Experimental report

20/04/2016

Proposal: 5-21-1089 **Council:** 10/2014

Title: Accurate site-occupancies of Cu and Zn in inverse CuxZn2 - xTiO4 spinel from powder neutron diffraction

Research area: Physics

This proposal is a new proposal

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Samples: CuxZn2-xTiO4 (0 < x < 1)

Instrument	Requested days	Allocated days	From	To
D2B	2	2	20/04/2015	22/04/2015

Abstract:

Zn2TiO4, pure or doped, is a versatile host material, ideal for engineering optical and magnetic properties. Our recent x-ray diffraction (XRD) and Raman spectroscopy experiments have revealed that Cu2+ incorporates in both the octahedral and tetrahedral sites of CuxZn2-xTiO4 inverse spinel up to x = 0.6, but the maximal concentration of Cu2+ in the tetrahedral sites is currently unknown. In order to understand the material for future applications, the site occupancies for solid solutions with different Cu-concentrations have to be determined. XRD is not appropriate to solve this question since in CuxZn2-xTiO4, Cu2+ substitutes Zn2+ and these two elements differ by only one electron. Hence, the XRD structure factors are nearly identical and site occupancies cannot be obtained from powder data. With a difference of the coherent neutron scattering cross section between Cu and Zn of 3.432 barns, neutron diffraction is ideally suited to resolve this question. To minimize the effect of temperature, the measurements should be performed at low temperatures. We propose to study the site occupancies of Cu2+ and Zn2+ in CuxZn2-xTiO4 inverse spinel solid solutions with neutron diffraction.

The aim of the experiment

According to our previous study [1], $Cu_xZn_{2-x}TiO_4$ with $0.0 \leqslant x < 1.0$ hold a cubic spinel structure with space group $Fd\bar{3}m$. Raman spectroscopy reveals that Cu^{2+} incorporated into both the tetrahedral $8a$ site and the octahedral $16d$ site (figure 1). XRD is not able to distinguish Cu^{2+} ($3d^9$) and Zn^{2+} ($3d^8$) in the same set of sites because they differ by only one electron. However, the neutron cross sections differ by 3 barns [2], which makes the neutron diffraction pattern of $Cu_xZn_{2-x}TiO_4$ sensitive to the distribution of the Zn/Cu cations (figure 2). Therefore, the aim of the experiment is to approach the accurate site occupancies of the studied spinels.

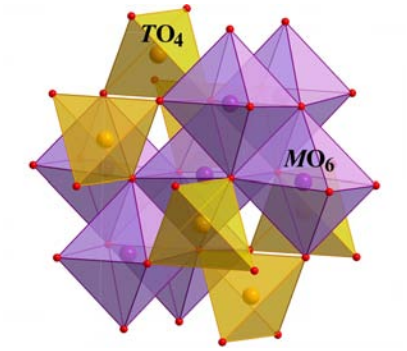

Figure 1: Crystal structure of the cubic spinel using TO_4 tetrahedra and MO_6 octahedra where T and M refers to cations occupying the tetrahedral and octahedral sites, respectively. Each octahedron shares all vertices with 6 tetrahedra and half edges with 6 octahedra.

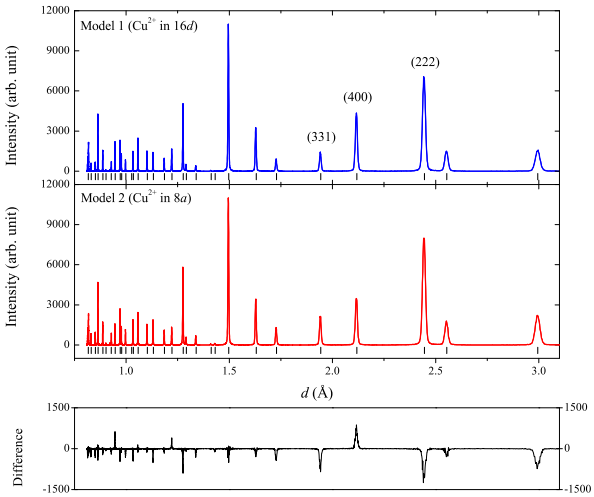

Figure 2: Calculated neutron diffraction patterns of the spinel $Cu_xZn_{2-x}TiO_4$ with x = 0.5 using different structural models where Cu^{2+} is exclusively incorporated into the $16d$ or $8a$ sites. The bottom curve indicates the intensity difference between model 1 and model 2.

Experiment at D2B

Neutron diffraction (ND) data of the spinels $Cu_xZn_{2-x}TiO_4$ with $0.0 \leqslant x < 1.0$ were collected at ambient conditions on the high-resolution powder diffractometer D2B at the Institut Laue-Langevin.

