Modulated Structures in the Ta_2O_5-WO_3 System

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X-ray and neutron powder diffraction data for a number of compositions within the $(1-x)Ta_2O_5 \cdot xWO_3$, $0 \leq x \leq 0.267$, solid solution were collected at the Australian National Beamline Facility, Tsukuba, and at ANSTO, Lucas Heights, respectively. The results of the structure refinements using the program JANA are presented.

1. Introduction

Systems that form modulated structures are a fascinating class of materials which lack lattice periodicity but may still be perfectly long-range ordered [1]. They are inherently more flexible than other systems and consequently many of them are found amongst interesting and technologically useful materials, *e.g.* high-T_c superconductors, organic conductors and intermetallic compounds, amongst others.

Composite modulated structures consist of two or more substructures, each with their own symmetry *etc*. and, in general, with an incommensurable periodicity along at least one of the unit cell directions. They can exist as line phases or wide-range non-stoichiometric solid solutions. The structures of such solid solutions have the ability to adapt continuously over an often extremely wide composition range, while maintaining the essential integrity of their structure type. Detailed chemical investigations as well as crystallographic results are required across such solid solution fields in order to better understand the crystal chemical origin of this extraordinary structural flexibility.

One example for a composite modulated structure, the wide-range, non-stoichiometric solid solution $(1-x)Ta_2O_5 \cdot xWO_3$, $0 \leq x \leq 0.267$, has been subject to intensive investigation over many years [2 - 7]. Owing to the phase transition at 1360 °C, large single-crystals of L-Ta_2O_5 were impossible to grow. Thus, attempts were made to stabilise the phase by the addition of other oxides. For WO_3, a series of anion-deficient α-UO_3-related 'line phases' with basic structure dimensions very similar to those of L-Ta_2O_5 was found within the composition range $(1-x)Ta_2O_5 \cdot xWO_3$, $0 \leq x \leq 0.267$.

It was shown that all diffraction patterns obtained at whatever composition within this composition range could be coherently indexed in terms of incommensurately modulated structures characterised by a smoothly varying, composition-dependent, primary modulation wave-vector (and average structure unit cell dimensions) and by the one specific superspace group symmetry – $Xmmm(0\beta0)s00$ [3]. An elegant description is possible in terms of two coherently intergrown, mutually incommensurable, component substructures. The two average substructures (an M substructure containing the metal and apical oxygen atoms and an O substructure containing the basal plane, or equatorial, oxygen atoms - see Fig. 2) both have *Cmmm* space group symmetry and identical **a** and **c** axes but are, in general, mutually incommensurable along their common *b* axis direction with a relative periodicity $b_M/b_O = \beta$ which ranges from ~1.635 for x = 0 (*i.e.* Ta_2O_5) to ~1.615 for x = 0.267 (*i.e.* $Ta_{22}W_4O_{67}$).

Until recently, structural analyses for modulated phases were essentially confined to investigations of single crystals, as only these allowed for sufficient numbers of weak satellite reflections to be collected in adequate quality. There was no easily manageable program available that allowed refinement of powder diffraction patterns from modulated structures.

Furthermore the difference between the real modulated structure and an underlying average structure, in most cases, only produces weak additional features in reciprocal space. These weak features (Fig.1), therefore, contain all the interesting information for the particular structure and need to be analysed carefully. Therefore, it is necessary to extend the capability to routinely solve and refine modulated structures to powder data.

The aim of this contribution is to establish accurate and reliable refinement procedures for ceramic materials with commensurate or incommensurate modulated structures using powder diffraction data.

2. Sample preparation and data collection

Ta_2O_5 (Aldrich, 99.99%) was tempered at 1300°C for two weeks to increase its crystallinity prior to data collection. $(1-x)Ta_2O_5 \bullet xWO_3$, x = 0.200, was prepared using solid state techniques. Component oxides (WO_3: Koch-Light Labs Ltd, 99.9%) were mixed in the required ratio, ground in a mortar and then heated in an alumina crucible at 1000°C for 3 days followed by a further heating at 1500°C for 2 hrs. Following this treatment the material appeared 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 1.88424(4) Å. Data were collected for 72 hrs each. For data collection at the synchrotron the samples were put into glass capillaries (0.3 mm nominal diameter). Owing to apparent absorption problems the data were collected at a wavelength of 0.704(1) Å (Fig. 1).

