Correlative X-ray microscopy measurements in CdTe solar cells

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Abstract

Synchrotron X-rays are considered ideally suited to studying PV systems. Because it allowed to research electronic defects at grain boundaries, what is a weakest part in solar cell.

The one of the most promising methods in correlative X-ray spectroscopy is XBIX methods, because it can be combine with X-ray fluorescence and XANES technique.

On this report we will focus on analyzing XRF measurements and finding chemical environment of Cu through 4 different samples of CdTe with incorporated Cu.

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1 Introduction

Throughout the history existence of human, the people have always tried to find new more efficient sources of energy, starts from coal fuel and all the way up to atomic energy. But unfortunately almost all of the sources were non-renewable resources and destructive to the environment.

Interest in new ways of generating energy increased due to the fact that starting from about 2000, environmental issues and economic issues started to become more and more important in the public discussion.

It is in has time that in interest in solar energy began to rise.

Solar energy begins with the sun. Light from the sun is a renewable energy resource that provides clean and cheap energy, produced by solar panels.

Already in 2012 the world-wide solar energy capacity surpassed the magic barrier of 100 GWp [1]. Between 1999 and 2012, the installed PV capacity hence has grown with a factor 100. In other words, in the last 13 years, the average annual growth of the installed PV capacity was about 40%. [1]

Despite this solar panels are still not as popular as it could be. It still require study and refinement to obtain the best characteristics and parameters for implementation in daily life.

The working principle of a solar cell is based on the photovoltaic effect, i.e. the generation of a potential difference at the junction of two different materials in response to electromagnetic radiation.

Working mechanism of a solar cell can be divided into several steps

- Photons in sunlight hit the solar panel and are absorbed by semiconducting materials, such as silicon.

- Electrons are excited from their current molecular/atomic orbital by absorbing incident photon. Once excited an electron can either dissipate the energy as heat and return to its orbital or travel through the cell until it reaches an electrode. Current flows through the material to cancel the potential and this electricity is captured. The chemical bonds of the material are vital for this process to work, and usually silicon is used in two layers, one layer being doped with boron, the other phosphorus. These layers have different chemical electric charges and subsequently both drive and direct the current of electrons.

- An array of solar cells converts solar energy into a usable amount of direct current electricity. inverter can convert the power to alternating current.

Solar cell can be of the following types: specifically single-crystal, polycrystalline and thin-film among many others. Different solar cell have different efficiency of light energy conversion. Figure 1 shows diagram of the comparison of efficiency for solar cells of different types.

There are many challenges to overcome the abundance of materials can be an issue [2] [**?**]; efciency and lifetime of modules need to be improved for lower levelized cost of electricity (LCOE) and a smaller ecological footprint; materials need to be recycled, and less energy-intensive processes and materials need to be found to reduce the energy-payback time. These challenges demand a high level of continuous research in the eld of PV, and although many of the effects are visible at the module level, their causes lie at the nanoscale, which elicits the need to investigate the materials
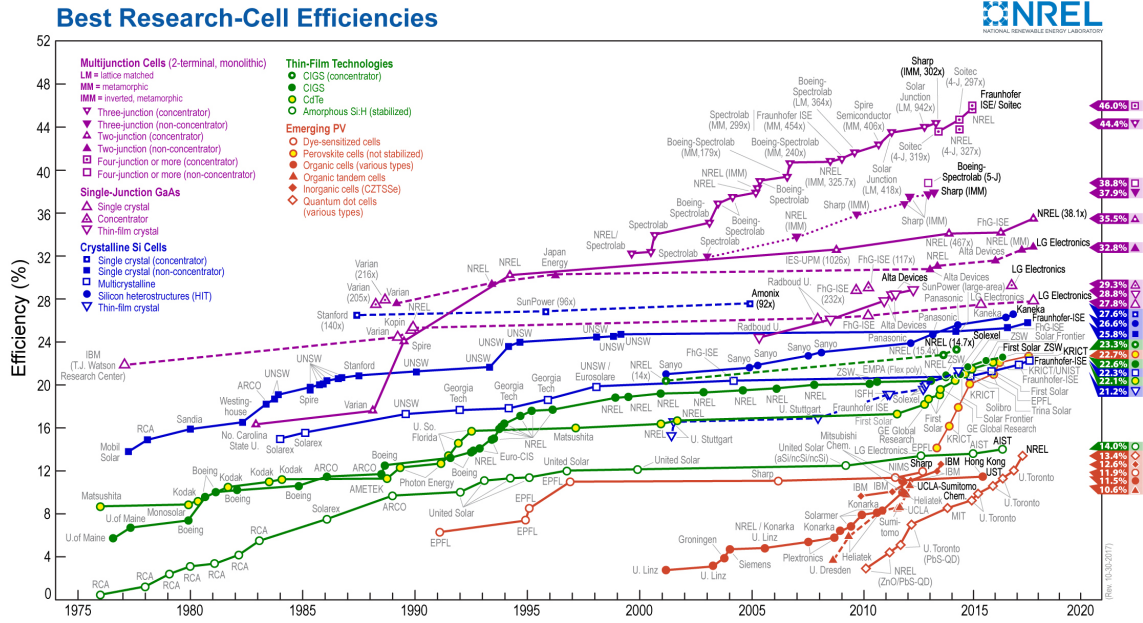
Figure 1: Reported timeline of solar cell energy conversion efficiencies (National Renewable Energy Laboratory).

