

Structural study and electronic band structure investigations of the solid solution $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ and its impact on the $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{In}_2\text{S}_3$ interface of solar cells

A. Lafond^{a,*}, C. Guillot-Deudon^a, S. Harel^b, A. Mokrani^a, N. Barreau^b, S. Gall^b, J. Kessler^b

^a Institut des Matériaux Jean Rouxel, UMR 6502 CNRS-Université de Nantes, 2, rue de la Houssinière, BP 32229, 44322 Nantes cedex 03, France

^b Laboratoire des Matériaux Photovoltaïques, Université de Nantes, 2, rue de la Houssinière, BP 92208, 44322 Nantes cedex 03, France

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Abstract

The present work reports investigations on the new In_2S_3 containing Cu and/or Na compounds, which are expected to be formed at the $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{In}_2\text{S}_3$ interface. The knowledge of these materials properties is very important in order to better understand the operation of the devices based on these junction partners.

It has been observed that a solid solution $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ exists from CuIn_5S_8 ($x=0$) to NaIn_5S_8 ($x=1$) with a spinel-like structure. The single crystal structure determination shows that indium, copper and sodium atoms are statistically distributed on the tetrahedral sites.

XPS investigations on the CuIn_5S_8 , $\text{Na}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ and NaIn_5S_8 compounds combined with the band gap changes reported in a previous work show that these variations are mainly due to valence band maximum shift; it is moved downward when x increases from 0 to 1. These observations are confirmed by the electron structure calculations based on the density functional theory, which additionally demonstrate that the pure sodium compound has direct gap whereas the copper-containing compounds have indirect gaps.

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1. Introduction

Solar cells based on $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGSe) are on the edge of large-scale production. Therefore, questions such as the use of non-toxic materials have gained importance. One of the means to achieve this goal is to replace cadmium sulfide (CdS) by indium sulfide (In_2S_3) as the buffer layer. When indium sulfide is deposited on CIGSe copper as well as sodium atoms diffuse from the CIGSe layer towards the In_2S_3 buffer layer and new compounds with general formula MIn_5S_8 ($\text{M}=\text{Cu,Na}$) are expected to be formed [1]. Because the actual composition of this buffer layer strongly influences the solar cell performance it is of great importance to study the properties of these compounds as bulk materials. The present study deals with the crystal structure characterization and electronic band structure investigations through XPS measurements and *ab-initio*

calculations. The impact of the properties of the MIn_5S_8 compounds on the CIGSe/ In_2S_3 thin film solar cells is also discussed.

2. Investigation methods

The experimental details for the preparation of the compounds $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ ($x=0, 0.25, 0.5, 0.75$) were given in a previous paper [1]. All the samples were manipulated in a dry box.

2.1. XPS measurements

The XPS measurements were carried out in a Kratos Axis Ultra Spectrometer using monochromatized $\text{Al K}\alpha$ radiation (1486.6 eV). The surface analysis chamber pressure was typically on the order of 10^{-8} Pa. The spectrometer was calibrated using sputter-cleaned Au and Cu thin films which have binding energy (BE) of 84 eV and 932.5 eV for $\text{Au 4f}_{7/2}$ and $\text{Cu 2p}_{3/2}$ respectively. The hemispherical analyser has been used in

* Corresponding author.

E-mail address: Alain.Lafond@cnrs-imn.fr (A. Lafond).

URL: <http://www.cnrs-imn.fr/>.

Table 1

Atomic coordinates and equivalent isotropic displacement parameters for $\text{Cu}_{0.644}\text{Na}_{0.356}\text{In}_5\text{S}_8$ (space group: $F-43m$, #216, $a=10.744(2)$ Å, agreement factors: $R=1.76$, $R_w=3.30$ for 319 reflections and 15 independent parameters)

Atom	Site	Coordination	s.o.f.	x	y	z	U_{eq}
In1	4a	Td1	0.5	0	0	0	0.0175(3)
Na1	4a	Td1	0.205(13)	0	0	0	0.0175(3)
Cu1	4a	Td1	0.295(13)	0	0	0	0.0175(3)
In2	4c	Td2	0.5	0.25	0.25	0.25	0.0107(2)
Na2	4c	Td2	0.151(13)	0.25	0.25	0.25	0.0107(2)
Cu2	4c	Td2	0.349(13)	0.25	0.25	0.25	0.0107(2)
In3	16e	Oh	1	0.62698(6)	0.12698(6)	0.12698(6)	0.01877(10)
S1	16e		1	0.86882(14)	0.36882(14)	0.36882(14)	0.0137(2)
S2	16e		1	0.38252(12)	0.38252(12)	0.38252(12)	0.0125(2)

constant analyser energy (CAE) mode for all of the spectra. The pass energy was 20 eV for narrow-scan and valence band spectra. The Ag $3d_{5/2}$ FWHM is 0.47 eV giving an instrumental resolution about 0.1 eV.

