inorganic compounds

SrZn$_{11}$: a new binary compound with the BaCd$_{11}$ structure

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Single crystals of strontium undecazinc, SrZn$_{11}$, were obtained when decomposing SrZn$_2$ under conditions of high pressure and high temperature. The new binary Sr–Zn compound crystallizes in the space group $I4_1/amd$ (BaCd$_{11}$ structure type) with one Sr position ($\overline{4}m2$) and three Zn sites ($\overline{4}m2$, .2/m., 1). The structure is described in terms of all-face-capped Zn$_8$ tetrahedra as the central building unit, defined by the Zn atoms on .2/m. and 1. The building units are condensed into chains by the central tetrahedra sharing edges, and the chains are interconnected by shared capping atoms. The resulting three-dimensional framework of Zn atoms yields channels that are occupied by Sr and Zn atoms on the high-symmetry $\overline{4}m2$ positions.

Comment

Alkaline earth and rare earth metals (M) display remarkably intricate phase diagrams with zinc (Massalski, 1996). This is particularly true on the Zn-rich side (>80 at.% Zn), where phases with similar compositions and complex structures often occur (e.g. M_3Zn_{22}, M_2Zn_{17}, MZn_{11}, MZn_{12} and MZn_{13}). For example, if M is Ca or an early rare earth metal (La, Ce, Pr, Nd or Eu), M–Zn systems contain both MZn_{11} (91.7 at.% Zn) and MZn_{13} (92.8 at.% Zn) with the BaCd$_{11}$ or NaZn$_{13}$ structure, respectively, as the most Zn-rich phases (Sanderson & Baenziger, 1953; Lott & Chiotti, 1966; Iandelli & Palenzona, 1967). If M is Sr or Ba, MZn_{11} is missing, and MZn_5 (83.3 at.% Zn) and MZn_{13} represent the most Zn-rich phases (Bruzzone & Merlo, 1983; Bruzzone et al., 1985). We obtained SrZn$_{11}$ unintentionally when exposing SrZn$_2$ to 7 GPa and 1273 K by means of multi-anvil high-pressure techniques. Instead of transforming into a high-pressure phase, SrZn$_2$ decomposed into a Zn-rich phase, SrZn$_{11}$, and presumably an Sr-rich melt which oxidized under the conditions applied.

The crystal structure of SrZn$_{11}$ corresponds to the tetragonal BaCd$_{11}$ type (space group $I4_1/amd$). Many structures of Mg- and Zn-rich compounds with M can be described using an

all-face-capped tetrahedron [tetrahedral star (TS)] as a central building unit which can be linked or condensed in many different ways (Häussermann et al., 1998). In SrZn$_{11}$, the central tetrahedron of a TS unit is formed by the Zn atoms (Zn3) occupying the general 32i position (Fig. 1). These tetrahedra are centred around the 16g position ($\frac{1}{4}$, $\frac{1}{4}$, 0) and form strands by sharing edges. Within a strand, each atom from a central tetrahedron also acts as a capping atom for the neighbouring TS unit, and vice versa (Fig. 2). The remaining capping atoms correspond to the Zn atoms occupying the site 8d (Zn2). The translational period of a TS strand consists of four units and the translational direction coincides with a 4_1 or 4_3 axis. The unit cell contains four tetragonally arranged TS strands, which are linked by the 8d capping atoms (Fig. 3). The resulting framework of Zn atoms features channels around (0, 0, z) and ($\frac{1}{2}$, $\frac{1}{2}$, z), which are filled alternately by the Sr and remaining Zn atoms (Zn1) on positions 4a and 4b, respectively (Figs. 4 and 5).

The Zn—Zn distances within the TS strands range from 2.68031 (15) to 2.963 (2) Å (Table 1). The longest Zn—Zn distances occur within central tetrahedra (Zn3—Zn3). The
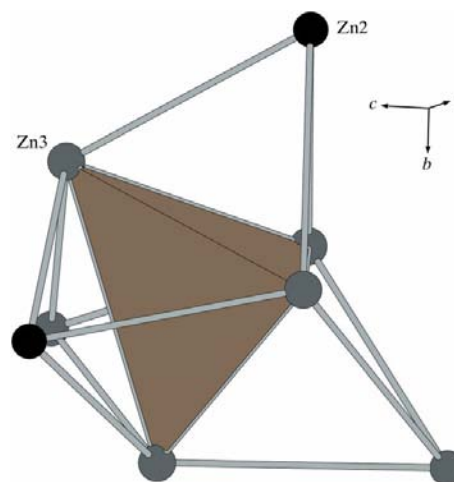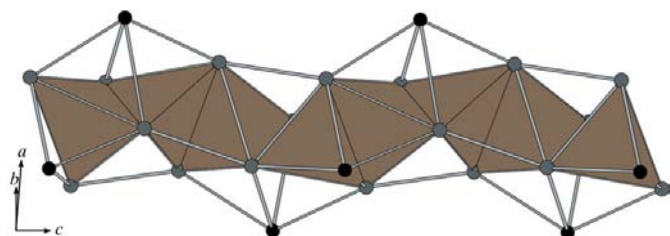