at that scale. Moreover, cell efciencies get closer to their theoretical limits and complex device architectures are being sought. Therefore, the engineering approach for the design and optimization of solar cells calls for advanced characterization methods [3] [4].

Given that optimization steps at higher levels are generally less efcient, these processes could directly benet from *in situ* and *operando* approaches, by which functional materials with defects can be understood rather than optimized by empiricism, and designed rather than found by chance.

Hard X-rays have unique capabilities well suited to probe complex materials and devices. They have excellent penetration of capping layers and interfaces, enabling 3D imaging of full devices and buried structures. They can penetrate gases and liquid, enabling studies at pressure, and under process conditions. They allow quantitative studies of sample composition with trace element sensitivity in structured materials and devices. Chemical-state information of individual atomic species can be obtained using X-ray spectroscopic techniques. X-rays do not interact with external elds, and thereby enable studies in electric or magnetic elds. With the development of optics capable of focusing hard X-rays to ever smaller dimensions, hard X-ray beams with sizes of 50 nm and well below now allow probing nanoscale regions of materials and devices. As such, they are capable of studying the compositional and structural properties of defects, inhomogeneities and gradients in devices and functional materials, under a large variety of synthesis and operating conditions.

Soft X-rays do not offer the high penetration of hard X-rays and related advantages for in situ measurements and probing of encapsulated solar cells. However, they are more sensitive to light elements that are particularly important for organic solar cells or as trace elements impurities in solar cells with inorganic absorber layers.

So in correlative microscopy there are a multitude of methods which performe different tasks and help can be used to achieve the desired goals.

One little-known but promising and significant method in the study of solar cells
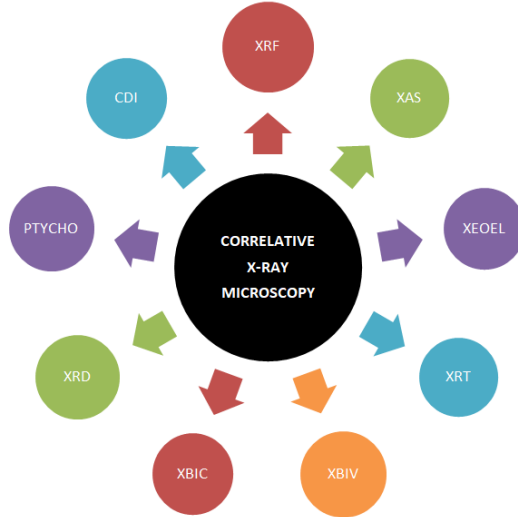
Figure 2: Methods of X-ray microscopy.

is XBIC. It was proposed and implemented in 2002 (reference) at the source of synchrotron radiation. In this method, a focused X-ray beam serves as a source of nonequilibrium carriers.
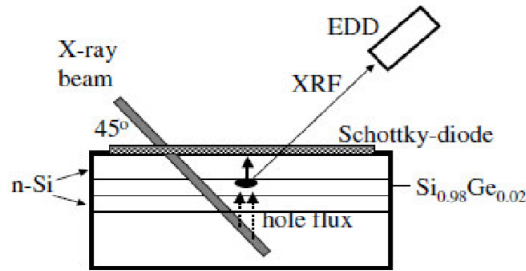

Figure 3: The scheme of measurements of the X-ray fluorescent signal realized on a synchrotron.

