Single-Crystal Perovskite CH₃NH₃PbBr₃ Prepared by Cast-capping Method for Light-Emitting Diodes

Van-Cao Nguyen¹, Hiroyuki Katsuki¹, Fumio Sasaki² and Hisao Yanagi¹

 ¹ Graduate School of Materials Science Nara Institute of Science and Technology (NAIST) 8916-5 Takayama, Ikoma, Nara 630-0192, Japan Phone: +81-743-72-6015 E-mail: nguyen.van_cao.nm5@ms.naist.jp
² Electronics and Photonics Research Institute National Institute of Advanced Industrial Science and Technology (AIST) 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

Abstract

We report on light-emitting diodes using single-crystal perovskites prepared by the cast-capping method. This method enabled us to simply fabricate ITO/single-crystal perovskite/ITO devices. The device showed sharp luminescence with FWHM ~ 20 nm and low operation voltage of 2 V at room temperature in ambient condition. This simple method is applicable to various diode structures in the solution process.

1. Introduction

There are a lot of studies indicating that perovskites are promising materials for light-emitting diodes (LEDs) due to their remarkable optical properties such as high luminescence yield and emission-wavelength tunability [1,2]. Furthermore, the perovskite LEDs can be fabricated by solution-processes at low temperature, and possess tunable bandgaps from visible to infrared region which are attractive for next generation optical devices. Up to now, spin coating is usually used to prepare perovskite thin films [3–5]. However, their small crystal grain size limited the performance of optical devices. Recently, we developed a new modified solution process to fabricate large-size single-crystal perovskite thin films, namely the cast-capping method [6,7]. It is a simple but useful method to grow high-quality and large-sized singlecrystal perovskites.

In this work, we demonstrate single-crystal perovskite LEDs prepared by the cast-capping method. The structure of LED is very simple, ITO/perovskite/ITO, without any carrier-transporting layers. X-ray diffraction (XRD) analysis was carried out to identify the crystal structure. I-V characteristics and emission spectra were measured to evaluate the LED performances.

2. Experimental

Based on refs. [6,7], we fabricated ITO/MAPbBr₃/ITO by the cast-capping method. A 40 wt% mixture solution of methylammonium bromide (MABr) and lead bromide (PbBr₂) in anhydrous N,N-dimethylformamide (DMF) with a stoichiometric molar ratio of 1:1 was casted on a ITO-patterned glass substrate (Luminescence Technology Corp.). Then, it was capped with another ITO-patterned substrate to make an emitting area of 3 x 3 mm². The samples were kept

at room temperature in a vacuum for few days to dry the DMF solvent and slowly grow single-crystal MAPbBr₃ between the two ITO substrates. After dried in vacuum, some of samples were cleaved to carry out the XRD measurements using a Rigaku RINT-TT III/NM x-ray diffractometer.

To fabricate LEDs, copper contacts were made to the top and bottom ITO patterns by an electro-conductive paste (D-500, Fujikura Kasei co., LTD.). Electroluminescence properties of ITO/single-crystal MAPbBr₃/ITO devices were investigated by I-V characteristics using an Agilent B2902A Precision Source/Measure and emission spectra using an Olympus MX-51 optical microscope equipped with a Hamamatsu Photonics multi-channel spectrometer PMA-12.

2. Results and discussion

Figure 1 shows an XRD pattern taken from the MAPbBr₃ grown on the ITO substrate. Two intense peaks at 14.95° and 30.15° correspond to the (100) and (200) planes of the cubic form MAPbBr₃, respectively. These growing planes are different from those (110) and (220) planes of MAPbBr₃ prepared by the cast-capping method on the glass substrate [7]. These results indicate that the stabilization of growing faces depends on the substrate surface properties.



Fig. 1 XRD pattern of single-crystal MAPbBr₃ grown between ITOpatterned glass substrates and schematic diagram of cubic MAPbBr₃ indicating the (100) and (200) planes.

Figures 2 shows I-V curves of the ITO/single-crystal MAPbBr₃/ITO device indicating that the currents start to increase around 2 V. The forward and backward currents gradually decrease while their hystereses are kept quite small in three repeated cycles. Figure 3 shows microscope images of emission taken from the ITO/single-crystal MAPbBr₃/ITO device when the applied voltage increases above 2 V up to 4 V. Bright pure green emission was observed at the voltage of ~ 2 V. Noted that the emission only occurred at the crystal edges and they were blinking in a quite regular interval of sub-second. The edge emission could be attributed to imperfect contact of the crystal with the ITO surface while the blinking might be related to ionic migration in the crystal.



Fig. 2 I-V characteristics of the ITO/MAPbBr3/ITO device.



Fig. 3 Microscope images of emission from ITO/MAPbBr₃/ITO at increasing voltages from 2V (I) to 4V (IV). The scale bar: $200 \mu m$.

Fig. 4 shows absorption, photoluminescence (PL) and electroluminescence (EL) spectra of the single-crystal MAPbBr₃ device. The exciton absorption peak appears at $\lambda = 535$ nm while the PL and EL peaks are red-shifted to $\lambda = 540$ and 544 nm, respectively. The EL spectrum displays a pure green emission with a narrow full width of half-maximum

(FWHM) ~ 20 nm which is similar to the PL spectrum.



Fig. 4 Absorption, PL and EL spectra of single-crystal MAPbBr $_3$ in the LED.

Our study realized a simple approach to fabricate solution-processable perovskite LEDs. However, the incomplete contact between the single-crystal perovskite and the ITO surface should be improved to achieve homogeneous and brighter emission. We are trying to replace the ITO/glass substrate with flexible top electrodes such as ITO/PET, Au foil and Au/mica to make better contacts with the perovskite crystals.

3. Conclusions

We have fabricated LED based on single-crystal perovskites prepared by the cast-capping method. Even its simple structure of ITO/MAPbBr₃/ITO without any other layers for carrier injection and transport, the devices showed green electroluminescence at voltage above ~2V. However, the blinking emission occurred at the crystal edges the reason of which should be more deeply investigated and discussed.

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