

## On the Existence of ZrOSe: Solid Solubility of Se in ZrOS

G. A. EISMAN, J. S. SWINNEA, AND H. STEINFINK

*Materials Science and Engineering Labs, Department of Chemical Engineering, The University of Texas, Austin, Texas 78712*

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Eisman and Steinfink (1) have described the synthesis of HfOS which, unlike the synthesis of ZrOS, required the presence of a mineralizer to form. A complete range of solid solubility exists between ZrOS-HfOS. We wished to synthesize ZrOSe, expecting that this compound would form easily, would be isostructural with ZrOS and would probably have a lower value for  $E_g$  [ZrOS:  $E_g = 3.5$  eV,  $\rho = 10^6 \Omega\text{-cm}$  at room temperature, (2)]. Analogous procedures which successfully yielded ZrOS, HfOS, and  $Zr_{1-x}Hf_xOS$  were fruitless. Since compounds  $ZrS_{2-x}Se_x$  can be prepared easily (3), experiments were undertaken to prepare  $ZrO(S_{1-x}Se_x)$ . If this solid solution can be prepared then presumably the phase  $x = 1$  might be approached by this technique. In any case the extent of solubility of Se in ZrOS can be studied.

Mixed Zr-dichalcogenides were prepared by mixing the appropriate ratios of the elements, sealing the mixtures in evacuated Vycor tubes, and heating to appropriate temperatures. Known lattice constants as a function of composition were used to determine the compositions of the products  $ZrS_{2-x}Se_x$  (3).  $ZrSe_2$  was prepared by the thermal decomposition of  $ZrSe_3$ . To prepare  $ZrO(S_{1-x}Se_x)$  a 1:1 mole ratio of  $ZrO_2$

and  $ZrS_{2-x}Se_x$  were mixed and sealed into evacuated Vycor tubes which also contained about  $5 \text{ mg/cm}^3 \text{ NH}_4\text{Cl}$ . The ampoule was slowly heated to  $450^\circ\text{C}$  and left at that temperature 12-15 hr. The temperature was subsequently raised to  $900^\circ\text{C}$ . The ampoule was situated in the furnace so that a temperature gradient of  $50^\circ\text{C}$  existed, the hot end being at the mixture. After about 3 days the tubes were slowly cooled to room temperature by shutting off power to the furnace. A crop of well-formed, small, yellow crystals could be collected from the cool end of the tube which looked identical with previously synthesized ZrOS crystals. The crystals from the various starting compositions were analyzed quantitatively using energy and wavelength dispersive X-ray fluorescence analysis. All crystals showed the presence of Zr, O, S, and Se, with Se about 6%. No concentration of Se exceeding this value was ever observed.

In order to check this limit of solid solubility a single crystal with nominal composition  $ZrOS_{0.94}Se_{0.06}$  having an approximately spherical shape with a volume of  $0.6 \times 10^{-3} \text{ mm}^3$  was mounted on a Syntex autodiffractometer equipped with a graphite monochromator and intensities for  $\frac{1}{2}$  of reciprocal space were collected with  $\text{MoK}\alpha$

TABLE I  
POSITIONAL AND ISOTROPIC THERMAL PARAMETERS  
FOR  $\text{ZrOS}_{0.94}\text{Se}_{0.06}$

| Atom | $x$           | $U$<br>( $10^4 \text{Å}^2$ ) | Occ. factor |
|------|---------------|------------------------------|-------------|
| Zr   | 0.32044(4)    | 44(2)                        |             |
| S    | 0.58409(9)    | 58(3)                        | 0.944(3)    |
| Se   | $x(\text{S})$ | $U(\text{S})$                | 0.056       |
| O    | 0.9053(3)     | 64(6)                        |             |

to  $60^\circ 2\theta$ . Equivalent reflections were averaged, taking care to keep Friedel pairs separate because the cubic space group is  $P2_13$ . A least-squares refinement of 15 reflections measured between  $24$  and  $30^\circ 2\theta$  yielded  $a = 5.710(2)$  Å as compared to  $5.696(4)$  Å for  $\text{ZrOS}$  (4). Of the 181 intensities collected by the variable  $\omega$ -scan technique at rates from  $2.0$  to  $5.0$  deg.  $\text{min}^{-1}$ , all  $F(hkl)$  were considered observed on the basis of having values exceeding  $2\sigma(F)$ . Lorentz, polarization, and absorption corrections,  $\mu = 74.6$   $\text{cm}^{-1}$ , were applied to the intensities. Absorption factors ranged from  $1.66$  to  $2.05$ . Estimated errors were calculated from  $\sigma(F^2) = [S^2(I_p + 1/R^2(I_{B_1} + I_{B_2})) + (pI_{hkl})^2]^{1/2}$ , where  $I_p$  = number of counts during peak scan,  $I_{B_1}$  and  $I_{B_2}$  = background counts on low and high  $2\theta$  side,  $S$  = scan speed, deg.  $\text{min}^{-1}$ ,  $R$  = total background counting time/scan time,  $p = 0.02$  and  $I_{hkl} = S[I_p - 1/R(I_{B_1} + I_{B_2})]$ . The starting parameters for the least-squares refinement were from McCullough *et al.* (5). The refinements converged quickly to  $R = 0.0126$ ,  $\omega R = 0.0132$ , using isotropic thermal parameters and an extinction coefficient  $g = 1.266 \times 10^{-4}$ . The use of anisotropic thermal parameters did not affect the values of  $R$ . Values for the scattering factors for neutral atoms corrected for the real and imaginary parts of dispersion were taken from International Tables for X-Ray Crystallography

(6). The final coordinates are shown in Table I and observed and calculated structure factors in Table II.<sup>1</sup> Scattering amplitudes for the inverse structure were also calculated yielding  $R = 0.0126$ ,  $\omega R = 0.0133$  so that the handedness of the structure could not be determined. The least-squares refinement contained as a variable parameter the occupancy for  $S$ . It converged to  $0.944$  in agreement with the analytically determined value. There is one Zr–S(Se) distance of  $2.6074(8)$  Å and three of  $2.7302(9)$  Å, the three Zr–O distances are  $2.085(2)$  Å. These distances agree with those reported in Ref. (4). We conclude that the extent of solid solubility is represented by  $\text{ZrOS}_{0.94}\text{Se}_{0.06}$ .

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### References

1. G. A. EISMAN AND H. STEINFINK, *J. Solid State Chem.* **43**, 225 (1982).
2. H. L. SÁNCHEZ, Ph.D. dissertation, The University of Texas at Austin, 1983.
3. C. R. WHITEHOUSE, H. P. B. RIMMINGTON, AND A. A. BALCHIN, *Phys. Status Solidi A* **18**, 623 (1973).
4. A. GLEIZES, Y. JEANNIN, AND N. MAIRE, *Bull. Soc. Chim. Fr.* **7-8**, 1317 (1974).
5. J. D. MCCULLOUGH, L. BREWER, AND L. A. BROMLEY, *Acta Crystallogr.* **1**, 287 (1948).
6. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England (1974).

<sup>1</sup> See NAPS Document No. 04259 for 1 page of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid.