

considered as twin interface modulated long period superstructure of calaverite.

#### MS41 O3

**Correlation between optical constants and crystal chemical parameters of  $ZrW_2O_8$**  Reinhard X. Fischer<sup>a</sup>, Olaf Medenbach<sup>b</sup>, Robert D. Shannon<sup>c</sup> <sup>a</sup>Fachbereich Geowissenschaften, Universität Bremen, Germany. <sup>b</sup>Institut für Mineralogie, Universität Bochum, Germany. <sup>c</sup>Geological Sciences/ CIRES, University of Colorado, Boulder, USA. E-mail: [rfischer@uni-bremen.de](mailto:rfischer@uni-bremen.de)

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$ZrW_2O_8$  is unusual because of its negative thermal expansion coefficient over the range 0.3 to 1050 K [1]. The refractive index,  $n_D$ , of  $ZrW_2O_8$  was reported to be 1.669 [1], but this value appears to be rather low for a tungstate which usually have values in the range between 1.84 and 2.27. The refractive index of  $ZrW_2O_8$  was redetermined at wavelengths between 435.8 nm to 643.8 nm yielding the  $n_D$  value at  $\lambda = 589.3$  nm. The corresponding  $n_\infty$  was extrapolated from the dispersion curve for  $\lambda = \infty$  using two forms of the one-term Sellmeier equation: (1)  $1/(n^2-1) = -A/\lambda^2 + B$  where A, the slope of the plot of  $(n^2 - 1)^{-1}$  vs.  $\lambda^{-2}$  in units of  $10^{-16} \text{ m}^2$  gives a measure of dispersion and B, the intercept of the plot at  $\lambda = \infty$ , gives  $n_\infty = (1 + 1/B)^{1/2}$ , and (2)  $n^2-1 = E_d E_0 / (E_0^2 - (\hbar\omega)^2)$ , where  $\hbar\omega$  = the photon energy,  $E_0$  = the average single oscillator (Sellmeier) energy gap and  $E_d$  = the average oscillator strength, which measures the strength of interband optical transitions. Refractive indices,  $n_D$  and dispersion values, A, were, respectively, 1.8794 and  $114 \times 10^{-16} \text{ m}^2$ . The high dispersion is attributed to the low value of  $E_0 = 7.7 \text{ eV}$ . The total polarizabilities,  $\alpha_{\text{total}}$ , were calculated from  $n_\infty$  and the Lorenz-Lorentz equation. The unusually large difference between the observed polarizability of  $20.087 \text{ \AA}^3$  and the calculated total polarizability  $\alpha_T$  of  $17.63 \text{ \AA}^3$  ( $\Delta = +12.2\%$ ) [2] is attributed to large M-O-M' angles resulting in a high degree of W  $5d - O 2p$  and Zr  $nd - O 2p$  hybridization, especially in the case of terminal oxygen atoms (Fig. 1) present in  $ZrW_2O_8$ . The relationship between atomic displacement factors B(O) of oxygen normalized to B(W) is discussed.

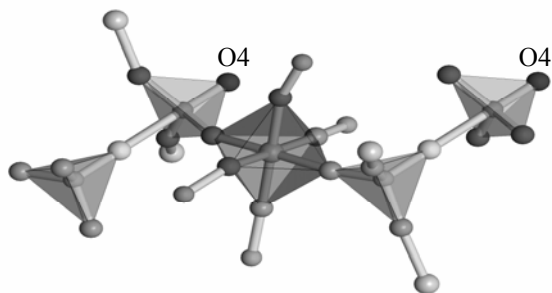


Fig. 1: Projection of the crystal structure of  $ZrW_2O_8$  [1] with terminal oxygen atoms O4.

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#### MS41 O4

**Simulating extended structures: a powerful crystallographic tool when interpreting X-ray absorption spectroscopy data** Maria-Ondina Figueiredo, Dept. of Materials Science, New University of Lisbon, 2829-516 Caparica & INETI/IGM, Portugal. E-mail: [ondina.figueiredo@ineti.pt](mailto:ondina.figueiredo@ineti.pt)

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Within the actual development of Materials Science, combining the crystal structure of selected model compounds with local atomic arrangement inferred by X-ray absorption spectroscopy is fundamental for a successful interpretation of either XANES (near-edge features) or EXAFS data. Currently used analytical (mathematical and physical) methodologies for theoretical data fitting have enhanced the need for an increased capability of idealizing and simulating appropriate atomic geometries. With no doubt, theoretical crystallography plays a unique role in predicting local environments suitable to match the structural information provided by an element selective approach like X-ray absorption spectroscopy with convoluted results obtained through a bulk technique, namely, X-ray diffraction [1].

Two examples are described to illustrate such novel role of Crystallography. One is the handling of cubic tetrahedrites,

[c P 58 :  $P \bar{4}3n$  (6d) (6c), (12f)<sup>x</sup>, (8e)<sup>x</sup>, (24i)<sup>xyz</sup>, (2a) ], with ideal formula  $M_{12}^I M_{12}^{II} (M^{3+})_8^{\pi} \{ [S_{24}]^{\pi}, [S_2]^{\pi} \}^{\leftarrow}$  (M = Cu, Ag, Zn, Fe, Cd, Pb;  $M^{3+}$  refers to Sb, As, Bi). In this structural formulation,  $\bar{I}$  stands for tetrahedral,  $\bar{II}$  for triangular,  $\pi$  for pyramidal coordination and  $\leftarrow$  denotes the cubic closest packing of sulphur anions where four vacant sites out of sixteen packing positions are replaced by one sole S-atom [2], towards a progressive approximation to the ideal tetrahedral array found in sphalerite structure-type,  $Zn^I [S^I]^{\leftarrow}$ , [c F 8 :  $F \bar{4}3m$  (4a), (4c)]. This approach is now being applied to interpret S K-edge XANES spectra and, desirably, the electronic structure of sulphur in this mineral group.

Another example concerns the partial and disordered of substitution of potassium by lead in the crystal structure of jarosite [3],  $K^{ic} Fe^o_3 (S^I O_4)_2 (OH)_{6-x} (H_2O)_x$ , where  $\bar{ic}$  stands for pseudo-icosahedral and  $\bar{o}$  for octahedral coordination. Kipping the trigonal space group  $R \bar{3} m$  and allowing for the replacement of potassium invariant position (3a) with site symmetry [  $\bar{3}m$  ] by the equipoint (18h) with free parameters  $\bar{x}, \bar{z}$  and lower site symmetry [  $\bar{m}$  ], it becomes possible to generate a local environment particularly suitable to accommodate the lone  $6s^2$  electron-pair of  $Pb^{2+}$  ions.

A detailed description is presented of these two type-cases illustrating the fruitful interplay between XAFS and Crystallography.

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