

Synthesis and crystal structure of $\text{Na}_{1-x}\text{Ge}_{3+z}$: a novel zeolite-like framework phase in the Na–Ge system

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A novel crystalline binary phase is reported in the Na–Ge system, with an entirely new, zeolite-like crystal structure solved and refined by the combination of synchrotron X-ray and neutron powder diffraction techniques.

Open-framework inorganic materials exhibit a range of unique and interesting chemical and physical properties, as well as distinctive structural features.¹ Such materials often crystallize in known zeolite types or closely analogous structures, and have the ability to host atoms or molecules inside cages or tunnels formed by the framework. ‘‘Closed-cage’’ guest-host framework structures such as the Group 14 clathrates^{2–4} (analogous zeolite structures⁵ MEP and MTN), have been studied extensively, in part due to interesting physical properties such as glasslike thermal conductivity⁶ and superconductivity,⁷ extremely unusual properties for sp^3 bonded solids. However, structures with host frameworks composed solely of Group 14 elements in which the guest species are not entirely encapsulated in closed cages, but rather in tunnel or channel frameworks are far less common.¹ In this communication, we report the synthesis and crystal structure of $\text{Na}_{1-x}\text{Ge}_{3+z}$, a new binary framework phase in the Na–Ge system, the structure of which has been solved and refined by the combination of synchrotron X-ray and neutron powder diffraction methods. This phase constitutes the first example in which an exclusively Group 14 framework crystallizes in a tunnel configuration, reminiscent of those found in the microporous zeolites. Moreover, the current framework structure does not correspond to previously known zeolite structures.

The new Na–Ge phase reported here was identified as the product of thermal decomposition under vacuum (or ‘degassing’) of the Zintl phase NaGe .[†] The resulting products are fine, grayish polycrystalline powders that, upon removal of any unreacted NaGe by washing with water and ethanol, are stable in air and moisture. Thermal analysis measurements under flowing nitrogen revealed the new phase decomposes exothermically above 400 °C, whereas decomposition begins under vacuum (10^{-4} Pa) at the lower temperature of 370 °C.

The structure of the new phase was determined using the combination of synchrotron X-ray and neutron diffraction

experiments. Preliminary structure determinations were performed using synchrotron X-ray diffraction data.[‡] The structure was indexed using a hexagonal unit cell with space group $P6/m$ (no. 175), with cell constants $a = 15.05399(5)$ and $c = 3.96845(2)$ Å. To confirm and further refine the structural model, a larger sample (≈ 5 g) was prepared for neutron diffraction experiments performed at both 295 and 4 K (see Fig. 1).[§] The preliminary structure as determined from synchrotron experiments was confirmed and the structural model refined using both high and low temperature neutron diffraction data.

The structure determination revealed that the new Na–Ge phase crystallizes in a complex zeolite-like structure, shown in Fig. 2. The framework can be viewed as built from covalently bonded Ge atoms, all of which are arranged in distorted tetrahedral configurations (see Fig. 3) with the exception of Ge1. As shown in Fig. 2, the framework forms large and small channels, akin to the channels found in some zeolites. The present structure, however, does not correspond to any of the known zeolite structure types.⁵ The large and small channels in the framework both run along the c -direction. The Ge framework sites (denoted by Ge1, Ge2, Ge3 and Ge4 in Fig. 3) were all found to be fully occupied. From neutron diffraction at 295 K, the Ge–Ge distances in the framework range from 2.438(8) to 2.527(6) Å, as compared to the ‘ideal’ 2.45 Å for elemental Ge in the diamond structure.

