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$Sr_{11}Ge_4N_6$: a new nitride composed of $[GeN_2Sr_7]^{4+}$ antiperovskite-type slabs and $[Sr_4Ge]^{4+}$ layers, separated by sheets of bent $[Ge^{II}N_2]^{4-}$ ions

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The layered nitride $Sr_{11}Ge_4N_6$ contains Ge^{4-} Zintl anions in both $[Sr_4Ge]^{4+}$ layers and $[GeN_2Sr_7]^{4+}$ antiperovskite-type slabs which are separated by sheets of bent $[Ge^{II}N_2]^{4-}$ ions; the observed range of formal germanium oxidation states in nitrides thus extends between +4 and −4.

A number of binary nitrides exhibit structural or electronic properties that make them technologically useful (*e.g.* Si_3N_4, TiN and GaN). More complex nitrides are expected to show new structures and useful properties complementary to those of complex oxides. Recent decades have seen a boom in efforts, both experimental and theoretical,[1] to understand ternary and higher order nitride systems, including the development of new synthetic routes.[2] One such technique uses sodium-rich mixed-metal melts as nitride growth media and has produced a range of alkaline earth (AE)–main group nitrides.[2–5] Several AE–Ge–N phases synthesised by this and other routes have structures analogous to those of silicates, containing, for example, isolated $[Ge^{IV}N_4]^{8-}$ tetrahedra in Ca_4GeN_4,[3] corner linked tetrahedral chains in $Ca_5Ge_2N_6$,[3] and a three dimensional β-cristobalite framework in $CaGeN_2$.[6] The use of the sodium-rich melt technique also stabilizes Ge in a wide range of lower oxidation states, sometimes combining them in the same structure, as in $Ba_3Ge_2N_2$,[4] where Ge^{2-} in the form of infinite zigzag chains and Ge^{2+} in the form of bent $[Ge^{II}N_2]^{4-}$ units coexist. The antiperovskite $GeNCa_3$[7] contains Ge in a formal oxidation state of −3. Here we report a nitride with an unprecedented intergrowth structure in which formal Ge^{4-} Zintl anions, isolated for the first time in a nitride, are present in $[GeN_2Sr_7]^{4+}$ antiperovskite-type slabs and in $[Sr_4Ge]^{4+}$ layers, the two layer types being separated by sheets of $[Ge^{II}N_2]^{4-}$ ions.

The elements† were sealed in a tantalum-lined nickel tube, heated at 900 °C for 2 days and cooled to room temperature at 0.1 °C min^{-1}. Excess sodium was evaporated from the tube under dynamic vacuum at 350 °C after which the products could be easily removed and analysed. Energy dispersive analysis of X-rays (EDX)‡ indicated an overall 75.1% Sr to 24.9% Ge atomic ratio (esds are ±1.7%) on several well-shaped crystals of an extremely air-sensitive material which constituted approximately 10% of the sample. Due to the absorption of the detector window, the nitrogen content could not be quantified. Attempts to synthesise pure bulk material by reactions between stoichiometric ratios of Sr_2N, Ge and Ge_3N_4 powders were unsuccessful.

Single crystal X-ray diffraction§ on the black prisms indicated a primitive tetragonal cell (a = 7.278(1) Å, c = 18.681(4) Å) and the systematic absences were consistent with only one space group: *P*4/*nbm* (no. 125). The initial structural model obtained by direct methods included seven "heavy" atoms while two additional nitrogen atoms were located from Fourier difference maps. Although the scattering power of Sr^{2+} is very similar to that of Ge^{4-} since they have isoelectronic closed shells, their greatly differing chemical environments and the information from elemental analysis allowed for a straightforward assignment. The fractional atomic coordinates for $Sr_{11}Ge_4N_6$ are listed in Table 1.

The layered nature of $Sr_{11}Ge_4N_6$ is depicted in Fig. 1. Red polyhedra represent Ge3-centred Sr_8Ge distorted square antiprisms which form a ${}^{2}_{\infty}[Sr_{8/2}Ge]^{4+}$ layer in the ab plane by edge sharing. All Sr2–Ge3 distances are 3.2637(5) Å. The Ge3–Ge3 separation of 5.15 Å ($a/\sqrt{2}$) rules out any Ge–Ge bonding in the plane. Such isolated Ge^{4-} anions have precedent in the intermetallic phase Sr_5Ge_3[8] which contains very similar Sr_4Ge layers (although with longer Sr–Ge distances of 3.44 Å) which carry a formal +4 charge and are separated by Ge_2^{6-} dumb-bells and Sr^{2+} cations.

