Investigation of Cation Ordering in High Pressure $Sc_4Ti_3O_{12}$

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$ScTiO_3$ crystallizes in the bixbyite structure (space group: *I-3a* (#206)) with Sc^{3+}/Ti^{3+} disorder on the *8b* and *24d* sites.[1,2] $ScTiO_3$ topotactically oxidizes to $ScTiO_{3.5}$.[2] $ScTiO_{3.5}$ is a cation disordered (Sc^{3+}/Ti^{4+})fluorite structure (space group: *Fm-3m* (#225)) with 1/8 oxygen vacancies and mimics potential high temperature solid state oxide ion conductors.[2] At elevated temperature $ScTiO_{3.5}$ undergoes phase separation into TiO_2 (rutile) and cubic $Sc_4Ti_3O_{12}$ (space group: *Fm-3m* (#225)).[2,3] $Sc_4Ti_3O_{12}$ is known to form either a disordered fluorite structure (space group: *Fm-3m* (#225)) with vacancies on the cation lattice as well as on the anion lattice.[2] This disordered structure can undergo oxygen vacancy ordering and results in confining Ti^{4+} to the octahedral sites only. The ordered $Sc_4Ti_3O_{12}$ structure is rhombohedral (space group: *R-3* (#148)).[4] All previous work on $Sc_4Ti_3O_{12}$ (cubic and rhombohedral phases) has been carried out with X-ray diffraction experiments. The order-disorder phase transition can be clearly identified from the powder X-ray diffractograms but no comments regarding potential partial cation disorder can be supported with the previous data.

The synthesis of the ordered rhombohedral phase of $Sc_4Ti_3O_{12}$ is usually carried out by means of sol-gel synthesis but often results in cubic – rhombohedral phase mixtures. We have predicted that the rhombohedral phase could be formed under high pressure due to the larger density of the rhombohedral phase.

The high pressure synthesis only provides samples of approximately 30 mg. Because of the limited sample size a zero background single crystal Si-sample holder was used for the powder neutron diffraction experiments on powder diffractometere C2 at the CNBC in Chalk River. We obtained high quality powder neutron diffratograms clearly indicating full oxide anion ordering for the rhombohedral $Sc_4Ti_3O_{12}$ phase. No Sc^{3+} was found on the octahedral cation site, consequently the 3a site only contains Ti^{4+}, whereas the 18f site contains disordered Sc^{3+}/Ti^{4+} cations with a 2:1 Sc^{3+}:Ti^{4+} ratio.

