



**HAL**  
open science

## Preparation of $\beta$ -CuGaO<sub>2</sub> thin films by ion-exchange of $\beta$ -NaGaO<sub>2</sub> film fabricated by a solgel method

Thomas Fix, Jean-Luc Rehspringer, Stéphane Roques, Abdelilah Slaoui

### ► To cite this version:

Thomas Fix, Jean-Luc Rehspringer, Stéphane Roques, Abdelilah Slaoui. Preparation of  $\beta$ -CuGaO<sub>2</sub> thin films by ion-exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated by a solgel method. Emergent Materials, 2023, 6, pp.167-174. 10.1007/s42247-022-00404-9 . hal-03799429

**HAL Id: hal-03799429**

**<https://hal.science/hal-03799429>**

Submitted on 5 Oct 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Preparation of  $\beta$ -CuGaO<sub>2</sub> thin films by ion-exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated by a solgel**  
2 **method**

3 T. Fix<sup>1\*</sup>, J.-L. Rehspringer<sup>2</sup>, S. Roques<sup>1</sup>, A. Slaoui<sup>1</sup>

4 <sup>1</sup> ICube laboratory, CNRS and Université de Strasbourg, 23 rue du Loess, 67037 Strasbourg,  
5 France

6 <sup>2</sup> Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS and  
7 Université de Strasbourg, 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France

8

9 \* Corresponding author. Tel.: +33 388106334, Fax +33 388106548. E-mail address:  
10 [tfix@unistra.fr](mailto:tfix@unistra.fr)

11

12

13 **Abstract**

14  $\beta$ -CuGaO<sub>2</sub> is a wurtzite-derived phase that is promising for ferroelectric and photovoltaic  
15 applications. Its bandgap measured in the form of powders is about 1.5 eV and is direct  
16 according to density functional theory calculations, making it an appropriate solar light  
17 absorber. In this work, we describe our attempts to grow this complex phase by pulsed laser  
18 deposition (PLD) that resulted in growing mostly CuGa<sub>2</sub>O<sub>4</sub> on various crystal substrates such  
19 as SrTiO<sub>3</sub> (STO), Al<sub>2</sub>O<sub>3</sub> (ALO), ZnO and ZrO<sub>2</sub>:Y (9.5 mol%Y<sub>2</sub>O<sub>3</sub>) (YSZ). In contrast,  $\beta$ -CuGaO<sub>2</sub> is  
20 obtained using ion-exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated with a cost-efficient spin coating by  
21 solgel method, on substrates composed of a SiN film on c-Si (001) wafer. The potential of the  
22 different films obtained is discussed in view of photovoltaic applications using Surface  
23 Photovoltage under white light and Surface Photovoltage spectroscopy. While we show that

24  $\beta$ -CuGaO<sub>2</sub> is a suitable photon absorber we conclude that the fact that the films are  
25 discontinuous is detrimental for electronic transport and additional dopants must be inserted  
26 in this material to promote its optoelectronic properties and charge carrier transport.

27 **Keywords:** thin films; oxide materials; photovoltaics; photon absorber

28

## 29 Introduction

30 Inorganic thin film photovoltaics is mainly based on cadmium telluride, amorphous silicon and copper  
31 indium gallium sulfide/selenide (CIGSSe). Recently, hybrid perovskites have emerged with efficiencies  
32 rivalling the record efficiencies of Si. However they still suffer from stability, reliability, scale up and  
33 toxicity issues, although progress is fast. An alternative could be offered by inorganic oxide absorbers.  
34 Two materials share the record laboratory conversion efficiency of 8.1 % for oxide solar cells: cuprous  
35 oxide  $\text{Cu}_2\text{O}$  and the double perovskite  $\text{Bi}_2\text{FeCrO}_6$  [1-5]. The former has a bandgap of 2.1 eV which is not  
36 optimal as the ideal bandgap for a single bandgap solar cell is about 1.3 eV for the solar spectrum [1].  
37 The latter,  $\text{Bi}_2\text{FeCrO}_6$ , is based on the concept of ferroelectric solar cells which do not require a *pn*  
38 junction as the ferroelectric behavior is responsible for carrier separation and migration towards the  
39 contacts [4]. Here we investigate an emergent material in the form of thin film,  $\beta\text{-CuGaO}_2$ . It contains,  
40 as in CIGS, copper and gallium but the scarce indium and toxic S/Se elements are not present. Its  
41 bandgap measured in the form of powders is 1.47 eV and is direct according to density functional  
42 theory calculations, making it an appropriate solar light absorber [6]. The ferroelectric properties are  
43 thought to be remarkable with a computed remanence polarisation of  $84 \mu\text{C}/\text{cm}^2$ , surpassing  $\text{BiFeO}_3$   
44 single-crystal ( $\sim 60 \mu\text{C}/\text{cm}^2$  along  $\langle 100 \rangle$ ) and comparable to  $\text{LiNbO}_3$  ( $\sim 80 \mu\text{C}/\text{cm}^2$ ) and  $\text{PbTiO}_3$  ( $\sim 90$   
45  $\mu\text{C}/\text{cm}^2$ ) [7]. Thus several studies pointed out this material as an excellent candidate for ferroelectric  
46 solar cells [6,7].  $\beta\text{-CuGaO}_2$  has a wurtzite structure which is not the most stable oxide compared to  
47  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  and  $\alpha\text{-CuGaO}_2$  [8]. Therefore  $\beta\text{-CuGaO}_2$  powders have been discovered by fabricating first  
48  $\beta\text{-NaGaO}_2$  powders and by further substitution of Na by Cu [6]. The only report on  $\beta\text{-CuGaO}_2$  thin films  
49 is using a similar method, by first depositing  $\beta\text{-NaGaO}_2$  films by sputtering and then by substitution of  
50 Na by Cu using  $\text{CuCl}$  vapour [9]. The fabrication of  $\beta\text{-NaGaO}_2$  films by sputtering is not very convenient  
51 because of Na contamination of the chamber and hygroscopy of the  $\beta\text{-NaGaO}_2$  compound. In this work,  
52 we investigate the direct growth of thin film  $\beta\text{-CuGaO}_2$  by pulsed laser deposition (PLD). We also  
53 present an alternative original method to obtain  $\beta\text{-CuGaO}_2$  using ion-exchange of  $\beta\text{-NaGaO}_2$  film

54 fabricated with a cost-efficient spin coating by solgel method. We studied the potential of the grown  
55 films using the surface photovoltage (SPV) technique.

