Determination of bandgaps of photoactive materials in perovskite solar cells at high temperatures by in-situ temperature-dependent resistance measurement*

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Normally, it is difficult to directly measure the bandgaps of perovskite based on methylammonium (MA) or formamidinium (FA) at high temperatures due to material decomposition. We prevent the decomposition by keeping the synthesized perovskite films ($MAPbI_3$ and $MAPbI_3$) in organic iodide vapors, then measure the in-situ resistance of the films at varied temperatures, and further evaluate the bandgaps of these two materials. The evaluated bandgaps are consistent with the results from ultraviolet-visible (UV-vis) absorption spectrum. The bandgap of $MAPbI_3$ decreases with temperature above 95 °C, whereas that of $FAPbI_3$ first increases with temperature from 95 °C to 107 °C and then decreases with temperature above 107 °C.

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Bandgaps of semiconductors play an important role in tuning the light absorption and determine the Shockley-Queisser limit of photovoltaic devices. Organic-inorganic hybrid perovskite solar cells (PSCs) have developed rapidly in the past decade since the first report by Kojima et al[1]. The certified efficiency of large-area PSCs (more than 1 cm^2) has reached 19.6%[2], which is comparable with that of traditional thin-film photovoltaic technology[3-5].

Methylammonium lead iodide ($CH_3NH_3PbI_3$, $MAPbI_3$) and formamidinium lead iodide ($CH(NH_2)_2PbI_3$, $FAPbI_3$) are two commonly used photoactive materials in PSCs. There are many ways to measure their bandgaps, including ultraviolet-visible (UV-vis) absorption (or transmittance)[6], photoluminescence (PL)[7], and ultraviolet photoelectron spectroscopy-inverse photoelectron spectroscopy (UPS-IPES)[8]. For example, Milot et al[6] have measured the bandgaps of $MAPbI_3$ from 8 K to 370 K using temperature-dependent PL spectra. Fang et al[9] have measured the bandgaps of $FAPbI_3$ from 5 K to 295 K in a similar way. However, the bandgaps of these two materials at higher temperatures have rarely been reported. It is important to measure the bandgaps of these materials because the optoelectronic devices made of these materials may be employed at elevated temperatures.

In the high temperature region, $MAPbI_3$ decomposes into methylammonium iodide (MAI) and lead iodide (PbI_2). The $MAPbI_3$ film can turn yellow (the color of PbI_2) in half an hour (or several seconds) in air on a hot plate (100 °C or 120 °C). Direct measurement of bandgaps above 100 °C will be largely influenced by the decomposition. Hence, it is impossible to measure the bandgap of a bare $MAPbI_3$ thin film at temperatures above 100 °C.

To overcome this issue, we keep the $MAPbI_3$ thin film in an MAI vapor. Previously, we have developed a parallel-hot-plate (PHP) method to synthesize high-quality perovskite thin films[10]. In this method, $MAPbI_3$ thin films are exposed to MAI vapor even when stoichiometric $MAPbI_3$ is formed, which makes it possible to avoid the decomposition. More importantly, excess MAI must be avoided because it will cause the degradation of stoichiometric $MAPbI_3$[10]. In PHP method, such an issue can be overcome as the MAI vapor can be easily controlled if we set the top plate and the bottom plate to the same temperature.

In this paper, we synthesized $MAPbI_3$ and $FAPbI_3$ using the PHP method, and then investigated their electric resistance with temperature T>90 °C by using the setup as shown in Fig.1(a). Details of the fabrication procedure can be found in Ref.[10]. The bandgap E_g is further estimated by plotting ln$R$ against $1/T$, where R is the resistance, and T is the temperature. Principle of this method can be found in

