JOURNAL OF CHEMICAL EDUCATION
Cite This: J. Chem. Educ. 2018, 95, 598−600
Activity
pubs.acs.org/jchemeduc

Using Cu $K_{\alpha 1}/K_{\alpha 2}$ Splitting and a Powder XRD System To Discuss X-ray Generation

N. Stojilovic[†,‡,*]

[†]Department of Physics and Astronomy and [‡]Department of Chemistry, University of Wisconsin Oshkosh, Oshkosh, Wisconsin 54901, United States

Supporting Information

ABSTRACT: When single crystals are probed by powder X-ray diffraction (PXRD) systems, the peak widths are smaller and signal intensities are greater than those from powdered samples. Instead of the expected single peak, a doublet can be observed, and undergraduate students face a big challenge explaining its origin. This activity is suitable as an inquiry-based, upper-level undergraduate laboratory activity. Students typically engage in an extensive literature search and reading in order to understand observed diffraction data. With a little bit of guidance from the instructor, students can learn how X-rays are generated, and which X-rays are used in PXRD experiments. They can also learn about the electronic transitions in the target electrode leading to characteristic X-rays and learn about the role of spin−orbit coupling.

KEYWORDS: *Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Inquiry-Based/Discovery Learning, Laboratory Equipment/Apparatus, X-ray Crystallography*

INTRODUCTION

Powder X-ray diffraction (PXRD) is one of the most widely used analytical instruments in chemistry, physics, and materials science research and can be a very valuable tool in undergraduate student education.[1−7] However, traditional undergraduate PXRD laboratory activities do not focus on how X-rays are generated, filtered, or the physical theory behind their generation. Therefore, activities that place focus on understanding generation of characteristic X-rays can nicely complement typical experiments that focus on the specimens or Bragg's law.

XRD is the experimental technique primarily used to determine the geometrical arrangement of the atoms or molecules within matter (crystal structure). When a crystal is bombarded by a beam of X-rays, X-rays are scattered by electron shells, and the angles through which the beam is diffracted reveal the shape and dimensions of the crystal's unit cell. Diffraction experiments require the use of monochromatic K_α (or very close to monochromatic) radiation. This nearly monochromatic K_α X-rays can be selected by the use of a filter or a monochromator. Since the wavelengths of $K_{\alpha 1}$ and $K_{\alpha 2}$ X-rays are so close in value, they are observed as a single K_α line when powder samples are probed. In PXRD systems, single crystals are sometimes used as reference samples for calibration purposes. However, single crystals have narrow diffraction peaks that, when collected at high resolution, reveal doublets. To understand the origin of these doublets one needs to understand how X-rays are generated in a typical PXRD instrument.

X-rays are generated by bombardment of a metal anode with high-energy electrons emitted from the filament. These electrons decelerate as they penetrate the target, generating radiation with a continuous range of wavelengths known as bremsstrahlung (breaking radiation). Superimposed on this continuum are several sharp characteristic peaks, crucial for diffraction experiments. These characteristic X-rays are produced when high-energy electrons knock out the inner shell electrons of the anode material. The electrons from higher shells of the target atoms then drop down and fill the created vacancies and, in this process, emit X-rays with well-defined energy. For example, if a 1*s* electron from the *K* shell of copper atom is ejected, the resulting vacancy can be filled by an electron from the *L* shell ($2p_{1/2}$ or $2p_{3/2}$) (I ask students why not from 2s orbital), the *M* shell ($3p_{1/2}$ or $3p_{3/2}$), or the *N* shell ($4p_{1/2}$ or $4p_{3/2}$). Subscripts 1/2 and 3/2 are the values of *j*, the total angular momentum quantum number. The corresponding X-ray lines are denoted $K_{\alpha 1}$, $K_{\alpha 2}$, $K_{\beta 1}$, $K_{\beta 2}$, $K_{\gamma 1}$, and $K_{\gamma 2}$. It is important that students know how characteristic X-rays are produced and to understand transitions leading to different K_α lines in order to "discover" the origin of the doublets observed from single crystals.