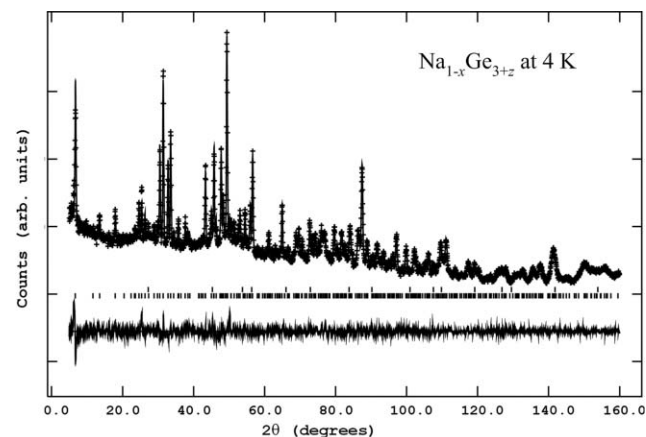


Fig. 1 Observed, calculated and difference patterns (plotted on the same scale) obtained from Rietveld refinement using neutron diffraction data collected at 4 K. Lower tick marks indicate calculated reflections for $\text{Na}_{1-x}\text{Ge}_{3+z}$. Upper tick marks indicate calculated reflections for elemental Ge, which was present in the sample as a minor impurity. Refinement results are given in the notes.[§]

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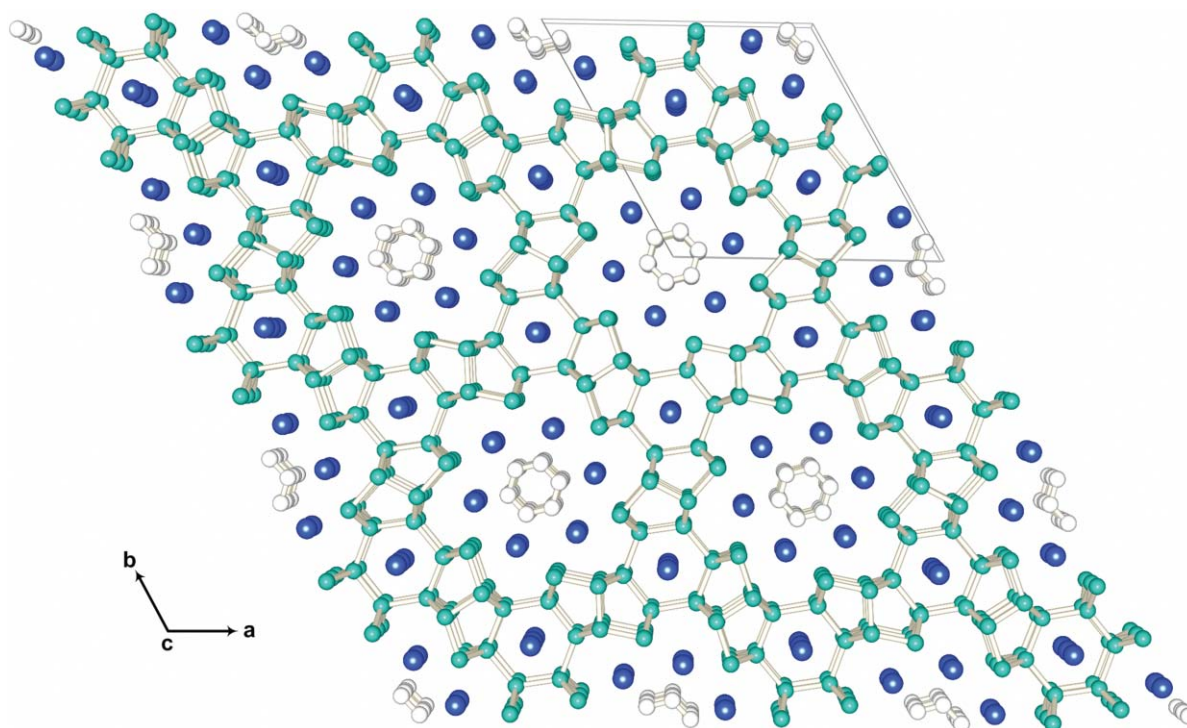


Fig. 2 Crystal structure of $\text{Na}_{1-x}\text{Ge}_{3+z}$, as viewed down the c -axis. Na atoms are shown in blue, while the framework Ge atoms are shown in turquoise. The Ge7 site, which is partially occupied, is shown in white. The hexagonal unit cell is outlined in the upper right.

