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The Effect of The Cerium Concentration On The Lattice Parameter of Cubic Cerium Tungsten Bronzes¹

J. J. TULLY, G. J. VOGT, and R. J. REULAND²

Abstract. Cerium tungsten bronzes, Ce_xWO_3 , were prepared by the high temperature, solid state reaction of CeO_2 , W, and WO_3 . The intimately mixed reactants were sealed under a vacuum in quartz ampoules and heated for not less than 100 hours at $1050^\circ C$. The lattice parameter a_0 of the cubic bronzes was determined from Debye-Scherrer X-ray powder patterns. The cerium content of the bronzes x was established by isotopic dilution techniques. Cerium tungsten bronzes of cubic symmetry were found to crystallize in the range $0.070 < x < 0.186$. The lattice parameter a_0 was found to increase linearly with x in the cubic range according to the relationship $a_0 = 0.2165x + 3.8008$.

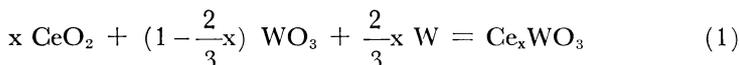
Tungsten bronzes, first prepared in 1823 by Wöhler (1), are in fact not bronzes but nonstoichiometric metal tungsten oxides of the formulation M_xWO_3 in which x may vary from zero to one. Among the large number of metals with which tungsten bronzes have been prepared are included most of the alkali, alkaline earth, and rare earth metals. The structure of a particular metal tungsten bronze depends upon the x -value. For example, sodium tungsten bronze assumes the cubic perovskite structure for x -values in the range $0.5 < x < 1$; is tetragonal in the range $0.07 < x < 0.5$; and is orthorhombic for $0.01 < x < 0.07$. Not all the metal tungsten bronzes prepared however have an x -value range in which the bronze crystallizes with cubic symmetry, and for those which do it is much less extensive than that observed for the sodium tungsten bronzes. The size of the unit cell of a tungsten bronze of a given symmetry is found to depend upon the x -value. Of those tungsten bronzes which exhibit cubic symmetry, the effect of changes in the x -value on the lattice parameter a_0 has been studied in detail only for the sodium (2, 3), lithium (4), lanthanum (5), gadolinium (4), and uranium (4) systems. For the sodium, gadolinium, and uranium systems, the lattice parameter has been observed to increase linearly with x ; while for the lithium system, it has been observed to decrease linearly with x . The lattice parameter of cubic lanthanum tungsten bronze has been reported to increase with x but in a nonlinear fashion. This occurrence of a cubic tungsten bronze system with a nonlinear a_0 - x relationship, especially in view of the linear relationship observed for the expectedly similar cubic gadolinium tungsten bronzes, prompted the investigation described herein. For this study, the cerium system was selected

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from among the rare earth bronzes mainly because of the availability of a cerium isotope with convenient decay characteristics. The cerium content of the cerium tungsten bronzes was to be determined by isotopic dilution techniques using Ce^{144} since the extreme chemical inertness of the tungsten bronzes makes accurate elemental analysis by the usual chemical methods difficult if not impossible.

EXPERIMENTAL PROCEDURE

Preparation of Cerium Tungsten Bronze. The cerium tungsten bronzes of this investigation were prepared by the high temperature, solid state reaction of tungsten trioxide, tungsten metal, and cerium dioxide, the latter tagged with Ce^{144} :



The finely powdered reactants were intimately mixed in a mole ratio calculated to yield a bronze with the desired x and sealed under a vacuum in a quartz ampoule. The ampoules were fashioned from 2-mm i.d. quartz tubing and were approximately $1\frac{1}{2}$ inches in length. The size of the charge was 100 mg. The charged ampoules were heated for not less than 100 hours at 1050-1075°C in a wire-wound resistance tube furnace. The cerium tungsten bronze so prepared was purified by successive digestions in 6M sodium hydroxide, 30% orthophosphoric acid, and concentrated nitric acid to which was added a small amount of 50% hydrogen peroxide. This treatment was designed to remove the unreacted reagents and side products. The bronze could not be easily purified of unreacted tungsten metal and care was taken to avoid this occurrence by adjusting the mole ratio of the initial charge to ensure complete reaction of the tungsten metal. Brown and Banks (2) have estimated that 0.5% tungsten by weight should be detectable in the X-ray powder photographs of the bronzes. A tungsten contamination of this magnitude would not seriously effect the subsequent calculation of the specific activity of the bronze. Only those cerium tungsten bronzes for which no extraneous lines could be observed in their X-ray powder patterns were considered further in this investigation.

