

Defect Perovskites in the SrO-ZrO₂-Nb₂O₅ System

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A number of samples have been synthesised in the SrO-ZrO₂-Nb₂O₅ system and investigated using laboratory X-ray and neutron powder diffraction data. It is evident that while structures in this solid solution are closely related to the cubic perovskite parent the symmetry for all investigated compositions is lowered to tetragonal or orthorhombic.

1. Introduction

Compounds that can reversibly intercalate lithium have the potential to be used as cathodes in rechargeable lithium ion batteries. Two characteristics, the availability of interstitial or defect sites for the incorporation of lithium and the presence of reducible cations are found in some defect perovskites. The aim of this study is to synthesise a number of defect perovskites, which might be useful as host materials for Li intercalation, and investigate their structures using X-ray and neutron powder diffraction.

The Sr_xNbO₃, 0.7 ≤ x ≤ 1, solid solution having 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.

Given the vacancies in the structure (particularly at the low strontium end of the solid solution) and the accompanying presence of niobium +V, which can be easily reduced by lithium metal, this solid solution appeared to be an interesting candidate to investigate Li-intercalation properties. Given that niobium +IV is not stable at high temperatures in air but rather gets oxidised, previous syntheses of the solid solution were conducted in high vacuum. Substitution of all niobium +IV by zirconium +IV allows syntheses to be carried out in air. Since previous studies have shown that niobium and zirconium are able to occupy positions in a structure at random [2-4], it was expected that a similar solid solution might be formed. Therefore an investigation was undertaken in the SrO-ZrO₂-Nb₂O₅ system to see whether an analogous solid solution is indeed formed, what the extent of the solid solution range is and whether this material has the potential to intercalate Li ions reversibly.

2. Sample preparation

Stoichiometric mixtures of SrCO₃, ZrO₂ and Nb₂O₅ were finely ground using a mortar and pestle, transferred to alumina crucibles and heated in a muffle furnace at 1150°C for 12 hrs. The slightly sintered powder was ground again and subsequently pressed into pellets and heated for a further 3 – 8 days at 1500°C, with up to three further re-grindings. Following this general procedure the samples were investigated using laboratory X-ray powder diffraction and found to be single phase and highly crystalline. The materials were loaded into vanadium cans (diameter 8mm, height 50mm) for data collection at HRPD, ANSTO, Lucas Heights, at a wavelength of 1.8846 Å. Data were collected for between 3 - 4 days each..

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3. Results

3.1 XRD Analysis

Investigation using laboratory X-ray data showed that in the SrO-ZrO₂-Nb₂O₅ system a solid solution similar to Sr_xNbO₃ was formed for Sr_{0.7+x}Zr_{0.4+2x}Nb_{0.6-2x}O₃, with $\sim 0.03 \leq x \leq 0.3$. Initially the symmetry appeared cubic across the solid solution field and Figure 1 shows the plot of ‘cubic’ cell dimensions as a function of composition. Only the sample with x = 0, representing a starting composition slightly outside the solid solution field, showed traces of a second phase.

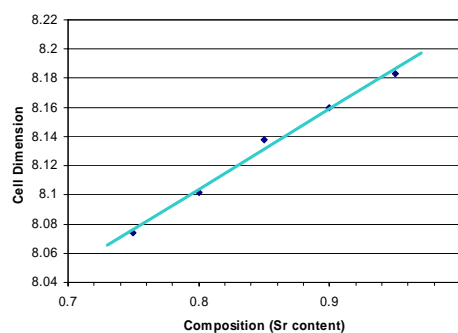


Fig. 1. Plot of the ‘cubic’ unit cell dimensions as a function of composition for Sr_{0.7+x}Zr_{0.4+2x}Nb_{0.6-2x}O₃ (the amount of Sr is given).

3.2 Transmission Electron Microscopy

An initial electron microscopy investigation of the low strontium end member of the solid solution confirmed the apparent cubic symmetry (to within the accuracy of the transmission electron microscope). Figure 2 shows a [100] zone axis (on the left) while the pattern on the right is tilted about 5° from the [100] zone axis and show a spectacular diffuse intensity distribution, indicating that there is additional short range order, which needs to be taken into account for a complete picture of the structure.

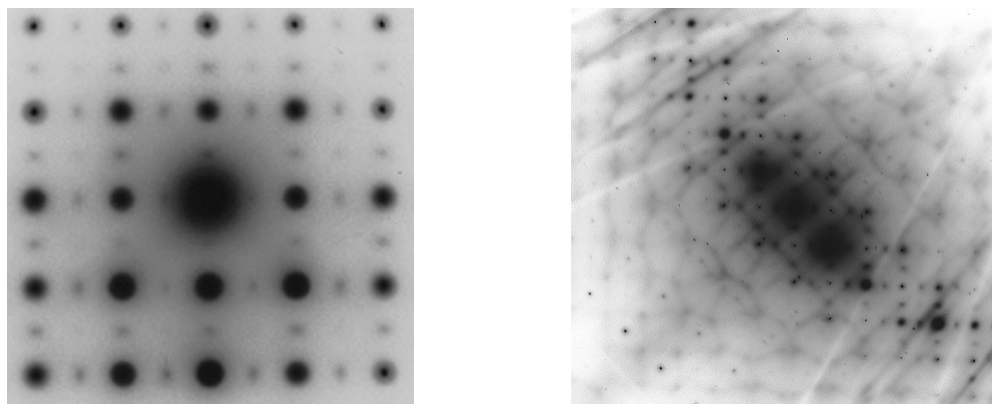


Fig. 2. Electron diffraction patterns showing the weak superlattice reflections (left) as well as a fascinating display of diffuse intensity (right) indicating additional short range ordering.

3.3 Neutron Powder Diffraction

Neutron powder diffraction patterns were collected at the HRPD instrument of HIFAR,

ANSTO, Lucas Heights. 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 and even monoclinic is required to fit the patterns satisfactorily. Given that the main difference to the phase 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 therefore appears that there is in fact no complete solid solution from $\sim 0.03 \leq x \leq 0.3$ but rather a series of smaller solid solutions the extent of which needs to be carefully examined.

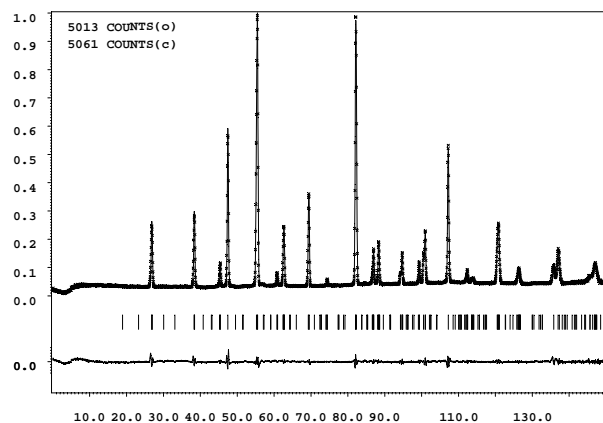


Fig. 3. Neutron powder diffraction pattern of the $x = 0.10$ member of the solid solution (HIFAR, $\lambda = 1.8846 \text{ \AA}$; $Cmcm$; $a = 8.1034$, $b = 8.1245$, $c = 8.1067 \text{ \AA}$).

Preliminary investigation of the Li-intercalation properties for members of the solid solution have shown that at least for the low strontium content end member a very significant amount of lithium can be intercalated reversibly [5]. These results will be presented in a separate publication.

Acknowledgments

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