The blue distorted octahedra in Fig. 1 are N2-centred Sr_6N units which are corner-linked to form a two-dimensional ${}^{2}_{\infty}[GeN_2Sr_7]^{4+}$ slab with the antitype of the ABX_3 perovskite structure in which the 12-coordinate "A" site in the slab is occupied by Ge2 atoms (isolated red spheres in Fig. 1). This unusual coordination environment for Ge has been observed previously in nitrides: Ca_3GeN[7] has the ideal antiperovskite structure with a ${}^{3}_{\infty}[Ca_{6/2}N]^{3+}$ framework and a formal −3 germanium valence for this 12-coordinate environment (Ca–Ge = 3.36 Å). In $Sr_{11}Ge_4N_6$ the N2 atom is octahedrally coordinated by Sr: 2.449(6) Å × 1(Sr3), 2.6029(7) Å × 4(Sr1) and 2.687(6) Å × 1(Sr4), Sr–N distances consistent with those previously reported in binary[1] and ternary[5] strontium nitrides. The two layers of Sr_6N octahedra in the ${}^{2}_{\infty}[GeN_2Sr_7]^{4+}$ slab in $Sr_{11}Ge_4N_6$ are contra-rotated by 6.4° around

Table 1 Fractional atomic coordinates and equivalent isotropic displacement parameters U(eq) for $Sr_{11}Ge_4N_6$

Atom	Site	x	y	z	U(eq)/(Å^2 × 10^3)[a]
Sr1	8m	0.47172(5)	0.52828(5)	0.12971(3)	14(1)
Sr2	8m	0.57881(4)	0.42119(4)	0.40170(2)	10(1)
Sr3	4g	¼	¼	0.2750(1)	10(1)
Sr4	2a	¼	¼	0	18(1)
Ge1	4h	¾	¼	0.2585(1)	10(1)
Ge2	2c	¾	¼	0	12(1)
Ge3	2b	¼	¼	½	12(1)
N1	8m	0.3951(4)	0.6049(4)	0.3163(2)	13(1)
N2	4g	¼	¼	0.1438(3)	11(1)

[a] U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor

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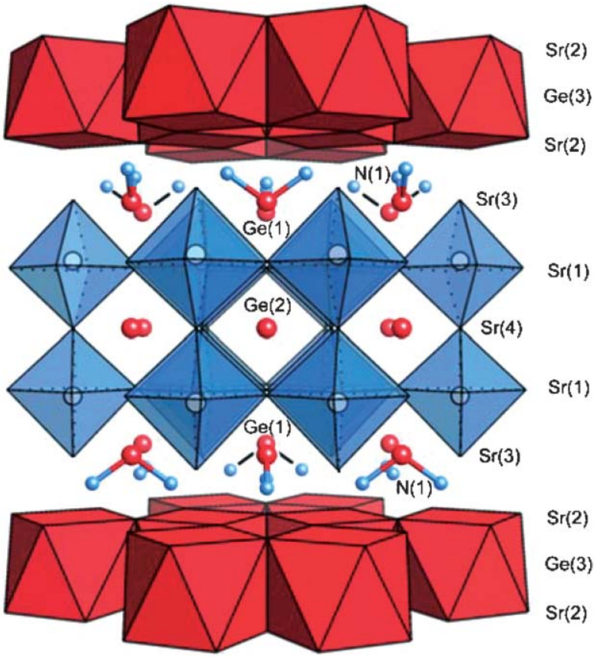

Fig. 1 Polyhedral representation of $Sr_{11}Ge_4N_6$. Red Sr_8Ge distorted square antiprisms edge share to form ${}^{2}_{\infty}[Sr_{8/2}Ge]^{4+}$ layers containing Ge^{4-} Zintl anions. Blue Sr_6N octahedra share corners to form antiperovskite type ${}^{2}_{\infty}[GeN_2Sr_7]^{4+}$ slabs also containing Ge^{4-} anions (red spheres). At the interface of the two cationic layers are bent $[GeN_2]^{4-}$ anions (Ge^{II}).