Preparation of Ce^{144} -Labelled Cerium (IV) Oxide. The cerium dioxide used in the preparation of the tungsten bronzes was isotopically labelled with Ce^{144} to permit subsequent determination of the x -value. This was accomplished by adding Ce^{144} as cerium (III) chloride to a solution of ammonium hexanitratocerate (IV). The cerium (IV) was reduced to cerium (III) with hydrogen peroxide and the cerium was precipitated as cerium (III) oxalate with oxalic acid. The cerium oxalate was calcinated to cerium dioxide by heating to 800-850°C under a 100% oxygen atmosphere.

The X-ray diffraction data obtained from a powder photograph of this cerium dioxide was in excellent agreement with that published for cerium dioxide (6).

It can be readily shown that the x-value of a cerium tungsten bronze can be calculated from a knowledge of the specific activity of the bronze and the specific activity of the cerium dioxide used in its preparation according to the following equation:

$$x = \frac{1.6546}{\left(\frac{S_0}{S}\right) 1.2284 - 1} \quad (2)$$

S_0 is the specific activity of the cerium dioxide in counts per minute per mg of cerium dioxide and S is the specific activity of the bronze in counts per minute per mg of cerium tungsten bronze.

Activity Measurement. In the determination of the relative specific activities, use was made of the decay characteristics of Pr^{144} which is in secular equilibrium with its precursor, Ce^{144} . The decay characteristics of both Pr^{144} and Ce^{144} are summarized in Table 1. (Some low intensity beta and gamma transitions in the Ce^{144} decay have been omitted.) It is desirable for comparison purposes to assay the activities of the bronze and the cerium dioxide under identical conditions. It appeared that this could be most readily accomplished by positioning the source in the well of a sodium iodide detector and counting the gamma-rays accompanying the decay of Ce^{144} with a pulse height analyzer and scaler. However, although the Ce^{144} gamma-rays are fairly abundant, their energies are all rather low and self-absorption effects were observed even with the small samples used in the assay. (Two to 25 mg was weighed into one-inch-long 62-mil i.d. polyethylene tubes which were then heat sealed.) Consequently, the activities of the bronze and cerium dioxide were measured by counting the energetic beta particles emitted in the decay of Pr^{144} with a GM-tube and scaler. Samples ranging in mass from two to 25 mg were weighed, using a microbalance, onto 1/4 inch diameter planchets, uniformly dis-

Table 1. Decay characteristics of Ce^{144} and Pr^{144}

Nuclide	Half-life	Beta Energy (Mev)	Beta Intensity ^a (%)	Gamma-Ray Energy (Mev)	Gamma-Ray Intensity ^a (%)
Ce^{144}	284 d	0.19	19	0.080	2
		0.24	5	0.134	11
		0.32	76		
Pr^{144}	17.3 m	0.80	1.0	0.695	1.5
		2.30	1.3	1.487	0.29
		2.98	97.7	2.186	0.71

^aPercentage of the total decay events.

persed, and fixed in place with a minute amount of Duco cement applied in acetone solution. The Ce^{144} beta particles were filtered with a 13 mil aluminum absorber. No self-absorption was observed when the samples were prepared in this manner. In each activity measurement, sufficient counts were accumulated to reduce the statistical error to less than one percent. The activities were corrected for coincidence losses and for background and converted to specific activities.

Lattice Parameter Measurement. The lattice parameter a_0 of the cubic cerium tungsten bronzes was determined from analysis of Debye-Scherrer X-ray powder patterns. The patterns were obtained with a Philips 114.59 mm camera using nickel-filtered copper $K\alpha$ radiation. The calculation of the precise lattice parameter was facilitated by computer handling of the diffraction data. The computer program includes a least-squares curve fitting to the Nelson-Riley function of the scattering angle—lattice parameter data. Each pattern was read at least twice by different experimenters and the deviation in the lattice parameter was rarely greater than $\pm 0.0004 \text{ \AA}$.

