UNIVERSITY OF GHANA

SCHOOL OF ENGINEERING SCIENCES

BSc. (Eng) MATERIALS SCIENCE AND ENGINEERING

END OF SECOND SEMESTER EXAMINATIONS: 2014/2015

MTEN 312: CRYSTAL CHEMISTRY OF CERAMICS (3 CREDITS)

TIME: THREE (3) HOURS

Answer only FOUR (4) Questions

Question 1

a) State Pauli's exclusion and Heisenberg uncertainty principles.
b) Distinguish between atomic structure and crystal structure.
c) Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4°C versus -85°C), even though HF has a lower molecular weight.
d) Using Figure 1,
   (i) Estimate the percentage ionic character of the following compounds: Magnesium Oxide (MgO), Calcium Oxide (CaO), Sodium Chloride (NaCl), Silicon dioxide (SiO_2) and Silicon Carbide (SiC).
   (ii) Arrange the preceding compounds in increasing ionic character.

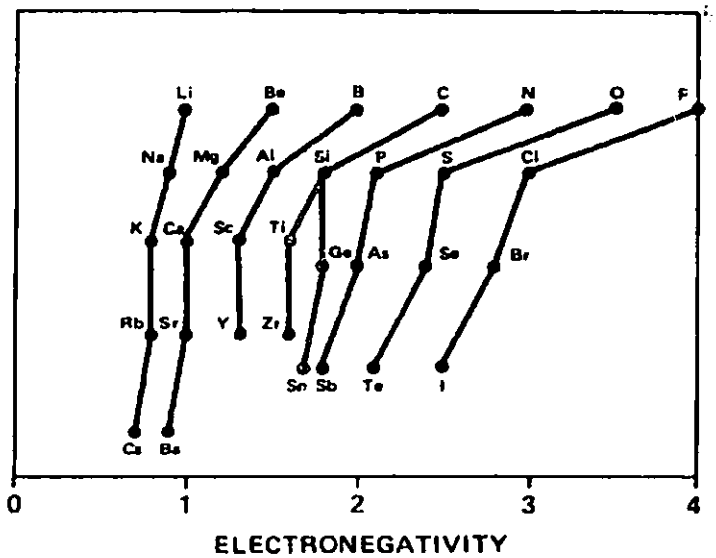


Figure 1: Pauling's electronegativity scale. Elements to the left have low affinity for electrons and those to the right have a high affinity. (Courtesy: Modern Ceramic Engineering, David W. Richerson.

e) The nearest approximation to free-electron model is the Group 1 and Group 2 metals, which are referred to as simple metals. Assuming an electron is restricted to an infinitely square potential (line length x= 0 to x= a) and also confined to motion on the x-axis.

(i) Show that the energy (for 1-dimensional analysis) of an electron is quantized (equation below). $E = \frac{n^2h^2}{8m_e a^2}$, where E is the energy of the electron, h is Planck's constant, m_e is mass of an electron.

(ii) Write down the quantized energy expression in three dimensional analysis.

[25 marks]

Question 2

a) Arrange in order of decreasing symmetry the 7 types of crystal structures found in nature.

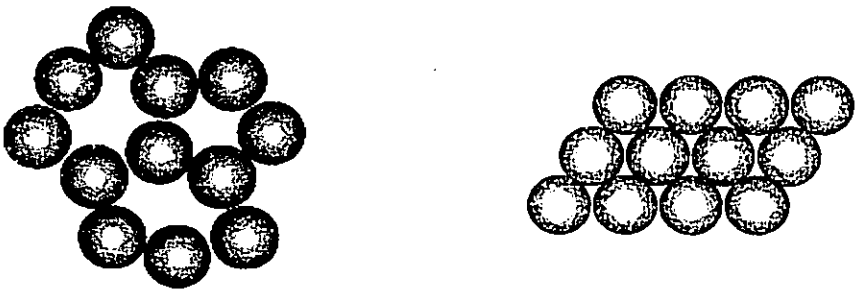
b) The face centered cubic (FCC) and hexagonal close packed (HCP) structures both have a packing factor of 0.74, consist of closely packed planes of atoms and have a co-ordination number of 12. The difference between the FCC and HCP is the stacking sequence.

(i) Deduce the atomic packing factor for FCC,

(ii) Explain why HCP structures are generally not as ductile as FCC.

(iii)Show that the ideal ratio of the unit cell height, c and the basal plane edge length, a, for HCP is 1.633.

c) Figure 2 has two different crystal packings; (i) is for a non-dense or random packing and (ii) is for a dense packing. Sketch graphically their energy (E) versus their inter-particles distances (r) and comment on these two parameters with respect to the structural packing in (i) and (ii).



(i) (ii)

Figure 2. Two different crystal packings for (i) non-dense and (ii) dense

d) On the same plot, sketch the energy-interatomic distance curve for two materials (i) strongly bonded and (ii) weakly bonded. Predict the melting temperature regimes of (i) and (ii).

