A Structural Study of the High Temperature Phases of Umbite and it's Derivatives

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The work present here analyses the structural chemistry of a wide variety of ion exchanged zirconium silicate phases subjected to high temperature. In this work the synthetic analogue of Umbite, $K_2ZrSi_3O_9.H_2O$, which can be prepared using hydrothermal methods and has an orthorhombic call with the space group $P2_12_12_1$, a = 10.2977(2) Å, b = 13.3207(3) Å and c = 7.1956(1) Å was ion exchanged with different cations.

A primary aim is to study the structural transformation of a variety of different ion exchanged Umbite subjected to high-temperatures to investigate how the structure collapses and traps the ions within the framework and how the different ions affect the structural phases formed and determine if there are any new intermediate phases formed. Nuclear waste streams contain Sr^{2+}, and Na^+ therefore it was decided to investigate the following ion exchanged phases; Ce-Umbite, Sr-Umbite and Na-Umbite. Ce^{4+} is also an inactive surrogate for Plutonium.

The ion exchanged Umbite is studied using a variety of solid state characterisation methods including synchrotron powder X-ray diffraction (XRD) and X-ray pair distribution function (XPDF). At high-temperatures certain charge balancing ions cause the structure to lose crystallinity, due to this powder XRD can no longer be used to determine the structure of these phases. To determine the structure of the amorphous phases XPDF will be used. This will allow the investigation of the local structure around the ion in order to fully understand the ion-exchange properties and determine a structural model. This information will be fundamental in determining if these materials have potential use as ion-exchangers for the nuclear industry. Investigating if the structure collapses is important because it is essential to determine if the ions are trapped into materials and whether the ions leach out during long term disposal for example in a geological disposal facility.

The samples behave differently depending on the nature of the ion exchanged cation. When heated K Umbite undergoes a phase transition at 650°C due to the loss of water. However, Na and Sr Umbite do not undergo a phase transition when subjected to high temperatures. Ce Umbite becomes amorphous when subjected to high temperature. For the K Umbite and exchanged phases the unit cells contract as the temperature increases displaying a negative thermal expansion, confirming upon heating the structure collapses and traps the ions within the material. There is also a loss of crystallinity at high temperatures. Less work has been carried out on microporous zirconium silicates, it is essential to investigate the phases formed at high temperature as theses phases could have a greater affinity towards cations present in nuclear waste.