A huge advantage of the XBIC method is that can be combined with other X-ray methods, such as X-ray fluorescent microanalyses$(\mu - XRF)$, and a method for analyzing the fine structure of the absorption spectra$(\mu - XAFS)$, which provides additional information on the chemical composition of the impurities in the sample. [5]

The behavior of solar cells is very often limited by inhomogeneously distributed nanoscale defects [6]. Furthermore, inhomogeneities in the elemental distribution of multi-component thin-lm semiconductors such as CdTe, CIGS, and perovskites can play an important role [7]. For decades, polycrystalline absorbers like CdTe and CIGS with adjacent junction and contact layers have been optimized following a trial-and-error approach, and the development of different layers for perovskite solar cells has followed similar trends. At the initial stages of a technology development this approach is powerful. It has led to remarkable solar cell efciencies of 22.6% (CIGS), 22.1% (CdTe), and 22.1% (perovskite);26 all of which now outperform multicrystalline silicon (mc-Si) solar cells with a maximum efciency of 21.3% [8].

The next step in device optimization requires ne tuning and signicant improvement of the fundamental understanding of limiting defects.

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Therefore, it is necessary to investigate the electrical properties of individual precipitates and structural defects in order to increase the efficiency of solar cells.

But for the quantitative characterization of recombination-active defects by the VLSI method, methods should be developed for calculating the induced current for extended defects so as to determine the defect parameters from a comparison with the measured contrast. However, for the XBIC method, such models have been developed poorly (have not yet been developed).

The analysis of thin film solar cells can also be successfully performed with XRF. It is possible to measure the structures both in air and under vacuum. The absorption in air for the lowest energies of interest is aceptable. Thus this method can be comfortably used for in-line control during the production process as well as for final testing. [9]

1.1 Method of X-ray fluorescence spectroscopy

The aim of this project was to study the XBIC method, and answer to the question what is the difference between XANES from XRF, and XANES from XBIC measurements. Unfortunately, due to lack of time, only X-ray fluorescence measurements have been studied. Thus, let us first look at this method in more detail
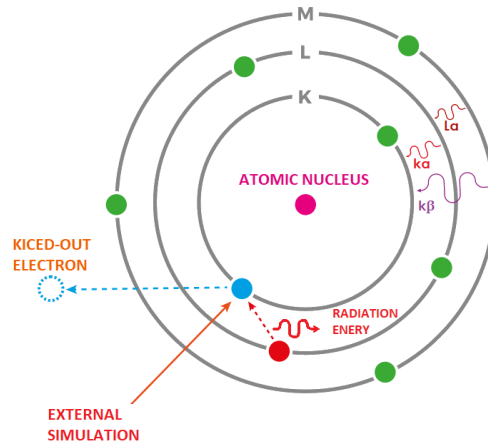

Figure 4: X-ray fluorescence process.

X-ray fluorescence (XRF) is the emission of characteristic "secondary" X-rays from a material that has been excited by bombarding with high-energy photons. When an atom is irradiated by electromagnetic radiation having suggestion energy, it absorbs an incident photon and expels an electron from an inner shell this is photoelectron. The rearrangement of the remaining electrons between the levels of the atom involves the emission of a photon X whose energy is characteristic of the emitter atom. The physical phenomenon of fluorescence X is widely used by modern spectrometers for elemental an chemical determination on materials like metals, ceramics, glasses etc.

The key components of a typical XRF spectrometer are:

- Source of X-Rays used to irradiate the sample.

- Sample.

- Detection of the emitted fluorescent X-Rays.
The resulting XRF spectrum shows intensity of X-Rays as a function of energy.

The X-ray fluorescence spectrum of atoms of one element will consist of several signals. The characteristic X-ray spectrum has a linear character; each line corresponds to a specific transition. In the spectra of X-ray fluorescence, the most intense are the radiative transitions to electron vacancies in the K shell (K-lines of the spectrum) for sufficiently "heavy" elements, also transitions to vacancies in the L-shell (L-lines of the spectrum)

For quantitative analysis, what is used is the so-called "fundamental parameter method", a numerical calculation algorithm that, from the theoretical knowledge of the fluorescence process, allows to obtain quantitative data on sample composition

1.2 Structure of CdTe solar cell

CdTe solar cell is II-VI semiconductor because it consists of the II valence electron element cadmium (Cd) and the VI valence electron element tellurium (Te). CdTe forms a zincblende lattice structure where every Cd atom is bonded to four Te atoms and vice versa. The band gap of CdTe is 1.44 eV, a value which is close to the optimal band gap for single junction solar cell. CdTe is a direct band gap material, consequently only a few micrometres of CdTe are required to absorb all the photons with an energy higher than the band gap energy.
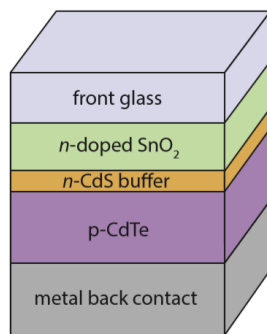
Figure 5: The layer structure of a typical CIGS solar cell. Band diagram data taken from.

