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A Phase Analytical Study of the Ge–W–O System near WO_3

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The phases occurring in the WO_3–WO_2–GeO_2 region of the Ge–W–O phase diagram at 1373K were determined by electron microscopy and X-ray diffraction. Preparations were heated for 3, 14, or 35 days. The structures found were WO_3, {102}*CS* structures, {103}*CS* phases, $W_{24}O_{68}$, W_5O_{14}, $W_{18}O_{49}$, and WO_2. The presence of GeO_2 was inferred. The tungsten oxides appear to contain very little Ge and are best regarded as pseudobinary phases. Equilibrium was slow to achieve and samples heated for up to 5 weeks were still not perfectly ordered. However, formation and ordering of the phases seemed faster than in equivalent binary samples, and either Ge or GeO_2 appears to act as a promotor in the reaction. The distribution of the {103} *CS* phase homologs is in good agreement with the predictions of stability based upon minimization of elastic strain energy.

Introduction

The crystal chemistry of the binary and ternary tungsten oxides has excited considerable interest in recent years because of the complexity of the nonstoichiometric phase regions and the intriguing crystal chemistry of the crystallographic shear (*CS*), pentagonal column (*PC*), and tungsten bronze phases that occur at compositions close to WO_3. Because of this, there have been a fair number of studies of the structures arising when WO_3 is reacted with small amounts of a different metal or metal oxide. These have been reviewed recently by Ekström and Tilley (*1*).

Despite this rather large amount of work not all systems have been investigated in depth. One of those still outstanding is the Ge–W–O system. Previous work has been limited to a study of the Ge_xWO_3 phases by Parmentier and Gleitzer (*2*) and a study of the reaction of germanium with $W_{18}O_{49}$ by Horyn (*3*). This is a little surprising as the crystal radii for Ge^{+4}, 0.054 nm for tetrahedral coordination and 0.068 nm for octahedral coordination, are quite similar to those of W^{+6}, viz., 0.056 nm for tetrahedral coordination and 0.074 nm for octahedral coordination (*4*). It is also true that both Ge and W will take both octahedral and tetrahedral coordination. This suggests that a more extensive study would be worthwhile. Such a view was reinforced by the fact that in a brief preliminary study we noted that the addition of Ge metal to reduced tungsten oxides appeared to give rise to the formation of an oxide of composition close to W_5O_{14}, which is not found in the binary tungsten–oxygen system (*5*). For this reason it seemed of interest to survey the WO_3

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region of the WO_3–WO_2–GeO_2 phase system to determine whether any other oxide structures were stabilized in this way. The results of this study are presented in this paper.

Experimental

Samples were prepared from specpure-grade WO_3, W metal, Ge metal, or GeO_2, supplied by Johnson Matthey Ltd., and $W_{18}O_{49}$ or WO_2 prepared from WO_3 and W metal from the same source. Appropriate quantities of these chemicals were weighted and sealed in evacuated silica glass tubes and subsequently heated at 1373K for periods of 3 days, 2 weeks, or 5 weeks. After heating, the samples were quenched in cold water. The compositions prepared are shown in Fig. 1 and are included in Tables I and II.

The samples were examined optically using a Zeiss Ultraphot optical microscope and electron optically using a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV and a JSM 35 scanning electron microscope. Some samples were analyzed for W and Ge using an ISI super IIIA scanning electron microscope fitted with a PGT XCEL-D energy-dispersive electron probe X-ray microanalysis facility. In addition, powder X-ray diffraction photographs of all samples were obtained using a Hägg–Guinier focussing camera using strictly monochromatic Cu$K\alpha_1$ radiation and KCl ($a_0 = 0.6292$ nm) as an internal standard. The X-ray data were refined using least-squares techniques.

Results

The results obtained from the various techniques employed were in good agreement with one another, and allowed the partial phase diagram shown in Fig. 1 to be constructed. They are also in accord with the data of Parmentier and Gleitzer (*2*) where overlap occurs.