As the samples were synthesized via high temperature solid-state reactions, in-situ XPS experiments were not possible.

The samples were mounted on double-sided carbon tape on top of a copper plate, which allows a good electrical contact with the spectrometer. The $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ powders were rapidly transferred to the XPS spectrometer. According to C 1s peak position, no charge effect occurs and charge neutralizer system was not used during spectra recording.

2.2. Electronic band structure calculations

The electronic band structures of bulk MIn_5S_8 ($\text{M}=\text{Cu},\text{Na}$) ordered compounds were calculated within *ab-initio* density functional theory. We used the scalar-relativistic tight-binding linear muffin-tin orbital method with the atomic spheres approximation [2]. The von Barth–Hedin local exchange correlation potential and the Langreth–Mehl–Hu non-local correction were performed [3]. The eigen-values and eigen-vectors were determined using the tetrahedron technique with an increasing number of k points in the irreducible Brillouin Zone until final convergence was obtained ($14 \times 14 \times 14$ k points are used).

3. Results and discussion

3.1. Structural study of the solid solution

The indium sulfide (In_2S_3) adopts the spinel-like structure in which 1/3 of the tetrahedral sites are empty. When the cationic vacancies are disordered the structure is cubic ($\alpha\text{-In}_2\text{S}_3$) with a lattice parameter of $a=10.774$ Å [4,5]. The formation of copper and/or sodium containing indium sulfide corresponds to the insertion/substitution process: $[\text{In}^{3+}]_{\text{Td}} + 2 \times [\text{vacancies}]_{\text{Td}} \rightarrow 3 \times [\text{M}^+]_{\text{Td}}$. The compounds studied here correspond to the composition $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$ in which all the tetrahedral sites of the spinel structure are filled.

The detailed study of the XRPD results has shown that there is a complete solid solution from CuIn_5S_8 ($x=0$) to NaIn_5S_8 ($x=1$) [1]. The linear increase of the cubic unit-cell parameter versus the Na-content is consistent with the relative values of the radii of In^{3+} (0.76 Å), Cu^+ (0.74 Å) and Na^+ (1.13 Å) [6].

The structural determination, from a single crystal of $\text{Na}_x\text{Cu}_{1-x}\text{In}_5\text{S}_8$, shows definitely that the structure of these compounds is cubic, closely related with that of $\alpha\text{-In}_2\text{S}_3$. The structure refinement, starting with the structure of CuIn_5S_8 [7], shows that there is a statistical distribution of In, Cu and Na cations on the tetrahedral sites (see Table 1). The indium cations are equally distributed on both 4a and 4c sites. The obtained composition of the studied crystal is $\text{Na}_{0.36}\text{Cu}_{0.64}\text{In}_5\text{S}_8$. The metal–sulfur distances are 2.4411(15) Å (S1 atoms) and 2.4659(13) Å (S2 atoms) for the 4a and 4c tetrahedral sites respectively. According to the cationic radii, it is clear that the tetrahedrally coordinated sites fit better with the Cu^+ size than the Na^+ size. This result could explain why the incorporation of monovalent cation in In_2S_3 is easier for copper than for sodium [8].

3.2. Electron band structure

In the XPS measurements, the core levels were recorded but only the valence band region will be discussed in detail. For all the samples the amount of oxygen is similar and low and the In 3d doublet is well-resolved with the usual intensity ratio of the $3d_{5/2}$ – $3d_{3/2}$ equal to 3/2. These doublets are located at the same energy (In $3d_{5/2}$: 445.2 eV). Nevertheless, for NaIn_5S_8 a supplementary low intensity ($\sim 3\%$) doublet appears on the high

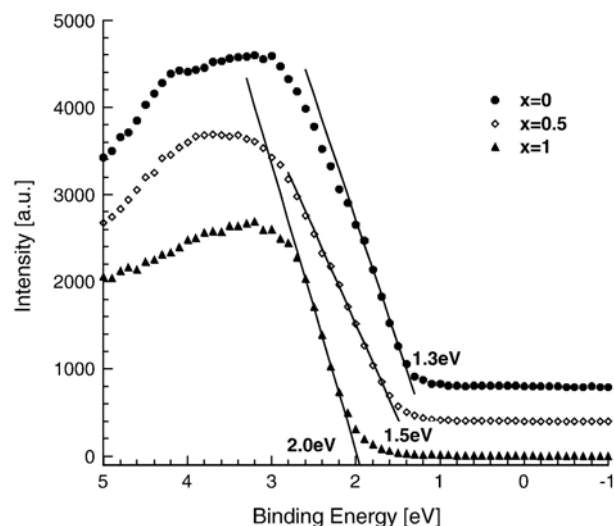


Fig. 1. XPS valence band spectra of NaIn_5S_8 , $\text{Na}_{0.5}\text{Cu}_{0.5}\text{In}_5\text{S}_8$ and CuIn_5S_8 . The spectra have been offset along the y axis for better viewing.

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