## 56 **1. Experimental procedure**

### 57 **PLD fabrication**

58 The substrates used for PLD deposition were SrTiO<sub>3</sub> (001) and (110) (STO), Al<sub>2</sub>O<sub>3</sub> (0001) (ALO), ZnO  
59 (0001) and ZrO<sub>2</sub>:Y (9.5 mol%Y<sub>2</sub>O<sub>3</sub>) (111) YSZ from Crystal GmbH. The PLD process was performed using  
60 a KrF laser (248 nm) with a 10 Hz repetition rate and a laser fluence of around 1-2 J/cm<sup>2</sup> (36000 pulses).  
61 The depositions were carried out at 700-800°C under an oxygen pressure of 10<sup>-2</sup> mbar. The films were  
62 naturally cooled down under the same atmosphere until room temperature. Around 20 samples were  
63 deposited by PLD for the study. The CuGaO<sub>2</sub> target was made by mixing CuO (99.995 % purity, Alfa  
64 Aesar) and Ga<sub>2</sub>O<sub>3</sub> (99.999 % purity, Alfa Aesar) powders in the required quantities, pressing into a pellet  
65 with a vertical pressure die and then with a cold isostatic press system (MIT Corporation YLJ-CIP-500M-  
66 30) at 460 Mpa actual pressure. The obtained pellet was then calcinated at 800°C for 3 h in air and  
67 used as a target.

### 68 **Solgel fabrication**

69 The β-NaGaO<sub>2</sub> films were prepared as follows. First, 5 g of gallium (III) nitrate hydrate (99.9 % purity,  
70 Sigma Aldrich) is poured in deionised water (~50 ml) together with 10 g of citric acid (99 %, Sigma  
71 Aldrich) and 10 g of ethylene glycol (> 99 %, Sigma Aldrich). The solution is heated while stirring with a  
72 magnetic bar until most of the excess of water is evaporated while releasing NO<sub>2</sub> gas. The obtained  
73 viscous and transparent solution is completed with 1.19665 g of sodium citrate tribasic dihydrate (≥  
74 99.0 %, Fluka). A part of the obtained paste was heated in a furnace at 700 °C for 1 h in air. The resulting  
75 white powder was analyzed by XRD which provided evidence of a β-NaGaO<sub>2</sub> phase.

76 Next, silicon nitride was deposited on 1-5 Ω·cm p-type (B-doped) c-Si (001) wafer by plasma-enhanced  
77 chemical vapour deposition (PECVD, Roth & Rau MicroSys 400 reactor). The Si substrates were etched

78 with HF (10% vol) before pumping (deoxidation). A SiN thickness of 157 nm was measured by  
79 spectroscopic ellipsometry. These films were then used as substrates for spin-coating with the  
80 aforementioned paste. The spin coating parameters were 2000 rpm speed, 2000 rpm/s acceleration  
81 and 30 min spin coating duration. The spin-coated samples were then heated in air at 700°C for 1 h  
82 with a heating rate of 3.3 °C/min and natural cooling. When the furnace cooldown reached ~40 °C the  
83 obtained  $\beta$ -NaGaO<sub>2</sub> films were placed in an alumina crucible and sprinkled with copper (I) chloride  
84 powder (purity  $\geq$  99 %, Sigma Aldrich). The powder was gently pressed onto the films. The crucible and  
85 samples were quickly inserted in a quartz tube and pumped until reaching a vacuum better than  
86  $1.5 \times 10^{-6}$  mbar. A furnace was placed around the quartz tube and set at 250°C for 17 h under dynamic  
87 vacuum. The final pressure after cooldown was  $5 \times 10^{-7}$  mbar. The samples were then rinsed with  
88 deionised water and dried under Ar gas flow.

89

## 90 **Film characterization**

91 Films grown by PLD on crystal substrates were investigated using at room temperature a Rigaku  
92 SmartLab diffractometer equipped with a monochromatic source delivering a Cu K <sub>$\alpha$ 1</sub> incident beam (45  
93 kV, 200 mA, 0.154056 nm). Films grown by the solgel method were investigated with a Bruker D8  
94 Discover X-ray diffractometer with Cu K <sub>$\alpha$ 1</sub> radiation (40 kV, 40 mA, 0.154056 nm) at room temperature.

95 The optical properties and thickness of the films were investigated by spectroscopic ellipsometry using  
96 a HORIBA Uvisel Lt M200 FGMS (210–880 nm) apparatus. The dispersion formula for SiN and  $\beta$ -CuGaO<sub>2</sub>  
97 are based on the classical and triple Tauc-Lorentz models respectively [10]. The goodness-of-fit values  
98 (Chi Square  $\chi^2$ ) was 4.5 for a  $\beta$ -CuGaO<sub>2</sub> film thickness of around 240 nm. Photoluminescence (PL)  
99 measurements were performed using a Horiba LabRAM ARAMIS spectrometer with 532 nm laser  
100 excitation (HeNe).

101 The surface of the films was investigated using atomic force microscopy (AFM) with a NT-MDT Smena  
102 B AFM in tapping mode. Scanning electron microscopy (SEM) was performed with a JEOL 6700F and a  
103 JEOL JSM-IT200LA apparatus and the stoichiometry was checked by Energy-dispersive X-ray  
104 spectroscopy (EDS). Kelvin Probe (KP) and Surface PhotoVoltage (SPV) measurements were performed  
105 with a single point Kelvin Probe system (KP Technology KP020) with a 2 mm diameter gold tip, and  
106 using either a halogen source with calibrated illumination for white light SPV or a GR50-605 (Thorlabs)  
107 monochromator of 600 g/mm grating for Surface Photovoltage Spectroscopy (SPS) mode.

