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Preparation and Structure of Mixed Tungsten Bronzes Containing Tin and Europium

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An isothermal section has been established for the system Eu_xWO_3–Sn_yWO_3 at 1000°C from X-ray powder and single-crystal data and Mössbauer spectroscopy and chemical analyses. A single-phase region with the (12 × 3) tetragonal structure has been established. Single-crystal X-ray analysis shows that the Sn and Eu occupy pentagonal tunnel sites. Mössbauer spectroscopy shows that both Sn(II) and Eu(II) are present. The extent of the single-phase field is controlled by two factors: First, the ratio Eu/Sn must be <1, and second, the supernumerary electron concentration per WO_3 must be <0.6.

Introduction

There are few detailed investigations of tungsten bronze phases containing more than one guest metal. A sodium–potassium phase $Na_xK_yWO_3$ was first prepared in 1883 (*1*) but no details were available until recently when Utsumi and Jujieda examined the extent of the phase boundaries (*2*). These workers found only a tetragonal (12 × 3)[1] structure with a lattice parameter varying linearly with potassium content but in no obvious manner with Na content. Phases were reported with $x + y$ values in $Na_xK_yWO_3$ up to 0.86, which is surprising in view of the expected limit of 0.60 guest ions if only four- and five-fold pentagonal tunnel sites in the WO_3 lattice are occupied. It is perhaps worthy of note that both the *a* and *c* lattice parameters reached a maximum at 0.60.

A sodium–barium tungsten bronze with a (12 × 3) tetragonal structure was prepared by Conroy and Yokokawa (*3*). Both lattice parameters increased with Ba content, but the extent of the phase field was not determined. A mixed bronze with hexagonal symmetry containing lithium and potassium was synthesized by Banks and Goldstein (*4*) in an attempt to extend the electron concentration range of the hexagonal structure by incorporating lithium into sites too small for other ions. This strategy appears to have been successful because the limit was increased from $x = 0.33$ to $x + y = 0.51$, implying that lithium could enter sites in triangular tunnels. A study of the expansion of the lattice with increasing lithium content supported the hypothesis that these latter sites were occupied.

Occasional references are found to mixed bronzes in studies on the effect of "doping" on crystal growth of well-established bronze phases (*5*), but few details have been reported. In general, no structural determinations of mixed bronzes have been made to enquire into such questions as the role of crystal structure on the symmetry requirements and the oxidation states of the guest ions.

Earlier detailed investigations on the tin tungsten bronzes (*6–8*) and europium tungsten

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[1] This nomenclature is explained in (*8*).

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bronzes (*9*) provided the basis for further study since these two systems contained unusual features that might prove dominant and prevent mixed bronze formation. First, tin in bronzes exhibits only divalency (*6*) and occupies asymmetric sites in tunnels in the (12 × 3) tetragonal structure. Second, europium is only tervalent in bronzes and occupies cage sites in the cubic structure (*9*). This unexpected tervalency of europium has been confirmed independently (*10*). Both systems show only a limited composition range with tin not exceeding 0.28 and europium not exceeding 0.125 atoms per WO_3. Accordingly we decided to investigate: (a) whether the limit of the total guest ions could exceed the limit in the parent bronzes; (b) whether tin would dominate and restrict the symmetry to (12 × 3) tetragonal; and (c) if this were the case, what would be the valency and site symmetry of europium atoms? The fact that both tin and europium are Mössbauer-active elements was an important further consideration in choosing this system since oxidation states could be determined directly *in situ*, and the technique has also proved very useful in assisting complex phase analyses in the past (*9*).

A practical difficulty was in selecting a temperature at which to study the system, since below 950°C, reaction is slow in the Eu_2O_3–WO_3 system, while above 750°C bronze decomposition products in the SnO_2–WO_3 system are molten and rapidly attack the silica reaction tubes (*8*). The best solution to this problem was to work at 1000°C and to keep the tin content below $y = 0.3$. By using a combination of X-ray powder, X-ray single-crystal analyses, microscopy, and Mössbauer spectroscopy we have been able to demarcate a mixed bronze area where the (12 × 3) tetragonal structure contains both tin and europium and with the interesting feature that the europium becomes divalent. This is the first time that Eu(II) has been found in a bronze and shows that the need for Sn(II) to occupy asymmetric tunnel sites is a dominant factor in deciding the structure type. Conversely, it demonstrates the effect of structure on the valency of a multivalent ion in a bronze phase. A description of the work leading to these observations is given below.

