Crystal Chemistry and Subsolidus Phase Relations in the System Eu–W–O

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Crystal chemistry and subsolidus phase relations in a portion of the system Eu–W–O have been investigated. The stoichiometry and symmetry determined for compounds on the Eu_2O_3–WO_3 join are: Eu_6WO_{12}, cubic or tetragonal depending on the conditions of preparation—structure related to fluorite; $Eu_{14}W_4O_{33}$, pseudorhombohedral; Eu_2WO_6, monoclinic—structure related to scheelite; $Eu_2W_2O_9$, monoclinic—isostructural with $Pr_2W_2O_9$; $Eu_2W_3O_{12}$, monoclinic—structure also related to scheelite. The only divalent europium tungsten oxide, $EuWO_4$, had the tetragonal scheelite structure. Because of the structural similarity of $EuWO_4$ and $Eu_2W_3O_{12}$ ($Eu_{0.67}WO_4$), there was actually a limited scheelite structure solid solution Eu_xWO_4 ($x \approx 1 \to 0.77$) between them. A cubic europium tungsten bronze, Eu_xWO_3, was found for $x \approx 0.07 \to 0.15$. The compatibility relations among all of these phases and those on the Eu–O and W–O binary system are presented in a subsolidus phase diagram.

Introduction

As part of a continuing study of rare earth–transition metal oxide chemistry, compound formation and subsolidus phase relations in a portion of the system Eu–W–O have been determined. A preliminary examination of this system for divalent europium tungsten oxides has already been reported (*1*). $Eu^{2+}WO_4$ was the only one which could be prepared.

The metal–oxygen binary systems are well known. Phillips and Chang (*2*) studied the system W–O and confirmed the existence of WO_2, $W_{18}O_{49}$, and $W_{20}O_{58}$ as well as WO_3. All of these oxides are present in the solid state and stable over the temperature range 950–1100°C. However, $W_{18}O_{49}$ and $W_{20}O_{58}$ undergo subsolidus dissociation at about 500 and 400°C, respectively. Studies of the Eu–O binary by Bärnighausen (*3*), McCarthy and White (*4*) and Bedford and Catalino (*5*) have all shown that over the temperature range 950–1100°C the only intermediate compounds are EuO, Eu_3O_4 and

Eu_2O_3. EuO and Eu_3O_4 show no significant range of stoichiometry, while Eu_2O_3 can have a slight oxygen deficiency. The Eu–W binary has not been studied.

Experimental

Starting materials for this study were Eu_2O_3 (99.99%, Molycorp), WO_3 (purified grade, Fisher), and W metal (purified grade, Fisher). EuO was synthesized from Eu_2O_3 and Eu (99.9%, Research Chemicals) by the method of Shafer (*6*). Batches with the desired bulk composition were prepared from the appropriate weights of EuO–Eu_2O_3–W or Eu_2O_3–WO_3–W, and ground in an agate mortar. Approximately 1/2 g of each of these mixtures was pressed into a 1/4-in. pellet at 28,000 psi and heated either in a sealed silica vial or in a molybdenum crucible suspended in a furnace through which a purified argon atmosphere was passed. Reaction times were either 2 days at 1100°C or 4 days at 950°C. The pellets which had been reacted in sealed silica vials were well sintered and showed no evidence of reaction with silica. To be sure, however, the surface of the pellet was removed before characterization studies were initiated.

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In order to ascertain that steady state conditions had been achieved with these heating schedules, several pellets were re-ground, re-pressed, and heated for an additional 2–4 days. In all cases the phase assemblage was the same as after the first heating.

The oxygen content of each run was checked by gravimetric oxidation to the Eu_2O_3–WO_3 join. The procedures have been described in detail elsewhere (7, 8).

