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Rare Earth Tungsten Bronzes

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Received November 12, 1965

Cubic rare earth tungsten bronzes of the formula $M_{0.1}WO_3$ have been prepared where M stands for the rare earth elements Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The bronzes were obtained by a solid-state reaction at 1100° with quenching to room temperature. The lattice parameters a_0 were found to decrease from $Ce_{0.1}WO_3$ (a = 3.828 A) to $Lu_{0.1}WO_3$ (a = 3.788 A). The extension of the homogeneity range of the cubic phase of Eu_xWO_3 and Gd_xWO_3 was studied by X-ray diffraction methods. The value of x was found to range from 0.085 to 0.16. Susceptibility measurements were carried out on all bronzes between 290 and 80°K. Measurements indicate that the rare earth ions account for the magnetic moment exhibited by these compounds. All rare earth ions are present in the trivalent state.

Introduction

The term "tungsten bronze" is used to represent nonstoichiometric compounds with the general formula M_xWO_3 where $1 > x > 0$. M can be an alkali metal,[1-3] barium,[4] lead,[5] thallium,[6] copper,[7] or silver.[8] Until recently, most of the studies on tungsten bronzes have been concerned with the alkali bronzes, especially the lithium and sodium bronzes. These bronzes are of great interest because of their unusual electrical properties, their wide range of homogeneity, and the high symmetry of their crystallographic modifications. The possibility of growing single crystals easily by electrodeposition makes them an ideal subject for studies of their semiconducting[9] and metallic behavior.[10] However, studies have been hampered by the difficulty in obtaining sufficiently accurate analyses of the single crystals.

It was the purpose of this investigation to find systems similar to those of Li_xWO_3 and Na_xWO_3, where the alkali metal M is replaced by elements which can be analyzed accurately using physical methods such as magnetic measurements. The rare earths (except Lu) were thought to be ideal because they exhibit magnetic moments which are high and relatively free from external influences. Since the ionic radii of the rare earth elements compare favorably with those of Li and Na, it was likely that these elements might enter the interstices of the WO_3 lattice to form the characteristic perovskite-type structures. In this paper, the preparation of a new group of tungsten bronzes will be described, and the results of the X-ray studies and magnetic measurements will be discussed.

Experimental Section

Preparation of Rare Earth Tungsten Bronzes.—Tungsten bronzes M_xWO_3, where M represents Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, were prepared by thermal reaction of the rare earth oxide, tungsten, and tungsten trioxide in the appropriate molar ratio. The carefully ground reagents were enclosed in an evacuated, sealed silica capsule and heated for at least 100 hr at 1050°. To guarantee homogeneity, the products were reground and reheated. All samples were cooled rapidly to room temperature. X-Ray examination of the products showed that single-phase compounds had formed. The bronzes obtained were blue-violet powders which were not attacked by hydrochloric acid.

Single crystals of Tm_xWO_3, approximately 2 mm in length, were obtained by electrolytic reduction of a fused mixture containing Tm_2O_3 and WO_3 at 1250°. The electrodeposition was carried out for 20 hr using a crucible of recrystallized Al_2O_3, Pt electrodes, and a cathode current density between 0.15 and 0.20 amp/cm^2.

Crystals of Gd_xWO_3 (8 mm long) were prepared by similar electrolytic techniques at 1000°. The melt was obtained from a mixture of $GdCl_3$ and WO_3. The electrolysis was started after an initial period of gas evolution (WO_2Cl_2).

Homogeneity Range of Cubic Eu_xWO_3 and Gd_xWO_3.—The extension of the homogeneity range for the cubic phase of Eu_xWO_3 and Gd_xWO_3 was studied by means of X-ray diffraction techniques. In both, the homogeneity range was found to vary from x = 0.085 to x = 0.16. X-Ray diffraction patterns of samples with rare earth concentrations lower than x = 0.085 showed the presence of a tetragonal phase whereas the X-ray photographs of samples with a rare earth concentration higher than x = 0.16 revealed reflections due to $R_2(WO_4)_3$, R_xWO_3, and WO_2. The disproportionation becomes obvious during prolonged heating at 1000°. After several days, these phases separated. It appears that for the europium and gadolinium bronzes, the values of x cannot exceed 0.16 at the temperature reported for their preparation. The possibility exists that bronzes containing higher concentrations of europium and gadolinium may be prepared if suitable techniques which would allow the rare-earth-richer bronzes to form at lower temperatures were developed.