Experimental

All samples were prepared by solid-state reactions according to the equation

$$xSnO_2 + (y/_2)Eu_2O_3 + (1 - 2/3x - 1/2y)\,WO_3 + ((2x/_3) + (y/_2))W = Sn_xEu_yWO_3.$$

The components were heated in sealed silica ampoules at 1000°C for times ranging from 3 days to 3 weeks. Eu_2O_3 was 99.99% pure (Rare Earth Products Ltd.), SnO_2 and WO_3 were specpure grade (Johnson and Matthey Ltd.), and W metal powder was 99.99% pure (Johnson and Matthey Ltd.).

The X-ray powder techniques and the Mössbauer apparatus have been described before (*6, 9*).

For all single-crystal X-ray investigations the integrating Weissenberg technique was employed. Copper $K\alpha$ radiation was used, and exposure times of up to 7 days were necessary when spot integration was carried out. Crystals having dimensions less than 50 μm were used in order to minimize absorption by the high atomic weight elements. Intensities were obtained from a Joyce–Loebl double-beam recording microdensitometer. All computing was undertaken at the SRC Atlas Computer Centre at Harwell using the "X-ray System" edited by Stewart, Kundell, and Baldwin.

Results and Discussion

A summary of the X-ray, microscopic, and Mössbauer analyses is given in Table I. These data are shown in Fig. 1 where it can be seen that, under these conditions, only one single-phase region exists. It is noticeable that outside this region the structures found (with the exception of the phase designated cubic II, which has a primitive cubic powder diffraction pattern from a cell of lattice parameter a = 4.29 Å) can be related to the single-component bronze systems. The position of this new cubic phase in Fig. 1 suggests that it is mainly europium-containing and serves as a reservoir for the excess metal when the europium and tin bronzes present exceed their upper composition limit and decompose. Attempts to

TABLE I

PHASES FOUND IN THE Sn–Eu–WO_3 SYSTEM

Composition		
x Sn	y Eu	Phases present (%, estimated)
0.02	0.10	Cubic bronze 100%
0.03	0.03	Orthorhombic 7-type + tetragonal (5 × 3)
0.05	0.05	Cubic bronze + orthorhombic 7-type
0.05	0.08	Cubic bronze 95% + uncertain
0.05	0.10	Cubic bronze 80% + $SnWO_4$ 20%
0.05	0.12	Cubic bronze 75% + tetragonal (12 × 3) 15% + WO_2 10%
0.05	0.15	Cubic bronze 70% + $EuWO_4$ + WO_3 + $SnWO_4$
0.07	0.07	Cubic bronze + orthorhombic 5-type
0.085	0.085	Cubic bronze + $SnWO_4$
0.10	0.10	Cubic bronze 75% + tetragonal (12 × 3) 25%
0.10	0.12	Cubic bronze 50% + tetragonal (12 × 3) 50%
0.10	0.15	Cubic bronze 70% + $SnWO_4$ + WO_2 + Cubic II + tetragonal (12 × 3) 5%
0.10	0.20	Cubic bronze 50% + cubic II 20% + $EuWO_4$ + WO_2 + tetragonal (12 × 3)
0.12	0.03	Cubic bronze 90% + orthorhombic 7-type 10%
0.12	0.07	Cubic bronze 40% + tetragonal (12 × 3) 60%
0.12	0.10	Cubic bronze 75% + $SnWO_4$ 25%
0.12	0.12	Cubic bronze 55% + tetragonal (12 × 3) 30% + $SnWO_4$ 15%
0.135	0.05	Cubic bronze 60% + tetragonal (12 × 3) 40%
0.14	0.05	Cubic bronze 60% + tetragonal (12 × 3) 40%
0.14	0.07	Cubic bronze 70% + tetragonal (12 × 3) 30%
0.15	0.10	Tetragonal (12 × 3) 100%
0.15	0.15	Tetragonal (12 × 3) 70% + cubic bronze 30%
0.17	0.07	Tetragonal (12 × 3) 100%
0.17	0.10	Tetragonal (12 × 3) 100%
0.17	0.15	Tetragonal (12 × 3) 85% + $EuWO_4$ + $SnWO_4$
0.17	0.17	Tetragonal (12 × 3) 80% + WO_2 + $EuWO_4$
0.18	0.12	Tetragonal (12 × 3) 100%
0.20	0.03	Tetragonal (12 × 3) > 90%
0.20	0.10	Tetragonal (12 × 3) 100%
0.20	0.15	Tetragonal (12 × 3) 70% + $SnWO_4$ 30%
0.20	0.20	Tetragonal (12 × 3) 90% + unknown 10%
0.21	0.07	Tetragonal (12 × 3) 90% + unknown
0.23	0.18	Tetragonal (12 × 3) 80% + $SnWO_4$
0.25	0.10	Tetragonal (12 × 3) 90% + $SnWO_4$
0.25	0.15	Tetragonal (12 × 3) 85% + $EuWO_4$ + WO_2
0.28	0.07	Tetragonal (12 × 3) 70% + $SnWO_4$ 30%
0.30	0.10	Tetragonal (12 × 3) + $EuWO_4$ + $SnWO_4$
0.30	0.20	$SnWO_4$ 75% + $EuWO_4$ 15% + W 10%
0.35	0.15	$SnWO_4$ 80% + $EuWO_4$ 10% + tetragonal (12 × 3)