Phase identification was by reflected and transmitted light microscopy and by X-ray diffraction. Most of the phases encountered were black, grey, yellow-orange, or purple-blue and could be readily distinguished. X-Ray powder data were obtained on a Siemens diffractometer using nickel-filtered Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The diffractometer was calibrated with high-purity silicon ($a_0 = 5.4301$ Å) and gold ($a_0 = 4.0786$ Å). Data were refined using the least-squares computer program of Appleman et al. (9). Only unambiguously indexed reflections were used in these refinements. Reported intensities are derived from relative peak heights.

Results and Discussion

Compounds on the Eu_2O_3–WO_3 Join

Two recent reviews of all rare earth sesqui-oxide–WO_3 compounds, including those on the Eu_2O_3–WO_3 join, are found elsewhere (10, 11). Only a brief summary is given here.

1. Eu_6WO_{12}. This compound was first synthesized by Potter et al. (12) and characterized by McCarthy (1). When prepared at 1100°C with 2 day heating it had a fcc powder diffraction pattern with $a_0 = 5.366(3)$ Å as reported earlier (1). However, when it was prepared at 1400°C with 4–6 day heating, a slight splitting of many of the fcc reflections was noted in the powder patterns. Since the (111) and (222) remained unsplit, the true symmetry is probably tetragonal or orthorhombic. All of the observed reflections could be indexed on a tetragonal cell with $a_0 = 5.384(1)$ Å and $c_0 = 5.362(1)$ Å. The powder data, except for the slight splittings, were identical to that reported by McCarthy (1).

2. $Eu_{14}W_4O_{33}$. Chang et al. (13) reported a compound of this stoichiometry in their study of the system Sm–W–O. Their powder data for $Sm_{14}W_4O_{33}$ corresponded closely to that of $Eu_{14}W_4O_{33}$, except that several of the reflections reported by Chang et al. were doublets in $Eu_{14}W_4O_{33}$. The powder data were also similar

to that of McCarthy and Fischer (14) for $Ho_{14}W_4O_{33}$. The observed reflections were indexed in reference to the pseudorhombohedral subcell proposed for that compound. These powder data and refined cell parameters are given in Table I.

3. Eu_2WO_6. This compound was recently prepared by Pokrovskii et al. (15). From single-crystal data they found the space group ($C2/c$, No. 15) and reported the following monoclinic cell parameters:

$$a_0 = 16.73(1) \text{ Å} \qquad c_0 = 5.447(4) \text{ Å}$$
$$b_0 = 11.225(5) \text{ Å} \qquad \beta = 110°39(6)'$$

More recently, Polyanskaya et al. (16) reported a structure determination of the isostructural Nd_2WO_6. They found a monoclinic cell with space group $I2/c$ (a higher symmetry form of No. 15) and $a_0 = 15.92$ Å, $b_0 = 11.39$ Å, $c_0 = 5.508$ Å, and $\beta = 92°$. A very satisfactory refinement was obtained from the powder data of Eu_2WO_6 based on a somewhat smaller version of this cell. The cell parameters are

$$a_0 = 15.686(3) \text{ Å} \qquad c_0 = 5.442(1) \text{ Å}$$
$$b_0 = 11.219(3) \text{ Å} \qquad \beta = 91°42(1)'$$

The powder data observed in this study were virtually identical to that given by Pokrovskii et

TABLE I

POWDER DIFFRACTION DATA FOR $Eu_{14}W_4O_{33}$

Hexagonal parameters of the pseudorhombo-hedral cell: $a_0 = 9.902(2)$ Å; $c_0 = 9.598(6)$ Å

$h\,k\,l$	d_{calc}	d_{obs}[a]	I/I_0[a]
0 0 3	3.20	3.20	40
2 1 1	3.076	{3.082 3.070	{ 50 100
1 2 2	2.689	2.689	55
2 1 4	1.930	{1.936 1.928	{ 30 35
4 1 0	1.875	{1.876 1.873	{ 25 30
1 2 5	1.652	{1.656 1.651	{ 16 14
4 1 3	1.618	{1.622 1.616	{ 20 35
2 4 1	1.601	1.601	16
4 2 2	1.538	{1.542 1.536	{ 4 5
2 4 4	1.345	{1.345 1.344	{ 18 16

[a] Overlapping reflections are indicated with a brace ({).

al. (15) for Eu_2WO_6 except that because they used a somewhat larger value a_0 and larger β angle, their indexing is generally incorrect. All of their observed reflections can be indexed on the higher symmetry $I2/c$ space group.

