Synthesis and Reactivity of a New Intermetallic Compound: Na_4Sn

Frédéric Guérin and Darrin Richeson*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5

The synthesis, crystallographic characterization and some preliminary reactivity (with main group elements and halides) of a new intermetallic phase, Na_4Sn, is reported and represents the first confirmation of an intermetallic compound of an alkali metal and group 14 element having a formal charge of -4.

Intermetallic compounds of alkali and alkaline-earth metals with main-group metal and metalloid elements have historically belonged to the realm of physics and metallurgy. Recently, as solid-state/materials chemistry has taken a higher profile, the synthesis and chemical properties of these materials have become of increasing interest. The appeal of these compounds stems from their unique structural features and properties and their ability to function as sources of unusual anions in solid-state synthesis.[1]

We are particularly interested in the Zintl phases formed between the alkali metals (M) and the metals/metalloids of group 14 (E) which possess single atom anions with a filled valence electronic shell (*i.e.* isolated E^{4-}). There are no confirmed compounds of groups 1 and 14 with the stoichiometry M_4E. A compound originally formulated as Na_4Pb has been proposed, based on powder diffraction data, to be either a body-centred cubic material with the formula $Na_{15}Pb_4$ or to have the stoichiometry $Na_{31}Pb_8$ with a face-centred cubic structure.[2-5] These results have been used for comparison with the Sn analogue thus leading to some discrepency in the assignment of the compounds in the binary Na–Sn phase diagram.[5] Compounds with isolated E anions bearing a formal charge of -4 have been prepared with the alkaline-earth metals (M′) as the M'_2E phases and crystallize in either the anti-$PbCl_2$ structure (M′ = Ca, Sr, Ba; E = Si, Ge, Sn, Pb) or the antifluorite structure (M′ = Mg; E = Si, Ge, Sn, Pb).[1,6-14] The recently reported structure of $Ca_{31}Sn_{20}$ also contains isolated Sn^{4-} atoms in both square prismatic and square antiprismatic coordination environments.[15]

Here we describe the synthesis and identification of a new intermetallic phase in the Na–Sn system along with its crystallograpic characterization. In addition to a structural determination, we report some preliminary reactivity studies on this compound.

The investigation of these materials began with the preparation of the binary compound by heating a 4 : 1 stoichiometric mixture of elemental Na and Sn under dynamic N_2 in a glass tube to 300 °C for 30 min. This procedure gave a quantitative yield of a lustrous metallic gray crystalline material. Similar results were obtained when a slight excess of Na is employed. In these cases, subsequent extraction with ethylenediamine or liquid ammonia was used to remove any unreacted metallic sodium. With sodium-poor mixtures, extraction gave dark red solutions which exhibited the characteristic ^{119}Sn NMR resonances for $Sn_9{}^{4-}$ (quintet 1230 ppm upfield from tetramethyltin).[16] Differential scanning calorimetry (DSC) analysis of the crystals, in sample pans sealed under inert atmosphere, showed a sharp endothermic event at 407 °C which we have assigned as the melting point of Na_4Sn. High quality single crystals suitable for X-ray diffraction studies were grown through a flux growth approach. The best results were obtained with slightly Na-rich (2% excess) mixtures of the reactants.