## 108 **2. Results and discussion**

### 109 **PLD growth**

110 Knowing that there is a small lattice mismatch of  $\beta$ -CuGaO<sub>2</sub> lattice with ZnO [8], we attempted to  
111 deposit  $\beta$ -CuGaO<sub>2</sub> by PLD using substrates that may provide an epitaxial relationship with  $\beta$ -CuGaO<sub>2</sub>,  
112 namely STO (001) and (110), ALO (0001), ZnO (0001) and YSZ (111). The original method of fabrication  
113 of  $\beta$ -CuGaO<sub>2</sub> powders uses a two-step method by first fabricating  $\beta$ -NaGaO<sub>2</sub> and then substituting Na  
114 by Cu [8]. This is because  $\beta$ -CuGaO<sub>2</sub> cannot be formed using conventional solid state synthesis from  
115 oxide powders as it is not the most thermodynamically stable phase. However, PLD is known for  
116 enabling the fabrication of metastable phases that would form from the plasma material onto the  
117 substrate. Furthermore, a principle called epitaxial stabilization helps synthesizing complex material  
118 by using an appropriate substrate playing the role of a template to promote the right phase formation.  
119 This has been demonstrated for example with h-TbMnO<sub>3</sub> thin film fabrication while orthorhombic  
120 TbMnO<sub>3</sub> is the most stable phase [11,12]. Films grown on STO (110) using a CuGaO<sub>2</sub>-stoichiometry  
121 target provided CuGa<sub>2</sub>O<sub>4</sub> films with the following orientation CuGa<sub>2</sub>O<sub>4</sub> (220)//STO(110) while films  
122 grown on ALO (0001) provided CuGa<sub>2</sub>O<sub>4</sub> films with CuGa<sub>2</sub>O<sub>4</sub> (222)//ALO(0001) orientation (Figure 1).  
123 This means that clearly the substrate has an influence on film growth, although the desired  $\beta$ -CuGaO<sub>2</sub>  
124 phase was not obtained. CuGa<sub>2</sub>O<sub>4</sub> is reported in [13] to grow along the (111) orientation on ALO (0001)  
125 substrate. This is because the observation along the [111] direction of the cubic CuGa<sub>2</sub>O<sub>4</sub> lattice is a

126 hexagonal sampling lattice matching with the hexagonal lattice of ALO [13]. As well  $\text{CuGa}_2\text{O}_4$  grows in  
127 the (220) direction on STO (110) because of the lattice match in plane between STO (001) and  $\text{CuGa}_2\text{O}_4$   
128 (002) and between STO ( $1\bar{1}0$ ) and  $\text{CuGa}_2\text{O}_4$  ( $2\bar{2}0$ ). EDS analysis (Figure S1 of the Supplementary  
129 Information (SI)) indicated a stoichiometry of Cu:Ga:O of 1:0.85:1.87 indicating that while the chemical  
130 composition of the films is close to  $\text{CuGaO}_2$ , the structural crystallized phase is  $\text{CuGa}_2\text{O}_4$ . This means  
131 that the deposition is rather congruent, preserving the chemical stoichiometry from the target to the  
132 film, which was an incentive to perform further depositions using alternative substrates. The  
133 evaluation of  $\text{CuGa}_2\text{O}_4$  films grown on STO (110) by SPV showed that these films provide a strong  
134 photoresponse, nearly as good under white light as 1-5  $\Omega\text{-cm}$  p-type c-Si wafers (Figure S2a). SPS was  
135 performed on the same sample and shows that the photoresponse originates from photons below 600  
136 nm, indicating that the electronic bandgap is above 2 eV (Figure S2b).

137 Further crystal substrates were used for film growth. Unfortunately, films grown on ZnO (0001) and  
138 YSZ (111) gave  $\text{CuGa}_2\text{O}_4$  (222)//ZnO (0002) and  $\text{CuGa}_2\text{O}_4$  (222)//YSZ (111) orientations respectively  
139 (Figure S3 of SI). In the latter film two XRD peaks could be also attributed to a delafossite  $\alpha\text{-CuGaO}_2$   
140 phase (rhombohedral R-3m (166), ICDD 04-010-0383). The case of STO (001) substrate gives a similar  
141 outcome (Figure S3). As pointed out in [8,9], deposition of  $\beta\text{-CuGaO}_2$  is difficult because  $\beta\text{-CuGaO}_2$   
142 transforms into stable  $\alpha\text{-CuGaO}_2$  at temperatures higher than 500°C under low  $\text{O}_2$  atmosphere and  
143 decomposes in CuO and  $\text{CuGa}_2\text{O}_4$  at temperatures higher than 300°C under  $\text{O}_2$  atmosphere. A phase  
144 diagram of Cu-Ga-O is proposed in [14,15] but again should be used with care due to the non-  
145 thermodynamic equilibrium of PLD deposition. Attempts to obtain the right  $\beta\text{-CuGaO}_2$  films by  
146 reducing the  $\text{O}_2$  pressure from  $10^{-2}$  mbar to  $10^{-3}$  or  $10^{-4}$  mbar were unsuccessful. A fine tuning of both  
147 the deposition temperature and the oxygen pressure could help promote the  $\alpha\text{-CuGaO}_2$  phase as  
148 evidenced in [16] but this strategy was not followed here as only the  $\beta\text{-CuGaO}_2$  phase is sought.  
149 Instead, we decided to investigate fabrication of  $\beta\text{-CuGaO}_2$  thin films by ion-exchange of  $\beta\text{-NaGaO}_2$  film  
150 fabricated with spin coating by a solgel method.