4. $Eu_2W_2O_9$. The existence of this compound has not been previously reported. Chang et al. (13) reported an analogous $Sm_2W_2O_9$ and Borisov and Klevtsova (17) have prepared and studied single crystals of $Ce_2W_2O_9$, $Pr_2W_2O_9$, and $Nd_2W_2O_9$. The powder data of $Eu_2W_2O_9$ could be indexed on a monoclinic cell (space group $P2_1/c$, No. 14) by analogy to the Borisov and Klevstova data for $Nd_2W_2O_9$. The refined cell parameters and powder data are given in Table II.

5. $Eu_2W_3O_{12}$. MacDonald et al. (18) first prepared this compound and studied its fluorescence properties. Templeton and Zalkin (19) performed a structural analysis and found the structure to be monoclinic with space group $C2/c$, $Z = 4$ and cell parameters

$$a_0 = 7.676(3) \text{ Å} \qquad c_0 = 11.396(5) \text{ Å}$$
$$b_0 = 11.463(3) \text{ Å} \qquad \beta = 109°38(2)'.$$

The structure may be most simply described as that of scheelite ($CaWO_4$) with one-third of the calcium sites vacant, i.e., $(Eu_{0.67}\square_{0.33})WO_4$. This is an oversimplified model, since the vacancies are ordered, and this leads to considerable distortion from the ideal scheelite structure and lowers the symmetry from $I4_1/a$

TABLE II

POWDER DIFFRACTION DATA FOR $Eu_2W_2O_9$

Monoclinic $a_0 - 7.590(1)$ Å
              $b_0 - 9.732(1)$ Å
$P2_{1/c}$ (14) $c_0 - 9.178(1)$ Å
              $\beta = 107°40(1)'$

h k l	d_{calc}	d_{obs}	I/I_0	h k l	d_{calc}	d_{obs}	I/I_0
1 1 0	5.80	5.80	10	0 4 0	2.433	2.433	16
$\bar{1}$ 1 1	5.49	5.49	5	0 4 1	2.344	2.344	7
0 2 0	4.87	4.86	8	3 1 0	2.340	2.340	30
0 0 2	4.37⎫	4.37	4	$\bar{1}$ 1 4	2.233	2.233	11
1 1 1	4.37⎭						
$\bar{1}$ 2 1	3.927	3.928	4	1 2 3	2.194	2.194	6
2 0 0	3.616	3.615	2	$\bar{2}$ 0 4	2.188⎫	2.187	10
				$\bar{3}$ 3 2	2.187⎭		
$\bar{2}$ 1 1	3.515	3.515	3	0 3 3	2.168	2.168	5
2 1 0	3.390	3.389	1	$\bar{3}$ 1 3	2.162⎫	2.160	6
				3 2 0	2.160⎭		
$\bar{2}$ 0 2	3.326⎫	3.324	100	$\bar{2}$ 3 3	2.078	2.078	7
1 0 2	3.321⎭						
$\bar{1}$ 2 2	3.254⎫	3.253	85	2 4 0	2.019⎫	2.018	10
0 2 2	3.252⎭			$\bar{3}$ 2 3	2.018⎭		
$\bar{2}$ 1 2	3.147⎫	3.145	90	$\bar{3}$ 3 1	1.994⎫	1.994	20
1 1 2	3.144⎭			0 2 4	1.994⎭		
0 3 1	3.041	3.041	20	3 2 1	1.976	1.976	4
$\bar{2}$ 2 1	2.980	2.980	20	1 4 2	1.963	1.963	25
1 3 0	2.959	2.960	50	1 3 3	1.959	1.959	20
$\bar{1}$ 1 3	2.904⎫	2.903	90	$\bar{3}$ 3 2	1.954⎫		
2 2 0	2.902⎭			2 3 2	1.953⎬	1.953	30
0 1 3	2.973	2.973	4	2 1 3	1.953⎭		
$\bar{2}$ 2 2	2.745⎫	2.744	15	1 0 4	1.936⎫	1.935	7
1 2 2	2.744⎭			3 3 0	1.935⎭		
$\bar{1}$ 3 2	2.606⎫	2.605	25	3 1 4	1.901⎫		
0 3 2	2.605⎭			$\bar{1}$ 4 3	1.900⎬	1.900	18
$\bar{1}$ 2 3	2.580	2.580	12	0 5 1	1.900⎭		
$\bar{3}$ 0 2	2.449⎫	2.449	8	$\bar{4}$ 1 1	1.853	1.853	15
$\bar{3}$ 3 1	2.449⎭						

