NPTEL Course on "Electroceramics

Problem Set (Part-I) **Total Marks: 65**

Data: Avogadro Number: 6.023×10^{23} mole^{-1}, Charge of electron (e) : 1.6×10^{-19} Coulomb
Boltzmann's Constant (k_B): 1.38×10^{-23} J.K^{-1}, Gas Constant (R): 8.314 J.mol^{-1}K^{-1}
mass of free electron (m_o) = 9.11×10^{-31} kg, Planck's constant (h): 6.6×10^{-34} J.s^{-1}

Question 1 **[10]**

Consider a cubic lattice in which atomic positions of metal ion is (0 0 0) and oxygen ions is (½00), (0½0) and (00½).

a) Draw the plan view of the lattice in the x-y plane with appropriate labels. 2
b) Determine the co-ordination number of metal and oxygen ions? 1
c) What is the formula unit and how many formula units are contained in an unit cell. 2
d) What is the lattice type? 1
e) Can this unit cell be represented in any other way? Justify your answer. 4

Question 2 **[4]**

Estimate the size of an interstitial atom (r) that can be placed in a tetrahedral void of a HCP unit cell touching all the surrounding host atoms of radii R without displacing them.

Question 3 **[8]**

Write the defect reactions for following cases:

a) Dissolution of MgO in an otherwise stoichiometric Al_2O_3 under ambient conditions. 4
b) Dissolution of Cr_2O_3 in an otherwise stoichiometric NiO under ambient conditions. 4

Question 4 **[6]**

Write the Schottky defect reaction for TiO_2 and then calculate the equilibrium oxygen vacancy concentration (per unit volume) in TiO_2 at 1400°C given that enthalpy of defect formation is 5.2 eV. You can neglect the entropy of defect formation. Atomic weights of Ti and O are 48 and 16 respectively, density of TiO_2 is 4 g/cc.

Question 5 **[14]**

TiO_2 has a band gap of 3 eV. Atomic weights of Ti and O are 48 and 16 respectively; density of TiO_2 is 4 g/cc. It is highly nonstoichiometric (oxygen deficient), compensated by creation of the Ti interstitials. The equilibrium constant for the defect reaction is

$$K = 6.55 \times 10^{122} \exp\left(-\frac{960\text{kJ/mole}}{RT}\right) \text{MPa.cm}^{-15}$$

a) Write the appropriate defect reaction for defect creation and the rate constant of the reaction in terms of pO_2 and the defects concentrations. 3
b) Calculate the extent of non-stoichiometry (in mole fraction of Ti interstitials) at 1690 K in air and at $pO_2 = 10^{-9}$ MPa. 3
c) Calculate electronic conductivity under both conditions if electron mobility is 0.2 cm^2/V-s. 4
d) Calculate the electronic conductivity at 1690K if TiO_2 was stoichiometric and compare the results with those obtained in (c)? 4

Question 6 **[13]**

NiO has rocksalt structure with bandgap of ~4.2 eV and Schottky defect formation energy of ~6 eV. It is a cation deficient oxide. Assume the defects to be completely ionized. The diffusivity of defects in NiO at 1000°C is 1.6×10^{-9} cm^2/sec and electron and hole mobilities are 24 cm^2/V-s. Density of NiO is 6.67 g/cc and molecular wt is 75 g/mole.

a) At 1000°C, what kind of conductivity will be in pure and stoichiometric NiO? 4
b) In the nonstoichiometric state, how will this deficiency be accommodated? Justify your answer by writing appropriate defect reaction and equilibrium constant. 4
c) Will the conductivity be of $Ni_{1-x}O$ be of p- or n-type? Explain. Show the dependence on pO_2? 5

Question 7 **[10]**

A sample of potassium ferrite with chemical formula $K^{+}_{1.25}Fe^{2+}_{0.25}Fe^{3+}_{10.75}O^{2-}_{17}$ is a mixed ionic/electronic conductor with the β-Alumina structure. It contains 4.07×10^{27} potassium ions per m^3 located in (001) planes. For this material, the total electrical conductivity at 573 K is 1.53×10^{-2} S/m and the diffusion coefficient at 573K for K^+ ions is 1.89×10^{-14} m^2/s. Calculate the transport number for K^+ ions at 573K. If the energy of migration of K^+ ions is 23 kJ/mol, what will be the ionic conductivity of the sample at 298 K?