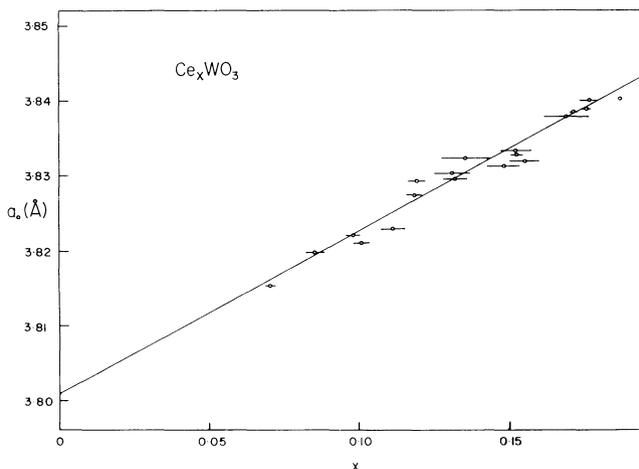


Figure 1. Lattice parameter versus x-value for cubic cerium tungsten bronzes.

RESULTS AND DISCUSSION

The results of the investigation are summarized graphically in Figure 1. Cerium tungsten bronzes were found to crystallize with cubic symmetry in the x-value range 0.070 to 0.186. This range is nearly identical to that reported for cubic gadolinium tungsten bronze (0.085 to 0.16) and cubic lanthanum tungsten bronze (0.08 to 0.19). Below $x = 0.070$, the cerium tungsten bronzes

Table 2. Parameters of the linear relationships, $a_0 = mx + b$, for the cubic tungsten bronzes.

Bronze	m	b
Ce_xWO_3	0.2165 ± 0.0099	3.8008 ± 0.0014
Na_xWO_3	0.0818	3.7850
Li_xWO_3	-0.134	3.782
Gd_xWO_3	0.230	3.785
U_xWO_3	0.278	3.785

exhibited symmetries lower than cubic. The x-value 0.186 represents the solubility limit of cerium in the tungsten trioxide matrix. The straight line in Figure 1 was fitted to the a_0 -x data by the method of least squares. The slope and intercept of this line are given in Table 2 together with those of the corresponding linear relationships for the sodium, lithium, gadolinium, and uranium tungsten bronzes.

Thus, it appears that, among the cubic tungsten bronzes studied, lanthanum tungsten bronze remains unique with its nonlinear lattice parameter dependency on x-value. However, the nonlinear relationship may be an artifact. The lanthanum content of the bronzes prepared by Broyde (5) in his investigation was inferred from the stoichiometry of the reactant mixture. That this may not be accurate is suggested in Figure 2. Here, the nominal x-value, that is, the x-value predicted from the stoichiometry of the reactant

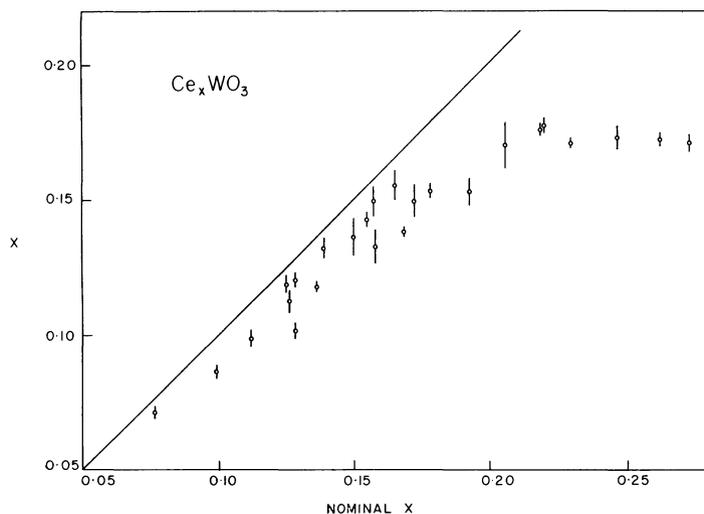


Figure 2. Nominal x-value versus x-value determined by isotopic dilution for cubic cerium tungsten bronzes. The line represents x equal to nominal x.

mixture, is plotted versus the x-value determined by isotopic dilution for the cerium tungsten bronzes of this investigation. The method of preparation of these cerium tungsten bronzes was the same as that used by Broyde in his study of the lanthanum system. Consequently, a re-investigation of lanthanum tungsten bronze similar to the study just described appears to be desirable and in fact has been initiated.

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