Several crystalline binary compounds have been reported previously in the Na–Ge system.^{8–15} Of these, NaGe and $\text{Na}_{12}\text{Ge}_{17}$ have been characterized in great detail,^{8,9} but the true nature or existence of some of the other Na–Ge phases has been disputed in the literature.^{9,15} The crystal chemistry of phases such

as NaGe and $\text{Na}_{12}\text{Ge}_{17}$ is understood in terms of Zintl–Klemm concepts,¹⁶ in which the compounds are composed of $[\text{Ge}_4]^{4-}$ (e.g. NaGe and $\text{Na}_{12}\text{Ge}_{17}$) or $[\text{Ge}_9]^{4-}$ (e.g. $\text{Na}_{12}\text{Ge}_{17}$) cluster anions and Na^+ cations.^{8,9} The covalent Ge framework of $\text{Na}_{1-x}\text{Ge}_{3+z}$ is in stark contrast to the ionic $[\text{Ge}_4]^{4-}$ or $[\text{Ge}_9]^{4-}$ cluster units found in other Na–Ge compounds such as NaGe and $\text{Na}_{12}\text{Ge}_{17}$. In $\text{Na}_{1-x}\text{Ge}_{3+z}$, Na atoms are situated inside the small hexagonal channels (Na5), as well as in the broad channels (Na6). The broad channel can be considered as consisting of alternating Ge and Na, connected *via* Na–Ge bonds, and may also be described as a 24-ring. Inside the broad channel, a maximum of six Na can occupy the Na6 sites that are related to each other by a sixfold symmetry. Moreover, it was found that additional Ge atoms are disordered in the middle of the broad channel, the nature of which was determined by neutron diffraction.

Neutron diffraction experiments at both 295 K and 4 K revealed the additional Ge in the broad channel can be located at sites (Ge7 in Fig. 3) which in fact possess a sixfold symmetry much like the Na atoms in this channel (Na6), yet closer to the center.¶ These Ge sites were not found to be fully occupied, however, in contrast to the Ge framework. Rather the Ge7 site was found to have an occupancy of 1/6, so that the Ge atoms are disordered on one Ge7 site per larger channel, per layer progressing along the c -axis.

An unique aspect of this new open-framework phase is the ability to vary the content of both species in the larger channel. For example, the Na6 site in the larger channel can be fully or partially occupied, and by successive degassing under high vacuum at 350 °C the Na content at this site can be reduced. The Ge content inside the broad channel (Ge7 position) can be varied as well. With the Ge framework, Na5 and Na6 sites all fully occupied the chemical formula of this new phase can be written as NaGe_3 . However,

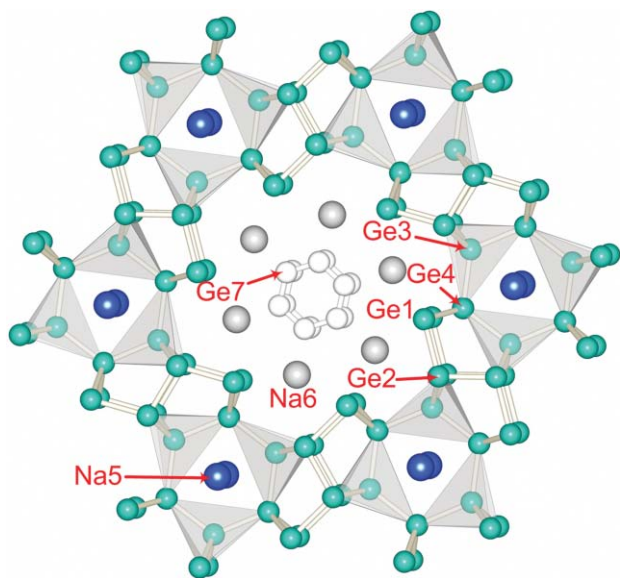


Fig. 3 Structure of $\text{Na}_{1-x}\text{Ge}_{3+z}$, in the vicinity of the broad channel as viewed along the c -axis at a slight tilt. Na atoms in the smaller channels are shown in blue, while the framework Ge atoms are shown in turquoise. The variable occupancy Na6 and Ge7 sites in the larger channel are shown in grey and white, respectively. Tetrahedral coordination of Ge3 is shown, while other tetrahedral arrangements are omitted for clarity.

since the Na6 and Ge7 occupancies inside the larger channel can be varied, the most general formula is $\text{Na}_{1-x}\text{Ge}_{3+z}$.

