Lewiński Group
Organometallic and Materials Chemistry

Mechanosynthesis of new lead-free perovskites as potential absorbers for photovoltaics.

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Introducion

In a remarkably short period of time, metal-halide perovskites have gone from relative obscurity to an intensely studied class of materials. The efficiencies of solar cells constructed from lead-halide perovskites have risen from 3,8% in a dye-sensitized solar cell configuration to NREL certified 21,2% in planar heterojunction cells [1]. Despite its good opto-electrical properties, $MAPbI_3$ possesses two main drawbacks that hampers further commercialization: (a) moisture sensitivity and (b) high toxicity due to lead content. Therefore finding good perovskite absorbers composed of non-toxic metals is one of main topics in perovskite chemistry.

One of the most promising candidates for Pb^{2+} replacement is Bi^{3+}, because it is **environment friendly** and both ions got **isoelectronic structure**. There are known several materials among perovskite family containing bismuth ions eg.: $Cs_2AgBiCl_6$ [2] (double perovskite) or $MA_3Bi_2I_9$ [3] (so called „0D" perovskite). Most of those materials got relatively high bangap ~2 eV, so their applications are limited to tandem solar cells.

a) $2\,CsBr + AgBr + BiBr_3 \xrightarrow[Cryst.]{DMF} Cs_2AgBiBr_6$

b) $3\,MAI + 2\,BiI_3 \xrightarrow[Cryst.]{DMF} MA_3Bi_2I_9$

Fig. 1. *Literature synthesis of bismuth(III) perovskites a) Cs_2AgBiX_6, b) $MA_3Bi_2I_9$*

Bandgap and t-factor tuning by ion mixing
- $MAPbI_{3-a}X_a$ (X = Cl, Br)
- $MA_{1-a}FA_aPbI_3$
- $MAPb_{1-a}Cd_aI_3$

Higher stability
- MA substitution with inorganic ions (eg. Cs^+)
- Layered perovskites
- Perovskite encapsulation

Tuning of halide perovskite properties

Lead substitution
- $A_2PbM(II)I_6$
- $Cs_2Ag(I)Bi(III)Br_6$
- $A_2M(I)\,M(III)X_6$

„0D" materials
- $A_aM_bI_c$ (M=Pb, Sn, Bi,…)
- $A_3Bi_2I_9$
- Other

Fig. 2. *General strategies of tuning the perovskite structure.*

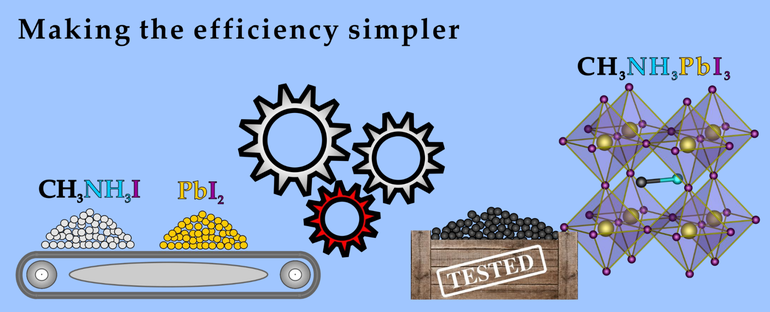

Fig. 3. *Idea of applying solvent free synthesis of perovskite by high-energy ball milling mechanochemistry [4]*

Experimental

Goal of work: *Design and preparation of bismuth perovskite, with bandgap shifted from ~2,0 eV (red colour) to ~1,5 eV (black colour), by mechanochemistry.*

