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EFFECTS OF CONTROLLED COOLING RATES ON $Cs_2AgBiBr_6$ SINGLE CRYSTAL GROWTH

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Introduction

As one of the most promising lead-free halide double perovskites, $Cs_2AgBiBr_6$ has received increasing attention, due to its high stability and nontoxicity. Nevertheless, it still suffers from a low power conversion efficiency (PCE) [1]. To further understand the nature of defects in $Cs_2AgBiBr_6$ and to improve the PCE, the effects of different cooling rates on the solution-based synthesis are investigated. $Cs_2AgBiBr_6$ single crystals were synthesized in various timeframes and analyzed by UV-Vis and Raman spectroscopy in order to determine the optical bandgaps and degree of defect formation.

Double Perovskite

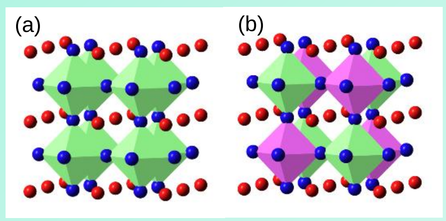


Fig. 1 (a) single perovskite and (b) double perovskite

The double perovskite composition of $A_2B'B''X_6$ has a similar structure as the ABX_3 perovskites [2]. But instead of one *B*-site atom, it consists of two different *B*-site elements that alternate in the lattice as it is shown in the figure above. These double perovskites have shown rich combinational variations with tuneable optical properties and thus studied with a great potential for various applications.

Crystal growth

For the synthesis of single crystals, it is essential to control the concentration and temperature. When the concentration of the precursor solution crosses the supersolubility curve, nucleation starts. This leads to further consumption of the precursor solution and thus decreases to the growth zone, In this zone the resulting nuclei keeps growing, without new nuclei being precipitated [3]. The key for successful single crystal growth is to stay in the growth zone. Above the super solubility curve, more nuclei are precipitated and under the solubility curve the crystals are dissolved.

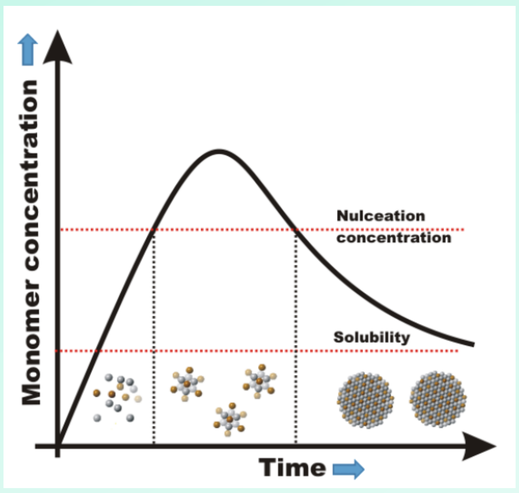
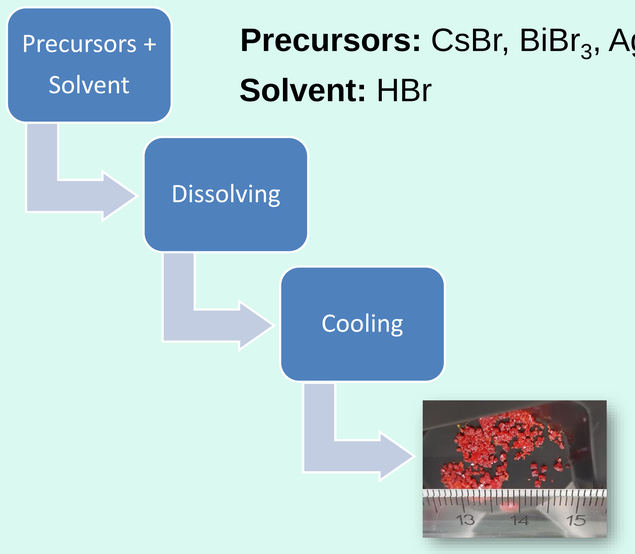


Fig. 2 LaMer diagram for nucleation [4]