## 151 **Fabrication by solgel**

152 Solgel fabrication of thin films is an inexpensive scalable method for fabricating oxides. In some cases  
153 this method provides better results than physical deposition, as in the case of  $\text{LaVO}_3$  [17]. Knowing that  
154 a simple mixture of  $\beta\text{-CuGaO}_2$  precursors in a traditional solgel experiment would not work for the  
155 aforementioned reasons, we decided to get inspired from the two-step fabrication in the way that the  
156 first  $\beta\text{-CuGaO}_2$  powders were produced: first the fabrication of a  $\beta\text{-NaGaO}_2$  film and second the  
157 substitution of Na by Cu [6]. As described in the experimental section, a precursor paste for  $\beta\text{-NaGaO}_2$   
158 was produced and spin coated on SiN//c-Si substrates. The spin coated samples were then heated in a  
159 furnace and resulted in the formation of  $\beta\text{-NaGaO}_2$  film as shown in Figure 2 and evidenced by XRD in  
160 Figure 3a). In contrast to the current method, the introduction of sodium citrate tribasic dihydrate at  
161 the same time as gallium (III) nitrate hydrate in water followed by heating does not lead to the right  $\beta\text{-}$   
162  $\text{NaGaO}_2$  phase. It should also be noted that  $\beta\text{-NaGaO}_2$  films degrade within few hours in air so that  
163 they need to be processed rapidly with the next step. A second remark is that spin coating and  
164 annealing on c-Si substrates without the SiN layer did not enable to obtain the  $\beta\text{-NaGaO}_2$  phase. It is  
165 believed that the SiN film acts as a barrier for Na diffusion into the substrate during the annealing at  
166  $700\text{ }^\circ\text{C}$ . The next step was to sprinkle CuCl powder on the  $\beta\text{-NaGaO}_2$  sample, pump the sample under  
167 dynamic vacuum and heat at  $250\text{ }^\circ\text{C}$  for 17 hours. It was found that a starting vacuum before heating  
168 of  $8\times 10^{-6}$  mbar was ineffective to form the  $\beta\text{-CuGaO}_2$  phase as CuCl was oxidized, while a starting  
169 vacuum better than  $1.5\times 10^{-6}$  mbar was satisfactory. The sample was naturally cooled down to room  
170 temperature before opening the furnace tube. The films obtained in this way present the right  $\beta\text{-}$   
171  $\text{NaGaO}_2$  phase as evidenced by XRD (Figure 3b). The composition was analyzed by EDS and provided a  
172  $\text{CuGa}_{1.06}\text{O}_y$  stoichiometry, very close to the perfect composition of  $\beta\text{-CuGaO}_2$  (Figure S4). Traces of Cl  
173 originating from the CuCl step were found, which could be further reduced by acetonitrile and ethanol  
174 washing as proposed in [9]. Although the films look visually uniform and flat (Figure 2), SEM performed  
175 on the samples shows that the films are discontinuous (Figure 4). Much smaller cracks were also  
176 observed in [9] and originate from lattice shrinkage during the ion exchange from  $\beta\text{-NaGaO}_2$  thin film

177 to  $\beta$ -CuGaO<sub>2</sub> thin film. AFM performed on the samples reveals a root-mean-square (RMS) roughness  
178 in the 300 nm range (Figure S5) which is rather high compared to films obtained by physical methods.  
179 Also the films look much darker than the initial SiN//c-Si substrates; and their optical properties were  
180 further investigated by spectroscopic ellipsometry. A thickness of about 240 nm and a bandgap of  
181 about 1.91 eV were found (Figure 5). Such a high film thickness was obtained because the precursor  
182 paste at step 1 was very viscous. The absorption coefficient was in the  $10^5 \text{ cm}^{-1}$  range in the 2-6 eV  
183 region, which is at 600 nm more than an order of magnitude higher than diamond Silicon. The optical  
184 parameters  $n$  and  $k$  were also determined (Figure S6). The optical properties were further investigated  
185 by PL (Figure S7). No sharp PL peak is observed around the bandgap or anywhere in the  $\beta$ -CuGaO<sub>2</sub>  
186 spectrum. The presence of a sharp peak would have indicated a high quality direct bandgap material.

187 We now focus in the electrical properties of the films. The work function was measured with the Kelvin  
188 probe system and was found to be in the 5.1-5.3 eV range. The value should be used with caution as  
189 the surface state of  $\beta$ -CuGaO<sub>2</sub> film is uncertain. Still, this value can be compared to the delafossite  $\alpha$ -  
190 CuGaO<sub>2</sub> reported value of 4.90 eV [18]. Unfortunately, no Hall effect could be performed because the  
191 samples were too insulating for the setup. This could be caused by the fact that the films are  
192 discontinuous as observed in Figure 4. To overcome these carrier transport limitations, we attempted  
193 to produce  $\beta$ -CuGaO<sub>2</sub> on conductive substrates. Because indium tin oxide (ITO) films would not  
194 withstand an annealing temperature of 700 °C, we opted for 50 nm thick Pt layers sputtered on quartz  
195 substrates and we followed the aforementioned procedure to produce  $\beta$ -CuGaO<sub>2</sub> films. While the right  
196  $\beta$ -CuGaO<sub>2</sub> phase could be obtained again, the surface of the films was severely damaged as shown in  
197 Figure S8. The adherence of  $\beta$ -CuGaO<sub>2</sub> on Pt is low and thus Pt areas are exposed after detachment of  
198  $\beta$ -CuGaO<sub>2</sub> fragments. To further investigate the potential of the  $\beta$ -CuGaO<sub>2</sub> films produced, we  
199 performed SPV measurements on films both on SiN//c-Si and Pt//quartz. Unfortunately no SPV signal  
200 could be extracted as shown in Figure S9. We believe that the main limitation for  $\beta$ -CuGaO<sub>2</sub> as a  
201 photovoltaic absorber is that the carrier transport is poor, probably due to the discontinuous nature  
202 of the film, although the optical properties are promising. A possible way to go forward would be to

203 study electrical doping of  $\beta$ -CuGaO<sub>2</sub>, which would be simple to adapt from the proposed solgel  
204 procedure.

