In situ variable temperature X-ray diffraction studies on Fe doped $CuGaO_2$ with applications in p-type dye sensitized solar cell

D. URSU[a,b], M. MICLAU[b], R. BANICA[a,b], N. VASZILCSIN[a*]

[a] *Politehnica University Timisoara, Str. Piata Victoriei, nr.2, 300006 Timisoara, Romania,*
[b]*National Institute for Research and Development in Electrochemistry and Condensed Matter, Str. Plautius Andronescu 1, 300224 Timisoara, Romania*

The aim of this study is to reveal the evolution and thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ compound obtained by hydrothermal method, using *in situ* variable temperature chamber (HT-XRD), and thermogravimetric curve (TG). The two temperature domains corresponding to the thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ (25 - 600°C) and to the destabilization of $CuGa_{0.95}Fe_{0.05}O_2$ phase (600 - 1000°C) have been determined. The unit-cell volume decreases with the increase of the temperature up to 200°C, and then increases with the increase of the temperature up to 500°C. Quantitative phase and microstructure analysis obtained from X-ray diffraction patterns are correlated with the results of scanning electron microscopy, where the morphology changes due to the temperature increase are emphasized.

1. Introduction

Dye-sensitized solar cells (DSSCs) are a third generation photovoltaic (solar) cell that converts any visible light into electrical energy [1]. DSSCs have been regarded the most promising solar cells, due to low production costs, ease of fabrication and tunable optical properties, such as color and transparency. In the last few years a lot of studies have been focused on the sensitization of *n*-type semiconductors, such as TiO_2, ZnO or SnO_2 [2-3].

Until now the efficiency of such *n*-type DSSCs has recently been improved, and it is about 12.3% [4]. Comparatively, there are very few studies on *p*-type semiconductor used in development of DSSCs due to the lack of choice of *p*-type semiconductors and organic sensitizers suitable for them. One of the most intensively studied materials used for dye-sensitized solar cell is NiO [5, 6], taking into account its special features, such as a wide band gap, large surface area, high surface chemical affinity, suitable valence band potential and high hole mobility [2].

Materials having delafossite structure ABO_2, including $CuAlO_2$ [7, 8] and $CuGaO_2$, [9, 10] are important transparent conducting oxides (TCOs), with a good optical transparency in the visible range and high electrical conductivity. It has been demonstrated that these materials are a very promising alternative to NiO in *p*-type DSSCs. Delafossite structure can be visualized as consisting of two alternate layers: a planar layer of A cation in a triangular pattern and a layer of edge-sharing BO_6 octahedra. Depending on the orientation of each layer in stacking, two crystalline forms can exist. By stacking the double layers with alternate A layers oriented 180° relative to each other, the hexagonal 2H type is formed which has P63/mmc space group symmetry [11]. If the double layers are stacked with the A layers oriented in the same direction relative to one another but offset from each other in a three layer sequence, the rhombohedral 3R type is formed that has a space group symmetry of R-3m [12].

Currently, *in situ* variable temperature chamber has been extensively employed to study the formation or characterization of $PbTiO_3$ [13], $BaTiO_3$ [13], calcium phosphate [14], hydroxyapatite (HA) [15, 16], sodium yttrium fluoride [17], $\gamma-Bi_2MoO_6$ [18], $CoAl_2O_4$ [18], silicon nitride compounds [19] and others.

In this work, we report the evolution and thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ compound obtained by hydrothermal method, using high temperature X-ray diffraction [20]. Variable temperature *in situ* diffraction is an ideal tool for studies of evolution and thermal stability for different compounds. An advantage of this characterization method *in situ* is given by the continuous monitoring of the system, thus avoiding problems associated with some irreversible changes in the material that may arise when the sample is cooled and taken out of the furnace for analysis.

The use of X-ray sources in the characterization of obtained materials by in situ diffraction provides important information about kinetics and reaction mechanism in solid state [21]. With this conventional X-ray instrumentation it is possible to realize various dynamic studies, including thermal decomposition and phase transformations [22].