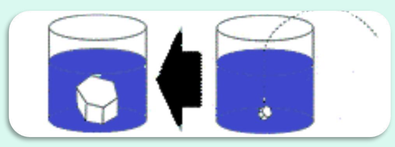
Synthesis



Precursors: CsBr, $BiBr_3$, AgBr
Solvent: HBr

Seeding method

- Seeding crystal synthesized beforehand in use
- Dissolve precursors
- placing the seeding crystal in solution
- Obtaining larger crystals

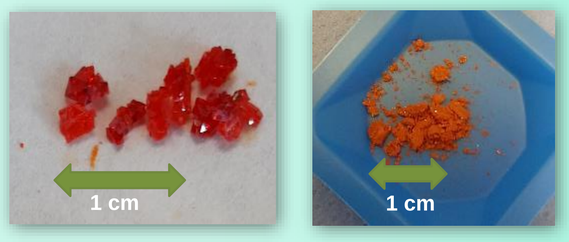


6 mm size via
slow cooling + seeding →

Cooling Rate

Slow Cooling
1°C/hr

Fast Cooling
30°C/min



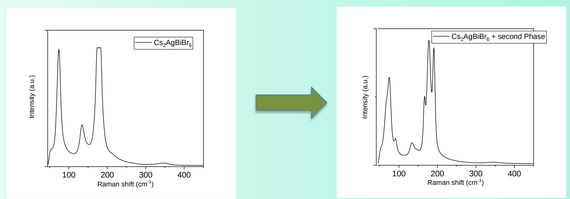
Resulting crystal size

- Slow cooling → larger crystals
- Fast cooling → smaller crystals

Additive

Sodium acetate is reported to enhance crystal growths [5]

- larger average size
- but formation of second phase is confirmed by Raman

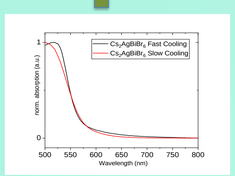


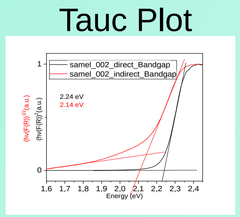
Analytics

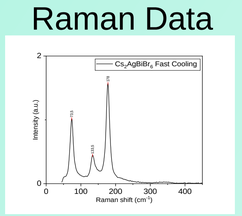
- UV/Vis spectroscopy to determine optical bandgap via Tauc plot
- Raman spectroscopy to confirm composition and get structural information's via FWHM

Absorbance | Tauc Plot | Raman Data

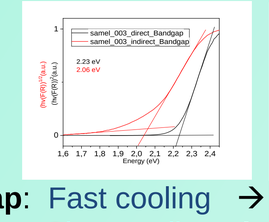
Fast cooling

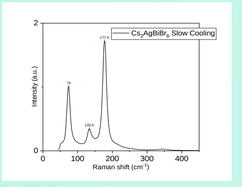






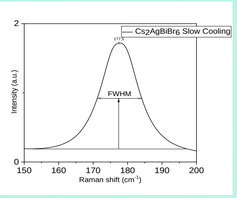
Slow cooling



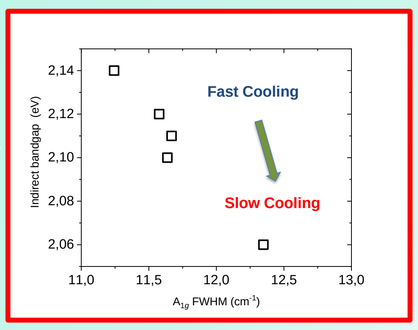


Indirect Bandgap: Fast cooling → 2.14 eV
Slow cooling → 2.06 eV

Comparison



- comparing FWHM of A_{1g} peak from Raman spectra with the estimated indirect bandgap from UV-Vis spectra.
- General trend observed depending on cooling rate
- The slower cooling rate results in a smaller bandgap and a more broadened Raman peak



Summary

By comparison of the peak broadening of Raman spectra and optical bandgap values from UV-Vis spectra:

- correlation between the indirect bandgap and defect formation with the controlled cooling rate applied during synthesis was confirmed
- **slow-cooling process resulted in more defects and disorder with a lower indirect optical bandgap**

References

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Acknowledgements

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