Materials 218/Chem 277 Take home final

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Please indicate the source of any material you might make use of (URLs, references . . .)

1. The crystal structure of a superconductor is described below:

   Space group $Pmmm$ (No. 47) a = 3.823 Å; b = 3.887 Å; c = 11.680 Å.

Y	$1h$	0.5	0.5	0.5
Ba	$2t$	0.5	0.5	0.18381
Cu1	$1a$	0	0	0
Cu2	$2q$	0	0	0.35489
O1	$1e$	0	0.5	0
O2	$2s$	0.5	0.	0.37855
O3	$2r$	0	0.5	0.37807
O4	$2q$	0	0	0.15896

   (a) What is it's chemical formula ? [1]

   (b) Describe the centering operation and nature of the symmetry associated with the space group. [2]

   (c) Sketch the structure in approximate sections along z [2]

   (d) Sketch the structure using VESTA showing coordination polyhedra around Cu1 and Cu2 [1]

   (e) What are the different coordinations around the cations? [2]

   (f) Calculate the bond valence sums of Cu1 and Cu2. Use these to assign charges on all the atoms. [BV parameters for Cu and O: use R_0 = 1.679 Å and B = 0.37. [2]

2. Explain briefly using the concept of *screening* why valence electrons in a metal do not crystallize, but remain mobile. On the same lines, explain the Mott-Hubbard metal-insulator transition in systems where the electron density is low. [4]

3. Using schematic DOS sketches, describe how:

   (a) TiO (rock salt) is a metal [2]

   (b) MoS_2 (MoS_2 strcuture) is an insulator [2]

   (c) $LaCoO_3$ (perovskite) is a diamagnetic insulator at low temperatures, but then as it is heated up, it becomes a paramagnetic metal. [2]

4. Transparent conducting oxides (TCOs):

   (a) Many oxides like TiO_2 are insulating because filled anion p states are separated from empty cation d states and the Fermi energy lies in the gap. Sketch the DOS of TiO_2. [2]

   (b) It is very difficult to hole dope a compound like TiO_2, and when one does achieve such hole doping, the holes are not very mobile because they are on oxygen. In order to make p-type transparent conducting oxide, one would rather work with insulators with filled d states below the Fermi energy. Name an insulating or semiconducting oxide with filled d states and sketch its DOS. [2]

   (c) When holes are doped on oxygen, two oxygen atoms tend to come together to form a peroxo species, which is two O with a short bond in-between and net shared charge of -2: $[O\text{-}O]^{2-}$. Suggest a possible structural reason why the reaction

$$AO + \frac{1}{2}O_2 \rightarrow AO_2$$

   [2]

   is known for A = Ba, but difficult for A = Mg, Ca or Sr.

   (d) The delafossite oxide $CuGaO_2$ (formulated $Cu^{+}Ga^{3+}O_2$) has the crystal structure described below, and is believed to represent a good candidate TCO material. Use VESTA to draw the crystal structure. If this compound is hole doped with excess oxygen (forming $CuGaO_{2+\delta}$), suggest where excess oxygens could sit in the unit cell? You must ensure that oxygen atoms are not too close to one another. On which cation states would the doped holes reside? [4]

   Space group $P6_3/mmc$ (No. 194) a = 2.942 Å; c = 11.325 Å.

Cu	1/3	2/3	1/4
Ga	0	0	0
O	1/3	2/3	0.0893

5. Polar and magnetic materials

   (a) Explain the notion of a supercell in an antiferromagnetic material. What technique would you require to observe the supercell? Why would simple X-ray diffraction not work? [3]

   (b) Explain the notion of a supercell in an antipolar material. How is it possible in this case to use X-rays to observe the supercell. [3]

   (c) In class you learned that in $PbTiO_3$, there are two contributing factors to driving the system off-center. Can you suggest a suitable modification (chemical) to $PbTiO_3$ that might render it magnetic as well as ferroelectric? You must be sensitive to ion size and oxidation state. [2]

(d) Consider the ordered spinel MCr_2O_4 where M is another (divalent) transition metal which sits in the tetrahedral site, and Cr is Cr^{3+} in an octahedral site. Suggest a number of different magnetic M cations. Which would result in the best paramagnet (highest number of overall spins in the formula). If the spins couple antiferromagnetically between M and Cr, which composition would result in a high net spin. [2]