2. Experimental

2.1. Material preparation

CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound was prepared according to the slightly modified hydrothermal route initially set up by Srinivasan et al [23]. Fe doped CuGaO$_2$ was synthesized in the hydrothermal conditions at 195°C for 60 h from 1 mmol copper (Cu(NO$_3$)$_2$·8H$_2$O (Alfa Aesar, 99%), 0.95 mmol gallium nitrates Ga(NO$_3$)$_3$ (Alfa Aesar, 99.9%) and 0.05 mmol Fe(NO$_3$)$_3$ (Merck, 99.9%) in a 16 mL aqueous solution adjusted at pH of 4.3 with 0.5 mmol KOH solution. The prepared mixture was diluted with an ethylene glycol/distilled water solution to fill up a total volume of 21 mL (35% filled Teflon bomb). The precipitate was filtered and washed with deionized water and stirring with liquid ammonia (30%) and distilled water in order to remove Cu$_2$O impurity phase. The product was dried in an oven at 80°C for 4 h.

2.2. Characterization

The effect of heat treatment on the structure of CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound prepared by hydrothermal method was followed by *in situ* XRD, thanks to a variable temperature chamber (Anton Paar HTK 2000 high temperature chamber) and connected to the diffractometer. The diffraction patterns were recorded in the [10° – 80°] (2θ) angular range, using 0.013 (2θ) step and a constant counting time of 165 s/step. The heating temperature was monitored by a type R thermocouple, which was welded to the bottom of the platinum heater strip (temperature accuracy was controlled within ± 1 K). These experiments allow the obtaining of better information on the composition of the materials. The sample was heated at the rate of 10°C/min, and diffractions spectrum of a sample was drown during one hour for every 100°C, from 25°C to 1000°C. The thermal stability of the material was performed in a vacuum chamber at 10^{-4} mbar. This vacuum has been made with vacuum pump (TRIVAC B D4B/D83) to the value of 10^{-2} mbar and with turbo pump (TURBOVAC 50) to the value of 10^{-4} mbar. The lattice parameters were obtained by Rietveld refinement of the collected XRD patterns. A Scanning Electron Microscope (SEM) was used to observe the microstructure of the sample. The thermal analyses were carried out on a thermo analyzer system Mettler TGA/SDTA 851/LF/1100. The measurements were conducted in a dynamic atmosphere of air (50 mL/min), using the alumina plates crucibles of 150 μL. The temperatures range was extent between 25 and 900°C and the heating rate was 10°C/min. The mass samples were about 25 mg.

3. Results and discussion

Fig. 1 shows the in situ XRD patterns of phase evolution CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound in air. The sample at 50°C shows a rhombohedral structure with R-3m space group [23].
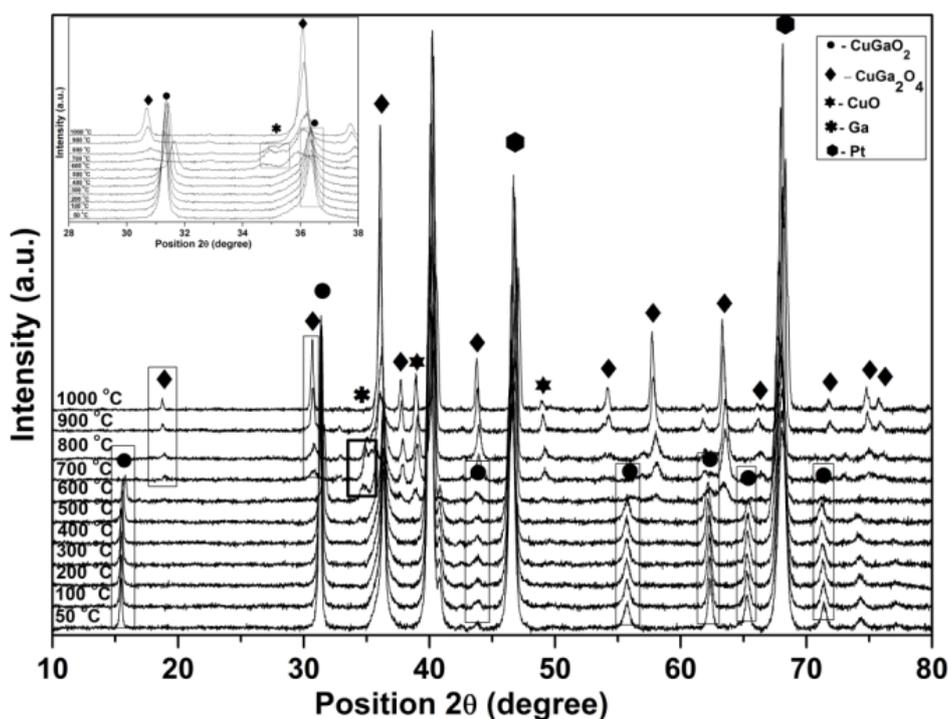
Fig. 1. X-ray diffraction patterns of phase evolution at different temperatures CuGa$_{0.95}$Fe$_{0.05}$O$_2$ in air