synthesize this phase by itself have so far failed and as a result accurate Mössbauer data for it have been difficult to obtain. However, it does produce a strong Eu(II) resonance, and it is possible that this phase is an ionic tungstate containing a large proportion of europium.

The results given in Table I are only those from what were considered to be "clean" runs. Experiments at 1000°C produced many

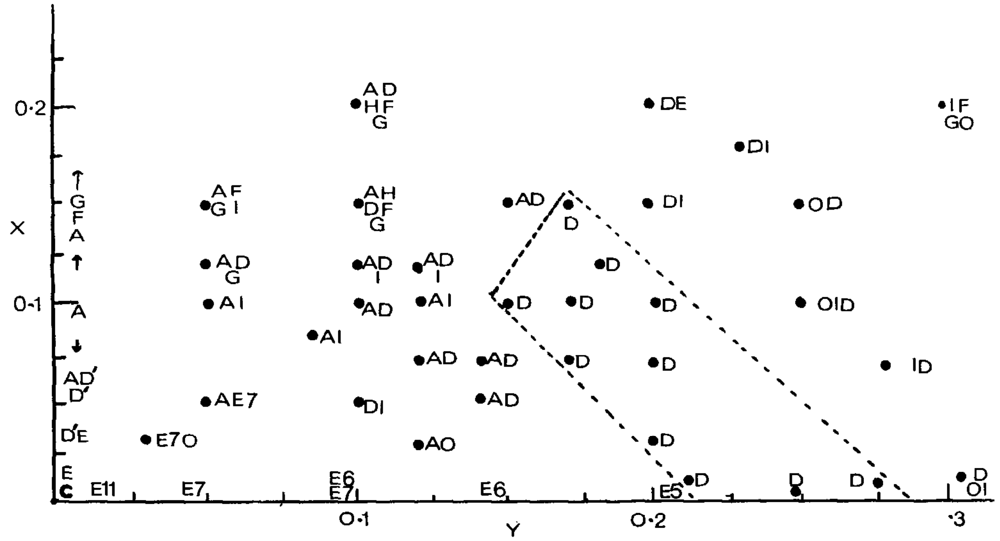

FIG. 1. Phases found in the Eu_x–Sn_y–WO_3 system at 1000°C. A = cubic, C = monoclinic, D = tetragonal (12 × 3), D′ = tetragonal (5 × 3), E = orthorhombic with the number equal to the size of the superlattice, F = $EuWO_4$, G = WO_2, H = Cubic II, I = $SnWO_4$, O = others.

ampoule failures, and when times greater than 3 days were used there was frequently visual evidence of reaction tube discoloration due to attack. Such specimens were discarded. At temperatures below 785°C these practical problems were not encountered, but all attempts to prepare the mixed bronzes at such temperatures resulted only in mixtures of $EuWO_4$, $SnWO_4$, tetragonal tin bronze, and oxides of tungsten. After several series of attempts it was concluded that a temperature of 1000°C was necessary to synthesize the mixed bronze phase.

