Experiment 4. Characterization of Nanomaterials by X-ray diffraction (XRD)

Leonardo Clemente, Arturo Cevallos, and Luis Garza
Tecnológico de Monterrey, Department of Chemistry and Nanotechnology, Campus Monterrey

Abstract. X-ray diffraction (XRD) is a very useful technique to identify crystalline materials. In this session Al, Si and two samples of PbI_2, obtained by two different procedures, were characterized using XRD. Their respective diffractograms were retrieved and later compared with data taken from the American Mineralogist Crystal Structure Database. The differences inbetween both samples of PbI_2 were studied in further detail.

I. INTRODUCTION

X-ray diffraction (XRD) is a macroscopic characterization technique developed in the XXth century; important for the study of the properties and structures of materials. Given it's nondestructive nature, it's helpful for when a large amount of information is needed from small and/or scarce samples. Also, it's unique in that components are identified as specific compounds [3]. Nowadays, XRD remains popular as it is practical, characterization times tend to be less than an hour, unambiguous, it doesn't require too much material and it relies on strong yet simple physical concepts [2].

There are some drawbacks though, given that since it involves diffraction, the identification of substances is limited to crystalline compounds [3]. A solid material whose constituents, be them atoms, molecules or ions, are arranged in a highly ordered microscopic structure. X-rays incident on these type of materials scatter in an specific way based on their internal structure or "cell". Bragg's model gives a basic explanation of the phenomena. However, if the need arises to identify, for example, a liquid organic compound it's frequently possible to transform it into a crystalline derivative that would have a characteristic, identifiable pattern. [3]

XRD relies on Bragg diffraction. This occurs when radiation, with wavelength comparable to the spacing between the atoms, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference. For a crystalline solid, the waves are scattered from lattice planes separated by the interplanar distance d. When the scattered waves interfere constructively, they remain in phase since the difference between the path lengths of the two waves is equal to an integer multiple of the wavelength (Bragg's Law, eq. 1) [7].

Bragg's Law gives the relationship among the angular positions of the reinforced diffracted beams in terms of the wavelength λ of the incoming X-ray beam and of the interplanar spacings d_{hkl} of the crystal planes.

$$n * \lambda = 2 * d_{hkl} * sin(\theta) \tag{1}$$

where n is the order of reaction (usually $n = 1$) and θ is the angular position.

Since h, k, and l are always integers, we can obtain values by dividing the 2 sin θ values for the different XRD peaks with the minimum one in the pattern (i.e., the 2 sin θ value from the first XRD peak) and multiplying that ratio by the proper integer.

$$a = \frac{\lambda}{2sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{2}$$

$$\frac{sin\theta_1}{sin\theta_2} = \frac{\sqrt{h_1^2 + k_1^2 + l_1^2}}{\sqrt{h_2^2 + k_2^2 + l_2^2}} \tag{3}$$

II. EXPERIMENTAL PROCEDURE

A. Synthesis of PbI_2

PbI_2 was prepared before the laboratory session and given to the team for characterization. Presumably, it was prepared using 100 mL of a 0.024 M KI solution, 100 mL of a 0.012 M $Pb(NO_3)_2$.

B. Apparatus and characterization

Characterization was carried out for films of Al, Si and both kinds of PbI_2. Additionally, it was also carried out over the adhesive tape used to hold the first two samples and the filter paper used to carry both lead compounds. This was in case aberrations showed up any of the crystals' diffractograms, since they may be linked to these utensils. All materials were centered inside the diffractometer of Rigaku exposed to monochromatic Cu K_α radiation ($\lambda = 1.54178\mathring{A}$). The tests were set up using the software Miniflex PDXL and the diffractograms were generated for a range of presumed angles of interest.

III. RESULTS

Data was obtained through XDR analysis software and exported into .txt files to be procesed and compared. Figures 1 through 6 show diffractograms with Intensity normalized to 100. Both scatter and plot graphs are included in order to show the frecuency of measurement and behavior respectively.

TABLE I: Values of θ for Intensity peaks.