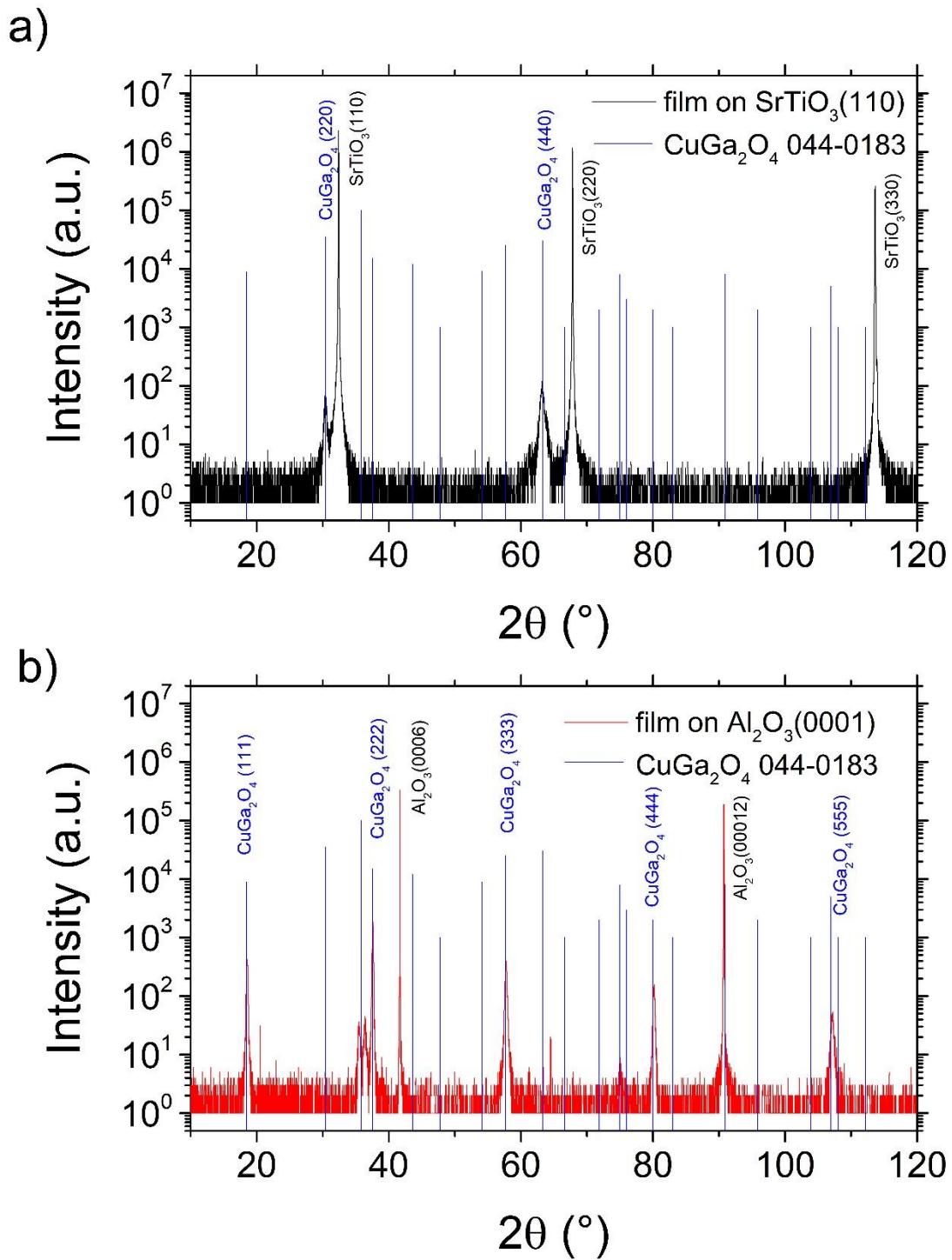
205

## 206 **Conclusions**

207 In summary, we first have attempted to grow  $\beta$ -CuGaO<sub>2</sub> by PLD. This was unsuccessful and the best  
208 films produced on various crystal substrates were CuGa<sub>2</sub>O<sub>4</sub>. Some of these films provided high SPV  
209 response and SPS spectroscopy indicates that this response is rather generated by photons below 600  
210 nm wavelength. In contrast,  $\beta$ -CuGaO<sub>2</sub> films were produced with an inexpensive ion-exchange of  $\beta$ -  
211 NaGaO<sub>2</sub> fabricated with spin coating by a solgel method which delivered well crystallized but  
212 discontinuous films. Although the optical properties obtained are interesting, further effort is  
213 necessary to obtain smoother films and improve carrier transport of  $\beta$ -CuGaO<sub>2</sub> by doping the material  
214 so that better optoelectronic response can be obtained in the future.

215

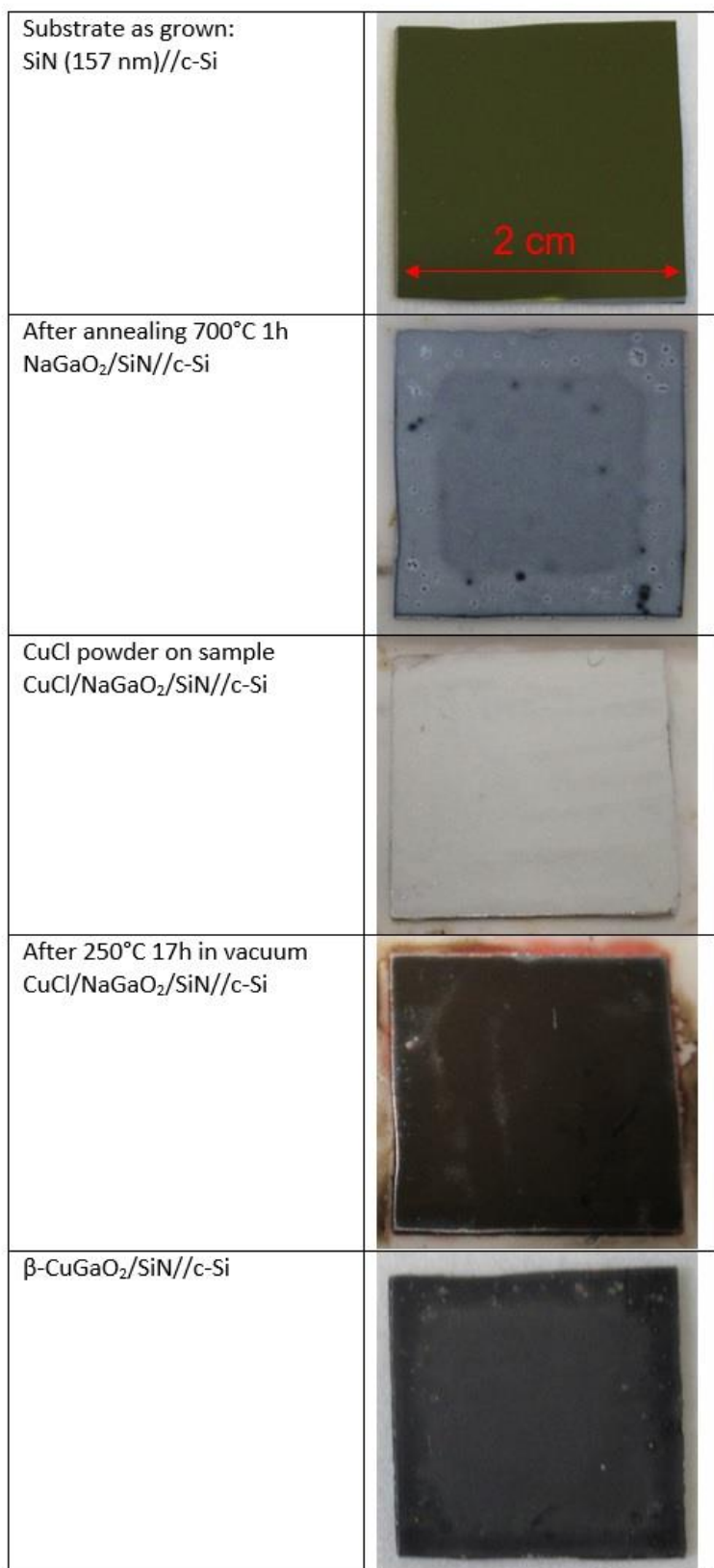
216 **Figure 1** XRD  $\theta$ - $2\theta$  patterns of films grown by PLD on a) STO (110) b) ALO (0001) from a  $\text{CuGaO}_2$   
217 target, and of the  $\text{CuGa}_2\text{O}_4$  ICDD reference