Refinement results

According to the structure factor of the $Cu_xZn_{2-x}TiO_4$ cubic spinels, intensity (I) of the reflections (331) and (400) are sensitive to cation occupancies in both sites while that of (222) is only sensitive to the octahedral cations. The theoretical neutron intensity ratios of $I_{(331)}/I_{(400)}$ and $I_{(400)}/I_{(222)}$ were calculated using the structure models 1 and 2 and compared with the experimental results, as shown in figure 3. With the increase of molar fraction of Cu^{2+} in the spinels, revolutions of the experimental results agreed well with model 1 while departed from model 2, indicating the main accommodation of

Cu^{2+} in the octahedral $16d$ sites.

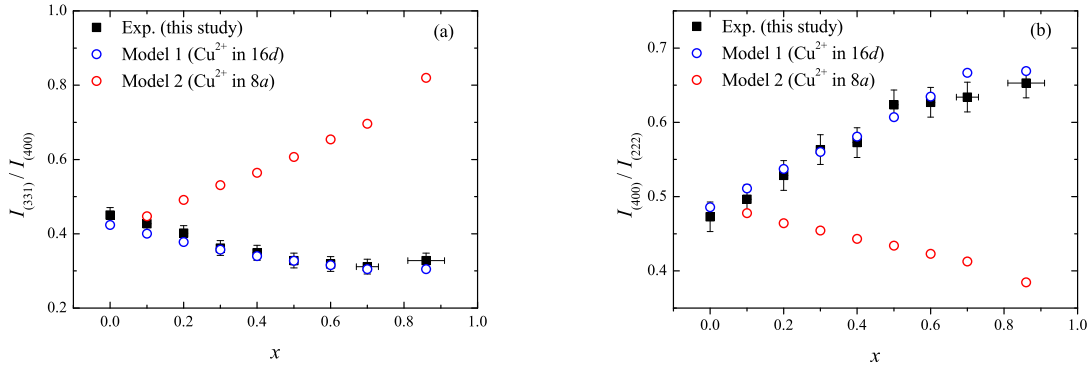

Figure 3: Experimental and theoretical neutron intensity ratios of $I_{(331)}/I_{(400)}$ (a) and $I_{(400)}/I_{(222)}$ (b) in the obtained $Cu_xZn_{2-x}TiO_4$ cubic spinels.

Rietveld refinement [3] was employed to analyse structural changes of $Cu_xZn_{2-x}TiO_4$ due to the substitution of Zn^{2+} for Cu^{2+}. U_{iso} of the cations in the same sites was constrained to be equal. A full occupancy of each site and an overall mass balance of each atom were achieved in the refinement results.

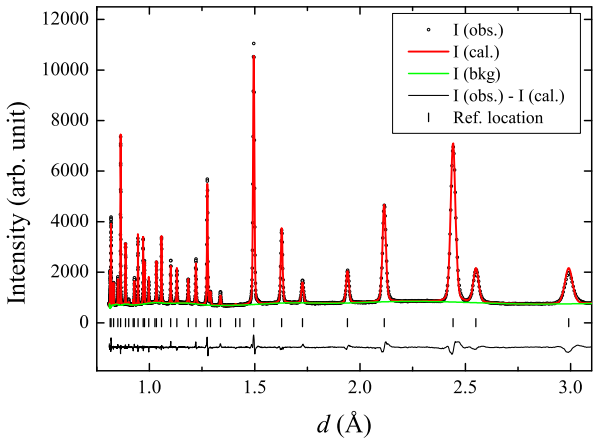

Figure 4: Rietveld refinement results of $Cu_xZn_{2-x}TiO_4$ with x = 0.5 using model 1 (all Cu^{2+} in the octahedral $16d$ site): R_{wp} = 3.26%, R_{wpb} = 4.53%.

Figure 4 gives the typical Rietveld refinement result of $Cu_xZn_{2-x}TiO_4$ with x = 0.5 using model 1. The refinement is very good, as indicated by the R-factors of R_{wp} = 3.26% and R_{wpb} = 4.53%. Another attempt was made to refine the tetrahedral site occupancy, which yielded very similar R-factors. Results showed that at maximum 0.014(1) Cu^{2+} and 0.011(6) Ti^{4+} occupied the tetrahedral sites.