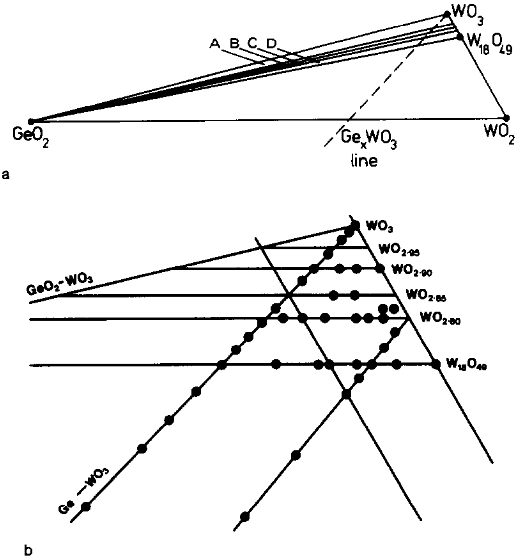

FIG. 1. (a) Phase relations in the ternary Ge–W–O system at 1373K. The small triangles A, B, C, and D represent phase regions containing A, GeO_2 + WO_3 + *CS* phases; B, GeO_2 + *CS* phases + disordered or ordered $W_{24}O_{68}$ structures; C, GeO_2 + $W_{24}O_{68}$ + W_5O_{14}; D, GeO_2 + W_5O_{14} + $W_{18}O_{69}$. The phase boundaries are not precise in triangles A and B due to the disorder present in the *CS* and $W_{24}O_{68}$ structures. (b) Part of (a) near WO_3 showing the compositions prepared.

There are a number of comments to make with respect to Fig. 1. First, it is seen that no phases are represented as having a significant Ge : W stoichiometry range. In general we assume that very little Ge enters into the tungsten oxides and that they can be regarded as pseudobinary oxides. A number of results contribute to this conclusion. For example, the X-ray diffraction patterns of the various structures produced in our preparations were carefully examined in order to observe whether there were any significant shifts in lattice parameters as the nominal compositions of the samples varied. None were found. In addition, the patterns were compared with those of corresponding phases in known binary tung-

TABLE I

ELECTRON MICROSCOPE PHASE ANALYSIS OF Ge–W–O SAMPLES

Gross composition	Heating time (days)	No. of frags.	Observed structures															
						Ordered {103} *CS* (n=)												
			WO_3	Disord. {102} *CS*	Disord. {103} *CS*	26	25	24	23	22	21	20	19	18	17	16	15	$W_{24}O_{68}$
$Ge_{0.005}WO_3$	3	14	4	10														
	14	15	3	12														
	35	15		15														
$Ge_{0.01}WO_3$	3	15	1	14														
	14	14		14														
	35	15		11	1	1		2										
$Ge_{0.02}WO_3$	3	16	2	8	1					3	1	1						
	14	14		10	2			1	1									
	35	15		8	1		1	5										
$Ge_{0.03}WO_3$	3	16		11	1			1		1	1	1						
	14	15		10	2			1		1	1							
	35	15		5		1		6	1	2								
$Ge_{0.04}WO_3$	3	17		2	2		1	3		4	1	3		1				
	14	15		2	1			1		4	1	4	1	3				
	35	15		1	3		1	9		2								
$Ge_{0.05}WO_3$	3	14				1		3		7		2		1				
	14	15			3					4	2	2	2	2				
	35	14			2			7	1	2	1	1						
$Ge_{0.06}WO_3$	3	15								1		2		10		2		
	14	15										1	1	12	1			
	35	15												11	1	3		
$Ge_{0.07}WO_3$	3	19										1	1	11	3	3		
	14	16												6		4		6
	35	14												4		2		8
$Ge_{0.125}W_{0.988}O_{2.90}$	35	17				2		6	1	8								
$Ge_{0.018}W_{0.982}O_{2.85}$	35	16												2	2	5	2	5

