

X-Ray Powder Diffraction and Raman Spectroscopy

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Abstract

This work reports two different Advanced Laboratory experiences in XAS facilities: XRPD and Raman spectroscopy. XRPD (X-ray powder diffraction) analysis is used on a nanocrystalline bismuth sample to estimate nanocrystallites average size. Characterizing a new instrument for Raman spectroscopy (Horiba iHR320), this device was set on different conditions varying magnification and grating. Then it was compared to spectra in literature.

X-ray diffraction analysis

Crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is a common technique for the study of crystal symmetries, the values of lattice parameters, the structure of the unit cell and crystallite size. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law $n\lambda = 2d \sin \theta$. A single crystal would produce only one family of peaks in the diffraction pattern. Using a polycrystalline sample, which contains thousands of crystallites, all possible diffraction peaks should be observed. Crystallites of the order of nanometers produce a spreading of diffraction peaks which allows to determine the average crystallite size L , using the Scherrer equation

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}, \quad (1)$$

where $B(2\theta)$ is the Full Width Half Maximum (FWHM), $K = 2\sqrt{\ln 2/\pi} = 0.94$, λ is the incident wavelength and θ is the diffraction angle.

Experimental setup

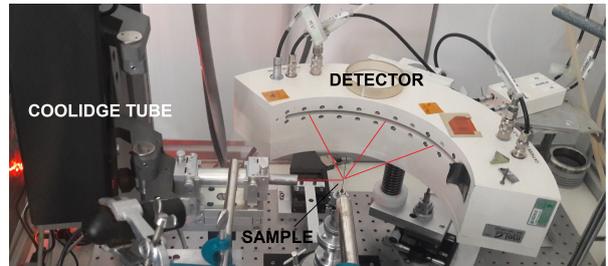


Figure 1: Experimental setup.

The X-Ray source in the setup (fig.1) is made by a Coolidge tube. The electrons are produced by thermionic effect from a tungsten (W) filament heated by an electric current of 15 mA under good vacuum condition (10^{-5} Pa). The electrons are thus accelerated by an high voltage potential

of 40 kV between cathode (the filament) and molybdenum anode. X-Rays emitted by the anode pass through a monochromator (graphite crystal) to have a beam of wavelength $\lambda = 0.7093\text{\AA}$ (the characteristic wavelength of radiation $K\alpha_1$ given by molybdenum) and through a divergence slit to limit the divergence of incident beam. After the sample there's a curved position sensitive detector (120 degrees). The diffracted beam ionizes the gas (Krypton) inside the detector; the electrons are thus accelerated by a voltage potential and generate an electric signal which, after an electronic counting (analog to digital converter an multi-channel analyzer), gives the exact matching intensity-angular position.

Measures and data analysis

The powder sample is nanocrystalline bismuth in antimony glass matrix. For this experiment bismuth has been prepared in a furnace for 50 hours, while reference sample spectrum (crystalline bismuth) was provided by professor. Because of high absorption of X-Rays, instead of filling a capillary (100 μm of thickness), it is coated by the powder using vacuum silicone for adhesiveness. The capillary is fixed perpendicularly to the instrumentation by an adjustable device (a microscope). Using this capillary as sample, after the calibration, it was obtained the diffraction pattern of the intensity versus 2θ (fig.2).

Using the Scherrer equation (1), with parameters of table 1, the average size of nanocrystallites is 6.37 nm. This is a lower limit of average dimensions of nanocrystallites because width of peaks must take into account the instrumental contribution.

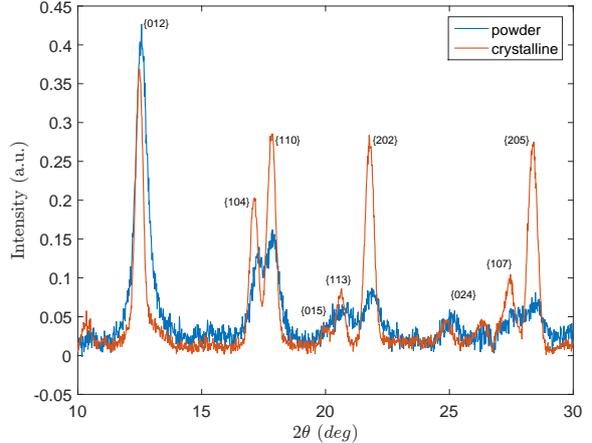


Figure 2: Diffraction pattern of nanocrystalline (blue line) and crystalline (red line) bismuth.

Peak	FWHM	2θ
{012}	0.61	12.45
{104}	0.61	17.31
{110}	0.61	17.98
{015}	0.61	20.22
{113}	0.61	20.82
{202}	0.61	21.94
{024}	0.61	25.06
{107}	0.61	26.51
{205}	0.61	27.19

Table 1: Parameters obtained by fitting experimental data using *Fityk* software. It was used a built-in tool for XRPD pattern, which determines a fixed FWHM for every peaks (Miller indices notation).

Conclusions

Comparing the two different diffraction patterns (fig.2), for nanocrystalline sample it can be observed a broadening of peaks, from which it was possible to estimate crystallites average size (eq.1), and a right shift in angle, related to cell parameters contraction [1].

Raman Spectroscopy

Raman spectroscopy is an investigation technique based on Raman effect [2]. Spectroscopy techniques' application field is wide, in particular Raman spectra are useful in determining molecular bonds in samples by phonon analysis.