From XRD diffraction spectra, it can be seen that the stability of the compound CuGaO$_2$ in air is up to 500°C. This temperature is about 140°C higher than the temperature reported by Kumekawa et al [24]. The peak position of 2θ = 15.671°, decreases in intensity with the increasing of the temperature. With increasing the
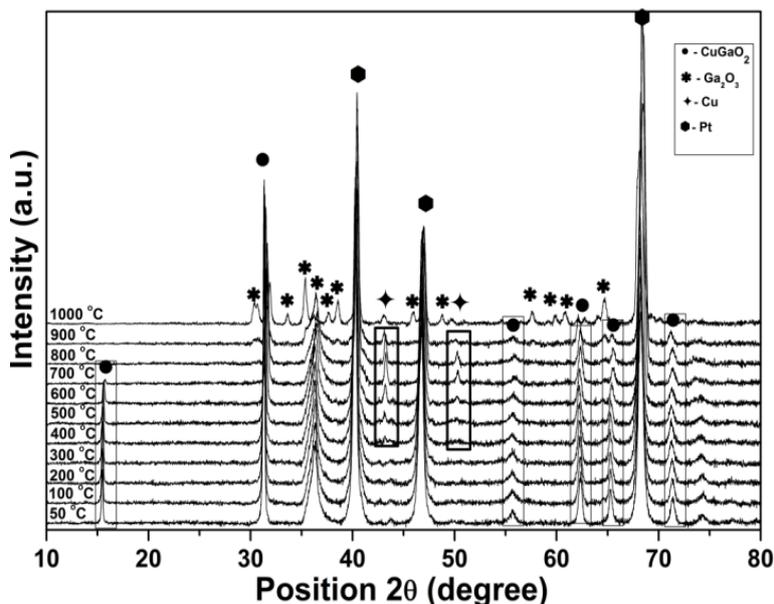
Fig. 2. X-ray diffraction patterns of phase evolution at different temperatures
$CuGa_{0.95}Fe_{0.05}O_2$ in vacuum

temperature over 600ºC, the peak disappears, thus forming other characteristic peaks (2θ = 18.910º, 30.784º, 37.878º, 43.867º, 58.068º, 63.546º) of spinel phase $CuGa_2O_4$ (00-026-0514), with a space group of Fd-3m and cubic symmetry. The intensity of these peaks increases with increasing the temperature. However, in the range of 600 - 1000ºC there is a transition of the delafossite structure in spinel structure, due to the copper (I) oxidation to cupper (II). The same thing was observed by Yong-Hun Cho et al [25], for $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ compound.

Besides the spinel phase appear two peaks (2θ = 38.898º, 48.945º) belonging to the CuO compound (00-001-1117). The oxidation of Cu_2O to CuO is due to the presence of oxygen in the atmosphere according to the reaction 1.

$$4CuGaO_2 + O_2 \xrightarrow{600ºC} 2CuO + 2CuGa_2O_4 \qquad (1)$$
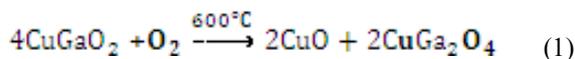
Between the temperatures 600-800ºC, appears a peak to 2θ = 34.945º, which cannot be identified. Platinum peak at (2θ = 40.766°, 47.327°, 69.005°) is given by the support that it provides sample.