the *c* axis in a manner designated ($00\Phi_z$) in the nomenclature describing octahedral tilts in layered perovskite-related materials such as Ruddlesden–Popper phases with an even number of octahedral slabs.[9] The tilting is a consequence of the mismatch between the ideal Sr–Ge and Sr–N distances: the Ge atom is slightly small for its perovskite-type "A" site and is surrounded by four Sr1 atoms at 3.3286(6) Å in a distorted tetrahedral arrangement, four Sr4 atoms at 3.6389(5) Å in a square plane and four Sr1 atoms at 3.7518(7) Å. This is not inconsistent with a higher formal valence on Ge2 than on the corresponding "A" site atom in Ca_3GeN, and we formulate the antiperovskite slab as ${}^{2}_{\infty}[GeN_2Sr_7]^{4+}$ containing chemically sensible Ge^{4-} Zintl anions.

The octahedral tilting removes the mirror plane normal to the *c* axis from an idealised double perovskite layer and the space group is *P4/nbm* as predicted for such a tilting scheme.[9] At the interface of the two positively charged layers are $[Ge^{II}N_2]^{4-}$ angular units which charge balance the overall structure. This unusual 18 e^- nitridometallate anion, also observed in $Ba_3Ge_2N_2$[4] and Sr_2GeN_2[5] is bent, as expected by analogy with the isoelectronic SO_2 and $SnCl_2$. These units, generated from Ge1 (4*h*) and N1 (8*m*) by a mirror plane, have C_{2v} symmetry with equal Ge1–N1 bond lengths of 1.844(4) Å and a N1–Ge1–N1 angle of 108.2(3)°, very similar to that previously found in nitrides[4,5] and molecular systems such as $Ge^{II}[N(SiMe_3)_2]$.[10] The Ge1 atom in this $[Ge^{II}N_2]^{4-}$ anion carries a lone pair which protrudes into the positively charged antiperovskite-type slabs and is coordinated by eight Sr atoms in that slab: 3.3154(8) Å × 2(Sr1), 3.6520(5) Å × 4(Sr3) and 3.7401(8) Å × 2(Sr1). Two Sr2 atoms in the ${}^{2}_{\infty}[Sr_4Ge]^{4+}$ layers actually lie closer (3.2039(8) Å) to the Ge1 atoms of the $[Ge^{II}N_2]^{4-}$ units, but these Sr atoms are more closely coordinated by three N1 atoms in $[Ge^{II}N_2]^{4-}$ units: Sr2–N1 = 2.474(4) Å × 1; 2.807(3) Å × 2. As well as being coordinated by three Sr2 atoms and by Ge1, the N1 atoms of the $[Ge^{II}N_2]^{4-}$ units are within bonding range (2.896(2) Å) of two Sr3 atoms in the antiperovskite-type slabs.

The coordination of both N1 in the $[Ge^{II}N_2]^{4-}$ units and N2 in the antiperovskite slabs is thus sixfold as is found in many nitrides.[1] Extended Hückel calculations carried out using the YAeHMOP software package[11] confirm that both Ge2 (in the ${}^{2}_{\infty}[GeN_2Sr_7]^{4+}$ layers) and Ge3 (in the ${}^{2}_{\infty}[Sr_4Ge]^{4-}$ layers) have complete octets and may be considered to be formally Ge^{4-}. The presence of unfilled Ge1-derived states above the Fermi level suggests that the material should be a narrow band gap semiconductor consistent with its physical appearance, although physical property measurements are hampered by the air sensitivity of the compound. This work extends the range of two-dimensional building blocks available for the construction of layered solids; we are investigating structure–composition–property relationships in other nitrides and non-oxide solids with low-dimensional crystal structures constructed from a range of well-defined layer types.

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Notes and references

† Operations were carried out in a Glove Box Technology argon-filled glove box (O_2 content < 2 ppm). 90 mg of Sr shavings cut from a freshly-cleaned surface of Sr chunk (Alfa 99.9%), 72 mg of Ge powder gained by pulverizing Ge pieces (Alfa 99.99%) and 48 mg of Ti powder (Alfa dehydrided 99.99%) were loaded in a nickel tube lined with Ta foil (Alfa 99.9% 0.025 mm thick) closed at the bottom and already containing 85 mg of NaN_3 (Aldrich 99.5%) as the nitrogen source. [**Caution:** sodium azide is highly toxic and is readily absorbed through the skin]. 200 mg of freshly cut sodium was added as the crystallization flux. The tube was transferred to an arc-welder and its top was welded closed under a stream of purified argon. To prevent oxidation the nickel tube was sealed under dynamic vacuum in a fused silica envelope.