to $C2/c$. Europium is surrounded in nearly regular eight-fold coordination by oxygen. There are two distinct kinds of highly distorted W–O tetrahedra. Powder data for these compounds were recently determined by Keester and Johnson (20) and will appear in Set 22 of the Powder Diffraction File (21).

Eu_xWO_4

McCarthy (1) described $Eu^{2+}W^{6+}O_4$ in his preliminary examination of the system Eu–W–O for divalent europium compounds. It has a tetragonal scheelite type structure with $a_0 = 5.411(1)$ Å and $c_0 = 11.936(1)$ Å. Since $Eu_2W_3O_{12}$ (which can be written as $Eu_{0.67}WO_4$) has a scheelite-related structure, one might expect that there could be partial solid solution between these phases. This was indeed found to be the case. At 1100°C the tetragonal scheelite structure was found for the solid solution Eu_xWO_4 with $x \approx 1 \rightarrow 0.82$. Over the range $x \approx 0.81 \rightarrow 0.77$ several reflections in the powder patterns showed a slight splitting which indicated that a phase change to lower symmetry occurs at $x \approx 0.82$. Only a slight stoichiometry range was noted for the monoclinic $Eu_{0.67}WO_4$ phase, from $x \approx 0.69 \rightarrow 0.67$. Between $x \approx 0.77$ and 0.69, the pseudo-tetragonal and monoclinic phase coexisted.

Cell parameters were determined for three representative members of Eu_xWO_4:

	a_0 (Å)	c_0 (Å)	V (Å³)
EuWO₄	5.411(1)	11.936(1)	349.4(1)
Eu₀.₈₃WO₄	5.300(1)	11.688(3)	328.4(2)
Eu₀.₇₈WO₄	5.264(2)	11.620(7)	321.9(4)

Only unsplit reflections of $Eu_{0.78}WO_4$ were used to determine the pseudotetragonal cell parameters.

There are two defect models which could account for the Eu_xWO_4 solid solution. In the first, an anion interstitial model, for each $2Eu^{3+}$ which replace $2Eu^{2+}$ in $EuWO_4$, charge compensation is provided by the addition of an interstitial oxygen:

$$(Eu^{2+}_{1-2y}Eu^{3+}_{2y})WO_4O_y{}^i.$$
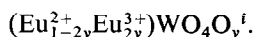
The second model involves cation vacancies. The substitution of each $2Eu^{2+}$ by $2Eu^{3+}$ in $EuWO_4$ is accompanied by the creation of one cation vacancy:

$$(Eu^{2+}_{1-3y}Eu^{3+}_{2y}\square_y)WO_4.$$
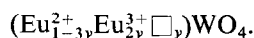
Since the structure of the end member $Eu_{0.67}WO_4$ is known to be a cation deficient scheelite type (19),

it is likely that the model for the solid solution between the scheelite $EuWO_4$ and this compound will also be of cation vacancy type. Work is in progress on the solid solution range, symmetry of phases and defect characterization in the $SrWO_4$–$Eu_{0.67}WO_4$ system in which $SrWO_4$ is size and charge model for $EuWO_4$. The advantage of working in this latter system is the elimination of the need for careful atmospheric control, since all reactions can be carried out in air.