If the light-excited charge carriers should be efciently collected at the contacts, their diffusion length has to be in the order of the thickness.

Figure 5 shows the structure of a typical CdTe solar cell. First, transparent front contact is deposited onto the glass superstrate. This can be tin oxide or cadmium stannate, which is a Cd-Sn-oxide alloy. On top of that the n-layer is deposited, which is a cadmium sulfide layer. Then, the p-type CdTe absorber layer is deposited with a typical thickness of a few micrometres.

Making a good back contact on CdTe is rather challenging because the material properties of CdTe do not allow a large choice of acceptable metals. Heavily doping the contact area with a semiconductor material improves the contact qualities, however, achieving high doping levels in CdTe is problematic.

CdTe can be p-doped by replacing Cd with a I-valence electron atom like copper, silver or gold.

Copper containing contacts have been used as back contacts, however, in the long term they may face instability problems due to diffusion of Cu through the CdTe layer up to the CdS buffer layer.

2 Experiment details

2.1 Material

For the study were selected 4 sample of high-efficiency solar cell with an absorber layer made of p-doped Cd with a I-valence electron atom like copper.

Of particular interest in these solar cells is the distribution of the dopant Cu, and its chemical environment.

It was been using two different methods to incorporate Cu into CdTe, what would called in further work method 1 and method 2. Both processes involve an annealing step.

2.2 Experiment

In the course of the experiment was measured the composition (by X-ray fluorescence) as well as the electrical performance (by X-ray beam induced current), at the nanoscale using the ESRF synchrotron beamline ID16B (France). And also was taken XANES measurements at different spots.

But we will consider experiments related with XRF measurement. During these experiment, 10 channels were used. All measurement data can be divided into two groups by length of energy scale: short spectra were obtained with an energy value of 8.95-9.10 keV and long ones with an energy value of 8.9-9.5 keV with the number of steps 300.

So for each measurement, we have a matrix of 300 x 2048 points that represent incident X-ray energy, and XRF energy channels.

The sample was examined in two positions of interest, namely in the part of the sample where the Cu quantity (intensity) was the largest (it is the brightest parts on element maps), the so-called Berg sites, and in the place where this intensity was the smallest - Tal sites(the darkest parts on element map). Figure 6 shows the element map with Te concentration.
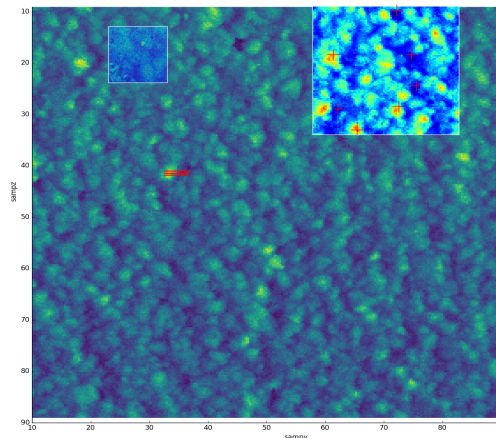

Figure 6: Element map for Te.

3 Analysis experimental data

3.1 Research

For data processing, it was first necessary to access them, since the synchrotron data is written in the "edf" type. To solve this problem, the code was written using the Python package.

First of all to read edf files was used python code, which is a part of the X-ray Fluorescence Toolkit developed at the ESRF by the Beamline Instrumentation Software Support (BLISS) group.

The direction of the matrix having 300 values is responsible for changing the intensity of the signal for different energy values, so summation over a scale of 0 to 300 for one column gives the intensity value for certain channel, that range from 0 to 2048.

These calculations were also performed using Python. The graph plotted from the obtained values is a fluorescent spectrum, with the difference that the intensity depends on the channel number, not on the energy as usual. To obtain the dependence of channel number on energy, we used the Pymca program [10].