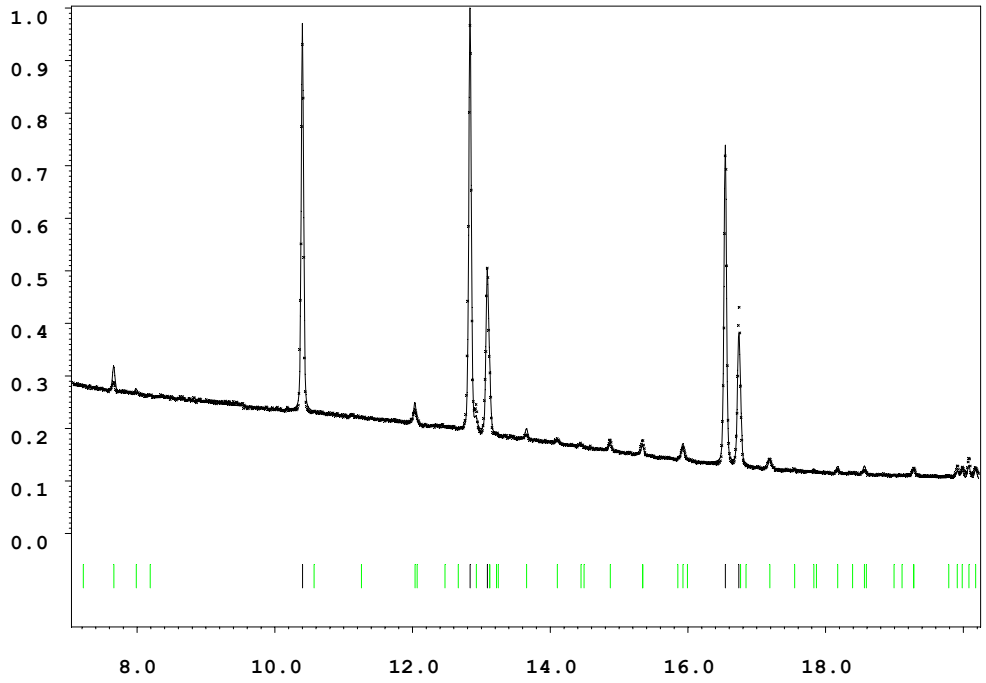

Fig. 1: X-ray diffraction pattern from the ANBF, Tsukuba (λ = 0.7 Å; rel. intensity *vs.* 2θ). Black markers are for main reflections of the metal substructure, while green markers are for satellite reflections thereof. From this typical pattern the weakness of satellite reflections is easily appreciated.

3. Results

JANA [8], the program of choice for refinements of modulated structures, was used to refine the structures. The average positions with respect to the underlying parent substructures are Ta/W (0,0,0), O_M $(0,0,\frac{1}{2})$ and O($\frac{1}{4}$, $\frac{1}{4}$, 0). The modulation functions were refined using starting values of ±0.0001 and the resulting parameters compared to values

available from previous single-crystal structure refinements, of other compositions within the solid solution. Refinements using X-ray powder diffraction data led to reasonable results when compared with previous refinements from single crystal data. Debye-Waller factors for the oxygen atoms, especially O_2, were not well behaved and strongly correlated with the absorption correction. Refinements using neutron diffraction data again led to reasonable results when compared to previous refinements.

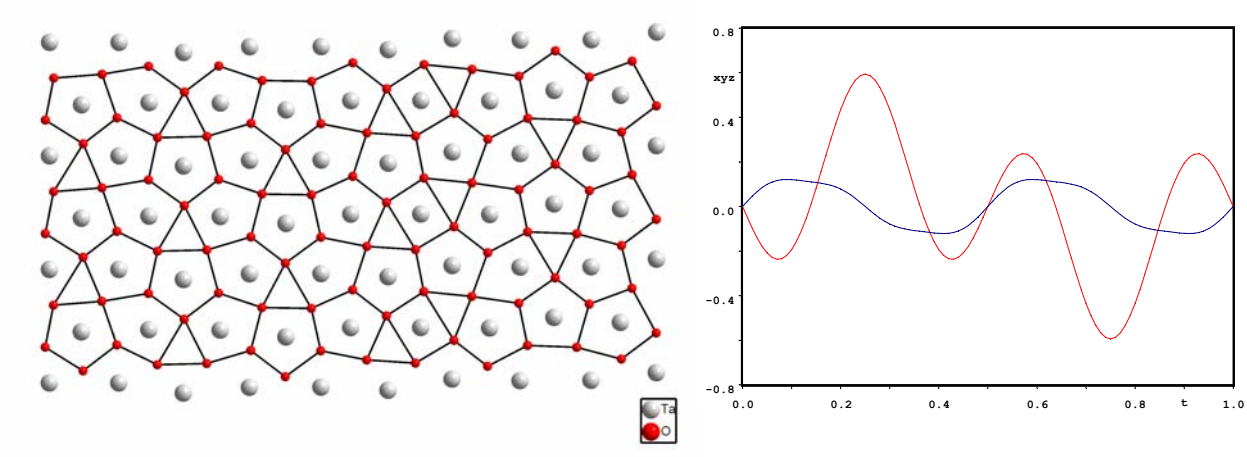

Figure 2: (a) Projection of the x = 0 structure along *c*. Oxygen atoms above and below the metal atoms are not shown; (b) Positional atomic modulation function for the metal atoms in Å as a function of the internal coordinate **t** (red = x; blue = y).

4. Conclusions

It has been shown that refinements using powder diffraction data lead to reasonable results, when care is taken. Especially the powerful combination of powder neutron and X-ray diffraction data ensures that good refinements are achieved. The final modulation functions are certainly entirely compatible with previous results for other compositions [4], refined using single-crystal X-ray diffraction data.

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