Synthesis and characterization of a hybrid perovskite to be applied as an absorbent layer in solar cell

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Abstract. This study is based on the synthesis and characterization of a hybrid perovskite based on tin chloride and methylammonium (CH₃NH₃SnCl₃) as an absorbent layer in solar cells. Preparation of the hybrid material was carried out using the wet method from a precursor of methylammonium chloride CH₃NH₃Cl and tin chloride (II) (SnCl₂). The solid obtained was heated to a temperature of 60°C in order to obtain the final product. The hybrid material was then characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The structural and morphological results showed the characteristic traits corresponding to the material. The formation of conglomerates with irregular spherical geometry and cubic forms associated with the precursor of tin chloride were also present. The application of this type of perovskite in solar cells is preferable due to its environmentally friendly impact, making it a promising material for photovoltaic technology.

1. Introduction

Research developed in the field of renewable energy has focused on the use and application of alternative sources of energy to remedy environmental issues arising from the excessive use of fossil fuels [1]. Alternative energy sources such as solar, wind, geothermal, and biomass among others, are considered as an alternative source of energy for the planet. Solar energy is widely considered to be the main source of clean energy due to its abundance [1]. Photovoltaic cells have allowed the conversion of sunlight to electricity [2]. Important advances have been made to photovoltaic cells in terms of lowering production costs and improving efficiency [3,4].

Photovoltaic cells are classified into four main groups: first generation (crystalline silicon), second generation (amorphous silicon, copper indium, gallium selenide, etc.), third generation (GaAs, GaInAs, etc.), and fourth generation (CZTS, perovskites) [1]. Silicon continues to dominate the photovoltaic cell market with energy efficiencies of up to 25% [5] and an expected product life of 20 years or more. Research has focused on the search for alternative materials with which to produce a new generation of solar panels that reduce manufacturing costs and improve efficiency. The use of organometallic perovskites has shown promise due to their efficiency and growth in recent years [6-9].

The organometallic perovskites are described by the general chemical formula ABX₃ [2-10], where the cation A is a small organic cation such as methylammonium (MA or CH₃NH₃⁺), formamidinium (FA or C₂H₇NH₃⁺), or caesium (Cs) to create hybrid organic-inorganic materials. The cation B uses divalent metal ions such as Pb²⁺, Sn²⁺, Ge²⁺, or Cu²⁺, and X can be X= Cl⁻, Br⁻, I⁻ [11-13], or BF₄⁻, PF₆⁻, or SCN⁻ [14,15].
This study attempts to synthesize and characterize a hybrid material of type CH$_3$NH$_3$SnCl$_3$, following a simple wet synthesis [16], in order to replace lead with a less toxic element such as Sn$^{2+}$ [17,18]. Based on this reduced toxicity and high efficiency there is the potential for its ability to be used in photovoltaic technologies. These advances along with the conditions of solar irradiation that Colombia has as well as their ability to be used in rural locations make it an ideal material for the economic, technological, and scientific advancement of the country.

2. Experimental

2.1. Preparation of CH$_3$NH$_3$Cl
CH$_3$NH$_3$Cl was synthesized by mixing 30 mL of methylamine (40% in methanol) and 32.3 mL of hydrochloric acid (57% by weight in water) in a 250 mL round bottom flask at 0°C for 2 hours with constant stirring. The precipitate was recovered by placing the solution in a rotary evaporator and carefully removing the solvents at 50°C. The methylammonium chloride CH$_3$NH$_3$Cl of the crude yellowish product was washed with diethyl ether by stirring the solution for 30 minutes. This step was repeated three times and the mixture was recrystallized in a mixed solvent of diethyl ether and ethanol [19].

2.2. Preparation of CH$_3$NH$_3$SnCl$_3$
0.395g of CH$_3$NH$_3$Cl and 1157 g of SnCl$_2$ were mixed at 60°C overnight with constant stirring. Afterwards, the small beaker was sealed and kept dark at room temperature using aluminum foil to cover the beaker to avoid a reaction with sunlight [20].