The existence of the single-phase mixed bronze region shown in Fig. 1 is the most interesting aspect of this work. Several specimens were synthesized in order to investigate the extent of this phase field and within the limits of the experimental difficulties and sensitivities it was found to be bounded by the compositions $Eu_{0.17}Sn_{0.175}WO_3$–$Eu_{0.11}Sn_{0.14}WO_3$ – $Eu_{<0.01}Sn_{0.21}WO_3$ – $Eu_{<0.01}Sn_{0.28}WO_3$.

Thus, it appears that the tetragonal (12 × 3) tin bronze structure can dissolve europium and extend the range of existence of this phase. These limits were determined by X-ray powder investigations, analysis by hydrogen reduction, neutron activation, and Mössbauer spectroscopy, all of which showed that the phase contained both tin and europium.

Mössbauer spectroscopy was used extensively in the investigation and the results are shown in Table II. Immediately striking is the divalent charge shown by the europium in the single-phase mixed tin–europium tungsten bronzes. This is in marked contrast to the parent europium bronze system where in all structures the guest ion was trivalent (*9*). Thus the charge state of the europium has been influenced by the presence of Sn(II) or by the (12 × 3) tetragonal structure.

It is perhaps not unexpected that the structure adopted by the mixed bronze is the tetragonal (12 × 3) since it must accommodate the asymmetrical divalent tin ions. The ionic radius of Eu^{3+} at (1.03 Å) enables it to occupy the square tunnel sites in the cubic europium bronze, and it would be possible for it to occupy the equivalent site in the (12 × 3) tetragonal structure. However, it appears that a valency change occurs, and the question to be answered is: Where do these europium (II) ions go in the structure? An answer to this is given below where a single-crystal structure analysis is described which shows that the

TABLE II

Mössbauer Parameters at 77°K for Various Compositions in the $Sn_xEu_yWO_3$ System[a]

Nominal composition		^{151}Eu[b]						^{119}Sn[c]		
		Eu(II)			Eu(III)			Sn(II)		
Sn x	Eu y	(%)	δ (mm sec^{-1})	Γ (mm sec^{-1})	(%)	δ (mm sec^{-1})	Γ (mm sec^{-1})	δ (mm sec^{-1})	Δ (mm sec^{-1})	Γ (mm sec^{-1})
0.05	0.10	0	—	—	100	0.0(2)	3.6	3.53(4)	1.39(6)	0.94
0.05	0.15	0	—	—	100	0.0(2)	3.1	3.56(8)	1.28(11)	1.15
0.10	0.10	11	−13.5(3)	3.0	89	+0.4(2)	1.8	3.67(3)	1.15(4)	1.05
0.10	0.15	63	−12.9(2)	5.0	37	+0.1(1)	3.3	3.54(8)	1.19(13)	1.00
0.10	0.20	53	−13.6(1)	4.3	47	−0.1(2)	2.8	3.54(5)	1.26(6)	1.00
0.12	0.10	0	—	—	100	+0.2(1)	1.4	3.53(3)	1.34(5)	0.91
0.12	0.12	50	−12.5(4)	6.9	50	+0.3(1)	2.7	3.62(4)	1.19(5)	1.05
0.14	0.07	0	—	—	100	−0.1(1)	2.3	3.64(3)	1.13(4)	1.05
0.15	0.15	77	−13.4(1)	4.8	23	0.0(1)	2.9	3.68(3)	1.16(4)	1.01
0.17	0.10	100	−13.3(2)	7.5	0	—	—	3.69(3)	1.12(4)	1.07
0.20	0.10	88	−13.0(1)	5.2	12	+1.5(6)	4.0	3.61(3)	1.05(4)	1.03
0.20	0.15	75	−13.8(1)	7.1	25	+0.3(7)	4.3	3.58(1)	1.26(2)	0.99
0.20	0.20	100	−13.6(1)	4.6	0	—	—	3.63(2)	1.22(3)	1.02
0.21	0.07	85	−13.8(2)	5.2	15	0.0(3)	1.6	3.67(2)	1.14(3)	1.07
0.25	0.10	100	−11.6(2)	10.2	0	—	—	3.73(4)	1.25(6)	1.15
0.25	0.15	100	−13.4(1)	4.1	0	—	—	3.60(2)	1.25(3)	0.98
0.28	0.07	69	−13.9(8)	11.0	3.1	0.4(2)	3.4	3.55(2)	1.29(3)	0.90

[a] δ = chemical isomer shift; Δ = quadruple splitting; Γ = full width at half-height; numbers in parentheses are estimated errors in the last significant figure.

