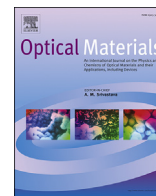




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# Cu-doped photovoltaic glasses by ion exchange for sunlight down–shifting

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## ABSTRACT

Ion exchange process is a widely studied synthesis technique for the controlled modification of silicate glass composition and properties, being moreover an easy and cheap approach. Silicate glasses containing copper are known to exhibit a broad luminescent band peaked around 500 nm, ascribed to  $3d^{10} - 3d^9 4s^1$  electronic transition of  $\text{Cu}^+$  ions; this band turns out to be much promising for the realization of down–shifting systems, being excited in the UV and near–UV region. Luminescent Cu–doped silicate glass sheets suitable as down–shifters to be used for covering solar cells have been prepared by thermal ion exchange. Synthesis of the Cu–doped glasses has been done by dipping pure silicate sheets (commercially used as cover of photovoltaic panels) into a fused copper salt mixture at temperature of 400 °C, for duration between a few minutes and some hours; two different types of copper chloride salt mixtures were explored, with the aim at obtaining luminescent glasses able to improve the Si cell yield. Absorption and luminescence glass features were collected and compared. The performance of the different samples was tested by a solar simulator, measuring the output power of a Si solar cell covered with the Cu–doped glass slides.

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## 1. Introduction

In a recent paper [1] we explored two different copper salt mixtures to dope commercial photovoltaic (PV) glass panels with copper ions by ion exchange, with the aim at inducing down–shifting phenomena to increase the total yield of the PV cells [2–5]. The first salt bath used was a  $\text{CuSO}_4:\text{Na}_2\text{SO}_4$  mixture (45:55 mol. %); after the exchange process the glasses resulted colored and characterized by high absorption in the UV–Vis range, due to presence of copper nanoparticles and  $\text{Cu}^{2+}$  ions. Being these features detrimental for a solar application of the doped glasses, the sulphate salt bath was discharged. More encouraging results were obtained by doping the glass panels starting from a  $\text{CuCl}:\text{ZnCl}_2$  salt bath (11:88 mol. %): in this case an improvement of the solar cell maximum output power was evidenced. On the basis of the exhibited optical properties and of the detected (and undesired)  $\text{Cu}^{2+}$  copper fraction – more and more present by increasing the exchange time, as revealed by the extended X–ray absorption fine structure (XANES) measurements – it was concluded that the best

conditions for doping the PV panels with copper should be an ion exchange around 400 °C for a duration of few hours. Starting from this point, the aim of the study here reported is to dope PV glass panels maximizing the  $\text{Cu}^+$  ions concentration and reducing as much as possible the  $\text{Cu}^{2+}$  presence, thus enhancing the glass spectral conversion. To avoid the formation of an important fraction of  $\text{Cu}^{2+}$  ions, the exchange duration was limited to few hours; moreover, the less dipping time inside the bath and the adopted stirring action of the bath should avoid salt islands formation on the glass surface.

## 2. Experimental

Samples cut from a commercial low–iron extra–clear float soda–lime silicate glass (Pilkington Optiwhite, 2.85 mm thick, used as photovoltaic panel cover glass) were doped with copper by thermal ion exchange process. The glass atomic % composition declared by the manufacturer is: 60.2O, 24.9Si, 9.0Na, 3.3Ca, 2.2Mg, 0.2Al, 0.2K, 0.03Zr, 0.005Ti, 0.003Fe + traces. Rutherford backscattering spectrometry analysis of the pure glass gave a comparable composition. Before the ion exchange, the glass slides were cleaned by a four–step process in ultrasonic baths (deionized  $\text{H}_2\text{O}$ ; trichloroethylene; acetone; isopropyl alcohol).

Samples were doped by dipping inside two different molten salt

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baths: 11:89 mol. % CuCl:ZnCl<sub>2</sub> (eutectic mixture) at temperature of 400 °C for 20, 80 and 320 min; 74.5:25.5 mol% CuCl:NaCl (eutectic mixture) at temperature of 400 °C for 20, 80 and 320 min.

UV–Vis optical absorption (OA) spectra were acquired with a JASCO UV–VIS dual beam spectrophotometer, in the 250–800 nm region (2 nm of spectral resolution).

Photoluminescence (PL) spectra were recorded with a Fluorolog–3 (Horiba–Jobin Yvon) modular system. Samples excitation was obtained by using a 450 W Xe lamp coupled to a double monochromator for wavelength selection ( $\lambda_{\text{exc-1}} = 260$  nm,  $\lambda_{\text{exc-2}} = 350$  nm). Samples were placed with the tin-free side facing the lamp. Photoluminescence excitation (PLE) spectra were recorded choosing the emission wavelengths at the values of emission bands collected in PL spectra.

Rutherford backscattering spectrometry (RBS) measurements were performed at INFN National Laboratories of Legnaro, Italy (LNL) with a 2.0 MeV He<sup>+</sup> beam at a scattering angle of 160°. Diffused atoms concentration was calculated by simulation of the RBS spectra with the RUMP code [6].

