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CONTROLLING THE DEFECTS OF LEAD-FREE DOUBLE PEROVSKITE $Cs_2AgBiBr_6$ BY VARIED PRECURSOR CONCENTRATIONS

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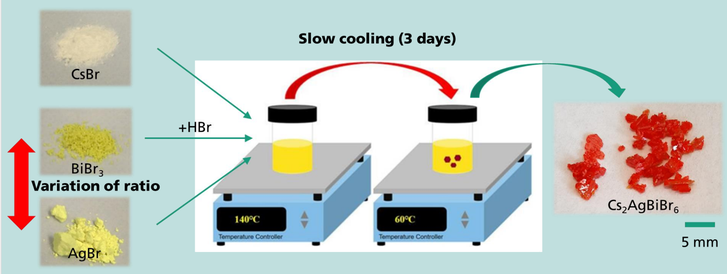
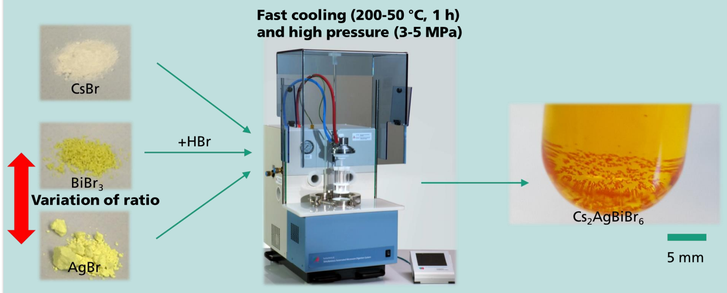
The double perovskite $Cs_2AgBiBr_6$ has been one of the most intensively studied Pb-free perovskite-type light absorbers for solar cells. Compared to the Pb-based counterparts $Cs_2AgBiBr_6$ exhibit currently lower power conversion efficiency (PCE) and external quantum efficiency (EQE), but its environment-friendliness and phase durability make it a viable alternative. It is known that the relative short carrier lifetime compared to the lead-based hybrid perovskites results in an insufficient PCE. (*ACS Energy Lett*. 2020, 5, 2200–2207) Main cause of this is found to be the high density of trap states, which bound the charge carriers or allow for non-radiative recombination. (*ACS Energy Lett*. 2020, 5, 3821–3827) In this work, by the variation of the precursor concentrations during the synthesis, the amount and type of the defects were controlled. This is realized by using two different synthesis routes, i.e., solution cooling method and microwave-assisted hydrothermal method. From the estimated Urbach energy by UV-Vis spectroscopy and peak broadening analysis in Raman spectroscopy, it is confirmed that the defect concentration is changed by a variation of the Ag/Bi precursor ratio. In addition, applying Ag-rich condition during the synthesis are found to be favorable for preventing the formation of $Cs_3Bi_2Br_9$. Our findings provide a guidance to decrease the trap densities and thus can be applied to the fabrication of $Cs_2AgBiBr_6$-based thin film solar cells.

Two synthesis approaches

Solution cooling method

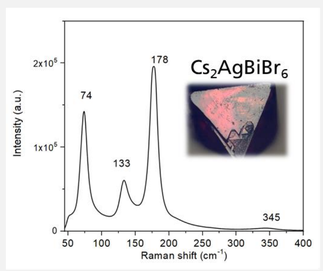


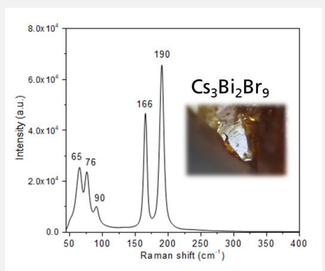
Microwave-assisted hydrothermal method



Raman spectroscopy

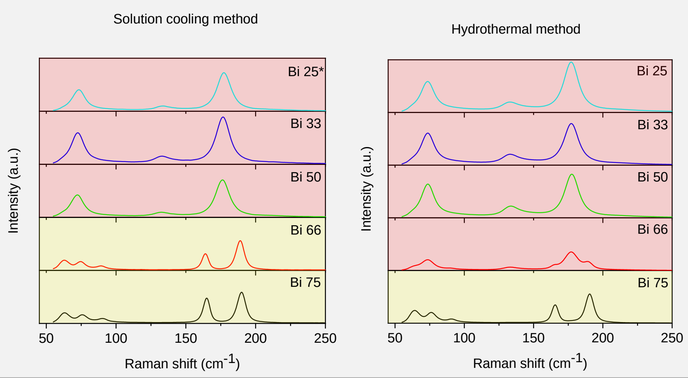
- Identification of $Cs_2AgBiBr_6$ and $Cs_3Bi_2Br_9$