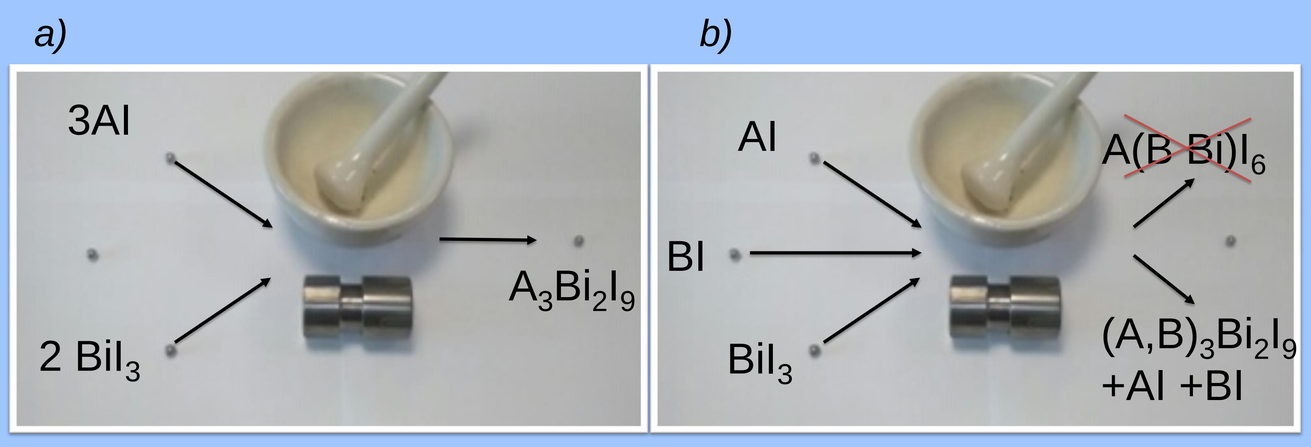

Fig. 4. *Synthetical procedure of perovskite synthesis (*A –big ion eg. Cs^+, $amines^+$, B – small ion eg. Li^+*) a) „0D perovskite", b) fail synthesis of double perovskite .*

Material type	E_g [eV]	Colour
$MA_3Bi_2I_9$	2,0	Red
$Cs_1MA_2Bi_2I_9$	1,95	Red
$Cs_{1,5}MA_{1,5}Bi_2I_9$	1,93	Red
$Cs_2MA_1Bi_2I_9$	1,90	Reddish-brown
$Cs_3Bi_2I_9$	1,85	Reddish-brown
$(PhNH_3)_2MA_2Bi_2I_{10}$	1,80	Brown
Several new compositions (not published)	2,1-1,8 1,7-1,0	Red to brown Black

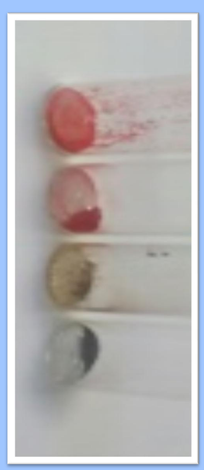

Fig. 6. *Bandgap and image of selected products determined by Reflectance UV-spectroskopy*

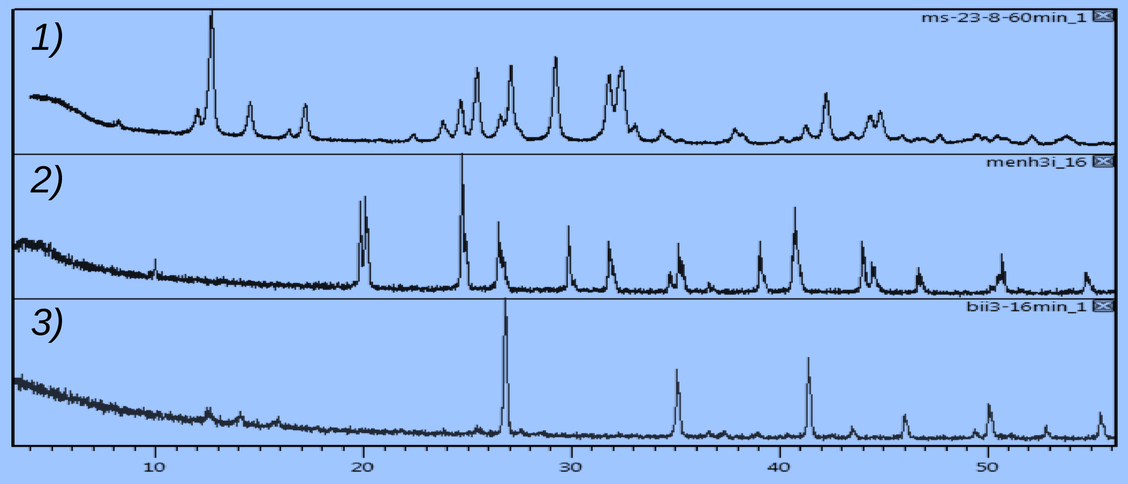

Fig. 5. *PXRD patterns of $MA_3Bi_2I_9$ (1) MAI (2), BI_3 (3)*

Literature

1. M. Grätzel et. al., Energy Environ. Sci., 2016, Advance Article,
2. Hemall I Karunadasa et al. J. Am. Chem. Soc., 2016, 138 (7), pp 2138–2141
3. S. Kaskel et al. Chem. Commun., 2016,52, 3058-3060
4. D. Prochowicz, (…), M. Grätzel and J. Lewiński et. al., J. Mater. Chem. A, 2015,3, 20772-20777

Conclusions

All materials were synthesized and charakterized by PXRD and UV spectroscopy. Some of them can be used for sollar cell preparation: (a) heterojunction architechture, (b) tandem architecture. Mechanochemistry can be applied to obtain several „0D perovskite" bismuth iodates with various compositions, but cannot be used for double perovskite synthesis.

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