

Quasi-2D lead-free halide perovskite materials

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Introduction:

Perovskites is a kind of mineral with a particular structure named after the Russian geologist Lev Perovski The first mineral found with this structure was calcium titanium oxide which was named as perovskite. Later this word is used as a joint name for all the materials with the same ABX₃ structure, including metal-halide (in which A, B are cations and X is a halogen anion) and oxide perovskites (in which X is replaced by the oxide anion O), and other derivative structures including layered and thin film. The great potentials of Perovskites in the fields of such as solar cells, light-emitting diodes and lasers have been discovered and explored in the last decade. The development of perovskites for LED devices manufacture did not drawn too much attention in the early stages but has received renaissance in recent years due to major promotion of light-emitting efficiency and stability [1]. The main goal of this Summer Research Project is to find a rather stable lead-free light-emitting perovskite which does not cause contamination problem in regard with the consideration of future commercialization. The motivation behind this goal is that one of the most primary pollution sources would be the lead left in the lead-based devices after their lifetimes. Therefore, the first direction settled would be that the device should be lead-free in terms of the materials chosen. The second consideration would be the stability of the intended perovskites. Three-dimensional hybrid perovskites have one major drawback is that they have relatively low stability when exposed to the ambient moisture [2]. The enhancement towards the stability of light-emitting devices could be achieved by using layered (or 2D) structure perovskites instead of 3D ones [3]. Layered perovskites are obtained by separating specific crystalline planes inside 3D perovskites structure using organic separator. For 2D perovskite layers, more energy for excitons binding is provided so that it is harder for excitons to become free charge carriers when exposed to ambient atmosphere hence more stable. Also, with greater portion of more bounded excitons, layered structured perovskites improve luminance quantum yields compared to 3D structured ones because excitons are more prompted compared to free charge carriers, indicating better light-emission efficiency, especially when the charge carrier concentration is low[4]. Therefore, the perovskites synthesized for this project should be organic-inorganic layered structured. In terms of the synthesis process and technique chosen, it had been decided to be solid-state reaction with no solvent used in regard with two major reasons. Firstly, for solid-state reaction, the error allowed for the mass of the materials is less restricted than solution synthesis because solution synthesis requires much more restricted precision for crystal to grow, therefore, it would be appropriate to choose the previous one for a time restricted project. Secondly, the solvent used for solution synthesis also cause contamination problem and other potential risks as it is one of the primary contributors from materials to environmental impact [5]. For perovskites synthesis, dimethylformamide is a common solvent and it is considered to be highly cancerogenic by IARC. It is also explosive once mixed with air. Finally, two types of layered structure were decided for the experiment, being A₂BB'X₆ (in which A is a +1 cation, B is a +1 metal cation, B' is a +3 metal cation and X is a halogen anion) and A₂BX₄ (in which A is a +1 cation, B is a +2 metal cation and X is a halogen anion). In order to shrink the range of the materials selected, the components that have been reported to have positive outcome in light-emitting perovskites were primarily been taken into consideration. For A₂BX₄, tin was decided to be the metal cation element, and for A₂BB'X₆, indium, antimony and bismuth cations were used [6].

Materials:

Methylammonium bromide (MABr), Xi'an; Cesium Bromide (CsBr), Alfa Aesar; Sodium Bromide (NaBr); Silver bromide (AgBr), Alfa Aesar; Potassium bromide (KBr), Sigma-Aldrich; Copper(I) chloride (CuCl), Aldrich; Methylammonium iodide (MAI), Dyesol; Bismuth(III) bromide (BiBr₃), Alfa Aesar; Antimony(III) bromide (SbBr₃), Alfa Aesar; Indium(III) chloride (InCl₃), Aldrich; n-Butylammonium bromide (n-BABr); Dyesol; n-Octylammonium bromide (n-OABr), Greatcellsolar; Benzylammonium bromide, Dyesol; Phenethylammonium bromide (PEABr), Dyesol; Propylphenylammonium bromide (PPABr), Xi'an; 1,6-Hexanediammonium bromide (HDABr₂), Xi'an; 1,8-Octyldiammonium bromide (ODABr₂), Xi'an, Tin(II) bromide (SnBr₂), Alfa Aesar