The unique crystal structure of this air-sensitive material has been elucidated by single-crystal X-ray diffraction analysis.† The compound crystallizes in the orthorhombic space group *Pnma* with all of the atoms on special positions. The asymmetric unit is presented in Fig. 1. The atoms Sn(2), Na(6), Na(7) and Na(5) lie on the same mirror plane while Na(1), Na(2), Na(3), Na(4), Na(8) and Sn(2) are positioned on a parallel mirror plane. An extended packing diagram of the structure is shown in Fig. 1.[17] Expansion of the asymetric unit by the symmetry operations gives rise to a columnar structure perpendicular to the crystallographic (010) plane with interpenetrating square planar Na(1)–Na(4)–Na(8)–Sn(1) subunits resulting in an overall ladder motif. The shortest intercolumnar interactions are between Na(8) cations [3.086(7) Å] of the overlapping square planar Na(1)–Na(4)–Na(8)–Sn(1) subunits. The shortest Na–Sn interaction with adjacent pillars are between Sn(2) with Na(4) [3.147(6) Å] and Na(5) [3.165(6) and 3.130(7) Å]. The two Sn anions occupy different coordination polyhedra: Sn(1) is positioned asymmetrically in a distorted eleven-coordinate arrangement with an average Sn(1)–Na distance of 3.31 Å (σ = 0.05 Å) while Sn(2) has a distorted nine-coordinate monocapped square antiprismatic coordination polyhedron with an average Sn(2)–Na distance of 3.30 Å (σ = 0.13 Å). In both cases, optimum electrostatic shielding of the Sn^{4-} anions is provided by their surrounding Na^+ cations. The shortest distance between Sn atoms is 5.54 Å in adjacent asymmetric units.

We have prepared two related intermetallic compounds, Li_4Pb and Li_4Sn, in order to investigate the generality of these results.[5,17-26] Preliminary powder X-ray diffraction data in both cases suggests similar structural features.

In order to examine the suitability of Na_4Sn as a starting material for the preparation of ternary phases, we have started to explore its reactivity with main group elements (*e.g.* P, S). In this regard, the general reactivity of Na_4Sn seems to take the course of a redox reaction. For example, reactions with both red and white phosphorus proceed at low temperatures (sealed tube 150 °C or reflux in toluene for 8 h), according to eqn (1), to yield black powders made up of Na_3P and Sn-rich Na/Sn alloys. Extraction with ethylenediamine leads to generation of a dark orange solution containing the $Sn_9{}^{4-}$ anion.[16]

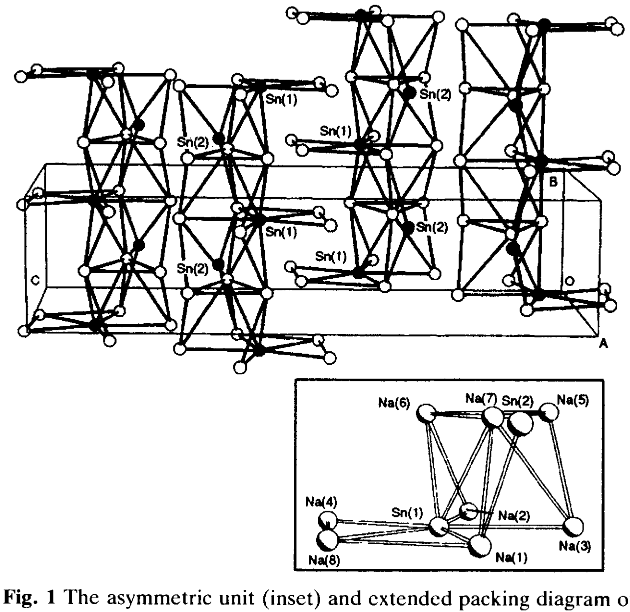

Fig. 1 The asymmetric unit (inset) and extended packing diagram of Na_4Sn in the *b* direction. Filled circles indicate Sn atoms and Na atoms are indicated by open circles. Some Sn–Na interactions have been omitted for clarity. See the inset for Na numbering scheme.