X-Ray Investigation.—The X-ray diffraction patterns were taken using a Philips 114-mm diameter Debye–Scherrer camera along with the standard Norelco X-ray equipment. Nickel-filtered copper radiation or iron-filtered cobalt radiation was employed depending on the absorption edge of the rare earth elements. The patterns of all $M_{0.1}WO_3$ compounds showed sharp diffraction lines corresponding to a simple cubic structure. All film patterns were corrected for shrinkage. The latttice parameters a_0 of the cubic unit cell were obtained by using the extrapolation method described by Nelson and Riley.[11] An attempt was made, without success, to find X-ray evidence of ordering.

Pycnometric density measurements were carried out on three samples ($Ce_{0.1}WO_3$, $Eu_{0.1}WO_3$, $Gd_{0.1}WO_3$) using doubly distilled water as the immersion fluid.

Magnetic Measurement.—The magnetic susceptibilities of the

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rare earth bronzes were determined at various temperatures between 290 and 80°K. The measurements were carried out with a Faraday-type balance using the horizontal-force method. A water-cooled 4-in. electromagnet along with a Varian power supply provided field strength in four steps up to 8000 gauss. The balance was calibrated with an $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ susceptibility standard. The calibration was reproducible to better than 1%. The observed susceptibilities were corrected in all cases for the values of the silica cup, containing the sample.

Results

Table I presents the lattice parameters a_0 of the series of cubic rare earth tungsten bronzes corresponding to the composition $M_{0.1}WO_3$ along with their atomic

TABLE I
CRYSTAL DATA OF CUBIC TUNGSTEN BRONZES

M_xWO_3	Lattice parameters, a_0, A	Unit cell vol, A^3	Calcd density, g/cm^3
$Ce_{0.1}WO_3$	3.828	56.09	7.28
$Pr_{0.1}WO_3$	3.827	56.05	7.29
$Nd_{0.1}WO_3$	3.822	55.83	7.32
$Sm_{0.1}WO_3$	3.817	55.61	7.37
$Eu_{0.1}WO_3$	3.815	55.52	7.39
$Gd_{0.1}WO_3$	3.810	55.31	7.43
$Tb_{0.1}WO_3$	3.808	55.22	7.45
$Dy_{0.1}WO_3$	3.805	55.09	7.48
$Ho_{0.1}WO_3$	3.801	54.92	7.51
$Er_{0.1}WO_3$	3.797	54.74	7.54
$Tm_{0.1}WO_3$	3.794	54.61	7.56
$Yb_{0.1}WO_3$	3.791	54.44	7.59
$Lu_{0.1}WO_3$	3.788	54.35	7.62
$Eu_{0.085}WO_3$	3.808	55.22	7.36
$Eu_{0.12}WO_3$	3.823	55.87	7.43
$Eu_{0.15}WO_3$	3.828	56.09	7.54
$Li_{0.36}WO_3$[12]	3.720	51.48	7.54
$Na_{0.32}WO_3$[1]	3.813	55.44	7.20

volumes and their calculated densities. It also lists the parameters a_0 of four europium tungsten bronzes which have varying values of x. For comparison, the X-ray data of $Li_{0.36}WO_3$[12] and $Na_{0.32}WO_3$[1] are listed. Table II

TABLE II
POWDER DIFFRACTION DATA OF $Eu_{0.1}WO_3$

d_{obsd}	I	hkl	d_{calcd}
3.820	s	0 0 1	3.815
2.698	s	0 1 1	2.698
2.203	m	1 1 1	2.203
1.907	s	0 0 2	1.908
1.706	vs	0 1 2	1.706
1.557	vs	1 1 2	1.557
1.348	s	0 2 2	1.349
1.272	s	3 0 0	1.272
1.206	s	0 1 3	1.206
1.150	w	1 1 3	1.150
1.101	w	2 2 2	1.101
1.058	m	0 2 3	1.058
1.020	s	1 2 3	1.020
0.954	w	0 0 4	0.954
0.925	vs	0 1 4	0.925
0.899	s	0 3 3	0.899

presents the indexing of the powder diffraction pattern of $Eu_{0.1}WO_3$ which is representative for all M_xWO_3 compounds with cubic crystal symmetry.