Test Material	1st	2nd	3rd	4th	5th	6th	7th
Adhesive Tape	6.97	8.37	12.77	x	x	x	x
Al	19.4	22.55	32.72	39.27	x	x	x
PbI_2	6.4	13.05	17.27	19.42	19.85	22.67	26.3
Si-ref	14.2	23.62	28.05	34.55	38.17	44	47.42
Filter	7.37	8.5	11.35	x	x	x	x
Recrystallized PbI_2	6.33	7.08	8.48	11.51	13.18	17.36	19.36

Intensity peaks for each diffractogram are shown in Table 1.

Adhesive tape diffraction pattern includes 3 peaks, being the second peak located in $\theta = 8.37$ the most intense one as shown in figure 1.

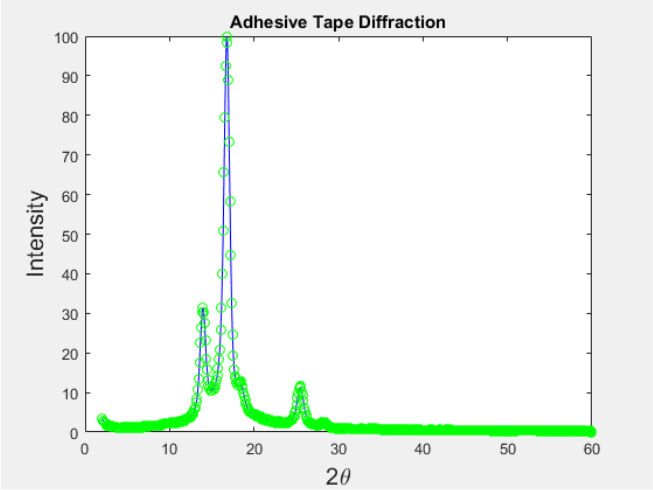

FIG. 1: Adhesive Tape X Ray Diffractogram

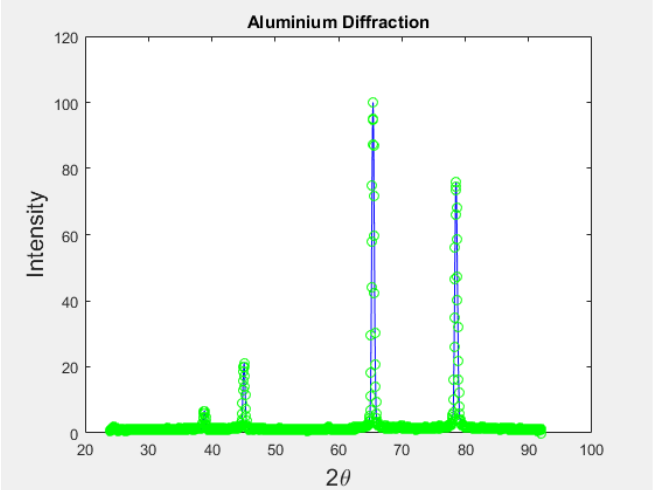

FIG. 2: Aluminium X Ray Diffractogram

Aluminuim diffraction pattern includes 4 peaks, being the second peak located in $\theta = 32.72$ the most intense one as shown in Figure 2.

PbI_2 diffraction pattern includes 4 peaks, being the second peak located in $\theta = 13.05$ the most intense one as shown in Figure 3.

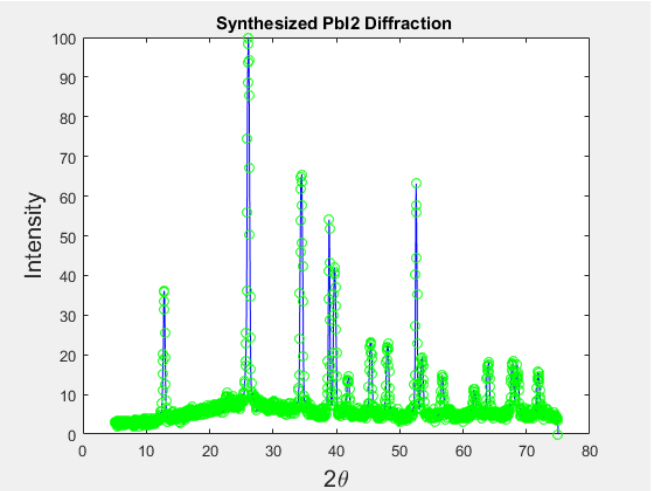

FIG. 3: Synthesized PbI_2 X Ray Diffractogram

Si-ref diffraction pattern includes several peaks, being the second peak located in $\theta = 14.20$ the most intense one as shown in Figure 4.