To convert it into energy, we need to make a calibration file. Knowing the composition of the sample, we found two bar corresponding to the energies of fluorescence line for Cu and Te, the mean energy are shown in the Table 1.

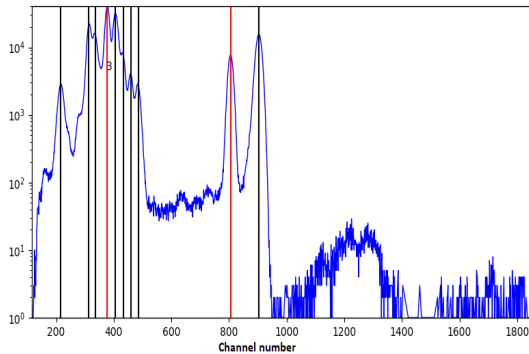| Chanel	Element	Line	Calc. Energy
805	Cu(29)	KL3 (0582)	8.0478
377	Te(52)	L3M5 (0.76151)	3.7693

Table 1: The value of energy for the fluorescent lines

This allowed us to compare the channel number and the known energy value. And the software will then calculate parameters to transform channels into energy by using function:
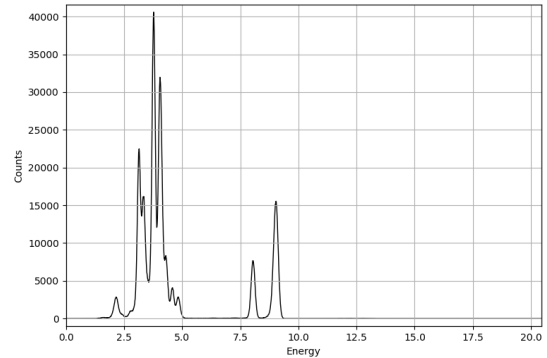
$$F(x) = A * energy + B$$

$$A = 0.00062$$

$$B = 0.00999$$

(a)   (b)

Figure 7: Fluorescence spectra depends on channel number(a) and on energy keV(b).

As a result, the dependence of the intensity on energy was obtained, which is a normal fluorescence spectrum.

The next step was to integrate the intensity peak for Cu. As the integration limits, the energy values from channel number 786 to 828 as shown on Figure 8.
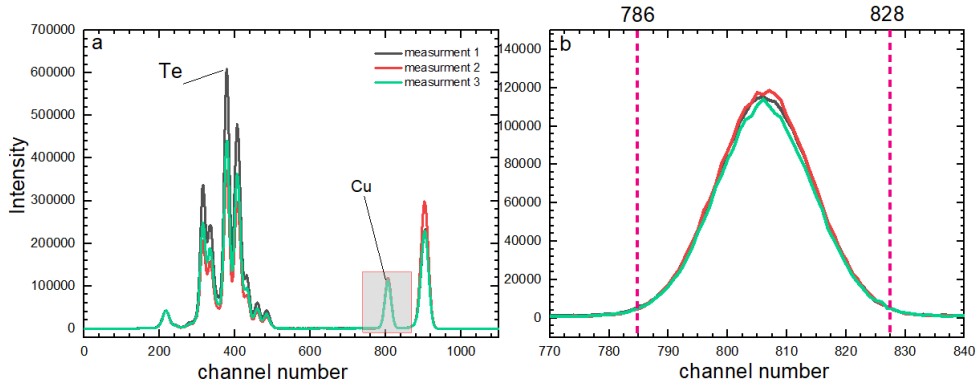

