

Experiment title: Synthesis and transformations of nanomaterials; time resolved in-situ powder diffraction studies.

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Report: Doping-dependent properties of lepidocrocite titanates

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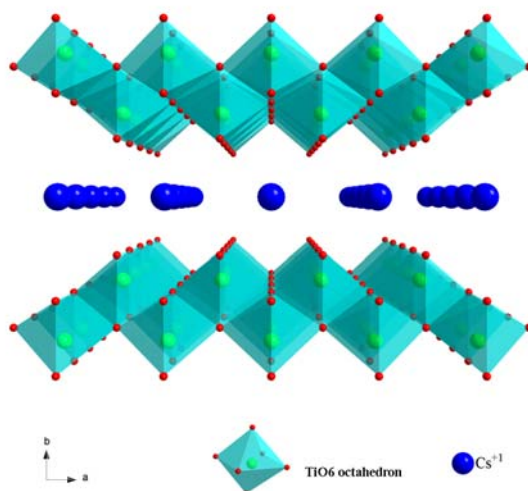


Figure 1. Polyhedral representation of the crystal structure of $\text{Cs}_x\text{Ti}_{2-x/2}\text{Mg}_{x/2}\text{O}_4$ ($x = 0.7$) viewed down along the c -axis. The Mg substitution is not shown for simplification.

The structure of several of lepidocrocite titanates $\text{Cs}_x\text{Ti}_{2-y}\text{M}_y\text{O}_4$, where M is any of vacancy, Li, Mg, Zn, Cu, Co, and Ni, has been determined from synchrotron XRD data collected at station BM01A, SNBL, ESRF. The lepidocrocite titanates studied usually crystallize into a body-centred orthorhombic layered structure, consisting of two-dimensional (2D) corrugated layers of edge and corner shared octahedra and interlayer Cs

ions, which compensate for the negative charge that arises from the substitution of M for Ti, as shown in Figure 1. The presence of interlayer Cs ions and the lattice substitution M indicates the lepidocrocite titanates are intrinsically heavy doped materials, where some doping-induced properties can be expected [1-2].

The structure of an Mg-doped titanate $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ has been determined by starting a Rietveld refinement with the high-resolution synchrotron XRD data. The final refinement on the basis of a body-centred orthorhombic structure (space group $Immm$) yielded a satisfactory convergence with the residual indices of $R_{wp} = 0.0754$ and $R_p = 0.0564$. The observed, calculated and difference profiles are illustrated in Figure 2. The refinement confirms that Mg^{2+} ions occupy the octahedral sites in the 2D corrugated host layers; substitution for Ti^{4+} ions in the nominal TiO_2 framework results in negative charge that is balanced by the interlayer Cs^+ ions.

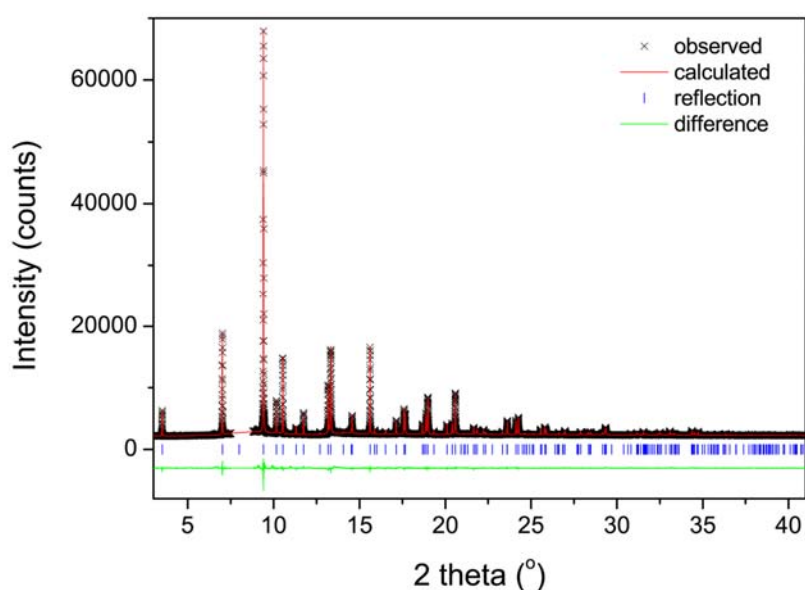


Figure 2. Final results of the Rietveld fitting of synchrotron X-ray diffraction data for $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($\lambda = 0.520193$ Å). The data region from 7.5° to 8.4° was excluded during the refinement due to a broad bump.

This compound shows interesting defect chemistry. Acid exchanging the $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ results in the protonic form, $H_xTi_{2-x/2}O_{4-x/2} \cdot H_2O$, which is notable for its extractable lattice Mg substitutions as well as the lattice O atoms [1]. The recent experiments indicate also the rich of defect chemistry in the isomorphous compounds with Zn and/or Ni doping [2, 3]. Further characterizations on these compounds are under way.

References

[1] Tao Gao, Helmer Fjellvåg, and Poul Norby, *Protonic titanate derived from $Cs_xTi_{2-x/2}Mg_{x/2}O_4$ ($x = 0.7$) with lepidocrocite-type layered structure*, **Journal of Materials Chemistry**, 19 (2009) 787-794.

[2] Tao Gao, Helmer Fjellvåg, and Poul Norby, *On the defect chemistry of lepidocrocite titanates: A zinc-doped titanate $Cs_xTi_{2-x/2}Zn_{x/2}O_4$ ($x = 0.7$)*, in preparation.

[3] Tao Gao, Helmer Fjellvåg, and Poul Norby, *Synthesis of nickel-doped lepidocrocite titanates and their doping-dependent properties*, in preparation.