Experimental evidence of the oxidation state through resonant Raman scattering

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INTRODUCTION

When atoms are irradiated by x-ray photons different kinds of interactions take place: the photn can be absorbed by the photoelectric effect or can suffer a Rayleigh or Compton scattering. However, under resonant conditions other low probability interactions can occur. One of these interactions is the resonant Raman scattering (RRS) [1].

The x-ray resonant Raman scattering is an inelastic process which presents fundamental differences compared to other scattering interactions between x-rays and atoms; when the energy of the incident photon approaches from below to the absorption edge of the target elemet, a strong resonant behavior takes place contributing to the attenuation of x-rays in matter. According to the absorption-emission model the RRS process can be represented by three steps [2]: 1) the initial state consists of an incident photon with an energy below, for example, the K threshold 2) a hole is produced in the K shell and the excited electron is ejected to an unoccupied state; an electron from a higher shell fills the vacancy and a photon is emitted 3) the final state consists of a hole in a higher shell, a scattered photon and an excited electron in the continnum or in a bound excited state

The resonant character of the process and the existence of an onset energy in the RRS spectrum enable the probing of the edge structure characteristics by tunning the incident energy towards the edge. In the case of oxide compounds, the Raman peak changes the maximum energy (corresponding to an excited electron with kinetic energy equal to zero); the Raman peak shifts to energies lower by a few elctron volts due to the change of the absorption edge energy [3]. By employing a low resolution detecting system, changes in the RRS structure can be observed, providing the possibility of identifying the elements of a sample and their oxidation state [4] [5]. This is an important fact since the chemical bonding of an element affects the emission of its characteristic x-rays; the formation of chemical bonding causes a migration of the valence electrons among participant atoms, reducing screenig effects and increasing their inner shell binding energies.

EXPERIMENT

The samples consisted of pure foils (> 99.99%) of Cu with a thickness of 7.5 μm oxide foils (> 99%) CuO and Cu3O with thicknesses 1.25 mm and 1.3 mm respectively.

These samples were irradiated with monochromatic photons of 8915 eV, i.e., below de absorption edge of the elements of interest (cooper) to inspect the Raman emissions.The measuring livetime was 2500 sec.

As a very good knowledge of the absorption edge energy is needed during the calculations, a further scanning in every sample was performed in order to determine the edge energy. It was attained by a scannings of about 40 eV in steps of 1 eV around the absorption edge with a measuring livetime of 5 sec.

The measurements were carried out in XRF station of the D09B-XRF beamline[6] at Brazilian synchrotron facility (LNLS, Campinas)[7]. The XRF beamline is equipped with a double crystal channel cut monochromator, the energy resolution of the monochromator is 3 eV at 10 keV using a Si(111) crystal. For the measurements performed in this work, the incident beam was collimated with orthogonal slits to 1x1mm and monitored with ionisation chambers. The detection systems are energy-dispersive setups composed by several solid-state detectors with different windows and different electronic chains. The detector used in this work was an Ultra-LEGe solid-state detector with a Be windows of 8 μm and an energy resolution of 158 eV for the Mn Kα line. The experimental geometry was the typical 45°+45° configuration on the electron orbit plane to reduce Compton and Rayleigh scattering.

Spectra were analyzed with specific programs for spectrum analysis (Peakfit[8]) using non-conventional functions for data fitting, i.e., modified Voight functions (for Compton peaks), gaussian functions for fluorescent peaks and for low intensity peaks , and polynomial functions for the background. Raman peaks were fitted using specific functions.

RESULTS AND DISCUSSION

The first step of the analysis is to determine the absorption edge energy of the target elements; this stage has the aim of establish certainly whether the sample is excited under resonant or fluorescent conditions. This stage is attained by applying the well-known method of inspecting the derivate change of the emitted intensity on the edge rising vicinity. The obtained values were (8.978+/-0.005) keV for Cu, which are in agreement with the tabulated (8.979 keV[9]). The measured absorption edge energies for the oxide oxides were (8.982+/-0.005) keV for CuO and (8.979+/-0.005) keV for Cu2O.

Figure 1, shows a spectrum of the RRS peak of Cu. Solid line represents the fitting curve described in previous papers. As it should be expected, the Raman scattering process is resonantly enhanced as the energy of the incident photons is closer to the K absorption threshold and the Raman peak (on the left)

is more intense, dominating over the Compton peak (on the right). This behavior was observed in all the samples. In the
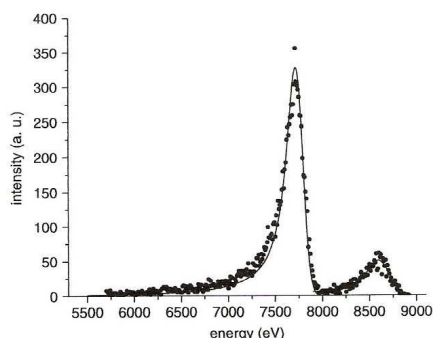

FIG. 1: RRS spectrum for Cu

case of oxides, the Raman peak changes the maximum energy (corresponding to an excited electron with kinetic energy equal to zero). Each Raman peak shifts to lower energies a few electron volts due to the change of the absorption edge energy. However, peak areas of pure elements were quite similar to those of oxides and no significant changes were observed.

After fitting, the residuals were calculated. Figure 2 shows these data starting on low energies and finishing right before the center of the Raman peak. A FFT smoothing procedure was applied considering a gaussian instrumental-function with a σ of 67 eV. The low energy tails of the Raman peaks, after smoothing are shown in Figure 3.
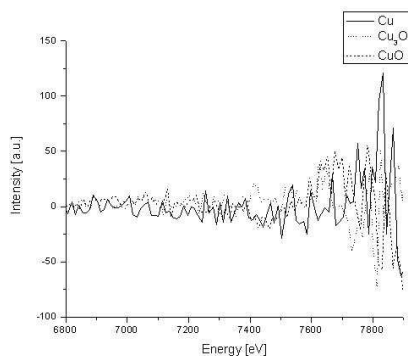

FIG. 2: RRS residuals before smoothing

CONCLUSION

The figures referred above show the existence of a clear difference among the measured samples, i.e. the oxidation states of copper. These results suggest the possibility of structural characterization by means resonant Raman scattering using

an energy-dispersive system combined with synchrotron radiation. Further investigations and measurements are needed
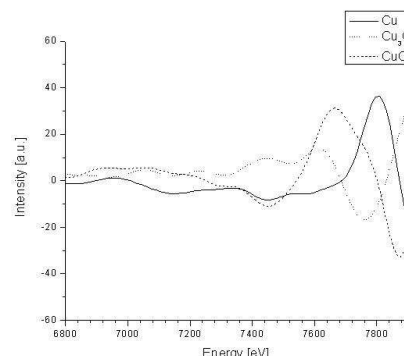

FIG. 3: RRS residuals after smoothing

for a better understanding of the processes involved and the implementation of a practical procedure.

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