

Materials 218 Take home final

Date: March 9 2016; Due date: March 16, 2016

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

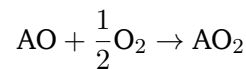
1. The crystal structure of a complex copper oxide material is described below:

Space group $Pmmm$ (No. 47) $a = 3.823 \text{ \AA}$; $b = 3.887 \text{ \AA}$; $c = 11.680 \text{ \AA}$.

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 the 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) Depict the structure with VESTA, showing coordination 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: use $R_0 = 1.679 \text{ \AA}$ and $B = 0.37$ for Cu–O. [2]
2. Explain briefly using the concept of *screening*, why valence electrons in a metal do not localize, but remain mobile. Along the same lines, describe the transition from metal to insulator in systems where the electron density falls below a certain threshold. Can this be explained in a band structure, and why/why not? [4]
3. Using schematic DOS sketches, describe how:
- (a) TiO_2 is an insulator. [2]
- (b) 1T-MoS_2 (where Mo is octahedral) is a metal. [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 Nb_2O_5 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 Nb_2O_5 . [2]
- (b) It is very difficult to hole-dope a compound like Nb_2O_5 , 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 : $[\text{O}-\text{O}]^{2-}$. Suggest a possible structural reason why the reaction



[2]

is known for $A = \text{Ba}$, but difficult for $A = \text{Mg}$, Ca or Sr .

- (d) The delafossite oxide CuGaO_2 (formulated $\text{Cu}^+\text{Ga}^{3+}\text{O}_2$) 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 $\text{CuGaO}_{2+\delta}$), suggest where excess oxygens could sit in the unit cell? You must ensure that oxygen atoms are not too close to one another. What are the cation orbital states that would the doped holes? [4]

Space group $P6_3/mmc$ (No. 194) $a = 2.942 \text{ \AA}$; $c = 11.325 \text{ \AA}$.

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

5. Polar and magnetic materials

- (a) X-rays cannot probe magnetism but neutrons can. Why does the neutron scattering of antiferromagnetic NiO resemble the structure of a layered oxide like LiCoO_2 ? [3]
- (b) Consider the ordered spinel $M\text{Cr}_2\text{O}_4$ 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 could stabilize the structure. Which of these would result in the best paramagnet (highest number of overall spins in the formula) and how many are these. If the spins couple antiferromagnetically between M and Cr , which composition would result in a high net spin (highest magnetization). [3]
- (c) State in simple terms, how phonons act as a “glue” to pair up electrons in a superconductor like Hg or Pb . [4]