‡ Elemental analyses on single crystals were carried out on a JEOL JSM-840A scanning electron microscope equipped with an Oxford Instruments ISIS300 energy dispersive X-ray analyser. No trace of titanium, tantalum or nickel was found in any of the crystals.

§ Single crystal XRD data were collected on a 0.08 × 0.06 × 0.04 mm^3 reflective black crystal using a Nonius Kappa CCD diffractometer: Mo Kα radiation ($\lambda = 0.71073$ Å); angular range $5.14^\circ \leqslant \theta \leqslant 29.13^\circ$; completeness to θ_{max}: 97.6%; $R_{int} = 0.081$; 26697 reflections measured (726 independent). Structure solution (direct methods): SHELXS-97,[12] absorption correction: numerical based on face indexing[13] ($\mu = 35.34$ mm^{-1}; max/min transmission: 0.27/0.12). Space group *P4/nbm*, $a = 7.278(1)$ Å, $c = 18.681(4)$ Å, $Z = 2$, $\rho = 4.491$ g cm^{-3}, $T = 173$ K, $M = 1338.24$. Full matrix refinement on F^2 using 36 parameters and no restraints: SHELXL-97[12] ($R_1 = 0.0236$, $wR_2 = 0.0473$ for $I > 2\sigma(I)$, Goodness of fit on $F^2 = 1.191$). CCDC 250041. See http://www.rsc.org/suppdata/cc/b4/b413534b/ for crystallographic data in .cif or other electronic format.

1 F. J. DiSalvo and S. J. Clarke, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 241; R. Kniep, *Pure Appl. Chem.*, 1997, **69**, 185; R. Niewa and F. J. DiSalvo, *Chem. Mater.*, 1998, **10**, 2733; D. H. Gregory, *J. Chem. Soc., Dalton Trans.*, 1999, 259; L. F. Mattheiss, *Phys. Rev. B: Condens.*

Matter, 1993, **47**, 8224; J. M. Oliva and E. Canadell, *Inorg. Chem.*, 2002, **41**, 4630.

2 H. Huppertz and W. Schnick, *Chem. Eur. J.*, 1997, **3**, 249; W. Schnick, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 806; M. Ludwig, J. Jaeger, R. Niewa and R. Kniep, *Inorg. Chem.*, 2000, **39**, 5909.

3 S. J. Clarke and F. J. DiSalvo, *Inorg. Chem.*, 2000, **39**, 2631.

4 H. Yamane and F. J. DiSalvo, *J. Alloys Compd.*, 1996, **241**, 69.

5 S. J. Clarke, G. R. Kowach and F. J. DiSalvo, *Inorg. Chem.*, 1996, **35**, 7009; S. J. Clarke and F. J. DiSalvo, *Inorg. Chem.*, 2000, **39**, 2631.

6 M. Maunaye, J. Guyader, Y. Laurent and J. Lang, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1971, **94**, 347.

7 M. Y. Chern, D. A. Vennos and F. J. DiSalvo, *J. Solid State Chem.*, 1992, **96**, 415.

8 R. Nesper and F. Zuercher, *Z. Kristallogr. New Cryst. Struct.*, 1999, **214**, 21.

9 K. S. Aleksandrov and J. Bartolomé, *J. Phys.: Condens. Matter*, 1994, **6**, 8219.

10 R. W. Chorley, P. B. Hitchcock, M. F. Lappert, W. Leung, P. P. Power and M. M. Olmstead, *Inorg. Chim. Acta*, 1992, **198–200**, 203.

11 G. Landrum, *Yet Another Extended Hückel Molecular Orbital Package (YAeHMOP)*, Cornell University, 1997, http://yaehmop.sourceforge.net/.

12 G. M. Sheldrick, *SHELX97: Programs for Crystal Structure Analysis (Release 97-2)*, University of Göttingen, Germany, 1997, http://shelx.uni-ac.gwdg.de/SHELX/.

13 N. W. Alcock, *Crystallogr. Comput.*, 1970, 271.