218

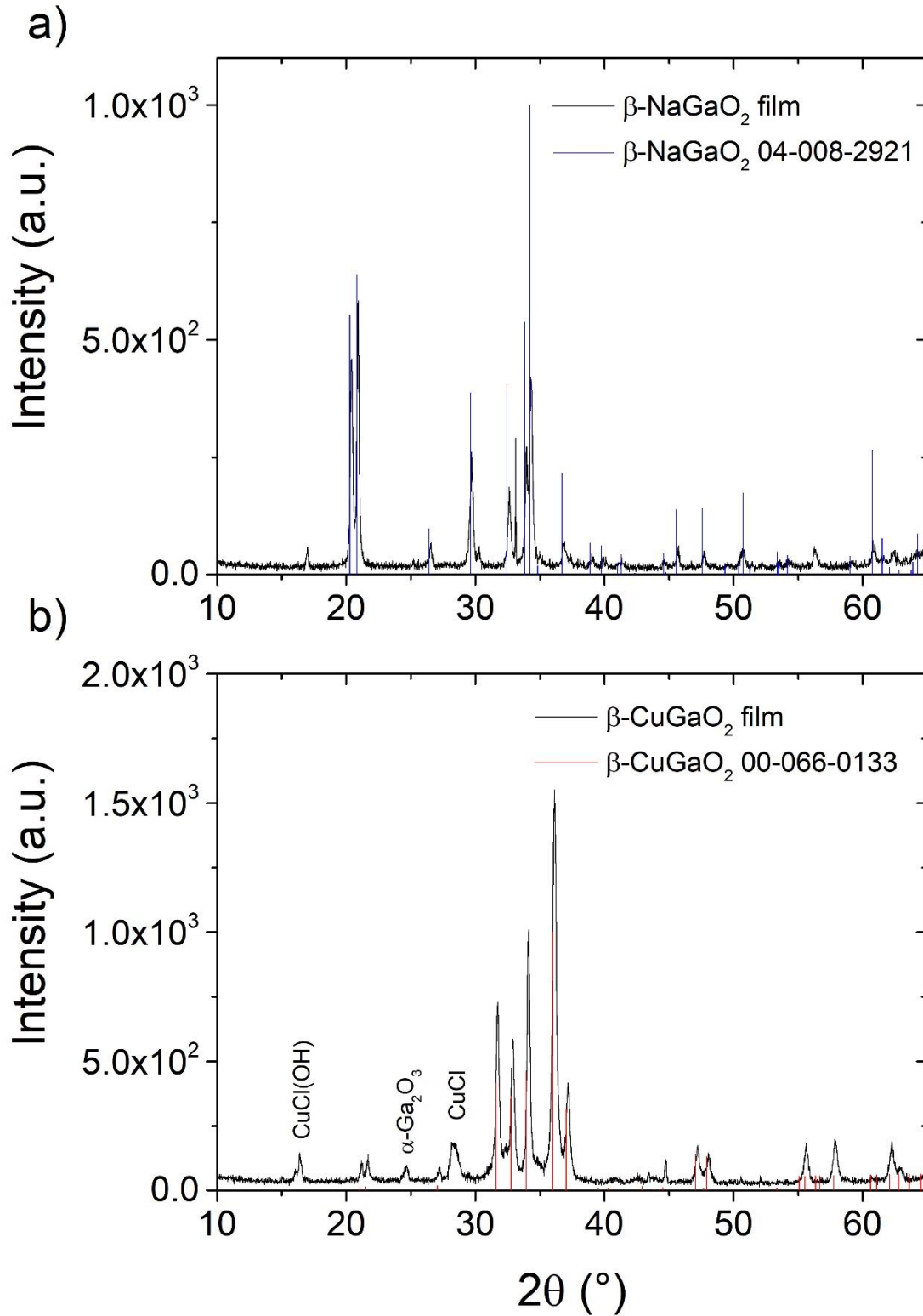
219

220 **Figure 2** Top-view photographs showing the fabrication of  $\beta$ -CuGaO<sub>2</sub> film obtained using ion-  
221 exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated with spin coating by solgel method on c-Si//SiN