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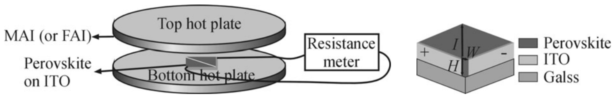
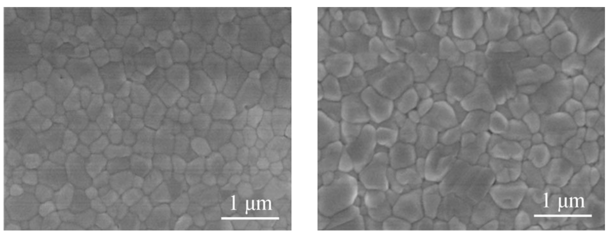
Ref.[11]. Schematic illustration of the channel between two indium tin oxide (ITO) electrodes is shown in Fig.1(b), which is used to measure the in-situ resistivity of the film, where *l* is the length of the channel (34 mm), *w* is the width (250 μm), and *h* is the height (150 nm).



(a) (b)

Fig.1 (a) Schematic diagram of the in-situ resistance measurement using a PHP method; (b) Schematic illustration of the channel between two ITO electrodes used to measure the in-situ resistivity of the film

Initially, the resistance of the film is beyond the measurement limit (250 MΩ), because it only contains PbI_2, and the electric resistivity of PbI_2 is at least 100 orders of magnitude higher than that of $MAPbI_3$[12,13]. As reaction proceeding, the resistance gradually decreases. After the resistance stops decreasing, we take out the thin films from the reaction chamber and investigate their surface morphology by scanning electron microscope (SEM) and crystal structure by X-ray diffraction (XRD). The results shown in Figs.2 and 3 reveal that the films are composed of well-crystallized $MAPbI_3$ without pinhole.



(a) $MAPbI_3$ (b) $FAPbI_3$

Fig.2 SEM images (×20 000) of PHP-processed (a) $MAPbI_3$ and (b) $FAPbI_3$ thin films

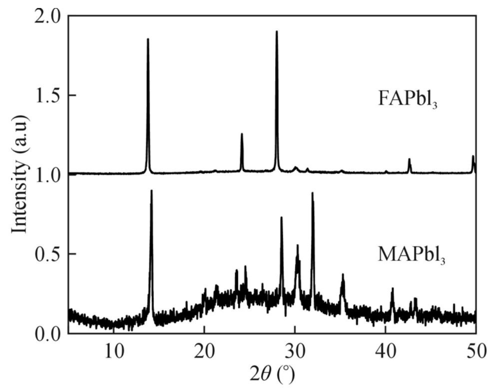
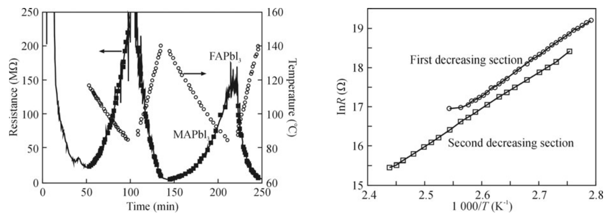


Fig.3 XRD patterns of PHP-processed $MAPbI_3$ and $FAPbI_3$ thin films

In order to measure the resistance of $MAPbI_3$, we set the temperature of the top hot plate to the same temperature as that of the bottom hot plate (120 °C) after the resistance stopped decreasing. Afterward, we decrease the temperature of both plates simultaneously from 120 °C to 90 °C step by step, during which the resistance increases from the initial value of about 20 MΩ to over 250 MΩ. It is worth noticing from Fig.4(a) that such a variation in resistance is reversible if the temperature is increased to 120 °C again. This means that electric property of the film is almost unchanged during the process. It can be obtained from Fig.4(b) that the bandgap E_g derived in this method stays around 1.5 eV. Nevertheless, it decreases with the increase of temperature, which is in contrary to the previous research result[7,8,14-17] that $MAPbI_3$'s bandgap increases with temperature, either in tetragonal phase or in orthorhombic phase.