INSTRUMENT AND SAMPLES

For this activity, a PXRD system with Cu $K\alpha$ radiation (λ = 0.154 nm) was employed. An Al_2O_3 (0001) single crystal was used, but many other single crystals will be suitable as well. Samples are directly mounted on the sample holder without any prior treatment, but care must be taken to ensure that the height of the sample is adjusted for diffraction measurements by using an appropriate sample holder. Wide and fast scans can be used to reveal the locations of the peak(s) and then narrow and high-resolution scans may be used to resolve the doublets. Samples are inexpensive, nonhazardous, and readily available.

Received: July 21, 2017
Revised: January 10, 2018
Published: February 19, 2018

DOI: 10.1021/acs.jchemed.7b00546
J. Chem. Educ. 2018, 95, 598−600

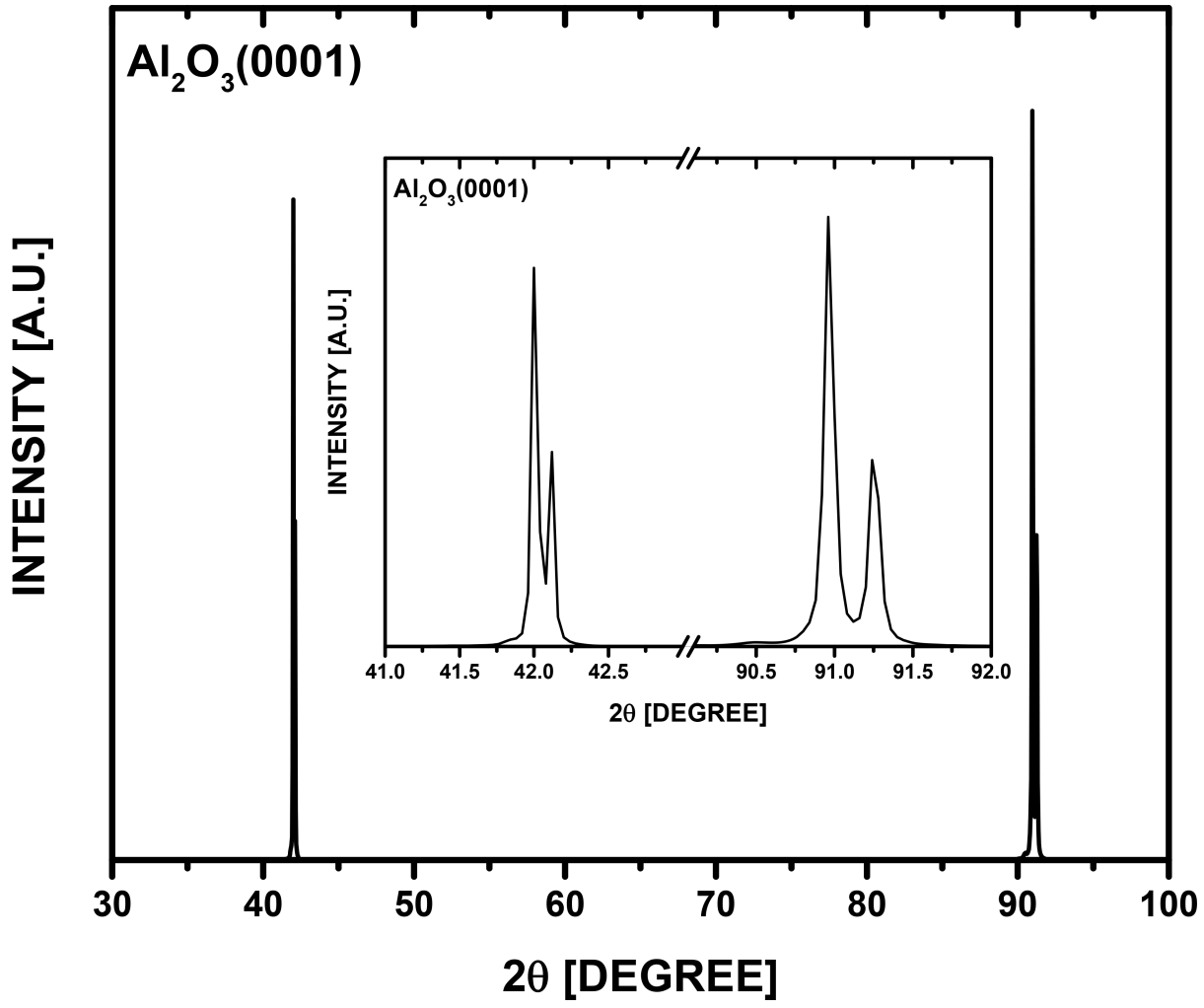

Figure 1. Diffraction pattern of an $Al_2O_3(0001)$ single crystal obtained using a PXRD system. To resolve the doublet, a narrow scan step size was set at 0.02°. Peak separation is greater at greater values of diffraction angle (see inset).

■ PROBING SINGLE CRYSTALS WITH PXRD

A typical X-ray diffraction measurement on a single crystal is expected to reveal only one peak. However, Figure 1 displays the diffraction pattern of an $Al_2O_3(0001)$ single crystal. The inset of the figure reveals doublets that are better resolved at higher diffraction angles. Students find this diffraction pattern rather puzzling, and they start engaging in discussions with fellow students. Single crystals generally produce very narrow and strong diffraction peaks that allow observation of closely spaced K_α lines. Wide scans often allow observation of different diffraction orders. In this activity, students are asked to perform X-ray diffraction experiments on single crystals, to assign not so trivial Bravais–Miller indices, to explain the origin of the doublet, to explain how spin–orbit coupling is related to characteristic X-ray lines, and to make sense of the observed intensity ratio. This type of activity motivates students and gives them a chance to develop scientific ways of thinking. At the end of the laboratory assignment or project, if completed correctly, students have the feeling of making a "discovery".