222

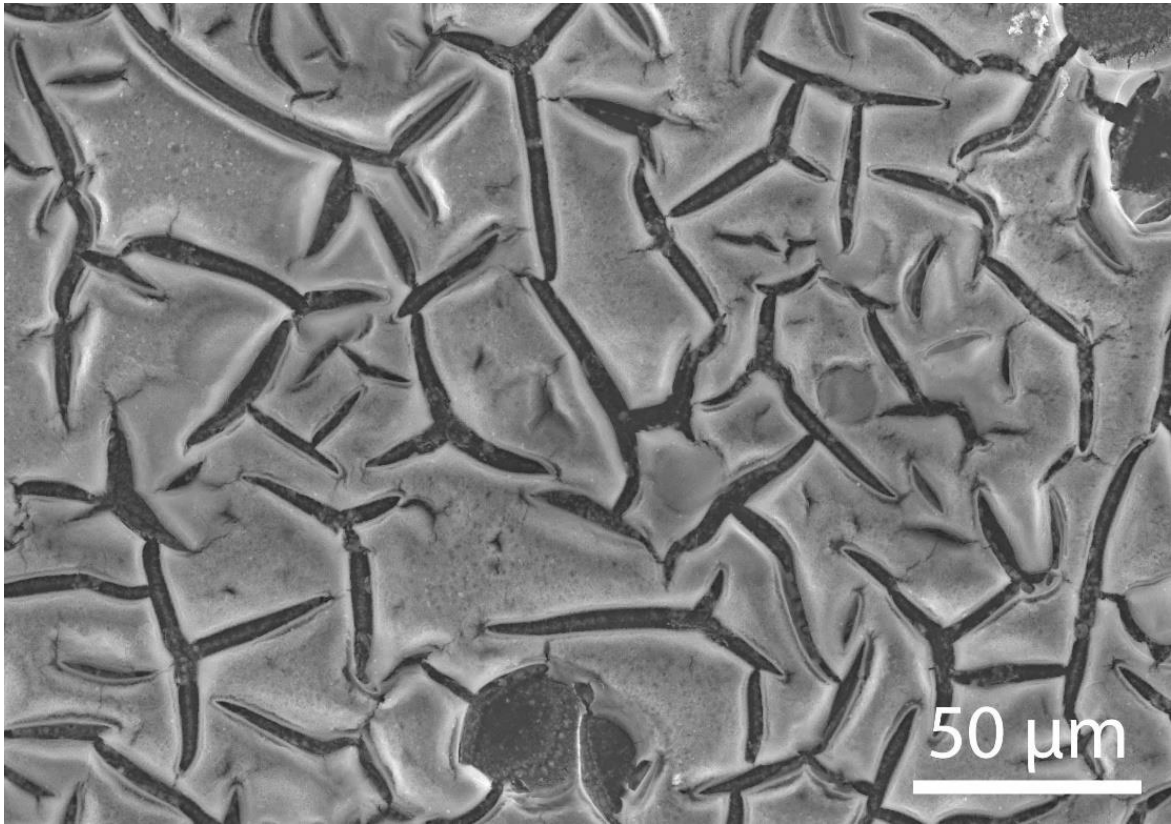
223 **Figure 3** XRD  $\theta$ - $2\theta$  patterns showing the  $\beta$ -NaGaO<sub>2</sub>, and  $\beta$ -CuGaO<sub>2</sub> films obtained using ion-exchange  
224 of  $\beta$ -NaGaO<sub>2</sub> film fabricated with spin coating by solgel method, and the ICDD references



225

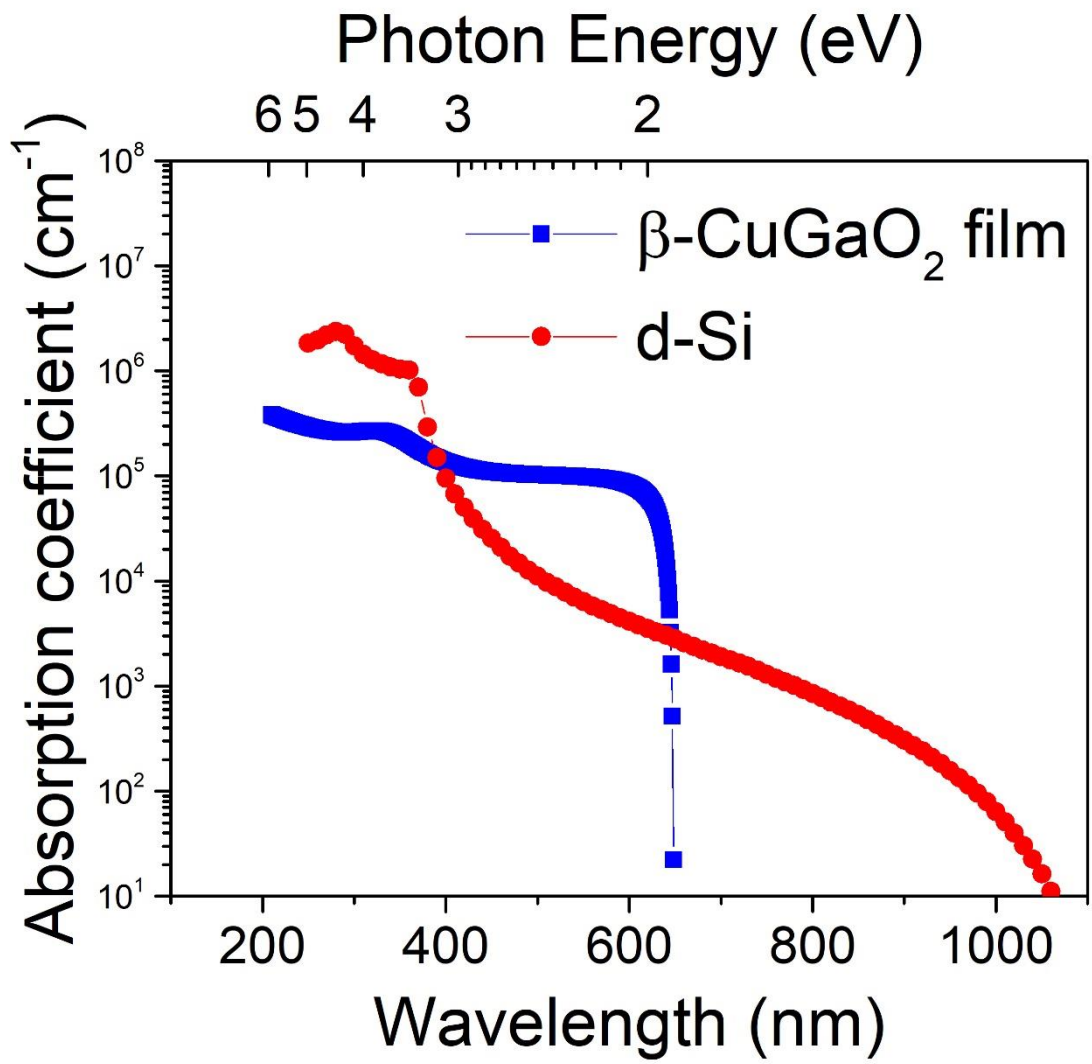
226

227 **Figure 4:** SEM top view of a  $\beta$ -CuGaO<sub>2</sub> film obtained using ion-exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated  
228 with spin coating by solgel method  
229