Figure 1
The tetrahedral star (TS) unit in SrZn$_{11}$. Atoms Zn2 and Zn3 are denoted by black and medium-grey spheres, respectively.
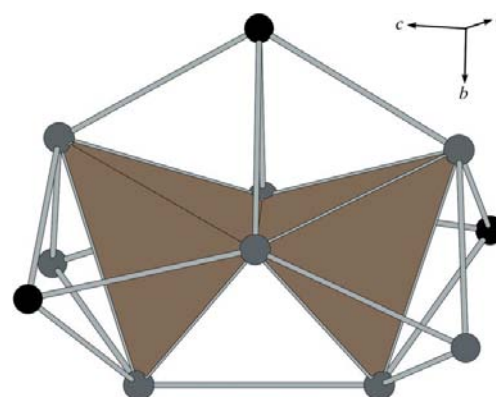
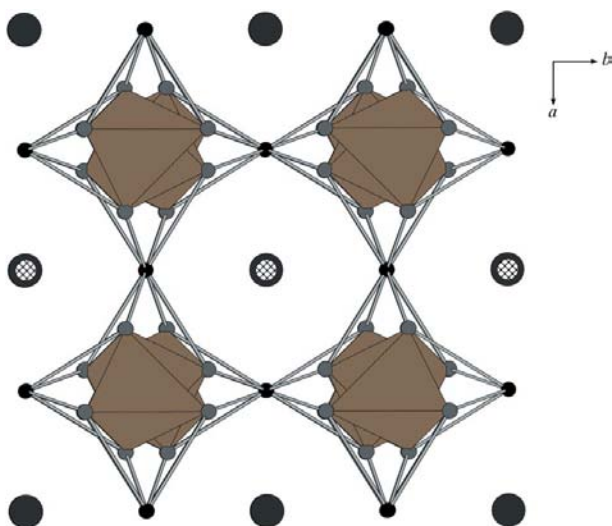**Figure 2**
Two TS units connected by sharing a common edge. Black spheres are Zn2 and medium-grey spheres are Zn3.

distances between atom Zn1 on 4b and neighbouring Zn atoms are 2.8223 (8) (to Zn2) and 2.9048 (12) Å (to Zn3). The Sr—Zn distances are 3.3350 (14) and 3.4396 (14) Å (to Zn3 and Zn3[i], respectively), and 3.7302 (12) Å to Zn2[ii] (all symmetry codes are as in Table 1). The unit-cell volume of SrZn$_{11}$ [797.1 (6) Å^3] is clearly the highest among binary Zn compounds with the BaCd$_{11}$ structure [M = Eu (789.8 Å^3), La

Figure 3
A strand of edge-sharing TS units. The repeat unit consists of four TS units and each unit cell is made up of four such repeat units. Black spheres are Zn2 and medium-grey spheres are Zn3.

Figure 4
A view of the TS arrangement in an SrZn$_{11}$ unit cell along [001]. Zn1, Zn2 and Zn3 are white hatched, black and medium-grey spheres, respectively, and Sr1 are represented as large dark-grey spheres.
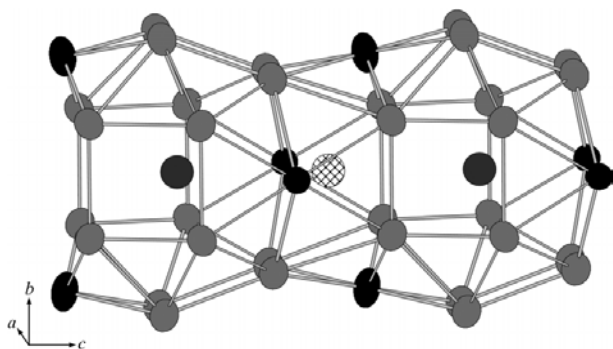
Figure 5
The channel arrangement of Sr and Zn atoms in SrZn$_{11}$ along the high-symmetry $\bar{4}m2$ positions, shown with 95% probability displacement ellipsoids. Sr1 is dark grey, Zn1 white hatched, Zn2 black and Zn3 medium grey.

(785.7 Å^3), Ca (781.8 Å^3), Ce (779.5 Å^3), Yb (771.9 Å^3), Pr (771.8 Å^3) and Nd (768.4 Å^3)]. It has been argued that the TS framework in BaCd$_{11}$-type compounds is rather rigid, giving little flexibility for the size of the voids around positions 4a and 4b (Sanderson & Baenziger, 1953; Iandelli & Palenzona, 1967). Therefore, the size of M is an important factor for the stability of MZn$_{11}$ phases.