[b] δ (^{151}Eu) is relative to EuF_3.

[c] δ (^{119}Sn) is relative to $BaSnO_3$.

Eu^{2+} ions occupy positions on the central axis of the pentagonal tunnels. The large size of this site does not impose the restriction on ionic radius of the four-fold tunnel site.

Electronic reasons for the change in oxidation state are not clear. It might be noted that a common feature in bronze systems seems to be a maximum in the total number of band electrons per WO_3 unit for the different structure types. When considering the (12 × 3) tetragonal structure the electron concentration per tungsten for K_xWO_3, Sn_xWO_3, Pb_xWO_3; and $Na_xK_yWO_3$ has an upper value of between 0.6 and 0.7, which is approximately the theoretical structural limit of 0.6 for occupancy of the pentagonal site by monovalent ions. However, no such limitation is imposed for the divalent ions, and it seems likely that an electron density of this amount corresponds to a minimum energy configuration within the band system. Because both tin and europium are divalent in the single-phase region it is seen that the upper composition limit of the mixed bronzes achieved in this work also give rise to a limit of about 0.65 electrons per tungsten in the bronze. Attempts to prepare mixed bronzes above this limit result in mixtures containing the mixed bronze at the upper composition limit with the relevant europium and tin "sink" phases. The other limiting factor in deciding the extent of the mixed bronze region is apparent in Fig. 1, where it can be seen that the Eu/Sn ratio never quite reaches unity. The reason for this last observation is not clear but it restricts the upper limit of europium content to about

0.17 atoms per WO_3, which is only a modest increase over the maximum value of 0.125 found in the parent Eu_xWO_3 system (*9*).

Single-Crystal X-Ray Analysis

One of the preparations with a composition $Sn_{0.15}Eu_{0.1}WO_3$ was formed with needle crystals of a suitable morphology and size for a single-crystal X-ray examination to be made to pursue further the question of the site of the Eu(II) ions. A Guinier focusing camera X-ray investigation of this sample produced the data in Table III, which showed the lattice parameter to be $a = 12.14$ Å, $c = 3.761$ Å.

Diffraction patterns were obtained for zero, first, second, and third layers of the reciprocal lattice when the crystal was mounted with its long edge parallel to the axis of rotation of the crystal. Other reflections were collected with the crystal remounted with a short edge parallel to the axis of rotation. In this way 616 unique reflections were observed out of a possible 635.

TABLE III

X-RAY POWDER DATA FOR $Sn_{0.15}Eu_{0.1}WO_3$

Intensity	Index $h\,k\,l$	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)
vw	2 1 0	0.0203	0.0202
vw	2 2 0	0.0326	0.323
s	3 1 0	0.0405	0.0403
s	0 0 7	0.0421	0.0420
w	1 1 1	0.0508	0.0501
s	3 2 0	0.0525	0.0524
w	2 0 1	0.583	0.0581
s	2 1 1	0.0624	0.0622
s+	4 1 0	0.0687	0.0686
w	3 3 0	0.0725	0.0726
vw	2 2 1	0.0743	0.0743
m	4 2 0	0.0809	0.0807
s	3 1 1	0.0823	0.0823
m	3 2 1	0.0945	0.0944
vw	5 0 0	0.1007	0.1009
vw	5 1 0	0.1044	0.1049
vw	4 0 1	0.1066	0.1065
m	4 1 1	0.1076	0.1106
m	4 2 1	0.1223	0.1227
w	5 3 0	0.1369	0.1372
s	6 2 0	0.1609	0.1614
s	0 0 2	0.1674	0.1680
s	6 3 0	0.1806	0.1815
s+	2 2 2	0.2005	0.2003