Before they can "discover" the origin of the doublet from single crystals using a typical PXRD system, students should be first advised to learn and write about Bragg's law and crystal planes (Miller and/or Bravais–Miller indices), how X-rays are generated, which X-rays are used in the PXRD experiment, how efficiently X-rays are filtered before they strike the sample, what causes the splitting of different K lines into doublets, and why different K lines have different intensities (for more details, please see Supporting Information).

When students determine the origin of the doublet, they are asked to verify their conclusions. This can be accomplished by using Bragg's law and the known $K_{\alpha1}$ and $K_{\alpha2}$ wavelengths to calculate the expected Bragg peak separations. For a Cu target, the wavelengths of K_α X-ray lines are $\lambda(K_{\alpha1})$ = 1.5405 Å and $\lambda(K_{\alpha2})$ = 1.5443 Å. For a Mo target, these values are $\lambda(K_{\alpha1})$ = 0.70926 Å and $\lambda(K_{\alpha2})$ = 0.71354 Å.[8] Instructors may ask students to think and explain why there is no $2s-1s$ transition, what causes splitting of energy levels, and why one K_α (or K_β) line has greater intensity than the other one. This would be a nice opportunity for instructors to have students encounter and learn more about terms such as selection rules,[9] spin–orbit coupling,[9] and transition probability.[10] In this activity, *fine structure*, that is typically seen in the emission spectra, can be observed in a PXRD experiment on single crystals. In my experience, upper–level undergraduate students generally fail to solve this doublet puzzle unless guided by the instructor. Therefore, these additional questions will guide students toward the solution of the puzzle. To ensure students' successful completion of this activity, instructors can provide

DOI: 10.1021/acs.jchemed.7b00546
J. Chem. Educ. 2018, 95, 598–600

or recommend the adequate reading material[8,11] and have discussions with students during this assignment/lab project.