[25 marks]

Question 3

(a) Assuming a cubic crystal system, make a sketch of the following planes

$$(111), (123), (\bar{1}10), (010), (\bar{1}\bar{1}\bar{1}), (0\bar{1}0).$$

(b) Distinguish between the following ceramic pair crystal structures:

(i) Zinc blende and Wurtzite

(ii) Fluorite and Anti-fluorite

(iii) Pyrosilicate and Metasilicate

(iv) Spinel and Inverse-spinel

(c) (i) Briefly explain the terms: Polymorphism and Polytypism.

(ii) Crystalline silica, SiO_2, exists mainly in three different polymorphic forms. The densities of these polymorphic forms are known to differ. Depending on the kind of changes occurring in the crystal and speed of transformation, the polymorphic forms can be classified.

(α) Name the polymorphic forms of Silica

(β) Explain the types of transformations that do occur during various transitions

(γ) Sketch a schematic diagram of the polymorphic transformations by stating the various transformational processes, polymorphic form and approximate temperature.

(d) The zinc blende crystal structure is one that may be generated from close-packed planes of anions. Describe briefly the stacking sequence for this structure.

[25 marks]

Question 4

(a) State Pauling's rules for ionic co-ordination

(b) State the main factors that affect ceramic crystal structures

(c)

(i) Using Tables 1 and 2 below, predict the structure of the following ceramic compound: MgO, KBr, CsCl, CaF_2, and MnS.
(ii) Deduce the co-ordination number of the anions in each material.
(iii)Draw the ceramic unit crystal structures of the materials in (i).

Table 1 – Ionic radii for several cations and anions (for a co-ordination number of 6).

Cation	*Ionic Radius (nm)*	*Anion*	*Ionic Radius (nm)*
Al^{3+}	0.053	Br^-	0.196
Ba^{2+}	0.136	Cl^-	0.181
Ca^{2+}	0.100	F^-	0.133
Cs^+	0.170	I^-	0.220
Fe^{2+}	0.077	O^{2-}	0.140
Fe^{3+}	0.069	S^{2-}	0.184
K^+	0.138		
Mg^{2+}	0.072		
Mn^{2+}	0.067		
Na^+	0.102		
Ni^{2+}	0.069		
Si^{4+}	0.040		
Ti^{4+}	0.061		

Table 2 – Co-ordination numbers and Geometries for various cation – anion radius ratio (r_c/r_a)

Co-ordination Number	Cation-Anion Radius Ratio	Co-ordination Geometry
8	0.732-1.0	Corners of a cube
6	0.414-0.732	Octahedral
4	0.225-0.414	Tetrahedral
3	0.155-0.225	Trigonal
2	Less than 0.155	Linear

Source: W.D Kingery, H.K. Bowen and D. R. Uhlmann, Introduction to Ceramics, 2nd Edition.

(d) Show that the minimum cation-to-anion radius ratio for a co-ordination number of 4 is 0.225.

[25 marks]

Question 5

a) Write out the symmetry elements present in the 'molecules' in Figure 3 and the corresponding point group of each one. Assume that the molecules are planar, exactly as drawn, and not three-dimensional. The shapes are: (i) pentagonal C_5H_5, in ferrocene; (ii) linear, CS_2; (iii) triangular, SO_2; (iv) square, XeF_4.

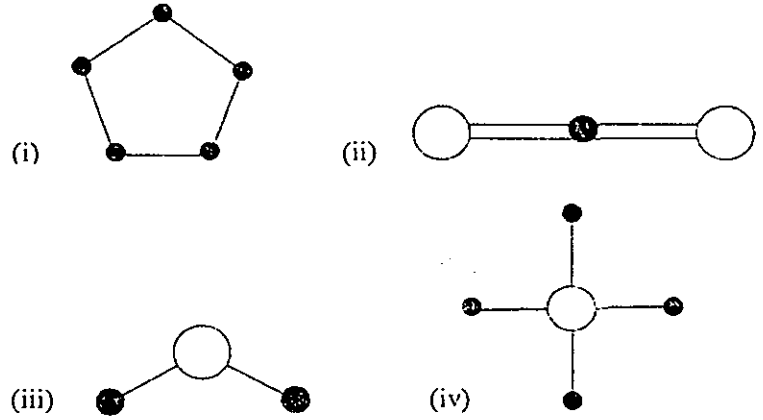


Figure 3. Molecular structures for (i) C_5H_5 (ii) CS_2 (iii) SO_4 and (iv) XeF_4

b) Briefly explain why x-rays are used in examining crystal structures?

c) You are to conduct an x-ray diffraction of a ceramic powder with cubic crystals of unit cell parameter 4.2 Å using a wavelength of 1.54 Å. At what angle (2θ) would you expect to measure the (111) peak?

d) Using Bragg's law, deduce the indices of the first three reflections in a powder diffraction pattern taken from a simple cubic crystal.

[25 marks]