TABLE II

X-RAY PHASE ANALYSIS OF Ge–W–O SAMPLES

Gross composition	Heating time (days)	X-ray phase analysis
$Ge_{0.005}WO_3$	3	WO_3 (disord. {102} *CS*)
	14	WO_3, (disord. {102} *CS*)
	35	WO_3, (disord. {102} *CS*)
$Ge_{0.01}WO_3$	3	WO_3 (disord. {102} *CS*)
	14	WO_3 (disord. {102} *CS*)
	35	WO_3, (disord. {102} *CS*)
$Ge_{0.02}WO_3$	3	quasiord. {103} *CS*, (disord. {102} *CS*)
	14	quasiord. {103} *CS*, (disord. {102} *CS*)
	35	103 *CS*, (disord. {102} *CS*)
$Ge_{0.03}WO_3$	3	quasiord. {103} *CS*, (disord. {102} *CS*)
	14	quasiord. {103} *CS*, (disord. {102} *CS*)
	35	{103} *CS*, (disord. {102} *CS*)
$Ge_{0.04}WO_3$	3	{103} *CS*, (({102} *CS*))
	14	{103} *CS*, (({102} *CS*))
	35	{103} *CS*
$Ge_{0.05}WO_3$	3	{103} *CS*
	14	{103} *CS*, (({102} *CS*))
	35	{103} *CS*
$Ge_{0.06}WO_3$	3	$W_{20}O_{58}$
	14	$W_{20}O_{58}$
	35	$W_{20}O_{58}$, ((GeO_2))
$Ge_{0.07}WO_3$	3	$W_{20}O_{58}$, ((GeO_2))
	14	{103} *CS*, ($WO_{2.83}$)
	35	$W_{20}O_{58}$, ($WO_{2.83}$), ((W_5O_{14}))
$Ge_{0.08}WO_3$	3	$W_{20}O_{58}$, W_5O_{14}
	14	W_5O_{14}, $WO_{2.83}$ ($W_{20}O_{58}$)
	35	W_5O_{14}, ($W_{20}O_{58}$)
$Ge_{0.09}WO_3$	3	$W_{20}O_{58}$, W_5O_{14}
	14	W_5O_{14}, $W_{20}O_{58}$
	35	$W_{20}O_{58}$, W_5O_{14}
$Ge_{0.10}WO_3$	3	$W_{20}O_{58}$, W_5O_{14}
	14	$W_{20}O_{58}$, (W_5O_{14})
	35	$W_{20}O_{58}$, W_5O_{14}
$Ge_{0.12}WO_3$	7	W_5O_{14}, (($W_{20}O_{58}$))
$Ge_{0.14}WO_3$	7	W_5O_{14}
$Ge_{0.16}WO_3$	7	W_5O_{14}, (($W_{18}O_{49}$))
$Ge_{0.20}WO_3$	7	$W_{18}O_{49}$, (W_5O_{14})
$Ge_{0.30}WO_3$	7	$W_{18}O_{49}$, (GeO_2), ((?))
$Ge_{0.010}W_{0.990}O_{2.90}$	7	{103} *CS*
	35	{103} *CS*
$Ge_{0.0125}W_{0.988}O_{2.90}$	35	{103} *CS*
$Ge_{0.020}W_{0.980}O_{2.90}$	7	quasiord. {103} *CS*, (disord. {102} *CS*)
$Ge_{0.030}W_{0.970}O_{2.90}$	7	quasiord. {103} *CS*, (disord. {102} *CS*)
$Ge_{0.0188}W_{0.982}O_{2.85}$	35	{103} *CS*, $WO_{2.83}$
$Ge_{0.030}W_{0.97}O_{2.85}$	7	$W_{20}O_{58}$, (($W_{18}O_{49}$))
	35	{103} *CS*, ($WO_{2.83}$)
$Ge_{0.005}W_{0.995}O_{2.82}$	7	$W_{20}O_{58}$, $W_{18}O_{49}$
$Ge_{0.01}W_{0.99}O_{2.82}$	7	$W_{20}O_{58}$, $W_{18}O_{49}$, ($WO_{2.83}$)
$Ge_{0.01}W_{0.99}O_{2.80}$	7	$W_{20}O_{58}$, $W_{18}O_{49}$
	35	$WO_{2.83}$, {103} *CS*
$Ge_{0.0125}W_{0.988}O_{2.80}$	35	$WO_{2.83}$
$Ge_{0.02}W_{0.98}O_{2.80}$	7	$W_{20}O_{58}$, $W_{18}O_{49}$, ((W_5O_{14}))
$Ge_{0.025}W_{0.975}O_{2.80}$	35	$W_{18}O_{49}$, $WO_{2.83}$, W_5O_{14}
$Ge_{0.04}W_{0.96}O_{2.80}$	7	W_5O_{14}, $W_{20}O_{58}$, ($W_{18}O_{49}$)
$Ge_{0.05}W_{0.95}O_{2.80}$	35	$W_{20}O_{58}$, (W_5O_{14}), ($WO_{2.83}$)
$Ge_{0.06}W_{0.94}O_{2.80}$	7	$W_{20}O_{58}$, (W_5O_{14})
$Ge_{0.010}W_{0.990}O_{2.772}$	7	$W_{18}O_{49}$, ($W_{20}O_{58}$)
	35	{103} *CS*, ($WO_{2.83}$)
$Ge_{0.020}W_{0.980}O_{2.745}$	7	$W_{18}O_{49}$, W_5O_{14}, ($W_{20}O_{58}$)
	35	{103} *CS*, $WO_{2.83}$
$Ge_{0.017}W_{0.983}O_{2.722}$	35	$W_{18}O_{49}$, W_5O_{14}
$Ge_{0.02}W_{0.98}O_{2.722}$	7	$W_{18}O_{49}$, (W_5O_{14})
	35	$W_{18}O_{49}$, $W_{20}O_{58}$, (W_5O_{14})
$Ge_{0.035}W_{0.965}O_{2.722}$	35	$W_{18}O_{49}$, $WO_{2.83}$
$Ge_{0.05}W_{0.95}O_{2.722}$	7	$W_{18}O_{49}$, W_5O_{14}
$Ge_{0.056}W_{0.944}O_{2.722}$	35	$W_{18}O_{49}$, $WO_{2.83}$, (W_5O_{14})
$Ge_{0.07}W_{0.93}O_{.2722}$	35	$WO_{2.83}$, ($W_{18}O_{49}$)
$Ge_{0.10}W_{2.90}O_{2.722}$	7	W_5O_{14}
$Ge_{0.111}W_{0.889}O_{2.722}$	35	W_5O_{14}, ($WO_{2.83}$)
$Ge_{0.029}W_{0.971}O_{2.718}$	7	$W_{18}O_{49}$, W_5O_{14}
$Ge_{0.038}W_{0.962}O_{2.692}$	7	$W_{18}O_{49}$; W_5O_{14}
$Ge_{0.048}W_{0.952}O_{2.667}$	7	$W_{18}O_{49}$, (W_5O_{14})
$Ge_{0.091}W_{0.909}O_{2.545}$	7	$W_{18}O_{49}$, ((?))
$Ge_{0.130}W_{0.870}O_{2.435}$	7	$W_{18}O_{49}$, ((?))
$Ge_{0.167}W_{0.833}O_{2.333}$	7	$W_{18}O_{49}$, (?)

