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LETTER TO THE EDITOR

*M*Sn and *M*SnO$_3$ (*M* = Ca, Sr, Ba): New Examples of Oxygen-Stuffed Alloys

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The normal pressure phases of *M*Sn (*M* = Ca, Sr, Ba) involve structures of the CrB type which are related to their respective bcc-*M* nets. At high pressure they undergo a transition to the CsCl type, which is just the array of *M*Sn cations in *M*SnO$_3$ perovskites. In hp-BaSn and BaSnO$_3$ the coincidence is not only in topology but also in the unit cell parameters (a = 4.10 and 4.05 Å, respectively) such that BaSnO$_3$ can be considered as a real BaSn stuffed alloy in which oxygen and high pressure seem to have the same effect on the *M*Sn arrangement. © 1994 Academic Press, Inc.

An alternative description of crystal structures of oxides, as oxygen-stuffed alloys, has been proposed (1, 2). In most of the examples given, the cation array in the oxides is related to the structure either of the elements or of simple alloys, but no general relationship could be established between the cationic substructure in the oxides and the structure of the corresponding alloy. Thus, the Mg$_2$Si array in Mg$_2$SiO$_4$ (olivine) is related to the Ni$_2$In structure but not to the Mg$_2$Si alloy itself, which adopts the antifluorite structure (3). Only in some of the reported examples (2) do the cation arrays in the oxides present the structure of either the parent metal or the alloy. In these cases, however, one must distinguish between those compounds for which the similarity is merely topological, as in SiO$_2$ (cristobalite), CuO, AlPO$_4$, and BaGeO$_3$, showing the expanded structure of the corresponding alloy (element), and those compounds in which both alloy and oxide have the same topology and dimensions as though the O atoms simply occupied the vacant sites of the corresponding alloy (element) structure (2). Within this group, we can include CaGeO$_3$, CaF$_2$, Y$_5$Si$_3$O$_{12}$N, and β-Ca$_2$SiO$_4$. In our opinion, this leads to a more strictly formulated concept of "oxides as stuffed alloys."

Other authors suggested a different model, which considers the structures of oxides as fragments or deformations of the parent metal by inclusion of other atoms (4). In this way, the Mg$_2$SiO$_4$ (olivine type) was described as a derivative of hcp-Mg with SiO$_4$ groups inserted between atoms (5). Similarly, the Ca$_2$Si structure (5) and hence the β-Ca$_2$SiO$_4$ is related to the structure of elemental calcium. However, in spite of the relation between a given cation array in an oxide and its parent metal, the question remains open as to whether the whole cation arrays in the oxides could be related in a more general manner to their corresponding alloys. We report here new examples of such a relationship between the high pressure phases of *M*Sn (*M* = Ca, Ba) and the cation arrays in the corresponding *M*SnO$_3$ (*M* = Ca, Sr, Ba) perovskites. At the same time, the structures will be compared to that of the parent metal.

The *M*Sn (*M* = Ca, Sr, Ba) structures are of the CaSi or CrB type, with Sn atoms at the center of face-sharing trigonal prisms of alkaline earth metals (7); however, they can also be related to their respective bcc parent metals, as previously reported for other CrB-type compounds (4).

The metal blocks have a structural unit equivalent to the bcc fragments, as can be seen in Ref. (4). In the latter, the *M–M* distances (a and $d = a\sqrt{3}/2$ values) are (4.48 × 4; 3.88 × 4 Å), (4.85 × 4, 4.20 × 4 Å) and (5.025 × 4, 4.35 × 4 Å) for bcc-Ca, Sr, and Ba respectively. In the *M*Sn alloys these structural units have *M–M* distances of (4.82 × 2, 4.35 × 2, 4.22 × 4), (5.03 × 2, 4.49 × 2, 4.40 × 4) and (5.31 × 2, 4.65 × 2, 4.60 × 4) Å, which deviate significantly from the values of the bcc nets. However, as reported for other compounds (8), the sum Σ of the eight distances (35.22, 36.67, and 38.32 Å for CaSn, SrSn, and BaSn respectively) compares well with the corresponding values in the pure metals (33.44, 36.20, and 37.50 Å for Ca, Sr and Ba respectively). The greatest deviation (5%) is observed for the Ca compound, which could also be regarded as distorted fragments of fcc-Ca (Σ = 34.90).

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At high pressure, BaSn and CaSn undergo a CaSi → CsCl type transition which has recently been reported (9). The unit cell parameter is given only for hp-BaSn ($a = 4.05$ Å). Consequently, the Ba–Ba distances are intermediate between the shortest Ba–Ba distances of bcc-Ba (4.35 Å) and hcp-Ba (3.90 Å), but closer to the value of the high pressure hcp-Ba phase. The topology, a primitive cubic array, is, however, closer to that of bcc-Ba. So far we have considered structural relationships between the MSn (M = Ca, Sr, Ba) compounds and their parent metals.

On the other hand, three perovskites $MSnO_3$ (M = Ca, Sr, Ba) have been reported. Those of Ca and Sr show orthorhombic distortions of the ideal perovskite (10), whereas $BaSnO_3$ has been reported to be cubic (11). It is well known that the metal array in perovskites has the CsCl-type structure. The unit cell parameters of $BaSnO_3$ (4.10 Å) and of hp-BaSn (4.05 Å) agree to within 1%: the coincidence is not only topological but also in dimensions. The lattice parameters for high pressure CaSn have not been reported, but the fact that it also undergoes the CaSi → CsCl transition leads us to conclude that the $MSnO_3$ (M = Ca, Sr, Ba) perovskites can be considered as oxygen-stuffed high pressure phases of the MSn binary compounds, and may represent new examples of "unaltered stuffed alloys." Although there are no experimental data for the hp-SrSn alloy, it presumably follows the same behavior.

In the examples discussed here, we point out that oxygen has the same effect as pressure in the structural arrangement of metals. Moreover, if Ba–Sn bonding interactions exist in the binary alloys and their structure remains in the oxide, one should consider the role played by oxygen in $BaSnO_3$. Although not strictly related to this phenomenon, the effect of isotopic substitution has recently been examined for NaOH (NaOD), and is considered to be equivalent to the application of pressure (12).

It is possible that a systematic check of β-brasses and perovskites as well as Laves phases and spinels would provide additional examples of "unaltered stuffed alloys." On the other hand, a detailed analysis of the structures of high pressure phases of alloys and oxides could lead to new examples of this relationship between oxidation and pressure. This could help us to understand better both the significance of Hyde's concept of oxides as stuffed alloys and the mechanism of phase transition in intermetallic compounds. We recall here the different behavior of the two related compounds $BaGeO_3$ and $CaGeO_3$.

Probably, new phases of alloys could be found, whose structures would correspond to the cationic arrays of known oxides. Consequently, new phases of oxides, having cationic substructures of known alloys, could be synthesized. Of great interest also would be a study of the oxidation process of the two MSn phases, as well as the reduction process of the $MSnO_3$ perovskites. All this will be the aim of forthcoming work.

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