(a) (b)

Fig.4 (a) In-situ resistance of PHP-processed $MAPbI_3$ and the temperature variations with time; (b) Plotting of ln*R* against 1/*T* in the first and second decreasing sections of temperature in (a)

Besides, some similar methods are further employed to evaluate the bandgap of $FAPbI_3$ in a temperature range of 95—135 °C. The $FAPbI_3$ thin film was synthesized between a top hot plate kept at 160 °C and a bottom hot plate kept at 150 °C in a PHP apparatus. The reaction time for synthesizing $FAPbI_3$ (a few hours) is longer than that of $MAPbI_3$ (about 1 h). The synthesized $FAPbI_3$ thin film contains larger grains with improved crystallinity compared with the $MAPbI_3$ thin film shown in Figs.2 and 3. It can be obtained from Fig.5(b) that the measured bandgap of $FAPbI_3$ is around 1.4 eV.

It is noted from Fig.5(a) that $FAPbI_3$ shows a resistance discontinuity at around 107 °C. Such an anomaly in the resistivity curve is usually accompanied with a phase transition. Based on Stoumpos's work, $FAPbI_3$ has two phase transitions at 130 K and 200 K[18]. But our investigation indicates that $FAPbI_3$ might have one more phase transition at 380 K. However, further examination is needed to confirm it.

For comparison, the optical bandgaps of perovskites are also estimated by UV-vis absorption measurement. It can be obtained from Fig.6 that the measured optical bandgaps of $MAPbI_3$ and $FAPbI_3$ are 1.60 eV and 1.50 eV, respectively. These two types of bandgaps are plotted together in Fig.7, which agree well with values reported in Refs.[6], [18] and [19]. The bandgap of $MAPbI_3$ decreases with temperature above 95 °C, whereas the bandgap of $FAPbI_3$ first increases with temperature from 95 °C to 107 °C and then decreases with temperature above 107 °C.

For most semiconductors, at high temperature, E_g is linearly proportional to temperature as $E_g=E_0-AT$, where A is advocated to be equal to $2Sk$. S is the entropy of formation of electron-hole pairs, and k is the Boltzmann constant[20]. A is positive in most cases, but it is negative for $MAbI_3$[7,8,14-17]. Nevertheless, as revealed here, A (also S) might be positive for $MAbI_3$ at temperatures higher than 95 °C.

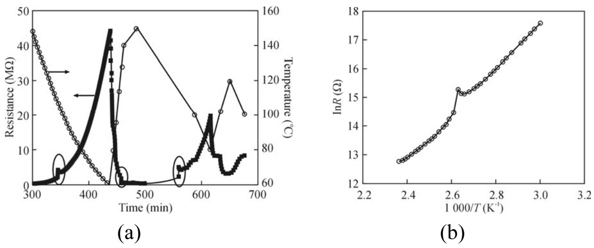


Fig.5 (a) In-situ resistance of PHP-processed $FAPbI_3$ and the temperature variations with time; (b) Plotting of ln*R* against 1/*T* of the first increasing section of temperature in (a)

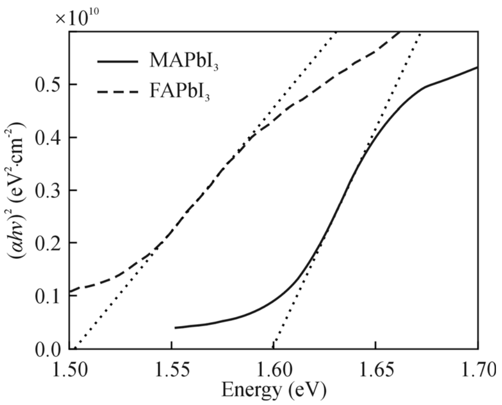


Fig.6 Tauc plots of the absorption spectra of $MAPbI_3$ and $FAPbI_3$

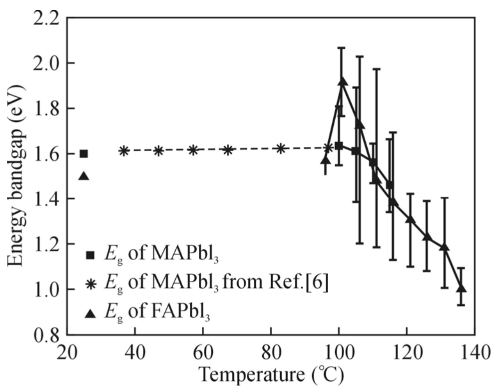


Fig.7 Bandgaps of $MAPbI_3$ and $FAPbI_3$ evaluated by UV-vis absorption measurement (room temperature) and the proposed method (high temperature), compared with those reported in Ref.[6]