Note. $W_{20}O_{58}$ refers to a phase or phases similar to $W_{20}O_{58}$ and not to a single material. $WO_{2.83}$ refers to a more or less ordered $W_{24}O_{68}$ phase. ( ) indicates a small amount, and (( )) indicates trace amounts of the phase enclosed in the parentheses.

sten oxides. Again no significant differences were found. From an X-ray point of view, therefore, we could find no evidence for Ge incorporation into the structures. In addition, a number of these reduced phases were oxidized by heating in air. The weight changes so produced were identical to that calculated for oxidation of the appropriate binary oxide rather than a ternary oxide, and X-ray examination of the oxidized products showed only the presence of WO_3. Finally, a number of samples were analyzed for Ge using electron microprobe techniques. This analysis revealed only trace amounts of Ge in any of the crystals studied. In particular, crystals of $W_{18}O_{49}$ were carefully examined in this respect, following the report of Horyn (*3*) that this oxide could take Ge into solid solution, but a negative result was again obtained. We are therefore led to consider that these materials contain only very small amounts of Ge, and certainly much less than 1 at.%.

A second point to make concerns the GeO_2 component of our samples. GeO_2 was only rarely identified on X-ray powder patterns and it was this absence that led us to check the Ge content of the crystals so carefully. To all intents and purposes the Ge seems to vanish from the reaction mixture. The most straightforward explanation of this is to assume that the Ge is oxidized to GeO_2, which reacts with the silica ampoules to form a $(Ge,Si)O_2$ glass. This same suggestion was made by Parmentier and Gleitzer (*2*) in their study of Ge_xWO_3 preparations. The oxygen for the formation of the GeO_2 comes from the tungsten oxides, which are correspondingly more reduced than if the Ge was able to enter into their structures. Calculation of the stoichiometry of these phases based upon this assumption yielded values which were in perfect accord with the X-ray and electron microscope phase analyses and we have no doubt that this was the dominant reaction which took place in our samples. The phase diagram in Fig. 1 were drawn accordingly.

Electron Microscope Phase Analysis

The electron microscope phase analysis showed that the products formed were similar to those found in the binary system (*6–10*), with the exception that a phase of composition $(Ge,W)_5O_{14}$ formed (*5, 11*). As with other crystals, this phase appears to have very little Ge in it and it is best regarded as a pseudobinary W_5O_{14} oxide. No other oxides were found in the system that have not been previously reported in the binary system. The overall sequence of phases found in the samples also mirrors that found in the binary system. As the microstructures of these materials appear to be identical to those found in the pure binary oxides, and have been well illustrated in the past (*6–10*), we will not include micrographs here.

