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Diffuse scattering in the cesium pyrochlore $CsTi_{0.5}W_{1.5}O_6$

Gordon J. Thorogood [a], Paul J. Saines [b], Brendan J. Kennedy [b,*], Ray L. Withers [c], Margaret M. Elcombe [d]

[a] Institute of Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia
[b] School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia
[c] Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia
[d] Bragg Institute, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW 2234, Australia

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Abstract

The structure of the defect pyrochlore $CsTi_{0.5}W_{1.5}O_6$ has been investigated using electron, synchrotron X-ray and neutron diffraction methods. The material is cubic $a = 10.2773$ Å with displacive disorder of the Cs cations along the ⟨1 1 1⟩ direction. The local structure, revealed by the diffuse structure in the electron diffraction patterns shows there is correlated displacement of the heavy Cs atoms along the ⟨1 1 0⟩ directions. The thermal expansion of the material is also described.

Keywords: A. Oxides; C. Electron diffraction; C. Neutron scattering; C. X-ray diffraction; D. Thermal expansion

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1. Introduction

Pyrochlore oxides display a remarkable range of physical properties, including catalytic activity, piezoelectric behavior, ferro- and ferrimagnetism, and giant magnetoresistance [1–3]. Pyrochlores display a similar wide range of electrical and ionic conductivities [4–7], including metallic, semiconducting and superconductivity [8,9]. Pyrochlores have been employed in fuel cells because of the high mobility of the oxygen ions [10], but perversely other pyrochlores form the basis of materials for nuclear-waste containment, presumably displaying very low cation mobility [11]. Some pyrochlore oxides undergo order/disorder transformations upon heating [12].

The pyrochlore oxides are a family of phases having the general formula $A_2B_2O_7$, although this is often written as $A_2B_2O_6O'$ or $B_2O_6{\cdot}A_2O'$ to highlight the two interpenetrating networks [1]. The corner-shared BO_6 octahedra giving rise to a B_2O_6 network with intersecting A–O′ chains having a formula A_2O'. These two networks only weakly interact and vacancies in the A_2O' network are common leading to defect pyrochlores such as $Pb_2Ru_2O_{6.5}$ [13], KOs_2O_6 [9] and $(NH_4)NbWO_6$ [14]. The A-type cations bond to six-oxygen atoms from the puckered hexagonal rings formed by the B_2O_6 network. In stoichiometric pyrochlores, the 8-fold geometry of the A-type cations is completed by two O′ anions from the A_2O' chains. Electro-neutrality can be achieved with several combinations of different valences for the

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* Corresponding author. Tel.: +61 2 9351 2742; fax: +61 2 9351 3329.
E-mail address: b.kennedy@chem.usyd.edu.au (B.J. Kennedy).

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A and B cations or by vacancies in the A_2O' network, and it is this flexibility of the pyrochlore structure that makes it so attractive for many applications in materials chemistry.

The ideal $A_2B_2O_6O'$ pyrochlore structure has cubic $Fd\bar{3}m$ symmetry with the four atoms occupying special positions, the A-type cations on 16*c* (½, ½, ½) at B cations on 16*d* at (0, 0, 0) O at 48*f* at (*x*, 1/8, 1/8) and O' at 8*b* (3/8, 3/8, 3/8). In a number of recent studies displacive disorder of the A-cations in the {1 1 1} planes has been observed [15–22]. The importance of such disorder is also emerging, for example displacive disorder is believed to contribute to the high relative permittivities displayed by $(Bi,Zn)_2(Zn,Nb)_2O_7$ that makes these materials attractive for use as capacitors. Neutron and X-ray diffraction studies suggest that the disorder involves displacement of the A-cation along the six $\langle 1\ 1\ 2\rangle$ or $\langle 1\ 1\ 0\rangle$ directions. The observation of diffuse scattering in electron diffraction patterns of such pyrochlores suggests there is strong local correlations among the disordered ions and Withers has suggested that the $O'A_4$ tetrahedra within the pyrochlore average structure type rotate as essentially rigid bodies with the O′ anion remaining in the centre of the tetrahedra [23].

A second class of pyrochlores is the AB_2O_6 materials [1] first described by Babel [24]. In these pyrochlores the A-type cation is typically described as occupying the 8*b* site. Such materials have attractive ion exchange properties [7,24]. The recent discovery of superconductivity in KOs_2O_6 [9] has lead to a resurgence in interest in these materials.

As part of their study of pyrochlores as hosts for the chemical immobilization of environmentally unfriendly waste Wittle and co-workers [25] recently described structural studies of the defect pyrochlores $CsM_{0.5}W_{1.5}O_6$ (M = Ti, Zr, Hf). The aim of the present paper was to examine the structure and possibility of disorder of Cs in one such oxide, $CsTi_{0.5}W_{1.5}O_6$.

2. Experimental

The polycrystalline sample of $CsTi_{0.5}W_{1.5}O_6$ was prepared by combining a stoichiometric mixture of $CsNO_3$, TiO_2 and WO_3 and sintering at 1123 K in air for 24 h. The calcined powder was then ball-milled for 16 h in cyclohexane, dried at 363 K, pressed into a pallet and then fired in air at 1123 K for 96 h.

Powder neutron diffraction data were recorded on the high-resolution powder diffractometer at ANSTO's HIFAR reactor [26]. Data were collected in 0.05° steps over the angular range $10 \le 2\theta \le 150^\circ$ using 1.337 Å neutrons. The sample was held in a thin-walled vanadium can. Synchrotron X-ray powder diffraction data were recorded using the Debye–Scherrer diffractometer on beamline 20B, the Australian National Beamline Facility, at the Photon Factory, Tsukuba, Japan [27]. Data were collected in 0.01° steps over the angular range $5 \le 2\theta \le 85^\circ$ using X-rays of wavelength 0.80088 Å. The sample was held in a 0.3 mm dia quartz capillary and rotated throughout the measurements. Temperature control was achieved using a custom built furnace. Structures were refined using the Rietveld method as implemented in the program RIETICA [28].

A JEOL JSM6400 scanning electron microscope (SEM) equipped with a Noran Voyager energy-dispersive X-ray spectroscopy system (EDS) was operated at 15 keV for microstructural analysis work.

Electron diffraction (ED) was carried out using a Philips EM 430 transmission electron microscope operating at 300 kV. Samples suitable for TEM work were prepared by the dispersion of finely ground material onto a holey carbon film.

3. Results and discussion

3.1. Analytical electron microscopy

The surface of a sintered and polished disc of $CsTi_{0.5}W_{1.5}O_6$ was decorated with a small number of well-formed needles (Fig. 1a) due to the disc having been polished with a polar liquid. The stoichiometry of the bulk sample determined using energy dispersive X-ray spectroscopy (EDS) was $Cs_{1.2}Ti_{0.4}W_{1.5}O_6$. EDS of the needles showed these to be cesium rich of stoichiometry $Cs_{2.0}Ti_{0.04}W_{1.6}O_6$, suggesting the loss of Cs from the sample. This could occur if the Cs diffused to the surface of the discs during sample polishing. In order to verify this, the surface of an unpolished disc was also examined before and after the final sintering step and this showed no surface decoration (Fig. 1b and c). Surface enrichment has been observed in the oxygen deficient pyrochlore $Pb_2Ru_2O_{6.5}$ with PbO_2 crystallizing on the surface following its use as an electrocatalyst [29]. That Bi does not segregate from the analogous Bi–Ru pyrochlore $Bi_2Ru_2O_{7-\delta}$ during electrolysis suggests the oxygen vacancies play a key role in the cation mobility [30]. The diffusion