When light (both visible and non-visible spectrum) shines a material, the most intense phenomenon is elastic scattering, also called Rayleigh scattering. In addition, there is an inelastic scattering and this effect is called Raman scattering. It's an inelastic process because incident radiation energy is different from emitted one. This difference energy is associated to vibrational states of the lattice of material.

$$\text{Raman shift} = \hbar\omega_{OUT} - \hbar\omega_{IN} = \pm\hbar\Omega. \quad (2)$$

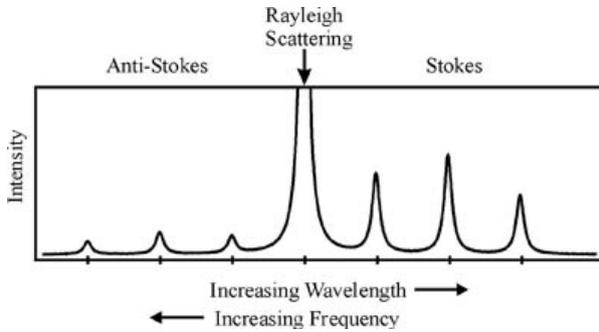


Figure 3: Simplified Raman spectrum.

Raman spectra shows two different behaviours for inelastic scattering: *anti-Stokes* branch ($E_{out} > E_{in}$) and *Stokes* branch ($E_{out} < E_{in}$).

Experimental setup

In this experience it was used a micro Raman technique which allows to collect the

maximum solid angle from the sample. The experimental setup is composed by a laser source which enters into microscope (with typical laser spot of 2-5 microns), through an optic fiber. Before and after the sample, the beam passes through optics to improve beam quality. So, the radiation passes into a spectrometer (using different gratings) and the photons are counted by a CCD camera.

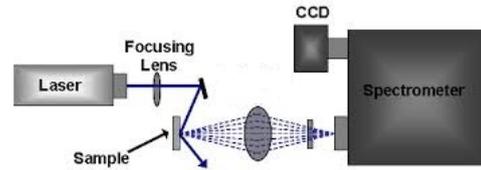


Figure 4: Experimental micro Raman setup.

Measures and data analysis

For this experiment it was used a red laser source of wavelength 633 nm to irradiate a silicon sample. Resulting spectra (intensity versus Raman shift) are obtained varying magnification (50x and 100x) and gratings (600 g/mm and 1800 g/mm). Spectra consider only Stokes branch because it is more intense than the Anti-Stokes one and a filter cuts the elastic scattering to avoid saturation of signal.

It can be observed that higher groove density of grating means greater spectral resolution.

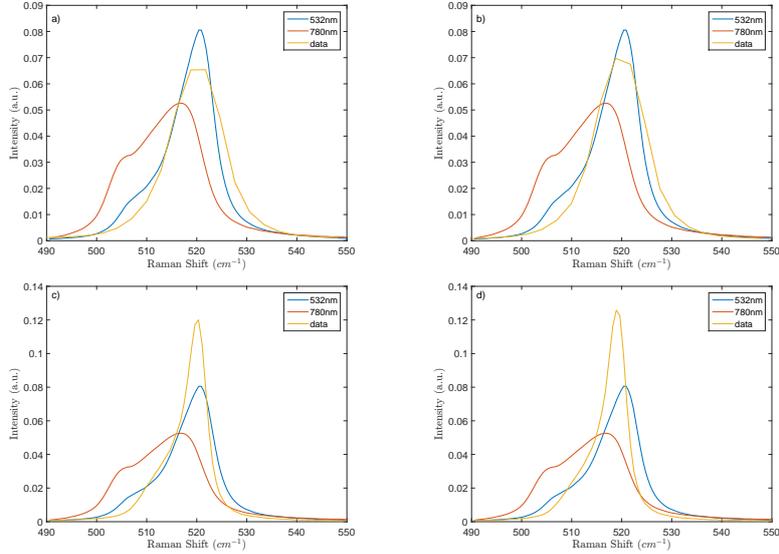


Figure 5: Experimental data (yellow line) for different magnifications and gratings: a) 50x 600 g/mm , b) 100x 600 g/mm , c) 50x 1800 g/mm and d) 100x 1800 g/mm .

Blue lines refer to RRUFF database with a wavelength of 532 nm , red ones refer to RRUFF database (<http://rruff.info/>) with a wavelength of 780 nm and yellow ones refer to data collected during this experience.

Magn. and grat.	Center	FWHM
50x 600 g/mm	519.13	30.34
	519.94	11.70
100x 600 g/mm	518.86	36.38
	519.64	11.74
50x 1800 g/mm	51673	13.74
	519.98	4.01
100x 1800 g/mm	515.89	13.69
	518.93	4.05

Table 2: Parameters obtained by fitting experimental data using *Fityk* software. For each configuration there are reported parameters of the two Gaussian peaks that compose the signal.

Conclusion

From the comparison of these Raman spectra (fig.5), for this experimental setup, it can be established that peak shape is more affected by resolution than magnification

(indeed 50x and 100x show same Raman peaks) and peak shape is strictly connected to source energy, because it is expected a greater penetration in sample for smaller wavelength.

References

- [1] Q. Jiang, L. H. Liang, , and D. S. Zhao. Lattice contraction and surface stress of fcc nanocrystals. *The Journal of Physical Chemistry B*, 105(27):6275–6277, 2001.
- [2] A. Zwick and R. Carles. Multiple-order raman scattering in crystalline and amorphous silicon. *Phys. Rev. B*, 48:6024–6032, Sep 1993.