INQUIRY-BASED LAB ACTIVITY

Traditional or "cookbook" laboratory activities are relatively ineffective in helping students learn and retain acquired knowledge on important concepts. Also, these laboratories do not help with development of analytical problem-solving skills and scientific reasoning that graduate schools need and many employers seek. Thus, preparing undergraduate students as scientists remains a challenge. On the other hand, the inquiry-based laboratory activity, where students perform experiments and try to interpret the data in a similar way as in a real scientific experiment, motivates them and brings an excitement of scientific discovery into the classroom, stimulates their curiosity, and improves their learning.[12] Here, an original, inquiry-based activity based on the use of PXRD instrument involving single crystals, is presented. Although trivial to carry out experimentally, the activity helps students learn about generation of X-rays and connect Bragg peaks with electronic transitions and spin−orbit coupling. This activity resembles performing research in the teaching laboratory and helps students start thinking like scientists. It can be implemented in upper-level laboratory courses like physical chemistry, analytical chemistry, or advanced physics lab. It was offered two times as part of advanced Physics III lab, mostly taken by physics students and is well suited as a physical chemistry lab. When guided, students will not only learn about Bragg's law but will also learn or strengthen their knowledge of electronic transitions, selection rules, and spin−orbit coupling.

CONCLUSIONS

An activity based on an atypical PXRD experiment and suited for upper-level undergraduate students is presented as an inquiry-based lab. The activity is straightforward to conduct, but the observations are challenging to interpret and will spark discussions among students. Students will review literature and develop an understanding of how X-rays are generated and filtered in a powder X-ray diffractometer. In a single, simple-to-run experiment, they encounter Bragg's law, different diffraction orders, electronic transitions, selection rules, transition probabilities, and spin−orbit coupling. This type of activity is expected to improve students' analytical problem-solving skills and scientific reasoning.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.7b00546.

Details of the experiment, some useful theory, and how this activity can be implemented (PDF, DOCX)

AUTHOR INFORMATION

Corresponding Author

*E-mail: stojilovicn@uwosh.edu.

ORCID

N. Stojilovic: 0000-0002-1751-6033

Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

I thank Professor Jennifer Mihalick for reading the manuscript and making some good points. I also thank anonymous reviewers for excellent suggestions and the UWO FDS498 grant for support.

REFERENCES

(1) Pope, C. G. X-Ray Diffraction and the Bragg Equation. *J. Chem. Educ.* **1997**, *74*, 129−131.

(2) Corsepius, N. C.; DeVore, T. C.; Reisner, B. A.; Warnaar, D. L. Using Variable Temperature Powder X-ray Diffraction To Determine the Thermal Expansion Coefficient of Solid MgO. *J. Chem. Educ.* **2007**, *84*, 818−821.

(3) Longo, E.; Espinosa, J. W. M; Souza, A. G.; Lima, R. C.; Paris, E. C.; Leite, E. R. Structural Order-Disorder Transformations Monitored by X-ray Diffraction and Photoluminescence. *J. Chem. Educ.* **2007**, *84*, 814−817.

(4) Epstein, P.; Dungey, K. E. Titration of a Solid Acid Monitored By X-Ray Diffraction. *J. Chem. Educ.* **2007**, *84*, 122−123.

(5) Butera, R. A.; Waldeck, D. H. X-ray Diffraction Investigation of Alloys. *J. Chem. Educ.* **1997**, *74*, 115−119.

(6) Rudman, R. X-Ray Diffraction Analysis (Part One-Safety and Generators). *J. Chem. Educ.* **1967**, *44*, A7.

(7) Rudman, R. X-Ray Diffraction Analysis (Part Three-Detectors). *J. Chem. Educ.* **1967**, *44*, A187.

(8) Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination A Practical Guide*; The Macmillan Company: New York, 1968.

(9) Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*, 3rd ed.; Oxford University Press: Oxford, 1997.

(10) Cohen-Tannoudji, C.; Diu, B.; Laloe, F. *Quantum Mechanics*; John Wiley & Sons: Paris, France, 1977; Vol. *1*.

(11) Azaroff, L. V. *Elements of X-ray Crystallography*; McGraw-Hill: New York, 1968.

(12) Ebert-May, D.; Brewer, C.; Allred, S. Innovation in Large Lectures − Teaching for Active Learning. *BioScience* **1997**, *47* (9), 601−607.

DOI: 10.1021/acs.jchemed.7b00546
J. Chem. Educ. 2018, 95, 598−600