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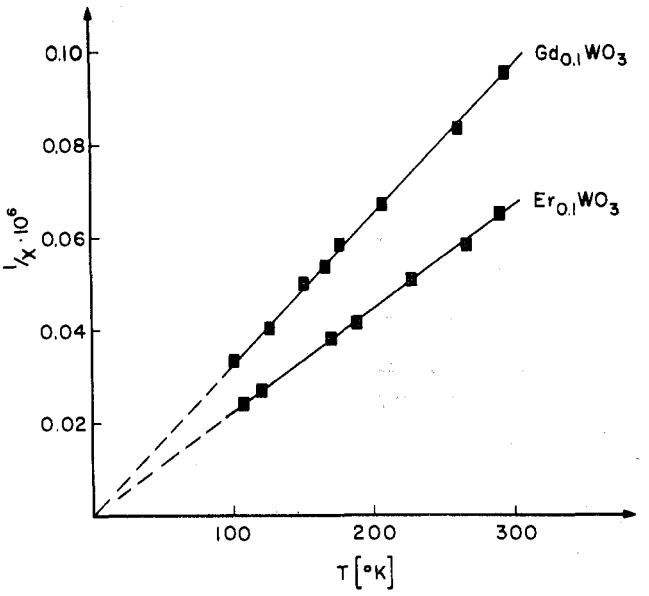

Figure 1.—Reciprocal susceptibility *vs.* temperature diagram of $Gd_{0.1}WO_3$ and $Er_{0.1}WO_3$.

Crystalline transformations from cubic to tetragonal were observed when the rare earth concentration was decreased below $x = 0.085$ or when the bronzes were slow-cooled rather than quenched from 1050°.

Pycnometric density measurements of $Ce_{0.1}WO_3$, $Eu_{0.1}WO_3$, and $Gd_{0.1}WO_3$ gave the values of 7.25, 7.38, and 7.42 g/cm^3, respectively. The measured densities are in good agreement with the densities calculated from the X-ray data.

All rare earth tungsten bronzes were found to be paramagnetic. The susceptibility values did not show any field dependency. Except for $Eu_{0.1}WO_3$ and $Sm_{0.1}WO_3$, the susceptibilities of the compounds were found to obey the Curie law. The plot of $1/\chi$ *vs.* T is illustrated for two representative samples, $Gd_{0.1}WO_3$ and $Er_{0.1}WO_3$, in Figure 1.

Table III presents the susceptibilities (χ_g and χ_{mol}) of the $R_{0.1}WO_3$ compounds at 290°K. The effective magnetic moment of the rare earth bronzes corresponding to the formula $R_{0.1}WO_3$ is listed for comparison along with the moments of the trivalent rare earth ions.

TABLE III
MAGNETIC DATA OF RARE EARTH TUNGSTEN BRONZES AT 290°K

R_xWO_3	$10^6\chi_g$	$10^6\chi_{mol}$	$10^{-1}\mu_{eff}$	$\mu_{M^{3+}}$
$Ce_{0.1}WO_3$[a]	1.08	265.6	2.5	2.6
$Pr_{0.1}WO_3$[a]	2.23	548.6	3.6	3.6
$Nd_{0.1}WO_3$[a]	2.46	606.0	3.8	3.7
$Sm_{0.1}WO_3$[b]	1.11	274.1	1.6	1.6
$Eu_{0.1}WO_3$[b]	1.95	481.9	3.4	3.5
$Gd_{0.1}WO_3$[a]	10.6	2624.7	7.9	7.9
$Tb_{0.1}WO_3$[a]	15.9	3940.2	9.6	9.7
$Dy_{0.1}WO_3$[a]	19.1	4740.0	10.6	10.6
$Ho_{0.1}WO_3$[a]	18.9	4695.0	10.6	10.6
$Er_{0.1}WO_3$[a]	15.6	3878.8	9.5	9.6
$Tm_{0.1}WO_3$[a]	9.7	2413.5	7.5	7.6
$Yb_{0.1}WO_3$[a]	3.45	859.8	4.5	4.5
$Lu_{0.1}WO_3$[a]	0.04	...	...	0

[a] μ_{eff} independent of temperature. [b] μ_{eff} dependent upon temperature.

