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NOTE

Vegard Relationships in Cubic Oxide Bronzes with the Perovskite Structure

The electronic expansion factor for bronze phases with the perovskite structure are derived from a wide variety of literature sources and shown to fit a curve when plotted against the Ahrens ionic radius of the non-network-forming cations. Examples are given which show how the curve can be used to characterize and compare bronze-like phases.

Oxide bronzes and in particular the tungsten bronzes M_xWO_3 are difficult to analyze by chemical methods due to their inertness. In such circumstances the availability of a reliable physical method of analysis, such as a linear relationship between lattice parameter and composition, is most convenient. It is perhaps because of such convenience that investigators of the physical properties use the method (*1*), often assuming that like the well-documented relationship for sodium tungsten bronzes, Na_xWO_3, that was first expressed by Brown and Banks (*2*) in the form of the equation

$$a_0 = 0.0819x + 3.7846 \text{ Å} \qquad (1)$$

an equally well established relationship exists for other bronze systems. A recent detailed study of Li_xWO_3 bronzes (*3*) has highlighted how inconsistent are data in the literature on the lattice-parameter composition relationships. In the Li_xWO_3 study two linear regions in the a_0 vs x relationship were found in the range $0.488 > x > 0.25$.

Lattice-parameter-composition data have been reported for cubic bronzes containing lithium (*3–8*), potassium (*9*), yttrium and the lanthanides (*4, 8, 10–15*), and uranium (*4, 16*), that show that with the exception of the lithium bronzes the structure expands as the concentration of the nonnetwork cation increases. This behavior is not immediately expected from purely geometrical considerations since the cation site in the perovskite ReO_3-type framework is much larger than all but the very largest cations. The expansion can be explained in terms of the occupation of the bronze conduction band by the valence electrons of the M cations which, since this is an antibonding W–O π^* band, leads to a weakening and expansion of the network cation–oxygen bonds.

Polaczkowa *et al.* (*11*), from studies on the sodium and lanthanide tungsten bronzes, have expressed this idea in an electronic expansion factor da_0/dc_e, where c_e is the electron concentration, which equals mx where m is the valence of the M cation.

The published data for cubic tungsten bronzes can be fitted to equations of the form

$$a_0 = \frac{da_0}{dc_e} mx + 3.7846 \text{ Å}, \qquad (2)$$

where 3.7846 Å is the lattice parameter of hypothetical cubic WO_3. The results of this analysis are presented in Fig. 1 in the form of a plot of da_0/dc_e against the Ahrens ionic radius (*17*) of the M cation. It is the aim of this note to show that this curve can be used to examine the bronze-like nature of materials and to highlight either a nonlinear composition-lattice parameter relationship, or the uncertain quality of some of the literature data.

The first use of the curve in Fig. 1 comes from considering the ranges of the da_0/dc_e

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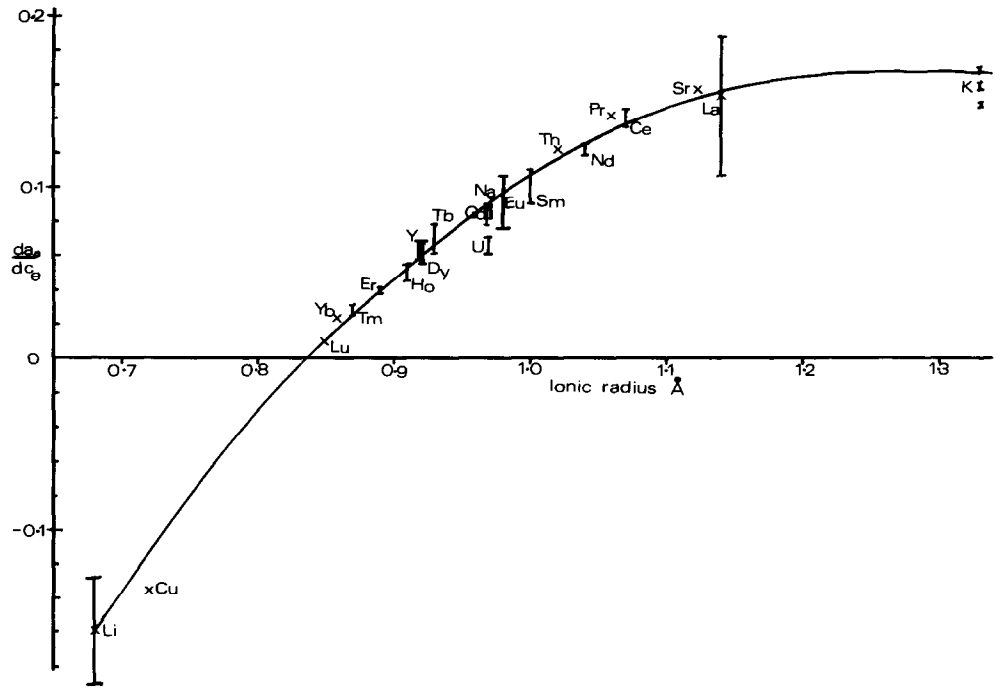

FIG. 1. A plot of electronic expansion factor versus Ahrens radius for bronze insertion ions in their highest normal valence state.

values for a given cation. Those cations exhibiting wide ranges are generally those for which a large number of lattice parameter measurements have been made, which combined with inaccuracies in the determination of x, as highlighted by the lithium work (*3*), produces scatter. For the more acidic cations, strong M–O interactions will result in trapping of conduction electrons (*30*) and may produce a nonlinear dependence of lattice parameter on composition. Even for basic cations when the value for x is large strong M–O interactions can become important (*31*). Changes in the degree of distortion of the octahedra in the perovskite structure could also contribute to the spread of values; Wiseman and Dickens (*8*) found that the WO_6 octahedra were increasingly tilted with respect to the c axis in the series of bronzes La_xWO_3 < Na_xWO_3 < Li_xWO_3. Whichever of the above reasons is responsible for the spread of the data, workers intending to use the X-ray method for compositional analysis should be wary when a large spread is indicated.