Depending on the refinement strategies, at maximum 0.04(1) Cu^{2+} and 0.04(1) Ti^{4+} occupied the tetrahedral sites of the $Cu_xZn_{2-x}TiO_4$ spinels. The lattice parameter and U_{iso} of the anions O^{2-} from the ND data agreed well with the XRD data [1]. Changes of the positional parameter and the average octahedral and tetrahedral bond lengths are shown in figure 5. Copper caused an increase of u and a

decrease of $d_{M-\mathrm{O}}$, and had no effect on $d_{T-\mathrm{O}}$.

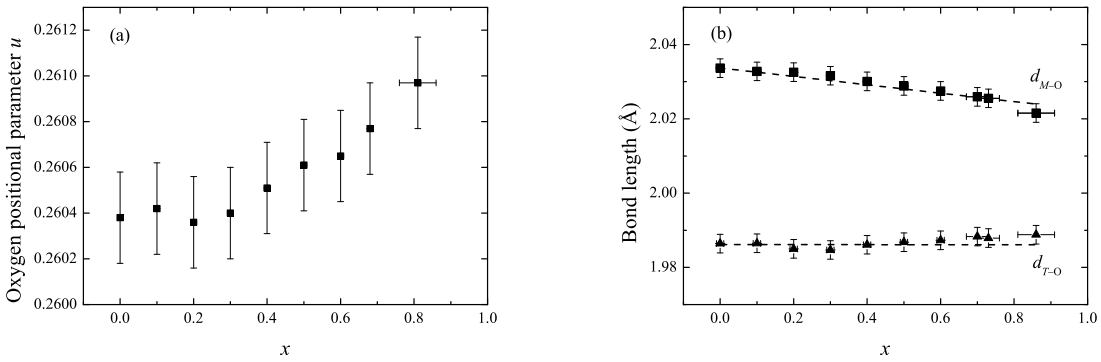

Figure 5: (a) Positional parameter u, (b) the average octahedral and tetrahedral bond lengths of the $\mathrm{Cu}_x\mathrm{Zn}_{2-x}\mathrm{TiO}_4$ cubic spinels.

Structural changes of the $\mathrm{Cu}_x\mathrm{Zn}_{2-x}\mathrm{TiO}_4$ cubic spinels were ascribed to local distortions around Cu^{2+}. Due to the d-orbital splitting, Cu^{2+} ($3\mathrm{d}^9$) induced local Jahn-Teller distortion of the CuO_6 octahedra [4]. Figure 6 shows local environments of the distorted CuO_6 octahedron.

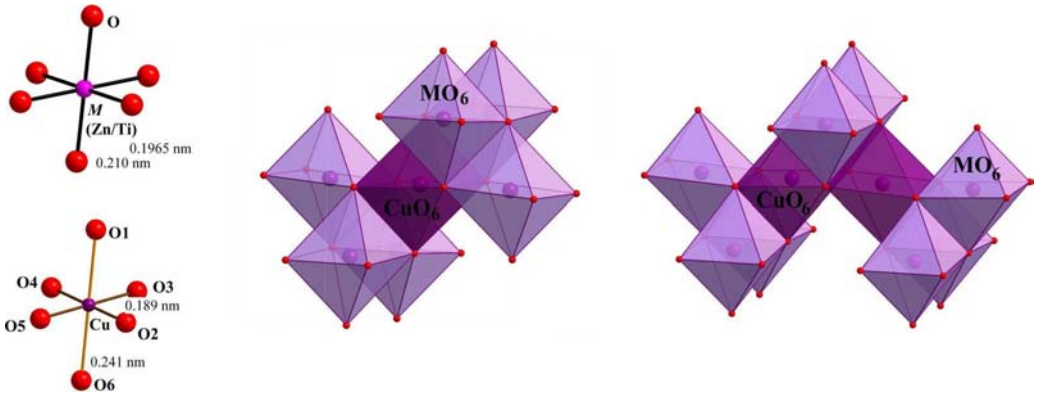

Figure 6: Local environments of the distorted CuO_6 octahedron.

References

[1] J. Ruiz-Fuertes, T. Bernert, M. He, B. Winkler, V. L. Vinograd, and V. Milman. Local structure of $\mathrm{Cu}_x\mathrm{Zn}_{2-x}\mathrm{TiO}_4$ inverse spinel. *Applied Physics Letters*, 105(7):071911, 2014.

[2] B. Grabcev, S. Todireanu, and V. Cioca. Total thermal neutron cross sections of Al, Si, Cu, Zn, Ge, Pb and Bi single crystals. *Journal of Applied Crystallography*, 12(4):399–400, 1979.

[3] H. M. Rietveld. A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2(2):65–71, 1969.

[4] Yu. V. Yablokov and T. A. Ivanova. The labile magnetic structure of JT copper and nickel complexes in the layered oxides. *Coordination Chemistry Reviews*, 190–192:1255–1267, 1999.