230

231 **Figure 5** Absorption coefficient determined by spectroscopic ellipsometry for a  $\beta$ -CuGaO<sub>2</sub> sample,  
232 obtained using ion-exchange of  $\beta$ -NaGaO<sub>2</sub> film fabricated with spin coating by solgel method on c-  
233 Si//SiN. The reference for diamond silicon is taken from [19]



234

235



236 **References**

- 237 1. T. Fix, in *Advanced Micro- and Nanomaterials for Photovoltaics*, edited by D. Ginley and T. Fix  
238 (Elsevier Science Bv, Amsterdam, 2019), p. 19.
- 239 2. A. Quattropani, D. Stoeffler, T. Fix, G. Schmerber, M. Lenertz, G. Versini, J. L. Rehspringer, A.  
240 Slaoui, A. Dinia, and S. Cois, *J. Phys. Chem. C* **122**, 1070 (2018).  
241 <https://doi.org/10.1021/acs.jpcc.7b10622>
- 242 3. A. Quattropani, A. S. Makhort, M. V. Rastei, G. Versini, G. Schmerber, S. Barre, A. Dinia, A.  
243 Slaoui, J. L. Rehspringer, T. Fix, S. Colis, and B. Kundys, *Nanoscale* **10**, 13761 (2018).  
244 <https://doi.org/10.1039/c8nr03137a>
- 245 4. R. Nechache, C. Harnagea, S. Li, L. Cardenas, W. Huang, J. Chakrabartty, and F. Rosei, *Nat.*  
246 *Photonics* **9**, 61 (2015). <https://doi.org/10.1038/nphoton.2014.255>
- 247 5. T. Minami, Y. Nishi, and T. Miyata, *Appl. Phys. Express* **9** (2016).  
248 <https://doi.org/10.7567/apex.9.052301>
- 249 6. T. Omata, H. Nagatani, I. Suzuki, M. Kita, H. Yanagi, and N. Ohashi, *Journal of the American*  
250 *Chemical Society* **136**, 3378 (2014). <https://doi.org/10.1021/ja501614n>
- 251 7. S. Song, D. Kim, H. M. Jang, B. C. Yeo, S. S. Han, C. S. Kim, and J. F. Scott, *Chem. Mater.* **29**, 7596  
252 (2017). <https://doi.org/10.1021/acs.chemmater.7b03141>
- 253 8. H. Nagatani, I. Suzuki, M. Kita, M. Tanaka, Y. Katsuya, O. Sakata, S. Miyoshi, S. Yamaguchi, and  
254 T. Omata, *Inorg. Chem.* **54**, 1698 (2015). <https://doi.org/10.1021/ic502659e>
- 255 9. I. Suzuki, H. Nagatani, M. Kita, and T. Omata, *Appl. Phys. Express* **10**, 4 (2017).  
256 <https://doi.org/10.7567/apex.10.095501>
- 257 10. F. Wooten, *Optical Properties of Solids* (Elsevier Inc., 1972).
- 258 11. T. Fix, G. Schmerber, J. L. Rehspringer, M. V. Rastei, S. Roques, J. Bartringer, and A. Slaoui, *J.*  
259 *Alloys Compd.* **883**, 6 (2021). <https://doi.org/10.1016/j.jallcom.2021.160922>
- 260 12. J. H. Lee, P. Murugavel, H. Ryu, D. Lee, J. Y. Jo, J. W. Kim, H. J. Kim, K. H. Kim, Y. Jo, M. H. Jung,  
261 Y. H. Oh, Y. W. Kim, J. G. Yoon, J. S. Chung, and T. W. Noh, *Adv. Mater.* **18**, 3125 (2006).  
262 <https://doi.org/10.1002/adma.200601621>
- 263 13. H. L. Wei, Z. W. Chen, Z. P. Wu, W. Cui, Y. Q. Huang, and W. H. Tang, *Aip Advances* **7**, 7 (2017).  
264 <https://doi.org/10.1063/1.5009032>
- 265 14. V. Varadarajan and D. P. Norton, *Appl. Phys. A: Mater. Sci. Process.* **85**, 117 (2006).  
266 <https://doi.org/10.1007/s00339-006-3667-0>
- 267 15. R. B. Gall and D. P. Cann, in *High temperature phase equilibria in the Cu<sub>2</sub>O-Ga<sub>2</sub>O<sub>3</sub>-In<sub>2</sub>O<sub>3</sub>*  
268 *system*, Cocoa Beach, FL, 2003 (Amer Ceramic Soc), p. 143.
- 269 16. T. Mine, H. Yanagi, K. Nomura, T. Kamiya, M. Hirano, and H. Hosono, *Thin Solid Films* **516**, 5790  
270 (2008). <https://doi.org/10.1016/j.tsf.2007.10.072>
- 271 17. M. Jellite, J. L. Rehspringer, M. A. Fazio, D. Muller, G. Schmerber, G. Ferblantier, S. Colis, A.  
272 Dinia, M. Sugiyama, A. Slaoui, D. Cavalcoli, and T. Fix, *Sol. Energy* **162**, 1 (2018).  
273 <https://doi.org/10.1016/j.solener.2017.12.061>
- 274 18. J. Wang, V. Ibarra, D. Barrera, L. Xu, Y. J. Lee, and J. Hsu, *J. Phys. Chem. Lett.* **6**, 1071 (2015).  
275 <https://doi.org/10.1021/acs.jpcllett.5b00236>
- 276 19. M. A. Green and M. J. Keevers, *Progr. Photovolt.* **3**, 189 (1995).  
277 <https://doi.org/https://doi.org/10.1002/pip.4670030303>

278

279 **Statements and Declarations**

280 *Funding*

281 This work has been partially funded by the CNRS Energy unit (Cellule Energie) through the project  
282 CIGALE-PV and by the IdEx University of Strasbourg.

283 *Declaration of Competing Interest*

284 The authors declare that they have no known competing financial interests or personal relationships  
285 that could have appeared to influence the work reported in this paper.

286