Sr and Ba have larger sizes than the M metals displaying phases MZn$_{11}$ in their M–Zn phase diagrams. This might explain why MZn$_{11}$ is absent in the Sr–Zn and Ba–Zn systems, and why the synthesis of SrZn$_{11}$ requires high-pressure conditions.

Experimental

The starting material, SrZn$_2$, was synthesized from the elements strontium (crystalline dendritic pieces, Alfa Aesar, 99.95%) and zinc (shots, Alfa Aesar, 99.9999%), which were weighed in the appropriate atomic ratio and sealed in a tantalum tube under an argon atmosphere. The tantalum tube was protected from air by a silica jacket sealed under vacuum, then heated at 973 K for 2 h and quenched in water. Subsequently, the sample was reheated and annealed at 773 K for 21 d, followed by quenching in water. Powder X-ray diffraction showed that the sample corresponded to phase-pure CeCu$_2$-type SrZn$_2$ (Bergman & Shlichta, 1964). SrZn$_{11}$ was obtained by subjecting SrZn$_2$ to high-pressure high-temperature conditions using a 6–8 Walker-type multi-anvil high-pressure module. SrZn$_2$ was ground in a mortar and a sample (57 mg) was loaded into a boron nitride (BN) capsule (4.555 mm diameter × 2.555 mm long). Thereafter, the BN capsule was positioned with a graphite furnace and a zirconia insulating sleeve in a magnesia octahedron with a 14 mm edge length (Leinenweber & Parise, 1995). The sample was pressurized to 7 GPa and then heated at a rate of approximately 400 K min^{-1} to 1273 K and kept at this temperature for 1 h. After 1 h, the sample was quenched isobarically by turning off the power to the furnace, and then slowly decompressed. The powder X-ray diffraction pattern of the recovered sample revealed SrZn$_{11}$ as the main product. The by-product(s) could not be identified, but may correspond to oxidation products of an Sr-rich melt also formed upon decomposing SrZn$_2$. The recovery of the high-pressure treated sample was not performed under air-free conditions. Single crystals investigated from the recovered sample corresponded to SrZn$_{11}$.

Crystal data

SrZn$_{11}$	Z = 4
M_r = 806.69	Mo Kα radiation
Tetragonal, $I4_1/amd$	μ = 38.97 mm^{-1}
a = 10.749 (3) Å	T = 298 (2) K
c = 6.899 (4) Å	0.09 × 0.06 × 0.06 mm
V = 797.1 (6) Å^3	

Data collection

Bruker SMART APEX diffractometer	3644 measured reflections
	258 independent reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 2003a)	214 reflections with $I > 2\sigma(I)$
	R_{int} = 0.113
T_{min} = 0.075, T_{max} = 0.101	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	18 parameters
$wR(F^2)$ = 0.077	$\Delta\rho_{max}$ = 1.04 e Å^{-3}
S = 1.08	$\Delta\rho_{min}$ = −1.21 e Å^{-3}
258 reflections	

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Table 1
Selected bond lengths (Å).

Sr1—Zn3	3.3350 (14)	Zn3—Zn3^{iv}	2.628 (2)
Sr1—Zn3^{i}	3.4396 (14)	Zn3—Zn3^{v}	2.672 (2)
Sr1—Zn2^{ii}	3.7302 (12)	Zn3—Zn3^{vi}	2.6803 (14)
Zn1—Zn2	2.8223 (8)	Zn3—Zn3^{vii}	2.717 (2)
Zn1—Zn3	2.9048 (12)	Zn3—Zn3^{viii}	2.905 (2)
Zn2—Zn3	2.6031 (15)	Zn3—Zn3^{ix}	2.963 (2)
Zn2—Zn3^{iii}	2.6528 (13)		

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{4}$; (ii) $y-\frac{1}{2}, -x, z-\frac{1}{4}$; (iii) $-y, x, -z+1$; (iv) $-x, y, z$; (v) $x, -y+\frac{1}{2}, -z+\frac{1}{4}$; (vi) $y, -x+\frac{1}{2}, z+\frac{1}{4}$; (vii) $-y+\frac{1}{2}, -x+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $-x+\frac{1}{2}, y, -z+\frac{3}{4}$; (ix) $y, x, -z+1$.

The origin choice 1 was used for correspondence with a standardized structure type comparison according to the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). Refinement was performed on F^2 for all reflections. The weighted R factor wR_2 and goodness-of-fit S are based on F^2, and conventional R factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R factors(gt), *etc.*, and is not relevant to the choice of reflections for refinement.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2003*b*).

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