$a = 12.14$ Å $c = 3.761$ Å

No systematic absences were found, and the possible space groups were $P4$, $P\bar{4}$, and $P4/m$; from previous experience of the structure $P\bar{4}$ was selected. The model for initial computation was based on atomic coordinates employed by Steadman (*11*) in a structure determination of a tetragonal tungsten bronze, and an initial R value of 0.28 indicated that an atom or group of atoms was present in the pentagonal tunnel sites with approximate coordinates $x = 0.33$, $y = 0.17$, $z = 0.0$. The height of the peak in the pentagonal site showed that it could represent an Sn atom with a population parameter of 0.14, which is equivalent to a composition $Sn_{0.28}WO_3$. This was incorporated into the model prior to a second least-squares refinement followed by a Fourier synthesis.

This second synthesis confirmed the presence of an atom in the pentagonal tunnel site, but also showed that the electron density contours were nonspherical. Refinement of both tin and tungsten positions and allowing variations in temperature factors and population parameter of tin atoms along with the temperature factor of the tungsten atoms produced a new R value of 0.12.

A closer examination of the "tin atom" in the pentagonal site showed it to consist of a central peak about the middle of the site with a tail toward the nearest apex of the pentagon. This is shown in Fig. 2. It has been shown that in pure tin bronzes the Sn^{2+} ions are found in asymmetric sites within the tunnel, and that one of these sites corresponds to the centre of the tail in Fig. 2. There is no evidence that europium prefers an asymmetric site since all pure europium bronzes are highly symmetrical (*9*). Thus it was felt that the electron density distribution in the tunnels arose from a europium ion near the geometrical center together with tin ions in an asymmetric position. As suggested for the tin bronzes (*11*), domains probably exist in which only one of the sites is occupied. This model gave an R value of 0.117, and no further refinement was carried

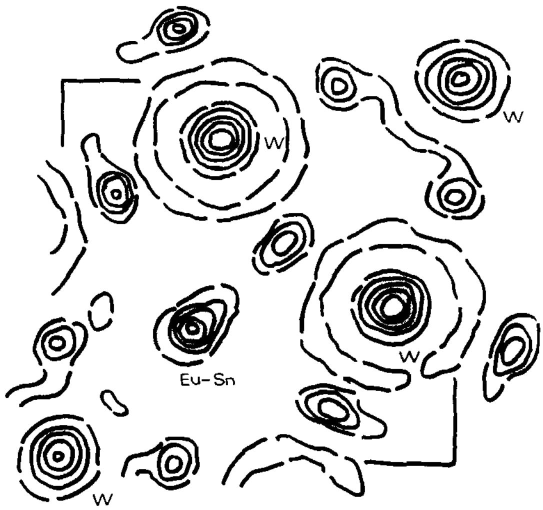

FIG. 2. Section of the electron density distribution for a single crystal of $Eu_{0.1}Sn_{0.15}WO_3$.

out. Complete lists of F_{obs} and F_{calc} are available.

It should be stressed that there was never any evidence for the presence of guest ions in cubic cage-type sites.

The concept of a domain structure consisting of asymmetric tin areas and symmetric europium areas in the tunnel sites may be important in determining the maximum Eu/Sn ratios of about unity found above, in that domains of europium (II) tetragonal bronze above a critical size would nucleate the stable cubic bronze structure with oxidation to the europium (III) state. Indeed cubic europium (III) bronzes are found to be among the decomposition products when high-concentration europium mixed bronzes are sought, as shown in Fig. 1.

Conclusions

Attempts to prepare mixed europium–tin tungsten bronzes at 750°C were not successful. At 1000°C, bronzes containing both europium and tin can be synthesized, the single-phase region is bounded by the compositions $Eu_{0.17}Sn_{0.175}WO_3 - Eu_{0.11}SN_{0.14}WO_3 - Sn_{0.21}WO_3$–$Sn_{0.28}WO_3$. Within this region all the samples have the tetragonal (12 × 3) structure.

In the mixed bronze, the europium is present in the europium (II) state and occupies pentagonal tunnel sites. A single-crystal X-ray analysis suggests that there is a domain structure present with tin on asymmetric sites and europium on tunnel center sites.

There appear to be two factors governing the composition of the mixed bronzes: first, an upper limit on the electron concentration per WO_3 unit of 0.6, and second, an Sn/Eu ratio of just less than unity.

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