Fig. 2 shows the in situ XRD patterns of phase evolution $CuGa_{0.95}Fe_{0.05}O_2$ compound in vacuum. From XRD diffraction spectra, we see that the stability of the $CuGa_{0.95}Fe_{0.05}O_2$ compound in vacuum is up to 300 ºC. The thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ compound in vacuum is about 200ºC low than thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ compound in air. Over the 300ºC is formed two characteristic peaks (2θ = 43.274º, 50.404º) of metallic copper (00-003-1005). This apparition of copper metal is due to the reduction of some Cu ions in cooper metal phase at high temperature. The same thing was observed by Te-Wei Chiu et al. when using a controlled gas environment (mixture of 5% hydrogen in nitrogen gas) [26]. This mixture of phases $CuGaO_2$ and Cu maintained
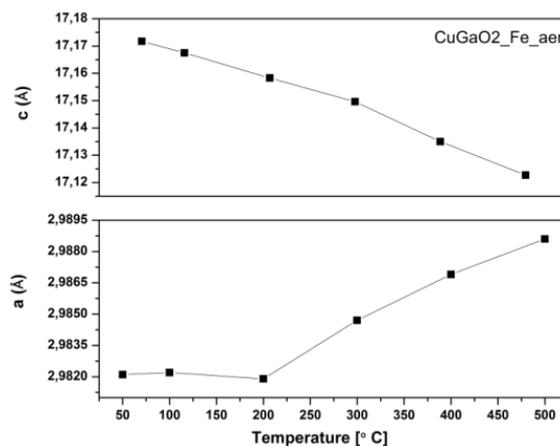
Fig. 3. Variation of a and c unit cell parameters for
$CuGa_{0.95}Fe_{0.05}O_2$ in air at different temperature
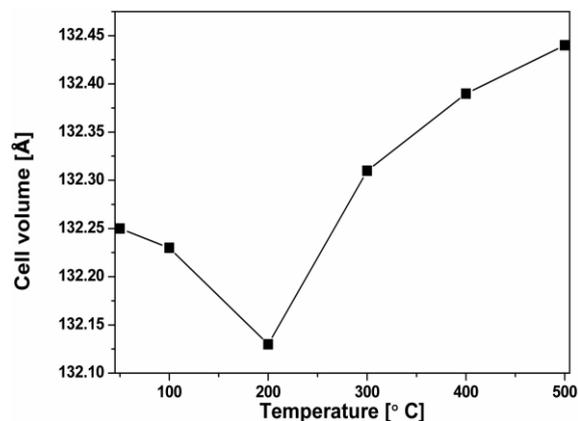
Fig. 4. Variation of cell volume parameters for
$CuGa_{0.95}Fe_{0.05}O_2$ in air at different temperature
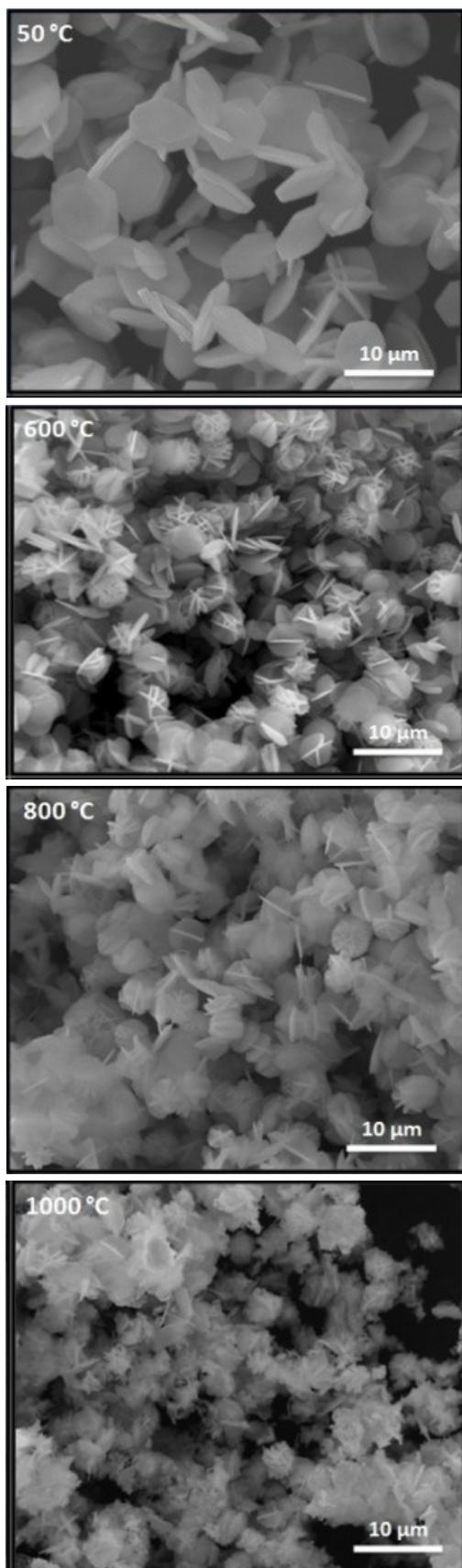
Fig. 5. SEM images of the CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound in air at different temperatures

until at a temperature of 900ºC. Above this temperature delafossite phase are destroyed thereby characteristic peaks appear Ga$_2$O$_3$.