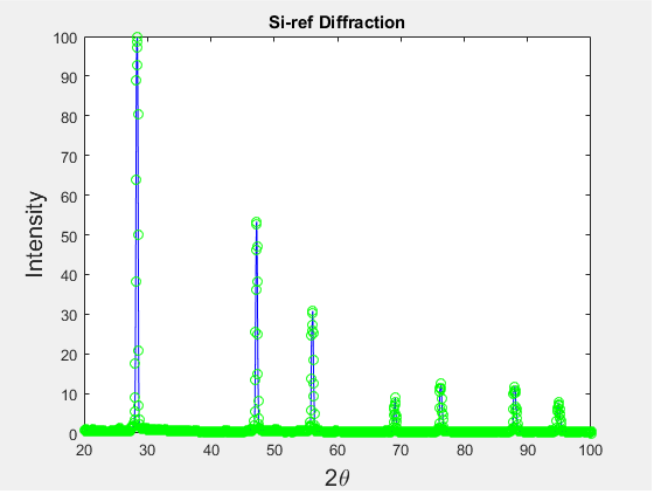

FIG. 4: Si-ref X Ray Diffractogram

Filter paper diffraction pattern includes 4 peaks, being the second peak located in $\theta = 11.35$ the most intense one as shown in Figure 5.

Recrystallized PbI_2 diffraction pattern includes 4 peaks, being the second peak located in $\theta = 6.33$ the most intense one as shown in Figure 6.

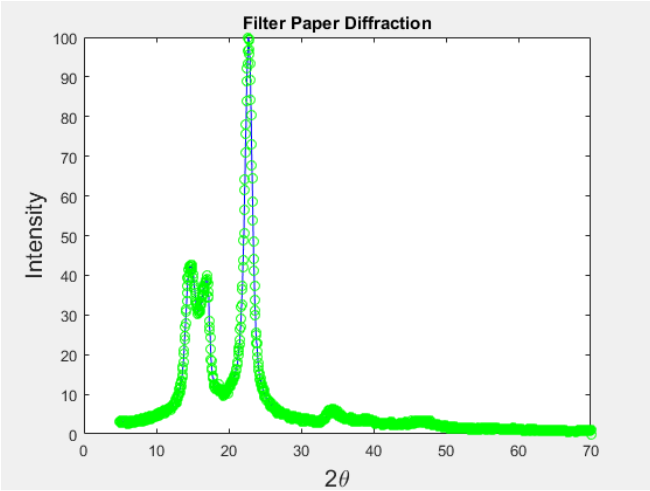

FIG. 5: Filter Paper X Ray Diffractogram

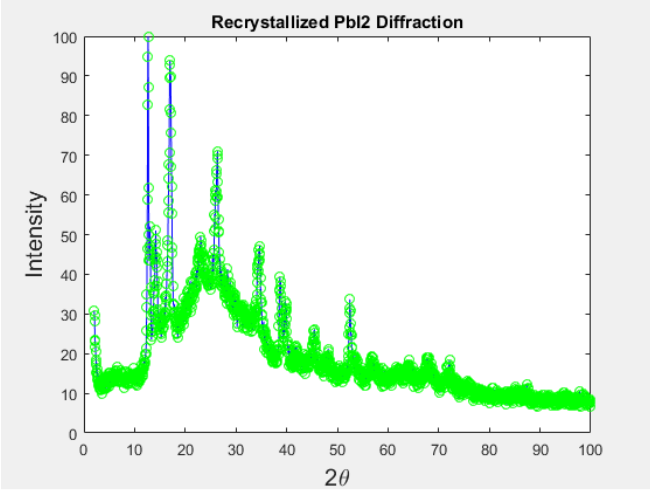

FIG. 6: Recrystallized PbI_2 X Ray Diffractogram

IV. DISCUSSION OF RESULTS

Miller indexes h,k,l and lattice parameters a were determined using equations 2 and 3. Lattice type was also computed based on the theory [9]. Values for aluminum, PbI_2-as and Silicon are displayed in tables II,III and IV.

Values for aluminum (FIG 2.) were compared based on data from the AMCSD [11]. Peaks corresponding to h,k,l indexes of 220, 311,200 and 111 were correctly derived. The peak corresponding to the 222 plane was not detected by the XRD diffractometer. This could be attributed to the fact that it is not as intense compared to the others (based on the relative intensity of AMCSD data). Values for the lattice parameter a were in average 4.02 angstroms. This is yet another confirmation as AMCSD reports values of 4.04 angstroms.

