Experimental report

27/08/2021

Proposal:	**5-21-1133**	**Council:**	10/2019
Title:	Enhancing near-infrared solar cellresponse using up-conversion materials over bare CsPbBr3		
Research area:	Materials		

This proposal is a new proposal

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Samples: Cs1-xPb1-x(Yb,Tb)xBr3

Instrument	Requested days	Allocated days	From	To
D2B	2	0		
D20	0	2	14/09/2020	16/09/2020

Abstract:

All-inorganic halide perovskites have emerged as promising materials in the application of optoelectronic devices. Cubic CsPbI3 has the narrowest band gap of 1.73 eV among all-inorganic lead halide perovskites, but it is only stable at high temperatures. A stable alternative is the orthorhombic CsPbBr3 perovskite, which unfortunately has a higher bandgap (2.3 eV). A strategy to achieve a lower band gap is the design of up-conversion bromide perovskites using lanthanides as dopants. We have succeeded in the preparation, by mechano-synthesis, of several members of the family of perovskites Cs1-xPb1-x(Yb,Tb)xBr3. Yb3+ has been selected as the sensitizer ion and Tb3+ as the activator ion. We aim to investigate the crystal structure features at RT, including the evolution of the tilting of the octahedra with rare-earth doping, and the accommodation of Cs vacancies and the structural evolution above room temperature, taking into account that the parent CsPbBr3 perovskite undergoes a phase transition from orthorhombic to tetragonal at 88ºC and then to cubic at 130ºC.

Over the last 5 years, hybrid perovskites (based on halides with organic and inorganic cations) have experienced a great development, reaching efficiencies close to conventional silicon solar cells. In comparison to hybrid perovskites, some totally-inorganic perovskite derivatives, like cubic $CsPbI_3$, present a greater capacity to modulate their composition, are less sensitive to ambient oxygen and water, yet having a high fluorescence quantum yield. All-inorganic halide perovskites have thus emerged as promising materials in the application of optoelectronic devices. The mentioned cubic $CsPbI_3$ has the narrowest band gap of 1.73 eV among all-inorganic lead halide perovskites, exhibiting the greatest potential in solar cell applications. However, the stabilization of the cubic α-$CsPbI_3$ phase at room temperature is challenging and remains unfulfilled because the synthesis reaction usually involves a phase change process, resulting in an undesired orthorhombic (δ) phase (non-perovskite) with a wider bandgap of 2.82 eV [1].

Recently, a stable totally inorganic orthorhombic $CsPbBr_3$ perovskite has been successfully prepared by our group, using the mechano-chemical synthesis method (working under N_2 inert atmosphere during the solid-state reaction of the precursors) [2]. This perovskite shows a high and constant photoresponse, being also more stable than $CsPbI_3$ to ambient atmosphere and humidity. However, $CsPbBr_3$ presents a higher bandgap (2.3 eV), that would hinder its application in solar cells devices [3]. Therefore, we were interested in the development of stable derivatives of $CsPbBr_3$ with a lower band gap that would promote their application in solar cell devices.

A strategy to achieve this goal is the design of up-conversion bromide perovskites using lanthanides as dopants [4]. Up-conversion is a process in which the sequential absorption of two or more photons leads to the emission of light at shorter wavelength than the excitation wavelength. Therefore, if upconversion is achieved using CsPbBr3 as the starting base material, it would be possible to increase the solar cell efficiency by harvesting a greater proportion of the solar spectrum. In order to reach this goal, certain pairs of lanthanides must be used as dopants.

In this work, we have succeeded in the preparation of several members of the family of perovskites $Cs_{1-x}Pb_{1-x}(Yb,Tb)_xBr_3$; in particular:

$Cs_{0.9}Pb_{0.9}Yb_{0.08}Tb_{0.02}Br_3$
$Cs_{0.85}Pb_{0.85}Yb_{0.12}Tb_{0.03}Br_3$
$Cs_{0.85}Pb_{0.85}\ Yb_{0.10}Tb_{0.05}Br_3$
$Cs_{0.8}Pb_{0.8}Yb_{0.16}Tb_{0.04}Br_3$

The preparation was carried out by mechano-synthesis, starting from bromides of the different metals involved. The samples were measured in the present experiment at D20 diffractometer with λ= 1.54 Å and a take-off angle of 90º, in order to enjoy a sufficient resolution in the mid-angle region. A criofurnace was available. At first, the samples were collected at room temperature in 6mm cylindrical vanadium sample holders, acquiring good quality diffraction patterns thanks to the high flux and resolution of the mentioned diffractometer, even for amounts of sample of less than one gram. The following strategy was then followed:

- After the RT acquisition, a ramp was defined from 300 K to 430 K in steps of 0.167 K every 60 s, in order to detect the orthorhombic to tetragonal and then to cubic transition the pristine $CsPbBr_3$ sample is well known to experience. The background was observed to decrease as temperature was increased. That accounted for 13 h of data acquisition for each of three samples.

- After this sequence, an extra measurement at 300K was taken, not corresponding with what was measured in the first place. The second measured (300Kb) was cooled down from 430K in a few minutes, perhaps retaining the HT structure. This still needs to be analyzed.