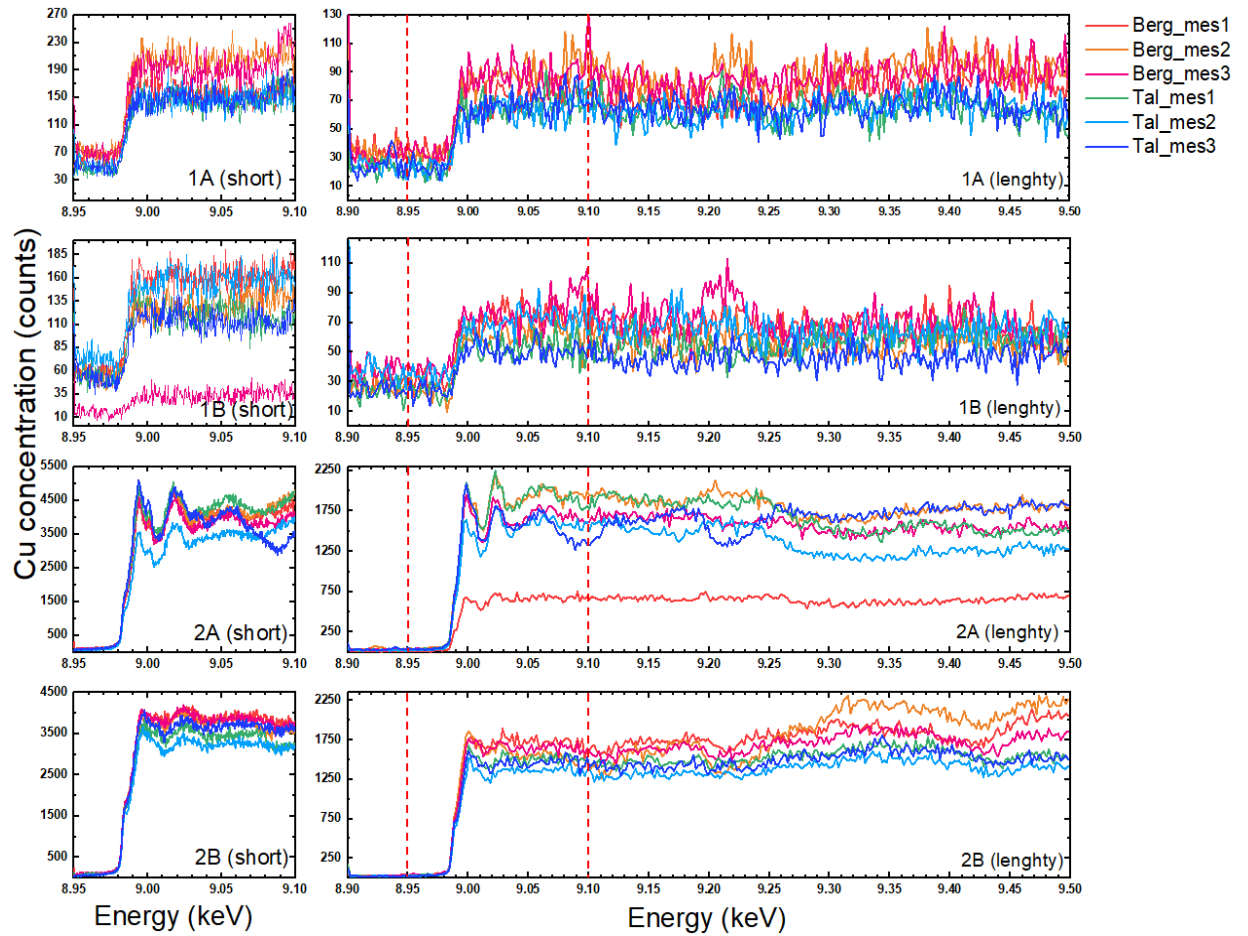Figure 8: Integration of Cu peak for sample 2A "Berg" zone.

Figure 9: Intensity of Cu peak for 4 samples by X-ray fluorescence.

This operation was carried out with all measurements. For each point in the sample three measurements were measured, so we summarized the obtained data for one measurement and constructed this dependence on the energy.

These steps gives to us graphics intensity for Cu peak for all samples that shown on Figure 9.

4 Conclusions

The intensity of Cu in samples 1A and 1B is smallest, so the first process of syntheses leads to less Cu concentration in solar cell.

In graphic for sample 1A we can observe difference between measurements from areas with the higher concentration (Berg zones) and less concentration (Tal zones). So Berg zones have higher Cu concentration than Tal.

But due to strong noise on the graphs for samples 1A and 1B we cant say much more about these samples. Graphics for sample 2A and 2B are much suitable for further analyzing.

There is a difference between annealing and not annealing samples, this is evident from the graphic for samples 2A and 2B. As sample 2A is annealing, then we can say that it leads to chemically well-defined state.

5 Future goals

It should be noted that these spectra are a little bit similar to XAS spectra. Therefore, in the future it is assumed that we will be able to analyze the spectra obtained with the help of Athena software (created specially to analyze XAS measurements) [11].

As the electrical performance was also measured by X-ray beam induced current and XANES measurements were taken at different spots on sample, our future goals are to analyze XBIC data and quantify and also analyze XANES.

Also as we know that annealing samples have chemically well-defined state it is interesting to find which state they have.

Future goals are to use the correlative X-ray spectroscopy methods to understand solar cells defects much more.

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