2.3. Characterization
The synthesized plates were characterized by X-ray diffraction (XRD), using a PANalytical X’pert PRO-MPD diffractometer, equipped with an Ultra fast X’Celerator detector in Bragg-Brentano arrangement, and using the CuK$_\alpha$ = ($\lambda$ = 1.54186 Å) radiation, between 5° and 90° with steps of 0.02°. Raman spectroscopy was performed using a Raman spectrometer, DXR smart Raman, which allowed the measurement of Raman transitions in the range of 50 cm$^{-1}$ to 3370 cm$^{-1}$, with a cooled CCD detector (-51°C) and a diode laser (785 nm). Analysis using scanning electron microscopy (SEM) to measure the morphology and thickness of the layer on the plates was obtained using a Carl Zeiss EVO-MA10 scanning electron microscope equipped with energy-dispersive X-ray spectrometry (EDS).

3. Results and discussion
The X-ray diffraction pattern for the CH$_3$NH$_3$SnCl$_3$, was analyzed by the X’Pert ® High Score software, demonstrating a crystalline phase oriented preferentially along the (1 1 0) facet, as illustrated in Figure 1. Using this intense signal, the determination of the crystalline size was made by means of the Debye-Scherrer equation, where the value of the average width of an observed peak ($\beta$) and a constant of 0.9 was used as a reference. The results indicated a crystal size of 34 nm, indicating the presence of nanoparticles.
The result obtained by XRD was compared with the diffraction pattern of \( \text{CH}_3\text{NH}_3\text{SnCl}_3 \) in a triclinic phase reported by Thuat et al., demonstrating that temperature is very influential on the formation of the material. At temperatures close to 487K, structures with cubic packing systems and lattice parameters \( a = 5.760 \text{ Å} \) were created, generating a greater consolidation of phases associated with \( \text{CH}_3\text{NH}_3\text{SnCl}_3 \) [21-24]. It is evident that the diffraction angles of the signals associated with \( \text{CH}_3\text{NH}_3\text{SnCl}_3 \) are transferred at slightly higher angles compared to the diffraction pattern reported by Thuat et al. This behavior may be attributed to the fact that there was no consolidation of material and the XRD results are more related to the precursors \( \text{SnCl}_22\text{H}_2\text{O} \) and \( \text{CH}_3\text{NH}_3\text{Cl} \) of the hybrid perovskite or the formation of tin oxides [25] produced by the contact of the material with the environment.

The Raman analysis is shown in Figure 2. The results show that the final perovskite product was formed, but with impurities. This is evidenced by the presence of other signals in the spectrum; primarily the bands that are between 300 cm\(^{-1}\) and 320 cm\(^{-1}\) which are assigned to Sn-O and Sn-O terminal vibrations [25,26]. This indicates that tin halide perovskites are very stable against oxidation. We can also observe a Sn-Cl rocking motion at around 100 \( \pm 0.7 \text{ cm}^{-1} \) [25,27] and a Sn-Cl bending motion at around 179.2 \( \pm 0.2 \text{ cm}^{-1} \) [28,29].

The obtained material was analyzed using scanning electron microscopy in order to study the morphological aspects and surface characteristics of \( \text{CH}_3\text{NH}_3\text{SnCl}_3 \). The results shown in Figure 3 ((a), (b) and (c)) show that the solids are made up of multi particle aggregates of irregular spherical geometry.
and some cube shaped aggregates. In contrast to the instability of the tin iodide perovskite, the Sn-Cl crystals (CH$_3$NH$_3$SnCl$_3$) mixed with tin were very stable after being synthesized from a dehydrated precursor of tin chloride (II) and methylammonium halide (CH$_3$NH$_3$SnCl$_3$) in an aqueous HCl solution.

Figure 3. SEM Micrographs of the material CH$_3$NH$_3$SnCl$_3$ ((a), (b) and (c)) and EDX Spectrum %Sn-Cl (d).

Additionally, elemental composition analyzes were performed using energy dispersive X-ray spectroscopy through an EDXA microprobe coupled to a scanning electron microscope. The results shown in Figure 3 (d) show that the composition of the organometallic perovskite is free of impurities.

4. Conclusions
This article showed an alternative method to synthesize an organometallic perovskite of type CH$_3$NH$_3$SnCl$_3$. The results showed that a pure product of the hybrid material was not formed. In order to achieve a completely pure product, some parameters, such as temperature, must be kept at temperatures above 60°C. The morphological results showed the presence of the material with irregular multiparticle morphology and the precursor of SnCl$_2$ with a geometry similar to a cube.

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