103

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES
B.Sc. (Special) Degree in Chemistry
Third Year Semester II Examination– April / May 2016
CHE 3212 – SOLID STATE CHEMISTRY

Answer all FOUR questions **Time: 02 hours**

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1. (a) i. State, major characteristics of bonds in an ionic solid.
ii. Draw a completely labeled plot for interionic energy vs. distance for a single ionic bond.
iii. Given the relationships for (i) energy of attraction (E_a) and (ii) energy of repulsion (E_r) between charge particles,

$$E_r = \frac{b}{r^n} \qquad E_a = \frac{-e^2}{4\pi\varepsilon_0 r_0}$$

Show that, the energy of a single ionic bond may be given by

$$E(r_0) = \frac{-(Z_+)(Z_-)\,e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

Identify all terms in the equation.

(50 marks)

(b) i. A metal (density = 7.86 g cm^{-3}) crystallizes in a BCC unit cell at room temperature. Calculate the radius of an atom in this crystal in nanometers.

ii. BCC Fe placed in an x-ray diffractometer using x-ray with $\lambda = 0.1541$ nm. diffraction from {110} planes was obtained at $2\theta = 44.704°$. Calculate lattice constant a.

(50 marks)

2 (a) Answer any THREE from i-iv

i. Silver bromide (AgBr) has rock salt crystal structure, i.e., FCC Bravais lattice with the ion pair, Ag^+ and Br^- as basis. The dominant defect in AgBr is the Frenkel disorder. Does the Frenkel disorder in AgBr create vacancies of Ag^+, vacancies of Br^-, or both? Explain. The ionic radii are 0.67 Å for Ag^+ and 1.96 Å for Br^-.

ii. Calculate the temperature in Kelvin at which the fraction of vacant sites in a crystal of Ag exceeds1 part per billion = 1 ppb = 10^{-9}. The activation energy for the vacancy formation in Ag has a value of 1.10 eV /defect.

iii. On each of three separate drawings of one face of an FCC unit cell, indicate one of each of the following:
(a) substitutional impurity; (b) vacancy; (c) interstitial impurity.

104

iv. Explain the conductivity that you would expect when pure Si is doped with
(i) Ge and (ii) B

(50 marks)

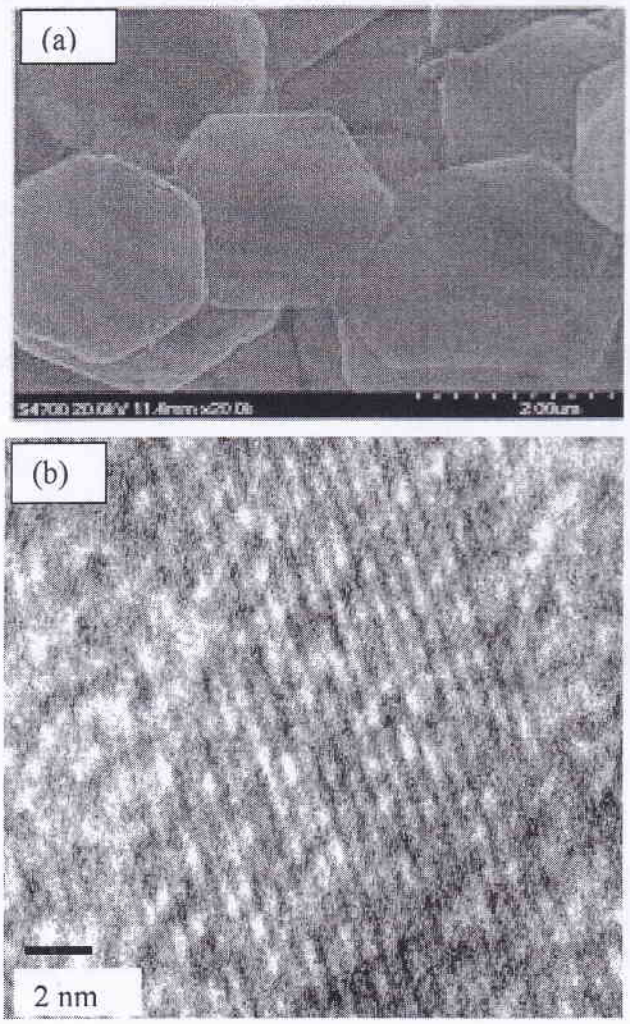
(b) Explain the following with the aid of necessary diagrams

i. A crystal of KCl is transparent to visible light but annealing in the vapour of K shows an absorption band at 565 nm.
ii. ZnO shows n-type conductivity.
iii. Grain boundary is a planer defect

(50 marks)

3. Layered double hydroxides (LDHs) are a class of clays which consists of cationic layers and interlayer charge balancing anions. Mg-Al based layered double hydoxide is a common candidate in this family. In Mg-Al LDHs cationic layers contain Mg and Al ions while the anion intercalate into the interlayer spacing. One example of such LDH is nitrate anion intercalated Mg-Al LDH.

The scanning electron microscopic and a transmission electron microscopic images of the Mg-Al-nitrate LDH are given below.



105

(a) Assigning the images to SEM and TEM techniques, explain the morphological characteristics of the Mg-Al layered double hydroxides.
(b) Explain how you would use the powder diffraction techniques to predict the interlayer spacing.
(c) What changes in the morphological features of the LDH may occur if the interlayer anion is replaced by benzoic acid, a larger anion.
(d) Explain what changes may occur in the powder diffraction pattern after benzoic acid is intercalated.

(50 marks)

4. (a) Explain the basic principle of (i) thermogravimetric analysis (ii) differential scanning calarimetry.
(b) An inorganic metal oxide undergoes the following thermal events during heating in an inert atmosphere;
Dehydration 150 °C, polymorphic transition 450 °C, melting 900 °C

(i) Sketch the resulting thermogram from a thermogravemetric analysis experiment.
(ii) Sketch the differential thermal analysis curve upon heating and cooling of the material.

(25 marks)

(c) A sample of chromium hydroxide was shown by chemical analysis to contain a few percentage of Al^{3+} impurities. What effect, if any, would the Al^{3+} ions have on the powder pattern if it were present

i. as a separate aluminium hydroxide phase

ii. substituting for Cr^{3+} in the crystal structure of $Cr(OH)_3$

iii. as an amorphous salt

Explain your answers.

(25 marks)