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# Anomalous ionic conductivity of $\text{Sc}_2(\text{WO}_4)_3$ mediated by structural changes at high pressures and temperatures

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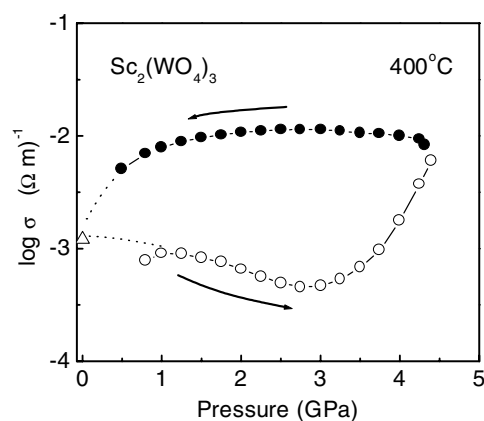
## Abstract

The ionic conductivity of  $\text{Sc}_2(\text{WO}_4)_3$  at 400 °C shows a normal decrease with increase in pressure up to 2.9 GPa but then increases anomalously at pressures up to 4.3 GPa. Synchrotron *in situ* x-ray diffraction results show that  $\text{Sc}_2(\text{WO}_4)_3$  undergoes pressure-induced amorphization at pressures coincident with the reversal in conductivity behaviour. The loss of crystal structure at high pressure may be associated with the property of negative thermal expansion in  $\text{Sc}_2(\text{WO}_4)_3$ .

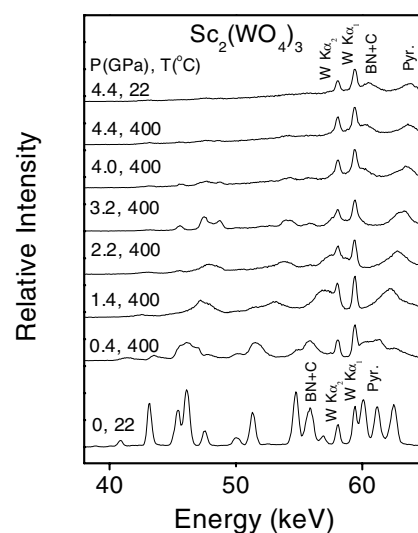
## 1. Introduction

In general, ionic mobility in solid electrolytes strongly depends on the valency and size of the mobile ion. Due to high electrostatic interaction with the surrounding framework structure of anions, such as  $\text{O}^{2-}$ , highly charged trivalent cations are often considered to be poor candidates for showing ionic migration. However, trivalent cationic conduction is possible in the  $\text{Sc}_2(\text{WO}_4)_3$ -type structure [1, 2]. This structure consists of a framework linked by corner-sharing  $\text{ScO}_6$  octahedra and  $\text{WO}_4$  tetrahedra which offers a large tunnel size for ionic migration.

It is common for ionic conductivity to increase with temperature since the normal effect of temperature is to expand the lattice, thereby facilitating motion of the mobile species. However,  $\text{Sc}_2(\text{WO}_4)_3$  belongs to a relatively small class of substances with negative thermal expansion coefficient [3, 4]. Since the mechanism of ion conduction is not affected by temperature up to 600 °C, the increase in  $\text{Sc}^{3+}$  mobility must be explained by structural accommodation resulting from the coupled tilting of the quasi-rigid framework polyhedra that causes contraction on heating [3]. In this context of enhanced conductivity resulting from overall lattice compression, we investigated the effects of high pressure ( $P$ ) on the conductivity of  $\text{Sc}_2(\text{WO}_4)_3$  as a means of exploring a new route to high-conductivity behaviour.



**Figure 1.** The  $P$ -dependence of the ionic conductivity of  $\text{Sc}_2(\text{WO}_4)_3$  at  $400^\circ\text{C}$  compared with the 1 atm datum [2].



**Figure 2.** High- $P$  XRD patterns of  $\text{Sc}_2(\text{WO}_4)_3$ .

## 2. Experimental details

The  $\text{Sc}_2(\text{WO}_4)_3$  sample used in this study was synthesized by standard solid-state techniques from the constituent oxides. Measurements of the ac conductivity in the frequency range 10 Hz–1 MHz at a temperature of  $400^\circ\text{C}$  and at pressures up to 4.3 GPa were carried out in a 1000 ton cubic press using a Solartron SI 1260 Impedance/Gain-Phase Analyzer. High- $P$ , *in situ*, synchrotron radiation x-ray diffraction (XRD) experiments were performed in a 250 ton DIA-type high- $P$  apparatus at the beamline 13 BM-D, Advanced Photon Source (APS), Argonne National Lab. An NaCl pressure standard was used for *in situ* measurement of  $P$ . Energy-dispersive XRD spectra were collected for 400 s at each  $P$ -setting with a Ge detector at a fixed  $2\theta$  angle of  $3.82^\circ$ . The small cross-section of the x-ray beam was  $30 \times 300 \mu\text{m}$  and permitted focusing of the beam on just the region of interest.