The electron microscope analysis of the phases present in our preparations is summarized in Table I. In general as many crystal fragments as was practical were observed for each sample in order to obtain as reliable statistics as possible. However, it is important to note that for crystals of a thin needle or whisker habit of the sort illustrated in Fig. 2, useful phase analytical information is only contained in projections parallel to the needle or whisker axis. Such crystals rarely fracture to give suitable thin flakes which may be oriented so that this projection is recorded in electron diffraction patterns, and for these materials the

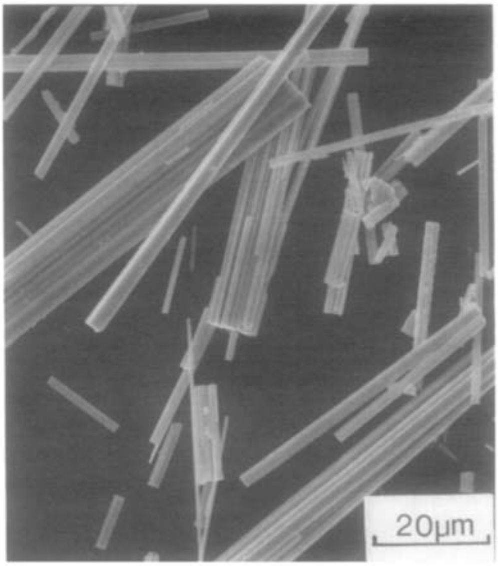

FIG. 2. Scanning electron micrograph of part of a sample of overall composition $Ge_{0.017}W_{0.983}O_{2.722}$ heated for 35 days. X-Ray analysis showed the sample to contain W_5O_{14} and $W_{18}O_{49}$. The needle-like habit of the crystals is apparent. The larger crystals appear to consist of bundles of smaller needles aligned parallel to one another.

statistics are far less reliable. For this reason the data presented in Table I is mainly concerned with the microstructures of the *CS* phases, as this data cannot be obtained readily by any other techniques.

A detailed examination of Table I suggests that equilibrium is very difficult to achieve in this system. For example, WO_3 is observed in samples of nominal composition $Ge_{0.005}WO_3$ heated for 3 days and 2 weeks, but not in samples heated for 5 weeks. Changes are also apparent in the *CS* phase distribution. In general the materials heated for only 3 days were somewhat more disordered than those heated for 5 weeks, and although the range of n values in the {103} *CS* phases, from 26 to 15, was similar for all samples examined, a definite trend in the distribution of these n values was found. This is illustrated in Figs. 3a, b, and c, which show, in histogram form, the distributions for samples heated for 3 days, 2 weeks, and 5 weeks, respectively. It is notable that n values which are even seem to be preferred, and that as the heating time lengthens, the amounts of $W_{18}O_{52}$ and $W_{22}O_{64}$ seem to increase relative to the other {103} *CS* phases present.