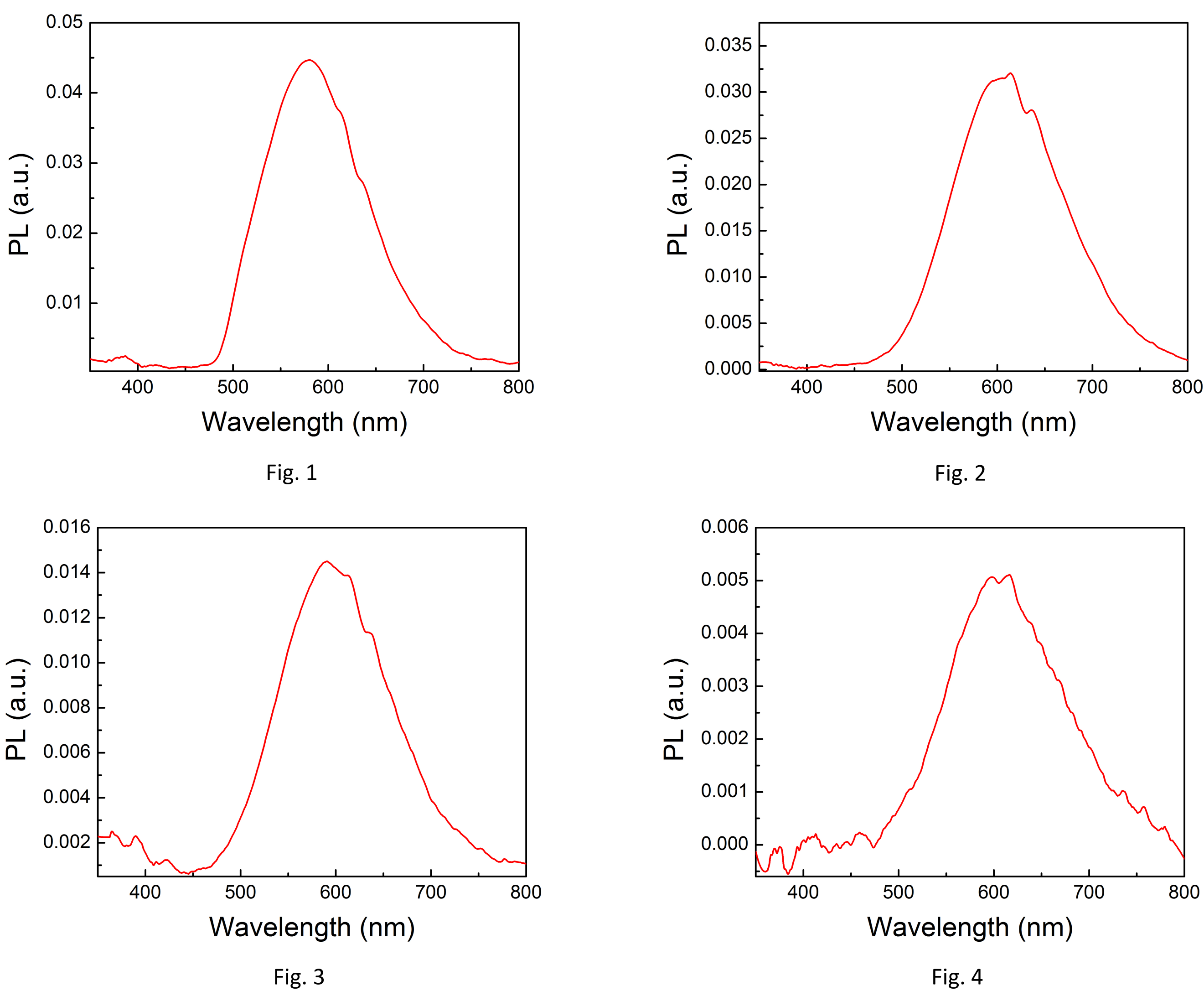
Methods:

The procedure of making samples was the same for both A₂BB'X₆ and A₂BX₄ structures. Samples were made by using solid-state reaction. The powder of chemicals was weighted according to the molar mass ratios in the intended compounds, using electronic balances with precision of 0.1 mg, and were mixed together sealed in plastic containers using parafilm after adding two smaller mixing balls and a larger one. For sodium bromide, bismuth bromide, silver bromide and methylammonium bromide powder, they are rather stable in normal room condition, therefore the weighting of these chemicals was done under room condition. For the rest of the chemicals, weighting and sealing were done in a glove box with argon environment. The sealed samples then were fixed on a vibrant device to let the chemicals inside mixed thoroughly with the aid of mixing balls. The time of mixing process was 30 minutes for each sealed sample. The mixed samples then were luminated under ultraviolet light to test whether it could emit visible light. Finally, the mixed samples were fixed on PL test set-up to run PL test for the numerical data.

Results and Discussion:

For this project, 21 samples were synthesized and tested in total. 14 samples of structure A₂BB'X₆ and 7 samples of structure A₂BX₄ were made. For the previous group, none of the samples of the first structure passed the UV light test and PL test. Among the 14 samples, only the one with intended compound Cs₂NaBiBr₆ showed apparent change in color so that it could be confirmed that the compound was synthesized successfully, as three of the chemicals used were white powder while the mixed sample appeared to be pure yellow. Whatsoever, there are reports of successful synthesis of compound mentioned above for their nanocrystal solution. For example, Cs₂NaSbBr₆ has been reported to be synthesized successfully and had a weak and broad PL emission [7]. The possible failure reason could be attributed to the solid-state reaction procedure used. The formation energy provided during mixing may not be sufficient for the chemicals to form perovskite nanocrystal structure. For the latter group, four of the samples passed the UV light test and PL test which were BA₂SnBr₄ (Fig. 1), OA₂SnBr₄ (Fig. 2), PPA₂SnBr₄ (Fig. 3) and ODA₂SnBr₄ (Fig. 4). All of the four samples showed visible yellow light for PL emission with broad peak wavelength ranges. However, the brightness of the light emitted by sample of ODA₂SnBr₄ decayed drastically after two weeks while other samples still retained similar level of brightness after two weeks, therefore, to be considered as relatively stable. The broad yellow light observed for the above samples may not be useful directly, yet it has great potential to be an essential component for better white light-emitting LED diodes [8].

Appendix:



Citations:

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