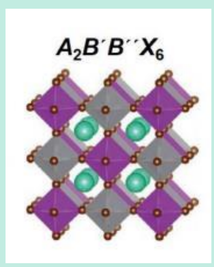


- $Cs_3Bi_2Br_9$ preferably formed under Bi-rich conditions
- $Cs_2AgBiBr_6$ preferably formed under Ag-rich conditions
- In hydrothermal method, $Cs_2AgBiBr_6$ forming range extended towards Bi-rich conditions

→ Ag-rich conditions further considered



Double perovskites



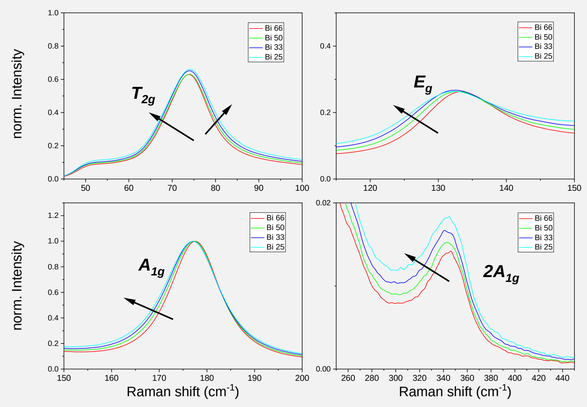
- Structure is similar to the simple perovskite structure with two different elements at *B*-site

Defects in $Cs_2AgBiBr_6$ and secondary phases

- The PCEs of the $Cs_2AgBiBr_6$-based PSCs are still low due to the defects
- The formation of deep defects needs to be prevented for efficient charge carrier transport
- Preferred Defects in $Cs_2AgBiBr_6$: V_{Ag}, V_{Br}, Ag_{Bi}
- Possible secondary phase: $Cs_3Bi_2Br_9$

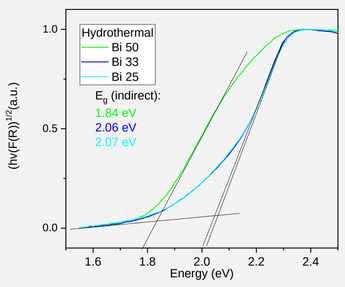
Goal: Controlling defects and preventing $Cs_3Bi_2Br_9$

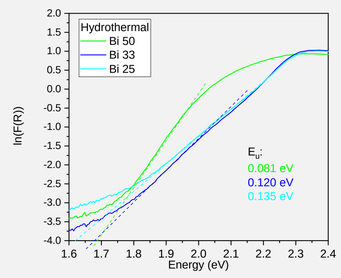
- All Raman bands show an increase of the band width at Ag-rich precursor conditions
- Peak broadening caused by defects



UV-VIS spectroscopy

- Absorption coefficient determined by Kubelka-Munk function
- Band gap estimation by Tauc-plot





- Urbach energy E_U was determined by slope of exponential part of the absorption edge
- It varies depending on crystal perfection and defect amount

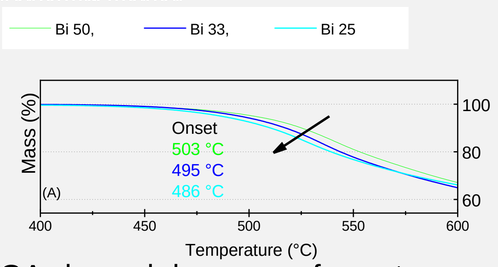
$$a(E) = a_0 \exp\left(\frac{E - E_c}{E_U}\right)$$

- Higher Urbach energy means more crystal imperfections
- Consistent wth the results of Raman spectroscopy

* Denotation: the number indicates the percentage of Bi in precursor solution. Bi 25 means 25% of Bi and 75% of Ag in precursor solution

Thermogravimetric analysis (TGA)

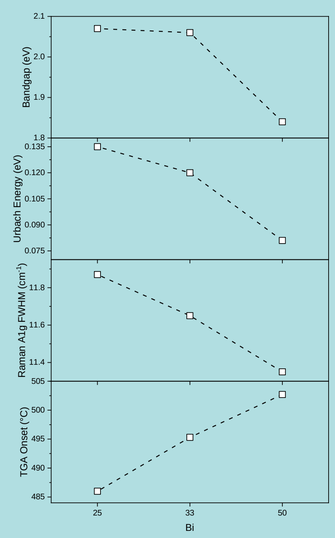
Hydrothermal method



- TGA showed decrease of onset temperature of thermal decomposition of $Cs_2AgBiBr_6$ on Bi-poor side
- Decrease of onset temperature indicated indirectly the degree of imperfection

Summary and Outlook

- Ag-rich synthesis conditions prevented formation of $Cs_3Bi_2Br_9$
- Ag-rich conditions lead also to increased defect concentration and apparently, the defect type is changed, which need further investigations together with the determination of the defect type



Acknowledgements
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