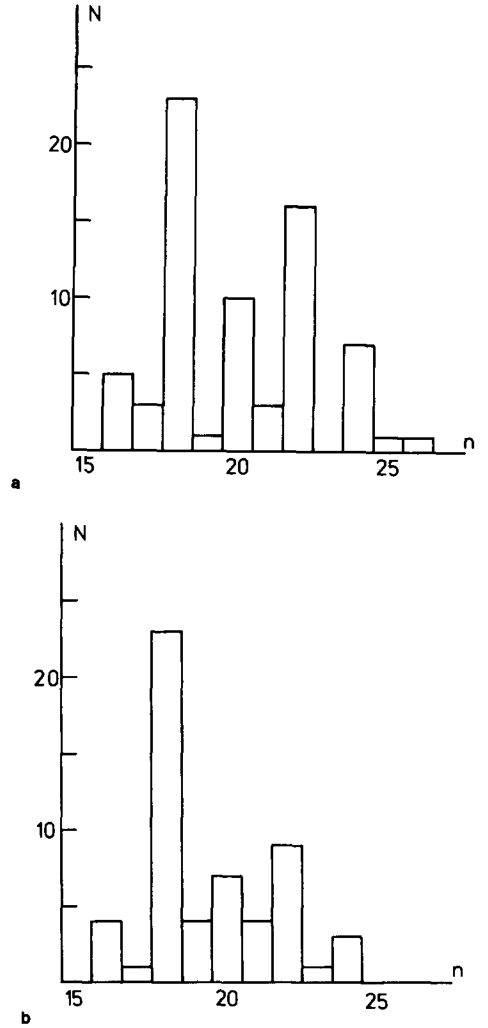

FIG. 3. Histograms showing the number of fragments of each of the 103 *CS* plane homologs W_nO_{3n-2} found in the preparations. (a) Samples heated for 3 days; (b) samples heated for 14 days; (c) samples heated for 35 days. The vertical axis represents the number of fragments of each homolog (N), and the horizontal axis the value of n in the series formula W_nO_{3n-2} for these oxides.

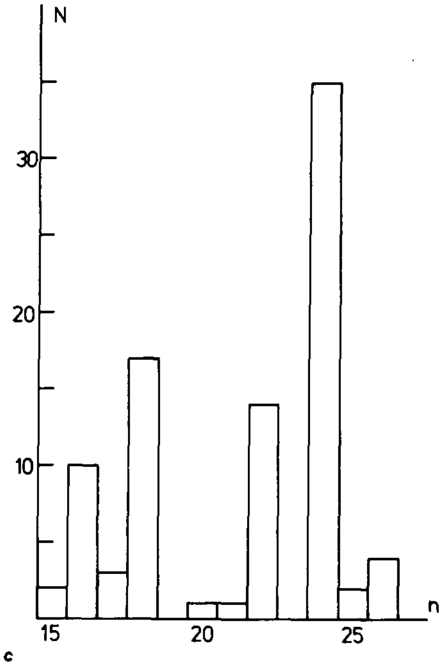

FIG. 3—*Continued.*

X-Ray Phase Analysis

The X-ray phase analysis of all samples is summarized in Table II. For X-rays the region of greatest uncertainty is the *CS* region close to WO_3 but even here the X-ray data are of some value. In the present study the appearance of the *CS* materials on the X-ray diffraction patterns did not differ from previous results for the binary W–O system itself (*12*). At the smallest degrees of reduction the presence of disordered {102} *CS* structures could only be inferred indirectly, as no distinct X-ray lines occur. However, the diffraction lines of the WO_3 become somewhat diffuse, and very diffuse weak bands appear on the photographs. In addition, the high-temperature orthorhombic form of WO_3 can sometimes be quenched to room temperature if the density of {102} *CS* structures is high enough (*13*). The diffraction patterns from the {103} *CS* area did not seem to differ from those produced by binary tungsten oxides, but they seemed to form rather more quickly and in a somewhat more ordered condition than in binary samples, so that the Ge seems to act in some way as a promoter in their formation.

This role was even more pronounced for the *PC* structures $W_{24}O_{68}$ and W_5O_{14}. In the binary system $W_{24}O_{68}$ forms slowly and is usually very disordered, which is why X-ray diffraction studies in the past often failed to detect this compound. In our Ge–W–O samples a $W_{24}O_{68}$ oxide also formed slowly and was only found in preparations heated for times longer than 1 week. The phase, though, ordered more rapidly in the ternary preparations. For example, powder patterns of this compound from binary W–O preparations were only of a quality suitable for indexing after the samples had been heated for 5 weeks, whereas in the present experiments samples heated for only 2 weeks gave reasonably sharp patterns. An indexed X-ray powder pattern of the pseudobinary $W_{24}O_{68}$ oxide obtained in our preparations is given in Table III. The data is in good agreement with data for the binary system (*12*).

The presence of Ge also has an important role to play in the formation of the pseudobinary W_5O_{14} phase, which is not found at all in the binary W–O system. The X-ray powder diffraction pattern of this material, taken from a sample of overall starting composition $(Ge_{0.05}W_{0.95})O_{2.80}$, is given in Table IV. The pattern and the tetragonal unit cell parameters $a = 2.327$, $c = 0.3791$ nm are not significantly different from other pseudobinary W_5O_{14} structures (*5*, *11*). No changes of these lattice parameters were found for Ge–W–O samples of different starting compositions. The X-ray analysis