At RT, all of the patterns can be perfectly fitted in the structural model of the orthorhombic perovskite $CsPbBr_3$, defined in the Pbnm space group, see Figures 1 and 2. As displayed in Table 1, the unit-cell parameters of the doped samples are comparable to those of the parent compound, with a slight volume expansion probably due to the presence of Cs vacancies, necessary to preserve the electroneutrality. There is a correlation between the relative proportions of $CsPbBr_3$ and the doping of lanthanides with the unit-cell size,

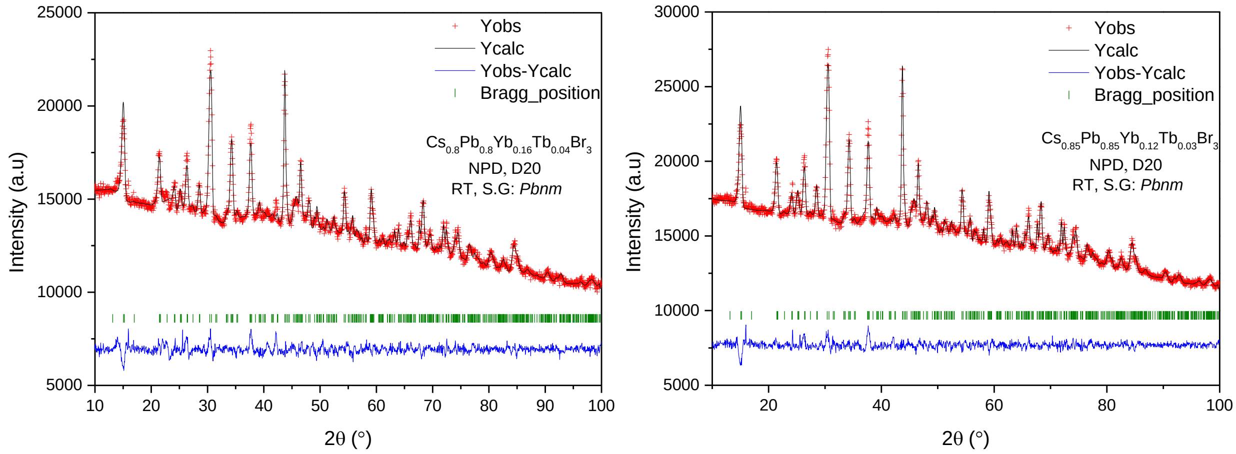

Figure 1. Observed (crosses) calculated (black line) and difference (blue line profiles after the Rietveld refinement from NPD data at RT for two different relative proportions between $CsPbBr_3$ and lanthanides (a) 20% $Cs_{0.8}Pb_{0.8}Yb_{0.16}Tb_{0.04}Br_3$ (b) 10% $Cs_{0.85}Pb_{0.85}Yb_{0.12}Tb_{0.03}Br_3$.

It is remarkable the effect of doping on the unit cell, being bigger as the proportion of the lanthanides increases. The effect of doping not only affects the crystal features, it also affects the bandgap of the sample; the effective bandgap is reduced as the rare earth doping increases, as desired.

	$CsPbBr_3$	***$Yb_{0.16}Tb_{0.04}$ (20%)***	***$Yb_{0.12}Tb_{0.03}$ (15%)***
a (Å)	8.19154(2)	8.2043(10)	8.2035(7)
b (Å)	8.24459(2)	8.2517(9)	8.2515(6)
c (Å)	11.73993(2)	11.7492(11)	11.7497(8)
V (Å^3)	792.87(1)	795.42(14)	795.35(11)

Table 1: Unit cell parameters and volumes of the parent and two doped compounds, all of them defined in the orthorhombic *Pbnm* symmetry.

Figure 2 displays the orthorhombic crystal structure of one of the doped samples, $Cs_{0.9}Pb_{0.9}Yb_{0.8}Tb_{0.02}Br_3$, characterized by the tilting of the $PbBr_6$ octahedra according to the $a^-a^-b^+$ Glazer's notation, characteristic of *Pbnm* perovskites. In this case, the Cs atoms are located in the 4*c* (*x*,*y*,¼) sites. The Pb atoms are located in the 4*b* (1/2,0,0) and are partially replaced Yb and Tb ions (up-conversors). The two types of bromine, Br1 and Br2, are located at 4*c* (*x*,*y*,¼) and 8*d* (*x*,*y*,*z*) sites, respectively.

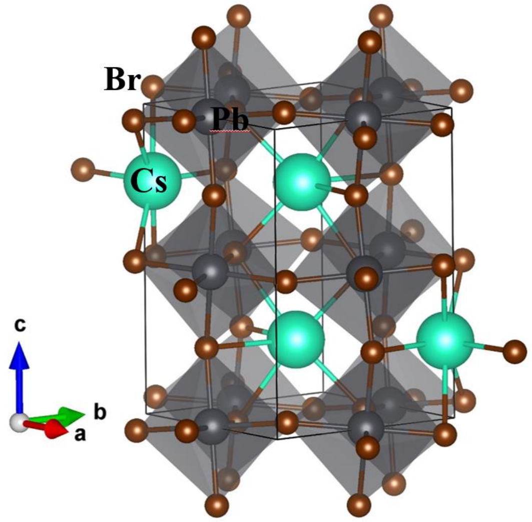

Figure 2. View of the orthorhombic structure of $Cs_{0.9}Pb_{0.9}Yb_{0.8}Tb_{0.02}Br_3$ at RT; Cs is deficient, whereas Pb is partially replaced by Yb and Tb

1. Z. Chen, L. Dong, H. Tang, Y. Yu, L. Ye and Jianfeng Zang, Cryst. Eng. Comm. (2019)

2. Saha, S.; Banik, A.; Sarkar, A; Biswas, K.; Pal, P., Chem. : A Eur. J. , 2018, Vol.24(8), p.1811-1815

3. Master Thesis of Bo-kyung Hong (September 2018) supervised by J.A. Alonso and M.C. Alvarez

4. Wu, Hao; Qiu, Jianbei; Wang, Jing; Wang, Qi; Ma, Jiao, et al / J. Mater Chem. C 7 (2019) 3751