

m30.p11**Defect perovskites in the SrO - ZrO₂ - Nb₂O₅ system**

Siegbert Schmid, Ivanka Barisic

*School of Chemistry, The University of Sydney, Sydney, Australia. E-mail: s.schmid@chem.usyd.edu.au***Keywords: perovskites, X-ray diffraction, Rietveld refinement**

The Sr_xNbO₃, 0.7 ≤ x ≤ 1, solid solution with niobium in both oxidation states +IV and +V whenever x < 1, has been reported to adopt the ideal cubic perovskite structure across the whole solid solution field. Despite intensive searching when data were collected on good quality single crystals no additional reflections were detected [1]. This indicates random ordering between strontium and vacancies on the perovskite A sites. Since there is evidence that niobium and zirconium are able to occupy positions in a structure at random [2], it was expected that a similar solid solution might be formed if niobium +IV is replaced by zirconium +IV. Therefore an investigation was undertaken in the SrO-ZrO₂-Nb₂O₅ system to see whether an analogous solid solution is indeed formed and what the extent of the solid solution range is. The composition range of Sr_{0.7+x}Zr_{0.4+2x}Nb_{0.6-2x}O₃ has been investigated in detail (as well as the Hf and Ta analogues) and specimens synthesised across the whole solid solution range (0.01 ≤ x ≤ 0.30). Substituting zirconium in its stable oxidation state +IV means that those syntheses can be carried out in air. X-ray and neutron powder diffraction patterns have shown that while there is an underlying pseudo cubic perovskite sub-structure the symmetry for all investigated compositions is lowered to tetragonal or orthorhombic. The low strontium content end member of the solid solution appeared to adopt cubic symmetry (in accordance with the laboratory X-ray and electron diffraction data), however, profile fitting clearly showed that the phase is actually tetragonal. The situation gets more complicated for the rest of the solid solution where symmetry lowering to orthorhombic is required to fit the patterns satisfactorily. Given that the main difference to the phase Sr_xNbO₃, 0.7 ≤ x ≤ 1, is the replacement of niobium +IV by zirconium +IV it is likely that the symmetry lowering for our new phase is driven by Nb/Zr ordering and accompanying octahedral rotation. It appears that there is no complete solid solution from -0.01 ≤ x ≤ 0.3, but rather a series of smaller solid solutions the extent of which needs to be carefully examined.

[1] Hessen B., Sunshine S.A., Siegrist T., Jimenez R., *Mat. Res. Bull.*, 1991, 26, 85.[2] Withers R.L., Schmid S., Thompson J.G., *Prog. Solid State Chem.* 1998, 26, 1.**m30.p12****Triangular Copper(II) TPPZ Supra-Molecular Species: Anion Encapsulation**

Laurette Schmitt, Helen Stoeckli-Evans

*Institute of Chemistry, University of Neuchâtel, Rue Emile-Argand 11, CH-2009 Neuchâtel, Switzerland. E-mail: laurette.schmitt@unine.ch***Keywords: crystal structures, copper complexes, antiferro magnetic properties**

Since the publication of the first binuclear Copper(II) complex of 2,3,5,6-tetrakis(2-pyridyl)pyrazine (TPPZ) [1] this ligand has been shown to be unusually flexible for the formation of mono- and binuclear compounds, and some polymeric and supra-molecular species. There are more than 60 crystal structures of transition metal complexes involving TPPZ deposited in the Cambridge Crystal Structure Data Base [2]. Recently, we have synthesized some unusual triangular Copper(II) complexes, using (TPPZ) as a η³ chelating ligand, that encapsulate mono-anions, such as, NO₃⁻, ClO₄⁻ and SO₃⁻. These compounds have been characterized crystallographically, and analyzed by UV-Vis spectroscopy and cyclic voltammetry. They also show weak antiferromagnetism.

[1] Graf, M.; Greaves, B.; Stoeckli-Evans, H. *Inorg. Chim. Acta.* 1993, 204, 239.[2] Allan, F.H. *Acta Crystallogr.* 2002, B58, 380.