## 3. Results and discussion

The  $P$ -dependence of the  $\text{Sc}_2(\text{WO}_4)_3$  conductivity at  $400^\circ\text{C}$  is plotted in figure 1 and compared with the 1 atm value [2]. Relative to the 1 atm datum, the high- $P$  data show a decreasing trend with increasing  $P$  up to  $\sim 3$  GPa. This is the expected effect of increasing  $P$  on the conductivity of an ionic conductor as observed in previous studies [5, 6]. As lattice volume decreases,  $\text{Sc}^{3+}$  hopping is impeded by a reduction in site volume and inter-site volume, or tunnel size. In addition, the bonding environment of available crystalline sites under  $P$  changes as inter-atomic distances are reduced leading to an increase in the activation energy of hopping. This is consistent with the observed increase in conductivity on heating if  $\text{Sc}^{3+}$  mobility is greatest between neighbouring  $a$ – $c$  planes [2]. The main effect of  $P$  then can be understood to reduce the volume between  $a$ – $c$  planes (i.e. reduction in the lattice constant  $b$ ) causing a decrease in  $\text{Sc}^{3+}$  mobility. The decrease in conductivity continues until a critical  $P$  of 2.9 GPa is reached, where the conductivity dependence on  $P$  reverses. Conductivity increases with increasing  $P$  up to the highest  $P$  of 4.3 GPa. This latter behaviour is unexpected for ionic conduction on

the basis of the above explanation. On decreasing  $P$ , conductivity decreases monotonically with a final trajectory in the low- $P$  region toward the 1 atm value.

In the search of an explanation of the positive  $P$ -dependence of conductivity above 2.9 GPa, an increasing electronic component of conduction may be considered but is very unlikely on the basis of the circular arc shape impedance spectra which are convincingly indicative of ionic conduction [7]. Another possibility is of structural origin, that is, a new crystalline phase. To our knowledge, the high- $P$ -temperature phase diagram of  $\text{Sc}_2(\text{WO}_4)_3$  has not been previously reported.

High- $P$  XRD patterns for  $\text{Sc}_2(\text{WO}_4)_3$  at 400 °C taken at several pressures up to a maximum  $P$  of 4.4 GPa are plotted in figure 2. At the experimental  $2\theta$  angle of 3.82° for the detector, the main diffraction peaks from  $\text{Sc}_2(\text{WO}_4)_3$  are localized between 40 and 50 keV. There are some additional strong peaks located in the energy range between 55 and 65 keV. The peaks at energies of 58.07 and 59.43 keV are easily identified as the fluorescence lines  $K\alpha_2$  and  $K\alpha_1$  of W, a strong x-ray absorber, respectively. Three additional peaks at energies of 55.87, 60.09 and 61.17 keV shift to higher energies with  $P$ , but persist over the entire experimental  $P$ -range. They are identified as BN and C at 55.87 keV and pyrophyllite at 60.09 and 61.17 keV, diffracted from the cell materials. The diffraction lines shift as a function of  $P$ , but the fluorescence lines are independent of  $P$  in this  $P$ -range. In contrast, the main diffraction peaks from the sample are completely absent at 4.4 GPa. Although the XRD patterns are not of sufficiently high quality for structure refinement purposes, structural changes in the sample with increasing  $P$  are clearly evident. On pressurization, the sharp peaks present at ambient conditions quickly broaden, intensities drastically decrease and the peaks shift to higher energy up to 2.2 GPa. There is another obvious change in the peak shapes and an increase in the peak intensities at  $P$  of 3.2 GPa, possibly indicative of a structural change or a new phase, as discussed later. The diffraction peak intensities decrease again with further increase in  $P$  to the maximum  $P$  of 4.4 GPa, where all diffraction peaks from the sample are absent. An XRD pattern at 22 °C and 1 atm of the decompressed and cooled sample showed no peaks, indicating acrySTALLINITY.

The decrease in peak intensity and broadening in peak shape observed for  $\text{Sc}_2(\text{WO}_4)_3$  with increasing pressure are interpreted as gradual  $P$ -induced amorphization. The structure of  $\text{Sc}_2(\text{WO}_4)_3$  is orthorhombic (space group  $Pbcn$ ) in which  $\text{ScO}_6$  octahedra and  $\text{WO}_4$  tetrahedra are linked through corner sharing to form a three-dimensional framework [8, 9]. Each  $\text{ScO}_6$  octahedron is corner shared with six  $\text{WO}_4$  tetrahedra and each  $\text{WO}_4$  tetrahedron is corner shared with four  $\text{ScO}_6$  octahedra. This results in a relatively open framework structure of metal atoms linked by the two coordinate oxygens. While several materials are now known to undergo  $P$ -induced amorphization, a study of amorphization in  $\text{ZrW}_2\text{O}_8$ , with an orthorhombic structure (space group  $P2_12_12_1$ ) above 0.2 GPa, was recently reported [10]. Our recent study of  $P$ -induced amorphization of  $\text{Sc}_2(\text{WO}_4)_3$  [11], as determined by XRD analyses on samples recovered from high- $P$  experiments at room  $T$ , is completely consistent with the results reported here by *in situ* synchrotron XRD. Whereas our room  $T$  study showed amorphization in the  $P$ -range 4–6 GPa, the present high- $T$  data show amorphization at a lower  $P$ . This is consistent with the negative thermal expansion property of  $\text{Sc}_2(\text{WO}_4)_3$  since both temperature and externally applied  $P$  act in the same direction to compress the lattice.

