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Structure and Properties of Organic-Inorganic Layered Perovskites based on MBr_4 (M=Pb,Cu)

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[Introduction]

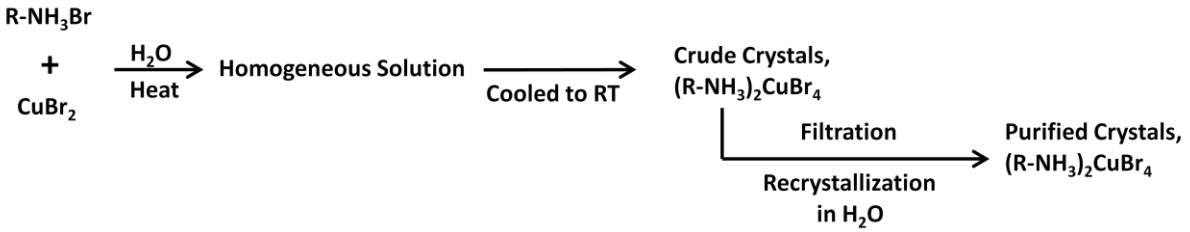
As can be seen in dielectrics and superconductors, the electronic structure of perovskite compounds, also known as a "storehouse of function" can be easily controlled by substitution of its constituent elements. Among these compounds, metal-halide perovskites are generally soluble in a variety of solvents. Therefore, they have the advantage for easy device fabrication. Our lab, has previously revealed that the spontaneous doping is the origin of high conductivity in exceptionally high conductive tin iodide organic and inorganic hybrid perovskite compounds, and also reported the rectification effect in mixed crystals with lead iodide due to the non-uniformity of chemical composition. Clarification of design guidelines for physical properties of these materials is important from the viewpoint of applications such as solar cells or field-effect transistors which are actively studied in recent years.

In this study, synthesis of organic-inorganic layered perovskites based on MBr_4 (M=Pb,Cu) were done. Single crystals of these hybrids were synthesized. The effects of changing the organic component in the synthesis of these hybrid materials were studied.

[Experimental]

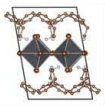
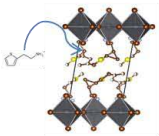
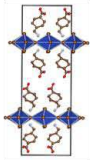
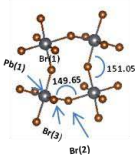
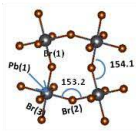
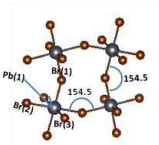
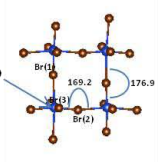
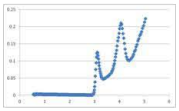
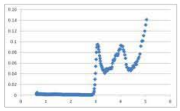
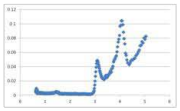
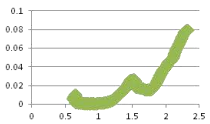
$(R\text{-}NH_3)_2PbBr_4$ Perovskite compounds can be easily synthesized by dissolving stoichiometric amounts of organic ammonium bromide and Lead(II) Bromide using a mixed solvent of DMF in Chloroform then slowly cooling of the heated solution. See schematic below:

$(R\text{-}NH_3)_2CuBr_4$ Perovskite compounds on the other hand, can be synthesized by simply dissolving stoichiometric amounts of organic ammonium bromide and Copper(II) Bromide and using H_2O as a solvent. Recrystallization using the same solvent allows for better crystal quality. See schematic below;



[Results and Discussion]

Crystal structure and Optical band gap of $(R\text{-}NH_3)_2MBr_4$ (M=Pb,Cu) Perovskites

*$(C_8H_{12}N)_2PbBr_4$	$(C_6H_{10}NS)_2PbBr_4$	$(C_8H_{16}NO_2)_2PbBr_4$	$(C_8H_{16}NO_2)_2CuBr_4$
Abbreviation $(PEA)_2PbBr_4$	Abbreviation $(THEA)_2PbBr_4$	Abbreviation $(PTA)_2PbBr_4$	Abbreviation $(PTA)_2CuBr_4$
Structure of $R\text{-}NH_3^+$ (PEA= Phenylethylammonium) 	Structure of $R\text{-}NH_3^+$ (THEA= Thiopheneethylammonium) 	Structure of $R\text{-}NH_3^+$ (PTA= Protonated tranexamic acid) 	Structure of $R\text{-}NH_3^+$ (PTA= Protonated tranexamic acid) 
Triclinic a = 11.549, b = 11.549, c = 17.346, α = 99.5677, β = 105.9780, γ = 90. 0590 	Monoclinic a = 8.25380, b = 8.2546, c = 15.97710, α = 81.9870, β = 83.0370, γ = 89.8630 	Triclinic a = 21.20400, b = 8.33190, c = 8.22420, α = 90.0000, β = 99.8862, γ =90.0000 	Monoclinic a = 10.91020, b = 41.84870, c = 11.53570 α = 90.000, β = 90.0243, γ = 90.000 
Inorganic layer Pb(1)—Br(1)→2.9784 Pb(1)—Br(2)→2.9827 Pb(1)—Br(3)→2.858 (Pb-Br-Pb) angle = 151.05 (Pb-Br-Pb) angle = 149.65 	Inorganic layer Pb(1)- Br(1)→3.002 Pb(1)- Br(2)→2.988 Pb(1)- Br(3)→3.003 (Pb-Br-Pb) angle = 154.13 (Pb-Br-Pb) angle = 153.27 	Inorganic layer Pb(1)- Br(2)→2.998 Pb(1)- Br(2)→3.003 Pb(1)- Br(3)→3.001 (Pb-Br-Pb) angle = 154.54 (Pb-Br-Pb) angle = 154.54 	Inorganic layer Cu(1)—Br(1)→3.333 Cu(1)—Br (2)→2.422 Cu(1)—Br (3)→2.423 (Cu-Br-Cu) angle = 176.9 (Cu-Br-Cu) angle = 169.2 
Optical Band Gap 	Optical Band Gap 	Optical Band Gap 	Optical Band Gap 

*was previously synthesized by Mitzi,1999

Organic - Inorganic layered Perovksites having the formula $(R\text{-}NH_3)_2PbBr_4$ show relative stability under ambient conditions. Analysis of crystal structure shows that regardless of organic cation used, these compounds show similar Lead-Bromide bond length as well as similar Lead-Bromide-Lead bond angle within the inorganic layer. Furthermore, these compounds show similar optical band gap value of about 3.0 eV.

Organic - inorganic layered perovskites based on $(R\text{-}NH_3)_2CuBr_4$, are also relatively stable under ambient conditions. Unlike $(R\text{-}NH_3)_2PbBr_4$ layered perovskites, analysis of the crystal structure of these compounds shows unequal Copper-Bromide bond length and Copper-Bromide-Copper bond angle within the inorganic layer which suggest the presence of Jahn-Teller distortion in these layered perovskites. Moreover, a relatively smaller gap was found in the optical spectra.

Due to the easy synthesis protocol, relative stability and possibility of being able to tune of the properties of these compounds, these organic-inorganic layered perovskites based on MBr_4 have the potential for easy device fabrication and manipulation.