In conclusion, we evaluate the bandgaps of two important photoactive materials $MAPbI_3$ and $FAPbI_3$ in perovskite solar cells at temperatures above 95 °C. The evaluated bandgaps are in good agreement with those measured by UV-vis absorption measurement. An abrupt change of resistance of $FAPbI_3$ at 107 °C indicates that $FAPbI_3$ might have a phase transition at this temperature. The bandgap of $MAPbI_3$ decreases with temperature above 95 °C, whereas the bandgap of $FAPbI_3$ first increases with temperature from 95 °C to 107 °C and then decreases with temperature above 107 °C.

References

[1] Kojima A., TeshimaK., Shirai Y. and Miyasaka T., Novel Photoelectrochemical Cell with Mesoscopic Electrodes Sensitized by Lead-Halide Compounds (II), 214th ECS Meeting, 7 (2006).

[2] Li X., Bi D., Yi C., Decoppet J.-D., Luo J., Zakeeruddin S. M., Hagfeldt A. and Gratzel M., Science **353**, 58 (2016).

[3] Polman A., Knight M., Garnett E. C., Ehrler B. and Sinke W. C., Science **352**, aad4424 (2016).

[4] Li F., Dang X., Zhang L., Liu F., Sun D., He Q., Li C., Li B. and Zhu H., Optoelectronics Letters **10**, 266 (2014).

[5] Lu G., Wang B. and Ge Y. W., Optoelectronics Letters **11**, 348 (2015).

[6] Milot R. L., Eperon G. E., Snaith H. J., Johnston M. B. and Herz L. M., Advanced Functional Materials **25**, 6218 (2015).

[7] Yamada Y., Nakamura T., Endo M., Wakamiya A. and Kanemitsu Y., Applied Physics Express **7**, 032302 (2014).

[8] Foley B. J., Marlowe D. L., Sun K., Saidi W. A., Scudiero L., Gupta M. C. and Choi J. J., Applied Physics Letters **106**, 243904 (2015).

[9] Fang H., Wang F., Adjokatse S., Zhao N., Even J. and Loi M. A., Light: Science & Applications **5**, e16056 (2016).

[10] Chen X., Cao H., Yu H., Zhu H., Zhou H., Yang L. and Yin S., Journal of Materials Chemistry A **4**, 9124 (2016).

[11] Ashcroft N. W. and Mermin N. D., Solid State Physics, Harcourt College: Orlando, 1976.

[12] Ponpon J. P. and Amann M., Crystal Research & Technology **42**, 253 (2007).

[13] Hao F., Stoumpos C. C., Chang R. P. H. and Kanatzidis M. G., Journal of American Chemical Society **136**, 8094 (2014).

[14] Zhang W., Saliba M., Stranks S. D., Sun Y., Shi X., Wiesner U. and Snaith H. J., Nano Letters **13**, 4505 (2013).

[15] Dittrich T., Awino C., Prajongtat P., Rech B. and Lux-Steiner M. C., Journal of Physical Chemistry C **119**, 23968 (2015).

[16] Miyata A., Mitioglu A., Plochocka P., Portugall O., Wang J. T.-W., Stranks S. D., Snaith H. J. and Nicholas R. J., Nature Physics **11**, 582 (2015).

[17] Tanaka K., Takahashi T., Ban T., Kondo T., Uchida K. and Miura N., Solid State Communications **127**, 619 (2003).

[18] Stoumpos C. C., Malliakas C. D. and Kanatzidis M. G., Inorganic Chemistry **52**, 9019 (2013).

[19] Eperon G. E., Stranks S. D., Menelaou C., Johnston M. B., Herz L. M. and Snaith H. J., Energy Environmental Science **7**, 982 (2014).

[20] O'Donnell K. P. and Chen X., Applied Physics Letters **58**, 2924 (1991).