Eu_xWO_3

Ostertag (22) has reported the preparation of a cubic tungsten bronze Eu_xWO_3 with $x \approx 0.085 \rightarrow 0.16$ at 1050°C. This was found to be one of the equilibrium phases in the present study. At 1100°C the cubic bronze was found over the approximate range of $x \approx 0.07 \rightarrow 0.15$. As noted by Ostertag, the stability range of the cubic phase varies as a function of preparation temperature and thus preparations at other temperatures will yield other composition ranges. X-Ray powder data for the cubic phase corresponded closely to that reported by Ostertag and the Powder Diffraction File (No. 19-465). Cell parameters were determined for two of the compositions, $Eu_{0.07}WO_3$ with $a_0 = 3.803(1)$ Å and $Eu_{0.12}WO_3$ with $a_0 = 3.813(1)$ Å.

A slight splitting of several reflections and broadening of high angle reflections in the powder pattern of $Eu_{0.15}WO_3$ probably indicate that a phase change to a lower symmetry form occurs near the upper limit of Eu solubility. For values of x lower than ≈ 0.07 the powder patterns became more complex. Crystallographic studies on these lower symmetry phases and Mössbauer spectra measurements on all Eu_xWO_3 phases are in progress elsewhere (23).

Subsolidus Phase Relations

Subsolidus phase relations for the portion of the system Eu–W–O bounded by EuO–Eu_2O_3–WO_3–W are shown in Fig. 1. A selected larger-scale view is shown in Fig. 2. The phase assemblages in both figures are numbered and listed in Table III.

Most of the phase relations were determined at 1100°C. However, due to partial melting at that temperature, the phase relations in the region just below $Eu_2W_3O_{12}$–WO_3 in oxygen content were determined at 950°C. Also, because the lower symmetry Eu_xWO_3 phases were not included in this study, the phase relations involving them and $Eu_2W_3O_{12}$, WO_3 and $W_{20}O_{58}$ were
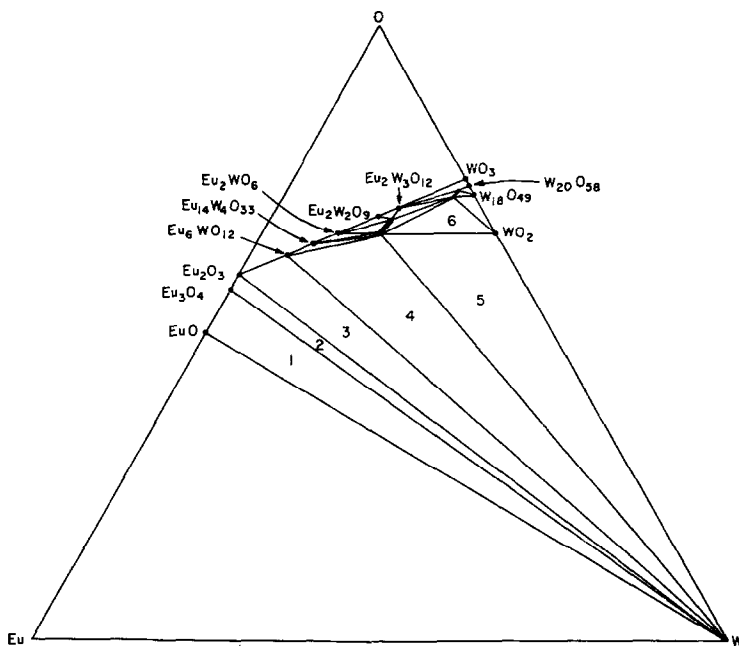
FIG. 1 Subsolidus phase relations in a portion of the system Eu–W–O. The solid solutions Eu_xWO_4 and Eu_xWO_3 are not labeled. Numbered phase assemblages are listed in Table III.

not determined. Only the stoichiometry range of the cubic Eu_xWO_3 phase is shown in Figs. 1 and 2.