$$Na_4Sn + xP \rightarrow xNa_3P + Na_{4-3x}Sn \quad (1)$$

The reaction of inorganic halides with reduced main group compounds may offer an alternative to the commonly employed, high temperature direct reaction of the elements.[21] Metathetical reactions of Na_4Sn with a variety of main group and transition-metal halides proceed quite rapidly at ambient or slightly elevated (*e.g.* 100 °C) temperatures. Of particular interest to us are the compounds in the binary Nb/Sn system which include the superconducting phase, Nb_3Sn. Interaction of Na_4Sn with $NbCl_5$ at 100 °C gives a self-sustaining reaction to yield a black powder. Removal of NaCl by successive washing with water, ethanol and ether yields a black solid with a composition, as determined by X-ray fluorescence, of Nb_3Sn. This material is amorphous by powder X-ray diffraction. The fact that there are no thermal events in DSC measurements (under inert atmosphere) up to 1200 °C clearly indicates that this material does not contain elemental Sn (mp = 232 °C) or NaCl (mp = 801 °C). Preliminary conductivity and magnetic measurements indicate semiconductor behavior and weak ferromagnetism respectively.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Received, 1st June 1994; Com. 4/03251I

Footnote

† *Crystal data* for Na_4Sn, M = 421.30, orthorhombic, space group *Pnam*, a = 9.744(3), b = 22.751(10), c = 5.5390(15) Å, $F(000)$ = 746.14, Z = 4, D_c = 2.279 g cm^{-3}. R = 0.071 for 1052 reflections with $I > 2.50\sigma(I)$.

References

1 H. Schäfer, *Ann. Rev. Mater. Sci.*, 1985, **15**, 1.
2 E. Zintl and A. Harder, *Z. Physik. Chem.*, 1936, **B34**, 238.
3 D. P. Shoemaker, N. E. Weston and J. Rathlev, *J. Am. Chem. Soc.*, 1955, **77**, 4226.
4 C. W. Stillwell and W. K. Robinson, *J. Am. Chem. Soc.*, 1933, **55**, 127.
5 *Binary Alloy Phase Diagrams*, 2nd edn. ed. T. Massalski, American Society for Metals International, Metal Park, OH, 1986.
6 A. Widera and H. Schäfer, *J. Less Common Met.*, 1981, **77**, 29.
7 G. Bruzzone and E. Franceschi, *J. Less Common Met.*, 1978, **57**, 201.
8 G. Bruzzone and E. Franceschi, *J. Less Common Met.*, 1977, **52**, 211.
9 A. Widera and H. Schäfer, *Z. Naturforsch., Teil B*, 1976, **31**, 1434.
10 A. Widera, B. Eisenmann and H. Schäfer, *Z. Naturforsch., Teil B*, 1976, **31**, 520.
11 B. Eisenmann, H. Schäfer and K. Turban, *Z. Naturforsch., Teil B*, 1975, **30**, 677.
12 K. Turban and H. Schäfer, *Z. Naturforsch., Teil B*, 1973, **28**, 220.
13 P. Eckerlin, E. Leicht and E. Wölfel, *Z. Anorg. Allg. Chem.*, 1961, **307**, 145.
14 P. Eckerlin and E. Wölfel, *Z. Anorg. Allg. Chem.*, 1955, **280**, 321.
15 A. K. Ganguli, A. M. Guloy, E. A. Leon-Escamilla and J. D. Corbett, *Inorg. Chem.*, 1993, **32**, 4349.
16 R. W. Rudolph, W. L. Wilson, F. Parker, R. C. Taylor and D. C. Young, *J. Am. Chem. Soc.*, 1978, **100**, 4629.
17 G. Masing and G. Tammann, *Z. Anorg. Allg. Chem.*, 1910, **67**, 183.
18 G. Grube and E. Meyer, *Z. Elektrochem.*, 1934, **40**, 771.
19 G. Grube and H. Kaliber, *Z. Elektrochem.*, 1934, **40**, 745.
20 A. Zalkin and W. J. Ramsey, *J. Phys. Chem.*, 1956, **60**, 234.
21 For examples using alkali-metal nonmetalides see: A. Hector and I. P. Parkin, *J. Chem. Soc., Chem. Commun.*, 1993, 1095; R. E. Treece, G. S. Macala, L. Rao, D. Franke, H. Eckert and R. B. Kaner, *Inorg. Chem.*, 1993, **32**, 2745 and references therein.