Perovskites and Spinels

Perovskite structure and applications:

Perovskites have the general formula ABX_3, and they are named after the mineral Perovskite, that has the composition $CaTiO_3$. In its ideal form, the perovskite structure is a cubic closed pack structure. In this structure the Ca cations are cuboctahedrally surrounded by 12 oxygen ions and the Ti cations are octahedrally surrounded by 6 oxygen ions. For the perovskite structure two different typs of unit cells are used. In the first unit cell the bigger Ca cations are in the middle and the smaller Ti cations are in the corners of the cube. The oxygen-anions are on the edges. In the second unit cell the Ti cations are located in the middle, the oxygen-ions are on the faces and the Ca cations are in the corners of the cube.
In some perovskite structures, as for example in $BaTiO_3$, the position of the Ti cations is not exactly located in the center of the octahedral hole. This leads to a polarisation and a high dielectric constant of the unit cell. This is the reason why these materials are used in capacitors, sensors and electronic components

High temperature superconductors:

Some high temperature superconductors can be viewed as variants of the perovskite structure. Superconductors enter below a critical temperature, T_c, the superconducting state. In this state they have zero electrical resistance.
One of the most important high temperature superconductor materials is the $YBa_2Cu_3O_7$. This material has a structure that is similar to the perovskite structure, with the difference that 2/9 of the oxygen ions are missing
In this structure the the Y- and Ba cations are the A ions of the original perovskite and the Cu-ions are the B cations. There are two kind of lattice sites for the Cu ions, a square pyramidal Cu(II) site and a square planar Cu(III) site. The Cu^{3+} ions can accept electrons from the Cu^{2+} ions and an internal charge transfer process can occur, which is very important for the superconductivity of $YBa_2Cu_3O_7$.

Spinel structure

In spinels the oxygen ions are forming a cubic close packed structure. Concerning the distribution of the cations we have to distinguish between two kinds of spinels:

1.) The first one ist the so called “normal spinel”, which has the general formula AB_2X_4. In this structure the A-Kations are occupying 1/8 of the tetrahedral holes and the B-Kations are occupying ½ of the octahedral holes. An example for a mineral that has a spinel structure, is the spinel-mineral itself with the composition $MgAl_2O_4$.

2.) The second type of spinels is the so called “inverse spinel”. It has the general formula $B[AB]O_4$. In this structure the B-Kations are occupying 1/8 of the tetrahedral holes and the second B- and the A-Kations are occupying ½ of the octahedral holes. An example for an inverse spinel is Fe_3O_4.

Literature:

1.) U. Müller, Inorganic structural chemistry, Wiley-VCH, **1999**
2.) D. Shriver, P. Atkins, Inorganic chemistry, Wiley-VCH, second edition, **1997**

Tasks:

1.) Sketch the unit cells of the perovskite structure and show the coordination of the Ca- and Ti- Kations.
2.) What is the reason for the superconductivity of the $YBa_2Cu_3O_7$