

- The compounds ZrO_2 (zirconia) and CeO_2 (ceria) can take on the ideal fluorite structure. Calculate the expected coordination numbers for Zr and Ce (based on the radius ratios) and compare it with that for the cation in the ideal fluorite structure. Which of these two compounds is more stable in the ideal fluorite structure? Why?
- [Changed]** In the perovskite structure, there are two cation-anion distances that are essential to the formation of the phase: A-O and M-O, for an AMO_3 perovskite. Consider an 'ideal' perovskite structure in which the M atom fits perfectly into the octahedral position at the center of the unit cell. Evaluate the lattice constant that is implied, $a_{(M-O)}$. Then also consider the perovskite in which the A cations and oxygen anions are well packed such that these two alone define the length of the unit cell. Evaluate the lattice constant that is implied, $a_{(A-O)}$. Evaluate the ratio of these two quantities, t , which is known as the perovskite tolerance factor. For an ideal perovskite, t is equal to 1.
- SnO_{2-x} an oxide of the rutile structure (cubic close-packed oxygen ions with one-half of the octahedral sites occupied by Sn^{4+}), reduces readily with a decrease in oxygen partial pressure. For the purposes of this exercise, you may assume that oxygen vacancies are the primary compensating defect. The material does not tolerate any oxygen excess to speak of.
 - Write formally correct (i.e., physically meaningful) defect reactions and, where appropriate, equilibrium constants for the following reactions. Assume all defects are fully ionized, that metal ion incorporation occurs substitutionally, and associates are not important.
 - the reduction of SnO_{2-x}
 - the creation of Schottky defects
 - the incorporation of Cr_2O_3
 - the incorporation of Nb_2O_5
 - What will be the Brouwer approximation in the cases where (i) reduction of SnO_2 dominates, (ii) the creation of Schottky defects dominates and (iii) incorporation of the dopant dominates?
- Assume the Schottky defect formation energy is much less than either Frenkel defects formation energies, and the electronic band-gap. Construct a Kroger-Vink diagram for chromium-doped tin oxide for the situation where $[Cr_2O_3] > K_s$.
- For the diagram of problem 2, take $[Cr_2O_3] = 2 \times 10^{-4}$ mole fraction (400 ppm Cr) and $T = 500^\circ C$. For this temperature, independent measurements have shown K_r [of **problem 3**, part (i)] to be 1×10^{-16} (units: concentration in mole fraction and partial pressure in atm) and K_s to be 1×10^{-14} . Determine the value of the oxygen partial pressure that separates the two regions in the Kroger-Vink diagram of **problem 4**.
- [Omitted.]**