TABLE II: Aluminum calculated indices and lattice constant.

θ	hkl	a
32.725	220	4.03E-10
39.275	311	4.03E-10
22.55	200	4.02E-10
19.4	111	4.02E-10

TABLE III: Si calculated indices and lattice constant.

θ	hkl	a
14.2	111	5.43677E-10
23.625	220	5.43E-10
28.05	311	5.43E-10

TABLE IV: My caption

θ	hkl	a
13.05	101	3.47734E-11
19.425	0,0,3	7.68243E-11
6.4	100	8.58311E-12
26.225	202	1.36104E-10

Values corresponding to planes with indexes 111, 220 and 311 for Silicon (FIG 4.) were experimentally found. They also correspond with literature based on the mineral database [1]. Here three peaks corresponding to 400, 331 y 422 are missing. Lattice constant a was correctly estimated at 5.43 angstroms.

PbI_2 (FIG 3.) data was analyzed only from values for 2θ of 0 to 50 degrees. XRD pattern was then compared to works from Condeles et Al.[10] Several peaks were found to happen at same values for θ. Unfortunately data corresponding to lattice values and h,k,l could not be directly calculated like for Al and Si (visual aid and references were needed to determine planes). For the case of recrystallized PbI_2 (FIG 6.) sample, no lattice parameters or hkl values could be determined. It is relevant to mention that samples used during XRD were not in their most pure form. In the case of Al, for example, it was necessary to use some tape and for other substances filter paper was used. This fact may add some perturbation to the measurement (FIG 1. and FIG 5.). Another reason may be impurities that remain from the original synthesis process. This result was puzzling for the team.

V. CONCLUSION

During this session XRD characterization tests were carried out for Al,Si, and PbI_2 and their diffraction patterns obtained. The team confirmed that Bragg's model, although simplistic, is an effective model that still works in the area of crystal characterization. These diffraction patterns were used to derive *hkl* values for the different components of the sample. Basic structures such as Al and Si were easily identified, whereas PbI_2 characterization turned more difficult based on the way the material was prepared.

XRD is a very resourceful method, which other applications include: determination of lattice mismatch between film and substrate and the inferring of stress and strain, measurement of superlattices in multilayered epitaxial structures, determination of thickness, roughness and density of film, etc. [2].

PbI_2 is currently a material of interest, given it's tunable dielectric and optoelectric properties affected by its lattice parameters. It's possible to obtain it through different synthesis processes [5][6], taking into consideration the desired characteristics. Many of the sources used in this report address these variation in its physical properties.

VI. REFERENCES

[1] Wyckoff R W, (Silicon) **1963** *7-83 Second edition.* Interscience Publishers, New York, New York

[2] Dutrow, Barbara. Better Living Through Minerals X-ray Diffraction of Household Products, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, *Mineralogical Society of America* p. 349-359.

[3] Ryland, Ada L. X-ray diffraction. *J. Chem. Edu.* **1958**, *35(2)*, 931-937

[4] Baibarac, M.; Preda, N.; Mihut, L.; *et al.* On the optical properties of micro- and nanometric size PbI_2 particles. *J. Phys.: Condens. Matter* **2004**, *16*, 2345-2356

[5] Preda, N.; Mihut, L.; Baibarac, M.; *et al.* Raman and photoluminescence on low-dimensional PbI_2 particles embeddded in polymer matrix. *J. Optoelect. Adv. Mater.* **2007**, *9(5)*, 1358-1361

[6] Salvati-Niasari, Masoud; Tavakoli, Farnish. Pb(OH)I-graphene composite: Synthesis and characterization. *J. Indust. Engineer. Chem.* **2015**, *21*, 1208-1213

[7] Myers, H. P. *Introductory Solid State Physics*, 2nd ed.; CRC Press: Boca Rata, 1997.

[10] Condeles, J. F., Stoichiometry, surface and structural characterization of lead iodide thin films **June 2006** *Brazillian Journal of physics*

[11] Wyckoff R, Crystal Structures (Aluminum) **1963** *7-83 Second edition.* Interscience Publishers, New York, New York