The framework topology is a critical factor in negative thermal expansion behaviour. The negative value of the expansion is related to transverse vibrations of bridging oxygens in the Sc–O–W linkages [3, 4]. Anharmonicity in these vibrations leads to cooperative tilting of the quasi-rigid framework polyhedra, causing an effective decrease in the average Sc–O–W bridging bond angle and a concomitant densification on heating. The driving force for polyhedral tilting in this lattice can be ascribed to the fact that the lowest-energy vibrational modes tend to cause an overall decrease in Sc–O–W bond angles.

The complex coupled twisting in three dimensions of the relatively rigid framework polyhedra on heating provides a possible route to  $P$ -induced disorder [11]. The overall three-dimensional framework structure can perhaps be best understood by breaking it down into two-dimensional slabs of corner-sharing polyhedra parallel to the  $a$ - $c$  plane, which stack together to form the overall structure. The  $c$ - and  $a$ -axes are more compressible than the  $b$ -axis on the basis of the flexible hinged Sc-O octahedra and W-O tetrahedra linkages. The Sc-O-W angles in the polyhedra within the  $a$ - $c$  plane are affected the most by  $P$ . This leads to the polyhedra exhibiting higher degree of anisotropy in the  $a$ - $c$  plane relative to either the  $b$ - $c$  or  $a$ - $b$  planes. This degree of anisotropy increases with compression, until the rigid polyhedra begin to oppose each other. The forces that tend to keep polyhedra regular are mainly the oxygen-oxygen repulsive interactions within the polyhedron. To accommodate further volume reduction as  $P$  is increased, the polyhedra must rotate or tilt, and eventually rupture the flexible Sc-O-W linkages. This is macroscopically identified as amorphization.

The observed amorphization, or so-called x-ray amorphization, refers only to the loss of long-range order. Length scales which give rise to the x-ray diffraction signal indicate translational symmetry of the crystal of the order of 500–1000 Å [12]. Therefore, the amorphization observed in this study is a result of the length scale of the crystallinity reaching values less than this approximate threshold scale length. It is interesting that there is an abrupt increase in the peak intensities at  $P$  of 3.2 GPa, just before the crystal becomes amorphous. Many members of the  $\text{Sc}_2(\text{WO}_4)_3$  structural family show a phase transition from orthorhombic to monoclinic symmetry with decreasing temperature [13]. No strong bonds are formed or broken during this transition and the framework topology remains unchanged. There is however an abrupt decrease in volume at the orthorhombic–monoclinic transition. A likely cause of this structural rearrangement is a reduction in the oxygen–oxygen repulsion. The effective charge on oxygen is directly related to the electronegativity of the cations present as discussed in detail by Evans *et al* [13]. In the case of  $\text{Sc}_2(\text{WO}_4)_3$ , the relatively high electropositive character of both Sc and W prevents a phase transition by electrostatic repulsion in the temperature range examined. However, under high externally applied pressures, the electrostatic interaction energy may be overcome by the  $P \Delta V$  energy term ( $V$  is volume) on compression. This suggests the possibility of an intervening phase preceding amorphization. The presence of an intermediate metastable crystalline phase, between a parent crystalline and daughter amorphous phase, has already been proposed for other systems [14].

At low  $P$ , the reduction in the  $b$ -axis of the orthorhombic structure is expected to cause reductions in bottleneck size leading to reduced ionic migration. But the conductivity results at  $P$  above 2.9 GPa suggest that amorphization enhances conduction. We interpret this as being the result of the increase in structural entropy and its concomitant effects on accessibility of neighbouring sites to mobile  $\text{Sc}^{3+}$ . There may be one or more of several factors enhancing site accessibility, including an increase in the number of sites available, a decrease in activation energy for inter-site hopping or changes in bonding states in vacant sites due to asymmetric accommodation of lattice volume reduction on pressurization.

#### 4. Conclusions

The effects of  $P$  on the ionic conductivity of  $\text{Sc}_2(\text{WO}_4)_3$  are mediated by structural changes. In the low- $P$  crystalline regime, conductivity decreases as volume reduction translates into reduced mobility of the charge-carrying  $\text{Sc}^{3+}$  ion. In the high- $P$  regime, conductivity increases with  $P$  following a structural collapse to the amorphous phase. This reversal in conductivity at a threshold  $P$  suggests the use of  $\text{Sc}_2(\text{WO}_4)_3$ , and possibly other materials with related structure in the  $\text{A}_2\text{M}_3\text{O}_{12}$  family, as pressure-sensing materials in device applications.

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