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR THE PSEUDOBINARY $W_{24}O_{68}$ PHASE OBSERVED IN THE Ge–W–O SYSTEM

d_{obs} (nm)	I_{obs}	*hkl*[a]	$\sin^2\theta_{obs} \times 10^5$	Δ[b]
1.900	vw	100	164	−3
1.434	vw	$\bar{1}01$	289	0
0.9445	w	200	665	−3
0.8364	w+	$\bar{1}02$	848	2
0.7181	vw	$\bar{2}02$	1151	−6
0.5376	vvw	$\bar{2}03$	2052	−1
0.4188	w	$\bar{2}04$	3383	−3
0.4122	w	004	3492	8
0.3939	m	$\bar{3}04$	3824	−15
0.3834	vs	104	4037	4
0.3786	vs	010, $\bar{5}02$	4140	0
0.3708	w	303	4316	−7
0.3592	w	111	4598	−22
0.3572	m	$\bar{4}04$	4650	26
0.3512	vw	210	4809	1
0.3473	m	204	4916	0
0.3446	vw	$\bar{1}12$	4997	11
0.3404	w	$\bar{1}05$	5120	−12
0.3398	w	$\bar{2}05$	5139	−15
0.3346	vw	$\bar{2}12$	5300	4
0.3301	s	005	5446	3
0.3285	w	$\bar{3}05$	5497	−14
0.3235	m	$\bar{6}01$	5669	14

[a] The pattern has been indexed using a monoclinic unit cell close to that originally given by Pickering and Tilley (*8*); $a = 1.947$, $b = 0.3785$, $c = 1.705$ nm, and $\beta = 104.5°$.

[b] $\Delta = (\sin^2\theta_{obs} - \sin^2\theta_{calc}) \times 10^5$.

TABLE IV

The X-Ray Powder Diffraction Data for the Pseudobinary W_5O_{14} Oxide

d_{obs} (nm)	I_{obs}	*hkl*[a]	$\sin^2\theta_{obs} \times 10^5$	Δ[b]
11.56	m	200	444	6
10.35	m	210	554	6
7.331	w	310	1104	8
6.424	vw	320	1438	13
5.811	w	400	1757	4
5.475	m	330	1979	7
5.185	vw	420	2207	15
4.559	vw	510	2854	5
4.312	vw	520	3191	13
4.115	vw	440	3504	−3
3.987	vw	530	3732	6
3.875	m	600	3951	7
3.826	w	610	4054	−1
3.782	vs	001	4148	20
3.678	w	620	4387	3
3.630	s	540	4502	9
3.467	w	630	4937	6
3.368	vw	311	5229	6
3.290	w	710	5481	2
3.225	w	640	5704	6
3.197	vw	720	5806	−2
3.177	vw	401	5879	−3
3.119	vw	331	6100	0
3.055	vw	730	6356	0
2.977	vw−	650	6694	9 9
2.910	w	800	7008	−5
2.887	m	810	7119	−3
2.848	vw	521	7313	7
2.822	vw	820	7452	1
2.713	w+	601	8058	−15
2.708	m	750	8088	−20
2.691	vw	611	8190	8
2.641	vw	621	8504	−7
2.624	m	541	8615	−6

[a] The tetragonal unit cell was refined to yield values of $a = 2.327$ and $c = 0.3791$ nm.

[b] $\Delta = (\sin^2_{obs} - \sin^2_{calc}) \times 10^5$.

also indicated that no extended substitution of Ge for W occurred along the $Ge_x W_{1-x})O_{2.80}$ line of the phase diagram and that no interpolation of Ge into the tunnels in the W_5O_{14} structure seemed to take place. As stated previously, very little Ge seems to be incorporated into this structure and the role of Ge or GeO_2 seems to be that of a promoter.

The lattice parameters found for the $W_{18}O_{49}$ structure in the ternary Ge–W–O samples did not vary from one preparation to another, being $a = 1.833$, $b = 0.3783$, $c = 1.404$ nm, and $\beta = 115.2°$ for the monoclinic unit cell. These are not significantly different from the lattice parameters of the binary $W_{18}O_{49}$ oxide (*12*). In addition, the phase analysis did not indicate that Ge was able to substitute for W in any significant amounts in this oxide, in contradiction to the results reported by Horyn (*3*).

Discussion

The most interesting and intriguing aspect of our study is the role that Ge plays in the system. A comparison with the binary system shows that Ge seems to act as a promoter, in that the *CS* and *PC* phases appear to form rather more quickly when Ge is present than when absent. There is also some evidence to suggest that the phases are somewhat better ordered in the ternary system. In addition, the W_5O_{14} structure is stabilized by the Ge present in the preparations.

