Revealing the origin of green light emission in Cs4PbBr6 by cathodoluminescence

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Background

Metal halide perovskite is expected as next-generation material for the application for solar cells and light-emitting devices due to their excellent optical properties. Among them, Cs_4PbBr_6 has obtained significant attention as a luminescent material for its high-efficiency green emission and ease of synthesis. However, the mechanism of this green luminescence from Cs_4PbBr_6 has not been understood so far since the bandgap energy of Cs_4PbBr_6 lies in the ultraviolet range, which suggests that the green emission originates from intermediate states formed by impurities or defects within the host phase [1].

Previous discussions have proposed that $CsPbBr_3$ nanocrystals embedded in the Cs_4PbBr_6 host phase are the primary candidates for the green light source [1]. However, conventional photoluminescence measurements cannot spatially resolve such nanocrystals, and thus definitive evidence has been lacking. Recently, cathodoluminescence (CL) studies taking advantage of nanoscale spatial resolution achievable by electron excitation have reported the presence of microcrystals dispersed within the host phase [2]. However, detailed information of these microcrystals as well as their luminescence mechanism remains unclear, necessitating further elucidation of local optical properties.

In this study, we evaluated the nano-scale optical properties of Cs_4PbBr_6 powder samples using CL with scanning transmission electron microscopy (STEM). CL spectral and lifetime mapping analysis with a temperature dependence validated the inclusion of $CsPbBr_3$ nanoparticles within the Cs_4PbBr_6 host phase.

Methods

CL Measurement: Light emitted from the sample by electron irradiation was collimated by a parabolic mirror inside the microscope and directed toward the spectrometer for the CL spectrum measurement and a Hanbury Brown-Twiss (HBT) interferometer for the emission lifetime measurement. By the HBT measurement, one can measure emission lifetime without pulsing the electron beam. In these measurements, the light detection and electron beam scanning were synchronized, enabling CL spectral and lifetime mapping.
Sample Preparation: Cs_4PbBr_6 powder samples, were synthesized via a solution method. CsBr and $PbBr_2$ precursors were prepared and held in dimethyl sulfoxide (DMSO) for one hour. The precipitate, grown by the anti-solvent method, was washed with DMSO to obtain a powdered sample. X-ray diffraction (XRD) analysis confirmed only peaks corresponding to Cs_4PbBr_6 in the crystal structure.

Results

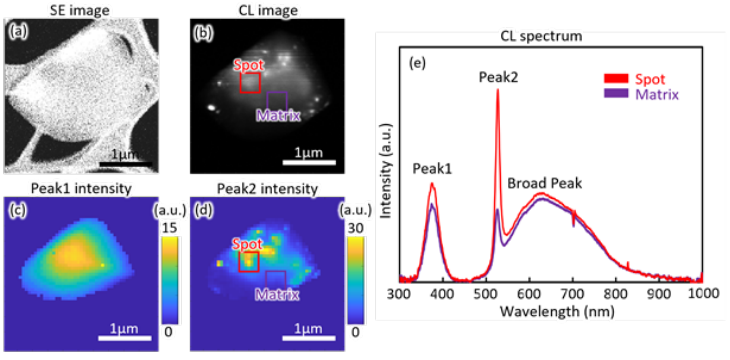
The secondary electron (SE) image of the measured powder is presented in Fig.(a). The CL image revealed the existence of bright spots with high luminescence intensity within the particle (Fig.(b)). Furthermore, the area-integrated spectrum showed peaks at emission wavelengths of 375nm, 520nm, and 700nm (referred to as Peak1, Peak2, and Broad Peak, respectively). According to previous studies, Peak1 is attributed to the optical transition of Pb ions originating from Cs_4PbBr_6 [3]. Broad peak can be attributed to emission derived from some other defects according to a radio-luminescence study by X-ray [4]. Peak2 is the green emission that we discuss in this study.

In the CL spectral mapping on the same measurement area that was conducted at low temperature (120K), the emission intensity of Peak1 exhibited a homogeneous distribution across the entire area, whereas Peak2 showed high intensity specifically in the bright spot regions (Fig.(c-d)). CL spectra were extracted from the region with single bright spot (Spot1), and regions without bright spots (Matrix), shown in Fig.(e). In all regions, the intensities of Peak1 and Broad Peak remained approximately the same, while the intensity of Peak2 changed depending on the presence of spots inside the signal extraction area in CL mapping (Fig.(d)). Particularly noteworthy is the significantly lower intensity of Peak2 in the Matrix region. On the basis of these findings, it is considered that nanoparticles forming the bright spots emit green light within the host phase of Cs_4PbBr_6.

To further investigate the optical properties of the green light emission, CL measurements were both performed at room temperature and low temperature (120K). It revealed that the emission wavelength is longer and the emission lifetime shorter at 120K than at room temperature. These trends are opposite to typical semiconductor materials but are consistent with $CsPbBr_3$ nanoparticles without a bulk host material [5]. This suggests that $CsPbBr_3$ nanoparticles surrounded by Cs_4PbBr_6 host phase are the origin of the highly effective green light emission.

Conclusions
In this study, we conducted nanoscale evaluation of the optical properties of Cs_4PbBr_6 using STEM-CL. By the spectral mapping, the presence of nanoparticles emitting green light within the Cs_4PbBr_6 host phase was observed. Furthermore, by measuring the spectra and lifetime under varying temperatures, it was confirmed that the characteristics of the green emission have the same tendency as bare $CsPbBr_3$ nanoparticles without a matrix. Thus, it is suggested that the highly effective green emission originates from $CsPbBr_3$ nanocrystals precipitated within the host Cs_4PbBr_6 material.

Graphic:



Keywords:

Cathodoluminescence, STEM, Perovskite, Lifetime

Reference:

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