Discussion

The structure data on the rare earth tungsten bronzes indicate that these compounds have a perovskite-like structure and crystallize with a moderate range of homogeneity isomorphous to the alkali-richest phases of Li_xWO_3 and Na_xWO_3. The data confirm observations made by previous authors[13] that the metal atoms M of the tungsten bronzes M_xWO_3 generally stabilize highly symmetrical arrangements of the WO_6 octahedra. (Tungsten trioxide has a distorted ReO_3-type lattice of low symmetry.) It can be seen from Table I that the parameter of the cubic unit cell decreases linearly from $Ce_{0.1}WO_3$ (a_0 = 3.828 A) to $Lu_{0.1}WO_3$ (a = 3.788 A) as a result of the lanthanide contraction. Table I also lists the lattice parameters of a number of cubic europium tungsten bronzes of different composition. The data give evidence that a_0 changes significantly with a variation of the value of x.

The crystalline transformation from cubic to tetragonal rare earth bronzes was found to be much the same as with the well-investigated sodium tungsten bronzes.[14] However, the x values, corresponding to the crystalline transformation, differ substantially in the system of Na_xWO_3 and R_xWO_3. For sodium bronzes, prepared by a quenching technique similar to that used for the preparation of the rare earth bronzes, the crystallographic change occurs between x = 0.25 and x = 0.30, whereas studies on Eu_xWO_3 and Gd_xWO_3 indicate that these bronzes have the structural change near x = 0.085. The values suggest that the crystalline transformation is not dependent upon the number of metal atoms, inserted into the WO_3 lattice, but on a certain concentration of quasi-free electrons. Since three sodium atoms are necessary to provide the same number of electrons as one rare earth atom, one may expect the crystallographic change for an x value ratio of 3:1. This was, indeed, observed. It may be mentioned at this point that recent studies on $U^{IV}{}_xWO_3$ showed that the transformation from cubic to tetragonal uranium bronzes occurs between x = 0.075 and x = 0.078.[15]

The magnetic moments of the rare earth bronzes are in excellent agreement with the moments of the trivalent rare earth ions (Table III). Although the formula of the rare earth tungsten bronzes implies that W has a valency between 5 and 6, it is evident that there is no magnetic contribution by the W ions. The data listed in Table III indicate that the rare earth ions account for the magnetic moment exhibited by these compounds. For the computation of the magnetic moment of the rare earth tungsten bronzes, all W ions were assumed to be hexavalent, and the valence electrons of the rare earths were regarded as quasi-free. This model may be justified since it was observed that the cubic rare earth bronzes have metallic behavior.[16] The magnetic moment of the rare earth bronzes was calculated considering (a) the paramagnetism of the trivalent rare earth ions, (b) the diamagnetism of the increments of the rare earth, tungsten, and oxygen ions, and (c) the weak, temperature-independent paramagnetism of the conduction electrons.

The effective moments of the trivalent rare earths were employed as calculated by Van Vleck.[17] The values used for the diamagnetic increments are those listed in Selwood's "Magnetochemistry."[18] A molar susceptibility of -51×10^{-6} was calculated for all rare earth tungsten bronzes of the formula $M_{0.1}WO_3$. The paramagnetic susceptibility of the electron gas was computed according to the equation $\chi_E = 1.25 \times 10^{-6} n^{1/3} V^{2/3}$,[19] where n is the number of the valence electrons and V is the volume available to these electrons. A value of 59×10^{-6} was obtained.

It may be noted that both the diamagnetism of the increments and the temperature-independent paramagnetism of the electron gas nearly cancel each other. This explains that the moments calculated for the rare earth tungsten bronzes are practically identical with those of the trivalent rare earths only.

Except for the samarium and europium compounds, the moments of all rare earth bronzes are independent of the temperature. The temperature dependence of the moments of Eu_xWO_3 and Sm_xWO_3 is caused by the multiplet width in Sm^{3+} and Eu^{3+} which is comparable to kT. Along with Lu_xWO_3, which exhibits no moment, Sm_xWO_3 and Eu_xWO_3 may therefore be excluded from any application of magnetic techniques for analytical reasons. However, the high and distinct moments of the other rare earth tungsten bronzes give rise to very accurate quantitative analyses of the rare earth content by means of susceptibility measurements. Magnetic techniques are particularly sensitive if the measurements are carried out at low temperature.

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