Despite this, very little Ge would appear to enter the crystals that are formed. We examined the W_5O_{14}, $W_{24}O_{68}$, and $W_{18}O_{49}$ phases especially carefully from this point of view and while we cannot rule out the possibility that a trace of Ge enters these structures, it is certain that it is a lot less than the amount originally present in the sample. Our findings here parallel those of Parmentier and Gleitzer (*2*) and as we found no trace of any Ge-rich phases, either by electron microscopy or by X-ray diffraction, we assume that a GeO_2 glass forms which is incorporated into the silica ampoule.

These results show that an excess quantity of Ge is unnecessary when the formation of the *CS* and *PC* phases are concerned, and particularly when it comes to the W_5O_{14} structure, which does not occur in the binary system. If the Ge is not required as an integral part of this and the other structures it is possible that Ge is involved in either the nucleation stage of crystal growth or else in facilitating transport of reactants to small crystallites. While GeO_2 may indeed help in material transport, although it is not clear how at this stage in our studies, it does not account for the formation of W_5O_{14}. We are led to conclude that the Ge somehow is significant in the formation of nuclei of this compound, which then proceed to grow into macroscopic crystals. If this is so then it is clear that the phase must be only slightly unstable in the binary system, as once formed the crystals persist and do not decompose even after 5 weeks of heating.

Because it would appear that the amount of Ge present in the samples is minimal we can compare the *CS* plane data with the calculations of *CS* plane stability made by Iguchi and Tilley (*14–16*) for binary oxides. We extracted the data from Table I and Fig. 3 and listed it in Table V, together with the relative stability of the oxides of the {103} *CS* series, which have a series formula of W_nO_{3n-2}, taken from Iguchi and Tilley (*14*). The theoretical stabilities are in good agreement with the experimental data with the exception of the $W_{15}O_{43}$ and $W_{16}O_{46}$ oxides, which will be considered below. For the rest of the table, we find that $W_{18}O_{52}$ is the most stable phase theoretically, and it also occurs most frequently in our preparations. Similarly, $W_{22}O_{64}$ and $W_{24}O_{70}$ are of similar stability, and both phases occur with an almost equal frequency in our samples. We also note from Table V and Fig. 3 that the amounts of these stable phases increase with heating time relative to the other unstable phases present. The only discrepancy comes at the low *n* value side of the phase diagram. The phase $W_{16}O_{46}$ is clearly not so unstable as the theoretical calculations suggest, while $W_{15}O_{43}$ is certainly less stable. These oxides, however, are close to the stability limit of the *CS* phase range and very close to the composition region where *PC* phases of the $W_{24}O_{68}$ and W_5O_{14} type are preferred. The approximations made in the theoretical calculations of the stability of these phases do not appear to apply in this extreme region, and, not surprisingly, the experimental data do not fit the theory well. The same is probably true of the $W_{26}O_{76}$ phase, which is at the extreme upper end of the phase region, and although it is expected to be just stable, it is not a strongly preferred homolog. Over the middle part of the phase range, though, the agreement between theory and experiment is very good. As the stability is calculated on the basis that the most stable materials are those with lowest elastic strain energy, the present results further substantiate the idea that elastic strain energy has an impor-

TABLE V

{103} *CS* PLANE STATISTICS

Oxide	*n*	Relative stability[a]	No. of fragments: 3 days	14 days	35 days	Total
$W_{26}O_{76}$	26	−5(s)	1	0	4	5
$W_{25}O_7$	25	+313(u)	1	0	2	3
$W_{24}O_{70}$	24	−111(s)	7	3	35	45
$W_{23}O_{67}$	23	+139(u)	0	1	3	4
$W_{22}O_{64}$	22	−137(s)	16	9	14	39
$W_{21}O_{61}$	21	+235(u)	3	4	1	8
$W_{20}O_{58}$	20	+133(u)	10	7	1	18
$W_{19}O_{55}$	19	+131(u)	1	4	0	5
$W_{18}O_{52}$	18	−742(s)	23	23	17	63
$W_{17}O_{49}$	17	+798(u)	3	1	3	7
$W_{16}O_{46}$	16	+1378(u)	5	4	10	19
$W_{15}O_{43}$	15	−2396(s)	0	0	2	2

[a] Negative values indicate that an oxide W_nO_{3n-2} will be stable (s), while positive values indicate that the oxide will be unstable (u) and disproportionate to the neighboring oxides. The units are arbitrary.

tant role to play in controlling the microstructures of the *CS* phases.

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