The phase assemblages numbered in Fig. 1 (Nos. 1–6) were determined by heating the appropriate mixtures in a flowing purified argon atmosphere. When this technique was used for determination of the phase relations involving Eu_xWO_4 and Eu_xWO_3, the original bulk com- position spontaneously lost some of its oxygen content. For example, a run of bulk composition in assemblage 16 ($Eu_2W_3O_{12} + Eu_xWO_3$) lost enough oxygen during the 2 days of heating to give products in assemblage 6 ($EuWO_4 + Eu_xWO_3 + WO_2$). This behavior has been des- cribed previously by McCarthy and coworkers in their studies of the system Eu–Ti–O (7), Sr–Ti–O (8), Sm–Ti–O (24), and Eu–Fe–O (25).
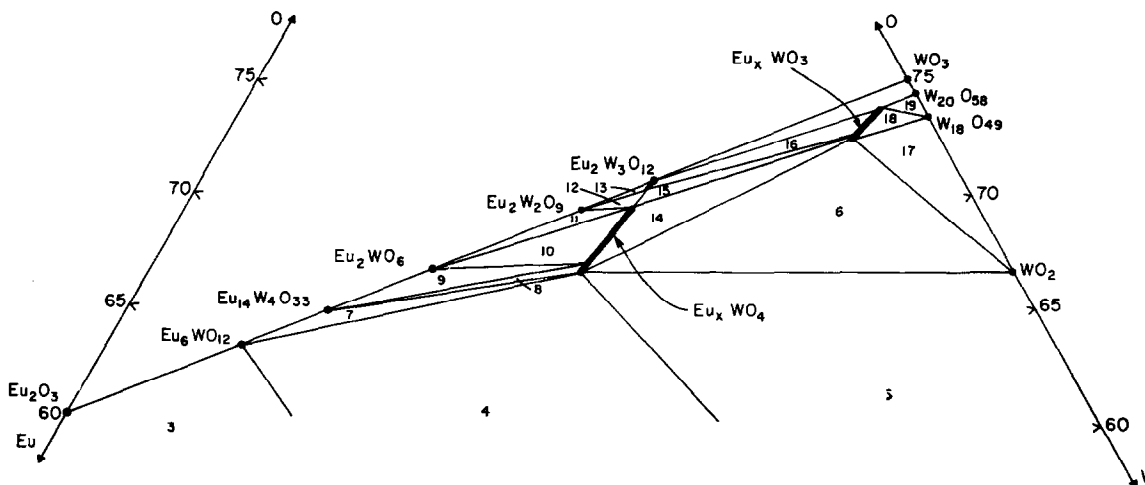

FIG. 2. Selected portion of Fig. 1 showing the detailed phase relations involving Eu_xWO_4 and Eu_xWO_3. Numbered phase assemblages are listed in Table III. The region bounded by $Eu_2W_3O_{12}$–$Eu_{0.07}WO_3$–$W_{20}O_{58}$–WO_3 was not studied.

TABLE III

PHASE ASSEMBLAGES IN FIGURES 1 AND 2

No.	Phase assemblage
1	$EuO + Eu_3O_4 + W$
2	$Eu_3O_4 + Eu_2O_3 + W$
3	$Eu_2O_3 + Eu_6WO_{12} + W$
4	$Eu_6WO_{12} + EuWO_4{}^a + W$
5	$EuWO_4 + WO_2 + W$
6	$EuWO_4 + WO_2 + Eu_xWO_3$
7	$Eu_6WO_{12} + Eu_{14}W_4O_{33} + EuWO_4$
8	$Eu_{14}W_4O_{33} + Eu_xWO_4$
9	$Eu_{14}W_4O_{33} + Eu_2WO_6 + Eu_xWO_4$
10	$Eu_2WO_6 + Eu_xWO_4$
11	$Eu_2WO_6 + Eu_2W_2O_9 + Eu_xWO_4$
12	$Eu_2W_2O_9 + Eu_2W_3O_{12} + Eu_xWO_4$
13	$Eu_2W_2O_9 + Eu_2W_3O_{12}$
14	$Eu_xWO_4 + Eu_xWO_3$
15	$Eu_xWO_4 + Eu_2W_3O_{12} + Eu_xWO_3$
16	$Eu_2W_3O_{12} + Eu_xWO_3$
17	$Eu_xWO_3 + WO_2 + W_{18}O_{49}$
18	$Eu_xWO_3 + W_{18}O_{49}$
19	$Eu_xWO_3 + W_{18}O_{49} + W_{20}O_{58}$

