Crystal Structure Analyses, **Take Home Exam-2**

Spring-2019, total 100 points, **Due Wednesday, May 1**

Instructions; Show all works. The answers should be in order (do not mix up the sequence of the answers). Answers should be organized and neat. Any book or computer programs may be used, but you may NOT consult with each other.

1. (10 points)

A certain tetragonal crystal has four atoms of the same kind per unit cell, located at $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$, $0\frac{1}{2}\frac{3}{4}$

(a) Derive simplified expressions for F^2.

(b) What is the Bravais lattice of this crystal?

(c) What are the values of F^2 for the 100, 002, 111, and 011 reflections?

2. (10 points) A phase is cubic with a composition of 50% Cu ad 50% Zn. There is one unit of CuZn per cell. The atoms in the unit cell can take on an ordered and a disordered form. In the ordered form Cu is at 000 and Zn is at 0.5 0.5 0.5. In the disordered form the same positions are occupied but randomly; that is, each position can be considered to be 0.5Cu and 0.5Zn.

(a) Derive simplified expressions for the structure factor F_{hkl} in the ordered form. What is the Bravais lattice of this structure?

(b) Derive simplified expressions for the structure factor F_{hkl} in the disordered form. What is the Bravais lattice of this structure?

(c) Briefly compare and discuss the results.

3. (12 points) Magnesium oxide (MgO) powder was ground by ball milling process to produce a fine powdered sample. XRD data of the powder was collected using Cu Kα radiation (1.5406Å) with a crystal monochromator, and the decrease of peak height as well as peak broadening was found. The values of FWHM of peaks corresponding to (200), (220), (311), (222) and (400) planes are summarized in Table 1. Similar XRD data were collected for the powder which was fully annealed to remove the lattice strain for comparison. The resultant FWHM values of the five peaks are listed in Table 2. What is the average size of the crystallites in the powder prepared by ball milling? Assume the annealed powder has no peak broadening from crystallite size and the shape of the diffraction peaks is approximated by Gaussian distribution.

Table 1 Diffraction data of ball milled sample

	hkl	2θ (degree)	FWHM (degree)
1	200	42.90	0.183
2	220	62.31	0.205
3	311	74.71	0.243
4	222	78.63	0.274
5	400	94.06	0.309

Table 2 Diffraction data of annealed sample

	hkl	2θ (degree)	FWHM (degree)
1	200	42.91	0.093
2	220	62.30	0.072
3	311	74.68	0.068
4	222	78.60	0.090
5	400	94.04	0.087

4. (12 points) Researcher finished collecting a powder diffraction pattern of an unknown crystalline substance. She used Cu Kα radiation, =1.54178Å. The first Bragg peak is observed at 2θ = 9.76°. Based on this information she makes certain conclusions regarding the length of at least one of the three unit cell edges. What are these conclusions?

5. (10 points) Vanadium oxide, V_2O_3, crystallizes in the space group symmetry $R\bar{3}c$ with lattice parameters a = 4.954Å and c = 14.00Å. Calculate the interplanar spacing, d, and Bragg peak positions, 2θ, for the 104 (the strongest Bragg peak) and for the 012 (the lowest Bragg angle peak) reflections assuming Cu Kα1 radiation with λ = l.5406Å.

6. (10 points) A student collected a powder diffraction pattern from an organometallic compound on a standard powder diffractometer equipped with a sealed Cu Kα X-ray tube. She noticed that scattered intensity decays rapidly and she cannot see any Bragg peaks beyond 2θ = 60º. Her goal is to have reliable intensities at 90º+ of 2θ. She thinks for a minute and then calls the crystallography lab at her university to schedule time on one of their units. The lab has three powder diffractometers, all equipped with Cu Kα X-ray tubes: a rotating anode unit operating at ambient environment, and two sealed tube units, one with a cryogenic attachment (the lowest temperature is 77 K) and another with a furnace (the highest temperature 1,100 K). Which unit will you recommend her to use if she asks you for advice and why?

7. (12 points) In the Rietveld refinement,

(a) The S_y in the equation below is to be minimized. What is the meaning of w_i in the equation? $S_y = \sum w_i (Y_i - Y_{ci})^2$

(b) What is R-weighted pattern (R_{wp}) and S (goodness-of-fit)?

8. (12 points) When measuring the XRD pattern of magnesium oxide(MgO) powder sample by Cu-Kα radiation (1.542Å), ten diffraction peaks were obtained in the scattering angle(2θ) as shown below. Index the pattern and compute the lattice parameter by referring to MgO having the NaCl-type structure. Use the systematic absence conditions.

2θ (degrees); 36.93, 42.91, 62.30, 74.64, 78.64, 94.06, 105.75, 109.78, 127.29 and 143.77

9. (12 points) If a simple cubic material has a peak at 42.908 degrees 2θ due to the (200) plane, where would the peak due to the (111) plane occur (using Cu Kα1 radiation; 1.54051Å)? What are the values of the lattice parameters a, b, and c?

At what angles will the reflections from these two planes occur due to Kα2 radiation? (wavelength 1.54433Å) The intensity of Kα2 peaks are generally 0.5 of the intensity of the corresponding Kα1 peaks. If the full width at half maximum (fwhm) is 0.1 degrees, sketch the two peaks clearly showing the relative intensity of 200 and 100 peaks. Based on the comparison of the difference between the peak locations and their fwhm's, will both peaks of the low angle doublet be visible? The high angle doublet?