A number of uses of the curve in Fig. 1 stem from its applicability to other bronze systems with the perovskite structure. Figure 1 contains results reported for rhenium, molybdenum, and uranium bronzes (*9*). Data are available for cubic rhenium and molybdenum perovskite bronzes M_xReO_3, M_xMoO_3 containing Na and K with $x \simeq 0.9$ (*19–21*) which can be fitted to equations similar to (*2*) but using 3.7477 Å for the lattice parameter of cubic ReO_3 (*19*), a value of 3.775 Å for the hypothetical cubic MoO_3, and 4.146 Å for cubic δ-UO_3 (*32*). Values for da_0/dc_e obtained in this way are given in Table I.

A cubic perovskite phase $Cu_{0.25}ReO_3$ (*24*) fits the curve if the copper is assumed to be divalent, which could be taken as

indirect evidence for such a valency state for copper in a bronze-like material. Likewise there are some data for a perovskite phase $RbUO_3$ (*33*) and although it is not clear whether it is a bronze a figure for da_0/dc_e of 0.177 can be derived which, with an Ahrens radius of 1.47, would fit on Fig. 1.

A similar application is found when considering available data for cubic bronze-type materials based on NbO_3 and TiO_3 containing strontium and lanthanum, respectively, (*22, 23*). Plots of a_0 vs x give good straight lines with intercepts of 3.80 Å for La_xTiO_3 and 3.88 Å for Sr_xNbO_3 which represent hypothetical cubic TiO_3 and NbO_3 and appear quite sensible. Fitting these lines to the standard type of Eq. (2) produces values for da_0/dc_e of 0.042 for La_xTiO_3 and 0.073 for Sr_xNbO_3 assuming that lanthanum has its usual valency of 3 and strontium is divalent. It can be seen that for La^{3+} and Sr^{2+} the da_0/dc_e values are too low by $\frac{1}{3}$ and $\frac{1}{2}$, respectively. However, if it is assumed that only one electron per cation is contributed to the conduction band then da_0/dc_e values become 0.126 and 0.146 for La_xTiO_3 and Sr_xNbO_3, respectively, which now fit the plot in Fig. 1. Thus accepting the bronze-like nature of these perovskites it might be concluded that for every lanthanum atom added two electrons are involved in covalent bonding with one electron contributing to the conduction band while strontium also contributes one electron to the band but only one to the covalent bonding.

Another example of this type of application concerns a number of reports that describe the preparation of cubic tungsten bronzes containing hydrogen, antimony, calcium, germanium, and cadmium (*25–29*). These phases have lattice parameters that do not fit Fig. 1. This is good evidence for not regarding them as bronzes in the strict sense but rather as perovskites with localized electrons or as doped WO_3 phases.

TABLE I

M	W	Re	Mo	U
Na_xMO_3	0.082	0.092	0.080	—
K_xMO_3	0.167	0.164	0.158	0.148

TABLE II

$Eu_xNa_yWO_3$		a_0 (Å)	
x	y	Observed	Calculated
0.08	0.05	3.806	3.806
0.10	0.10	3.815	3.815
0.06	0.20	3.818	3.814
0.08	0.20	3.816	3.819
0.06	0.30	3.820	3.822

Finally there is not much data available on the lattice parameters of cubic tungsten bronzes containing more than one cation with which to test whether the da_0/dc_e factors are additive. Data for mixed uranium–thorium (*16*) and lanthanum–gadolinium (*14*) tungsten bronzes suggest that this might be so although data for sodium–lithium and sodium–potassium bronzes (*6*) show poor correlation. Some results from our work with mixed sodium–europium bronze systems are shown in Table II, where the additive nature of the da_0/dc_e parameter can be seen. In order to calculate a_0 the expansion factor for sodium bronzes was taken from the Brown and Banks (*2*) equation and the europium value of 0.074 was taken from Dimbylow *et al.* (*15*).

This example suggests an ideal nature for this mixed bronze system containing mono- and trivalent cations even when the total electron concentration exceeds the maximum of 0.375 reported by Dimbylow for the europium bronze system.

Summary

A number of examples of the use of an

"electronic expansion factor" for perovskite bronzes have been presented which show how the relationship between this factor and the Ahrens ionic radius of the non-network-forming cations, that is, the "included" cations, can be used to classify the compounds. Deviations from a good fit to the curve in Fig. 1 can serve as a beginning to more detailed discussions on the bonding and structure in bronzes and bronze-related phases, or more practically might cause a careful reappraisal of existing data and the generation of better-characterized material.

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