The solar simulator system, used for measuring the power delivered by a Si solar cell covered with the Cu–doped glass samples, was made of a DC power supply, a halogen dichroic reflector lamp DECOSTAR 51 ECO SST 14 W 12 V 36 GU5.3 (Osram) as light source without UV filter, a solar panel, and a digital multimeter (Tektronix Keithley 2410). The DC supply was directly linked to the lamp and a multimeter was connected to the cell. The light source was hold on the top of an iron structure, and the cell was placed under the light source at 14 cm of distance. The solar cell used in this apparatus is a 2 × 1 cm<sup>2</sup> Si–based commercial device. The cover sample was put without matching fluids on the Si cell (with the tin-free side in front of the solar simulator) and the power–against–voltage P–V curve was obtained by simultaneously measuring the flowing current I and the cell voltage V ( $P = V \times I$ ). A specific data acquisition procedure was adopted to minimize fluctuations: for each sample, the curve was measured several times by removing and putting again the glass slide on the cell, alternating every measurement with that of the pure glass used as reference (thus checking the stability of the whole apparatus). This procedure was repeated several times during the different measurement runs, to take also into account the fluctuation of the light source. The final estimated uncertainty was found to be lower than 0.5% of the measured power values.

### 3. Results

#### 3.1. CuCl:ZnCl<sub>2</sub> salt bath

The diffusion profile of copper inside the glasses doped by CuCl:ZnCl<sub>2</sub> is reported in Fig. 1a, as obtained by RBS data. Increasing the exchange time the penetration depth becomes greater but the shape of the in–depth concentration profile changes significantly. In the sample doped for the shortest time the copper is mainly present immediately under the surface, as expected, and its maximum atomic concentration is about 1.3%. After 80 min of exchange, the first 100 nm below the glass surface resulted depleted of dopant; the highest copper concentration is reached at about 300 nm of depth and it is close to 0.5 atomic %.

In the sample exchanged for the longest time, the concentration of copper below the surface is very low and it decreases from the surface towards the bulk, following an almost flat distribution; here copper seems diffused well over 1 μm in depth. In all samples the dynamic of exchange is compatible with the process  $1\text{Cu}^+ \leftrightarrow 1\text{Na}^+$ . Optical absorption spectra (not reported) of the doped samples are almost indistinguishable from that of the pure soda–lime glass: this agrees with the hypothesis that copper inside the glass is

mainly in Cu<sup>+</sup> oxidation state [7,8], being Cu<sup>0</sup> and Cu<sup>2+</sup> usually originating absorption bands easily detected in the visible range [8,9].

In Fig. 2 the photoluminescence analysis under an excitation wavelength of 260 nm is reported. The pure glass shows two emission bands at 450 nm and 510 nm and after the exchange an increasing of the emitted intensity is recorded, due to the typical green emission of cuprous ions in the matrix [5]. The signals observed in the pure glass sample could be due to copper traces present as bulk contamination, therefore originating a detectable signal.

The excitation spectra were then collected at both emission maxima observed on the emission spectra (457 nm and 510 nm, respectively): in both cases, the absorption profile shape was not modified by the exchange process but the intensity increased due to the Cu<sup>+</sup> ions absorption (Figs. 3a and 3b). This result confirms the correlation between the increase of the detected emission and the green emission of Cu<sup>+</sup> ions in the matrix; moreover the absorption and the emission spectra follow the same intensity trend, related to the total amount of copper inside the samples.

The luminescence properties were also studied using an excitation of 350 nm, with the aim to investigate the presence of copper pairs originating the “orange band” centered around 610 nm of wavelength [10–13]. Actually, both the structured band around 400–450 nm and the large band centered at about 500 nm show a small but evident increase of their intensity, following the total amount of copper inside the different samples (Fig. 4), but only faint emissions over 600 nm were recorded.

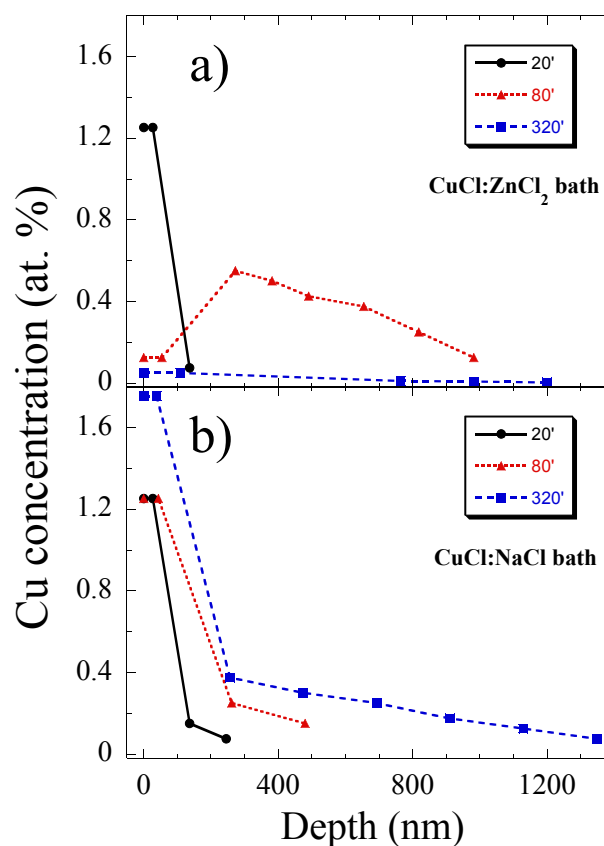


Fig. 1. Copper concentration depth profile of the PV panel glass doped by ion exchange for different time, as obtained by RBS measurements. The relative uncertainty on the concentration values is about 10%. a) doping by CuCl:ZnCl<sub>2</sub> molten salt bath; b) doping by CuCl:NaCl molten salt bath.

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