Fig. 4(a). The calculated patterns (solid lines) agree very well with the experimental one. The fitting factors are ${}_{w}R_p = 10.5\%$ and $R_p = 8.2\%$. The unit-cell parameters obtained from the Rietveld refinement are $a = 10.46$ Å, $b = 4.80$ Å, and $c = 17.78$ Å, respectively. The space group belongs to *Pnma*, which is consistent with the previous reports [19,20]. Only one set of $(0\ 0\ L)$ peaks for single crystal samples are exhibited in Fig. 4(b).

3.2. Optical properties and self-trap behaviors

The optical properties of resulting $CsPbI_3$ crystals have been studied at room temperature. Fig. 5 shows the transmission spectra from 350 to 750 nm. A sharp rise in the curve is observed at around 460 nm, with an average transmittance of ~48% from 500 to 750 nm. By fitting the Tauc plot, the energy band gap (Eg) was calculated to be ~2.69 eV, demonstrated in the inset of Fig. 5, which is in good agreement with the previous reports [18,21].

Fig. 6 reveals the temperature dependent photoluminescence (PL) spectra from 10 K to 100 K. At 100 K, there is a small peak at around 440 nm and another broad peak at around 580 nm. With the temperature decreasing, only one peak at 540 nm exists. According to the previous reports, the peak at 440 nm should be assigned to the free exciton and the broad one is possibly attributed to the formation of self-trapped excitons (STE) [21–26]. At low temperatures, only STE emission is observed. Upon heating over 50 K, the excitonic emission peak appears. The excitonic peak red-shift with increasing temperature suggests a strong electron–phonon coupling contribution dictates band gap behavior. This is consistent with the self-trapping of excitons. Increased

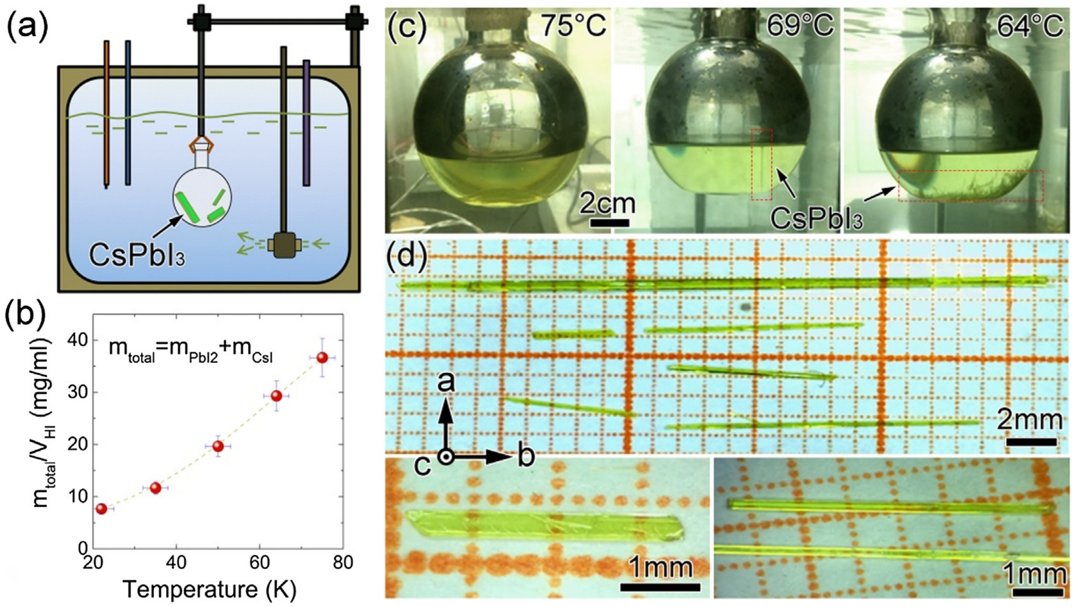

Fig. 2. (a) Schematic of experimental apparatus for $CsPbI_3$ crystals grown from HI aqueous solution. (b) Solubility curve of $CsPbI_3$ in HI solution. (c) The pictures of the processes for the crystal growth at 75 °C, 69 °C and 64 °C. (d) As-grown stick-like $CsPbI_3$ crystals.