Fig. 3 shows the variation of *a* and *c* unit cell parameters for CuGa$_{0.95}$Fe$_{0.05}$O$_2$ in air at different temperature. The value of *a* and *c* parameter values for CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound are in very good agreement with most of those previously reported for powders a = 2.9821(6) Å and c = 17.1717(3) Å [23].

The unit-cell volumes (figure 4) decrease with the increase of the temperature up to 200°C, and then increase with the increase of the temperature up to 500°C. The decrease of the unit cell volume is due to the difference of the ionic radius as Ga (r_{Ga}^{3+} =0.63 Å) is substituted for Fe (r_{Fe}^{3+} =0.645 Å) [27, 28].

The morphology of the compound CuGa$_{0.95}$Fe$_{0.05}$O$_2$ in air was observed by scanning electron micrography at high resolution as shown in figure 5. From SEM image, it is obvious that the size distribution of the product is micrometric. With the increase of the temperature it can be seen that the morphology of the particles are change up to 600ºC and then at 1000 ºC phase is destroyed.

The thermogravimetric (TG) curve of crystalline CuGa$_{0.95}$Fe$_{0.05}$O$_2$ compound in the range of 25–900ºC are shown in Fig.6. According to the literature a different behavior can be seen at CuGaO$_2$ in air compared with CuCrO$_2$ and CuAlO$_2$. From 25°C to 600°C it can be seen a loose mass around the -1.58 % (x= 0), and -0.36% (x= 0.05). According with Kumekawa et al. the decomposition reaction takes place when the temperature is higher than 350°C; after this temperature the oxidation of Cu(I) in air would cause the formation of CuO and CuGa$_2$O$_4$, according to the reaction (1) [24].

Starting with the temperature of 700°C, there was an increase of mass of 3.49 % for (x= 0) and 3.77 % for (x= 0.05). The results are consistent with HT-XRD study performed in air which highlights the appearance of CuO crystalline phase at 700 ºC (Fig.1).
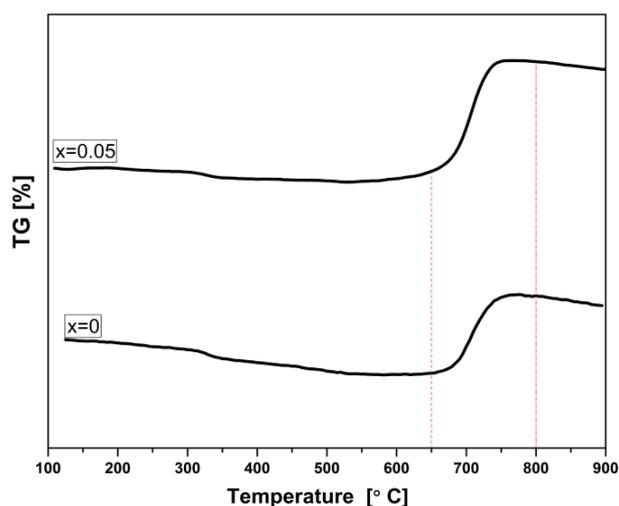
Fig. 6. TG-DTA curves of Fe doped CuGaO$_2$ at heating procedure with rate of 10 °C/min in air

4. Conclusions

The thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ compound obtained by hydrothermal method was performed using *in situ* variable temperature chamber (HT-XRD), and thermogravimetric curve (TG). The temperature at which the material tends to become unstable was found to be 600°C. According to the XRD and TG measurements exist two temperature domains corresponding to the thermal stability of $CuGa_{0.95}Fe_{0.05}O_2$ (25 - 600°C) and to the destabilization of $CuGa_{0.95}Fe_{0.05}O_2$ phase (600 - 1000°C) have been determined.

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*Corresponding author: nicolae.vaszilcsin@upt.ro