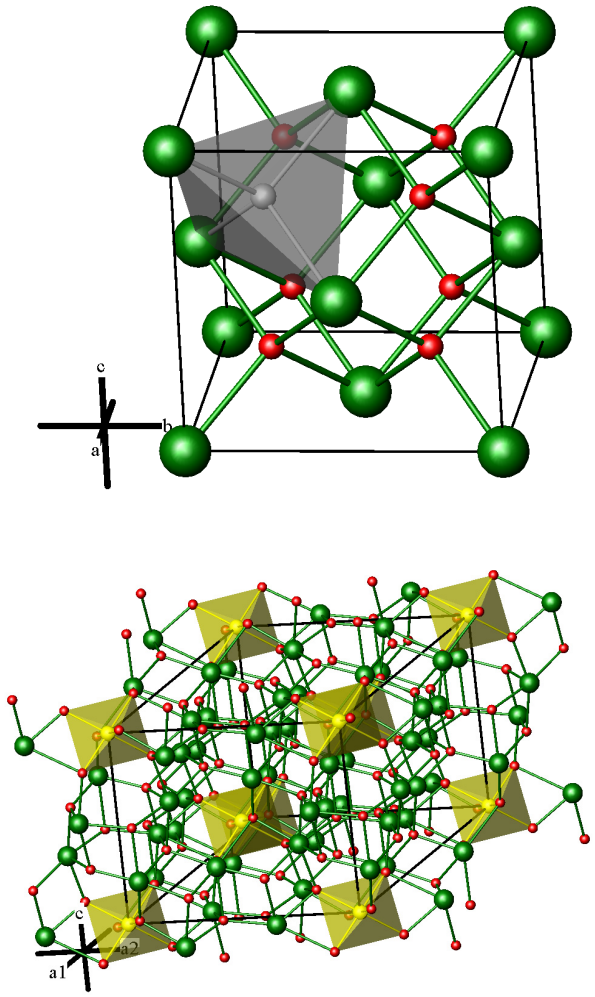

Fig. 1 (top) Cubic $Sc_4Ti_3O_{12}$ (*Fm-3m*) structure with fully disordered Sc^{3+}/Ti^{4+} cations and oxide defects. (bottom) Rhombohedral $Sc_4Ti_3O_{12}$ (*R-3*) structure with ordered oxide anions and only Ti^{4+} in octahedral sites. Green = Sc^{3+}/Ti^{4+}, yellow = Ti^{4+}, red = O^{2-}, grey = vacancy.

To our knowledge this is the first powder neutron diffraction experiment that can clearly describe the ordered phase. The experimental diffractogram for the high pressure $Sc_4Ti_3O_{12}$ sample is shown in figure 2 and is contrasted with simulated powder neutron diffractograms for the fully ordered and the fully disordered $Sc_4Ti_3O_{12}$ structures. The data clearly show

that the structure is ordered. Further details will be reported elsewhere.

References

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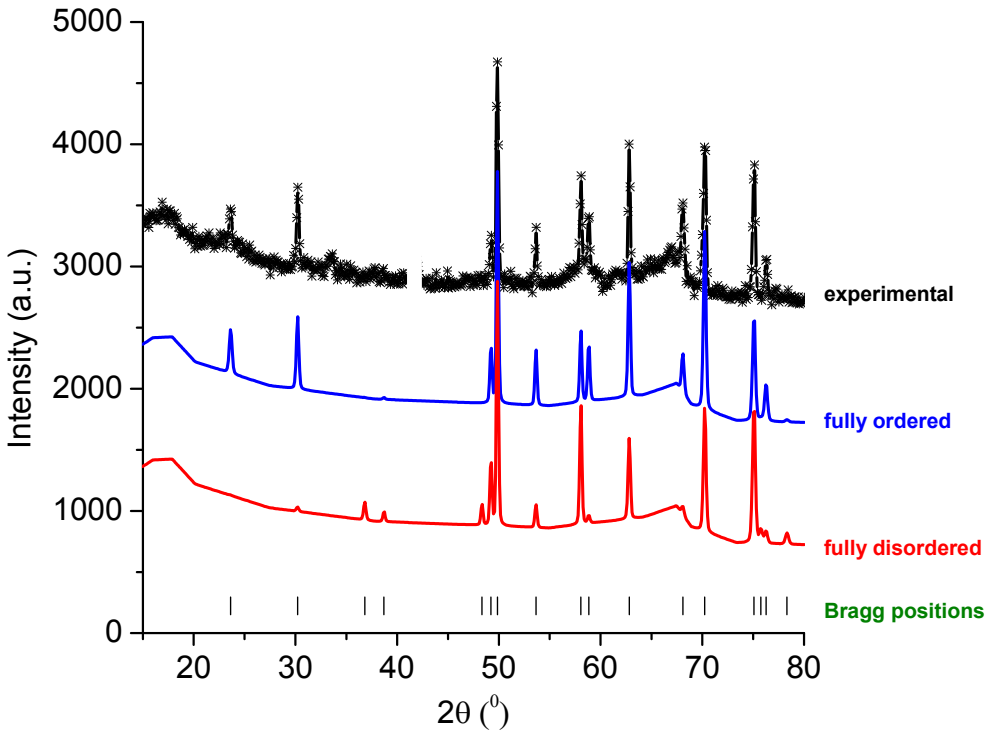

Fig. 2 Powder neutron diffractogram (λ=2.37Å) of Sc4Ti3O12 prepared at high pressure and high temperature (black crosses), simulation of the fully ordered structure (blue line) and of the fully disordered structure (red line).