^{a} EuWO₄ is used instead of Eu$_x$WO₄ to indicate the stoichiometric end member of the solid solution.

The solution to this problem was the same as that used previously, namely, the utilization of evacuated, sealed silica capsules. In this closed system the oxygen content of each bulk composition was fixed. Throughout the study, the oxygen content of each run product was checked by gravimetric oxidation as previously described by McCarthy et al. (7). Therefore, if one wishes to prepare Eu_xWO_4 or Eu_xWO_3 (these phases should be of interest in magnetic, electrical, or Mössbauer studies), one should do so in silica vials. It might also be noted that in the Eu_xWO_4 solid solution preparations, equilibrium was established more readily with the appropriate mixtures of $EuWO_4$ and $Eu_2W_3O_{12}$ ($Eu_{0.67}WO_4$) than with mixtures of Eu_2O_3–WO_3–W.

The general features of the subsolidus phase relations can be seen in Fig. 1. Tungsten metal coexists with EuO, Eu_3O_4, Eu_2O_3, Eu_6WO_{12}, stoichiometric $EuWO_4$, and WO_2. The phase relations involving Eu_xWO_4 and Eu_xWO_3 are shown in detail in Fig. 2. The solid solution Eu_xWO_4 coexists with Eu_6WO_{12}, $Eu_{14}W_4O_{33}$, Eu_2WO_6, $Eu_2W_2O_9$, cubic Eu_xWO_3, and WO_2. The small range of stoichiometry of $Eu_2W_3O_{12}$

is shown as well as its coexistence with $Eu_2W_2O_9$ and cubic Eu_xWO_3. Apparently the ordered defect monoclinic scheelite structure of $Eu_2W_3O_{12}$ can tolerate only a slight excess of Eu. Cubic Eu_xWO_3 coexists with $W_{18}O_{49}$ and $W_{20}O_{58}$.

The phase diagram also indicates what happens if one attempts to prepare europium tungsten bronzes with $x > 0.15$ at $1100°C$. One will derive a mixture of $Eu_{0.15}WO_3$ with $EuWO_4$ and WO_2 (assemblage 6).

Missing from the phase diagram is another compound which one might have predicted would exist, based on knowledge of the Sr–W–O system. Chang et al. (26) reported a phase diagram for the system SrO–WO_3 in which the two intermediate phases are $SrWO_4$ with the tetragonal scheelite structure and Sr_3WO_6 with a distorted $(NH_4)_3FeF_6$ structure. The compounds $SrWO_4$ and $EuWO_4$ are isotypes with very similar cell parameters and powder diffraction patterns (1). This would be expected from the virtually identical ionic radii of Sr^{2+} and Eu^{2+} (27). However, the Eu_3WO_6 isotype of Sr_3WO_6 is not stable at $1100°C$. The phase assemblage ($Eu_6WO_{12} + W$) precludes the existence of this compound. Attempts at synthesizing Eu_3WO_6 at temperatures over the range 900 to $1400°C$ also yielded the ($Eu_6WO_{12} + W$) phase assemblage.

Shafer (6) also attempted to synthesize Eu_3WO_6. He was unable to prepare the pure compound but succeeded in stabilizing it by partial substitution of Eu^{2+} with Sr^{2+}. The most europium-rich member of the solid solution was Eu_2SrWO_6.

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