In summary, a new crystalline binary phase in the Na–Ge system has been synthesized and its crystal structure determined. In contrast to other binary Na–Ge compounds such as NaGe and $\text{Na}_{12}\text{Ge}_{17}$, the new phase is comprised of a covalently bonded, zeolite-like Ge framework, in which Na atoms and also additional Ge atoms reside in small and broad channels formed by the framework. The general chemical formula may be written as $\text{Na}_{1-x}\text{Ge}_{3+z}$, with the values of x and z dependent upon the synthesis conditions, specifically the degas time. The unique and interesting structure of this material warrants further investigation of its physical properties, currently underway by the authors.

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Notes and references

† *Synthesis*: NaGe (monoclinic, space group $P2_1/c$) was first synthesized by direct reaction of the high purity elements at 650 °C. The reaction was carried out inside a tungsten crucible, sealed under ultra high purity nitrogen inside a stainless steel canister, which was in turn sealed inside a fused quartz ampoule. The resulting NaGe product is highly reactive with moisture and air, thus all handling was performed inside a nitrogen-filled glove box. The phase $\text{Na}_{1-x}\text{Ge}_{3+z}$ was then synthesized by heating of NaGe powder under vacuum ($\approx 1.33 \times 10^{-4}$ Pa) at 350 °C for several days.

‡ *Synchrotron X-ray powder diffraction and structure determination*: Synchrotron X-ray diffraction data were collected from 2 to 43.7° 2θ in 0.001° steps on the 32ID beamline at the Advanced Photon Source at Argonne National Laboratory (APS) using a wavelength of 0.4958 Å (25 keV). The pattern was indexed on a primitive hexagonal unit cell (figures of merit of $M(25) = 270$, $F(25) = 1503$) using DICVOL04.¹⁷ Attempts to solve the structure by applying single crystal techniques to extracted structure factors were unsuccessful, as were attempts to solve the structure in an orthorhombic sub-cell. Several space groups yielded essentially the same structure. The lowest residual was obtained in space group $P6$, but analysis of the refined structure suggested that $P6/m$ (no. 175) was the correct space group. The structure was solved using Monte Carlo simulated annealing techniques as implemented in the program Endeavour 1.3 (Crystal Impact).¹⁸ Rietveld refinements were carried out using the GSAS suite.¹⁹ Refined unit cell parameters: $a = b = 15.05399(5)$, $c = 3.96845(2)$ Å. Refinement results: $wR_p = 0.0445$, $R_p = 0.0257$, $\chi^2 = 2.164$. No. of variables: 28. Total no. of data points: 40 699. CCDC 622638. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614048c

§ *Neutron powder diffraction*: The neutron powder diffraction intensity data were collected using the BT-1 high-resolution powder diffractometer at the National Institute for Standards and Technology Center for Neutron Research. A Cu(311) monochromator was employed to produce a monochromatic neutron beam of wavelength 1.5403 Å. Collimators with horizontal divergences of 15, 20 and 7° arc were used before and after the monochromator, and after the sample, respectively. The intensities were measured in steps of 0.05° in the 2θ range 3–168°. Data were collected at 295 and at 4 K. All data processing and Rietveld structural refinements

were carried out using the GSAS suite.¹⁹ The neutron scattering amplitudes used in the refinements were 0.363 and 0.818 ($\times 10^{-12}$ cm) for Na and Ge, respectively. Approximately 1% elemental Ge (CCDC 627148 (4 K) and 627149 (295 K)) was found as an impurity phase. Refined unit cell parameters at 295 K: $a = b = 15.06406(32)$, $c = 3.96727(13)$ Å. Refinement results at 295 K: $wR_p = 0.0204$, $R_p = 0.0171$, $\chi^2 = 1.195$. No. of variables: 57. Total no. of data points: 3119. CCDC 622640. Refined unit cell parameters at 4 K: $a = b = 15.0052(4)$, $c = 3.95456(13)$ Å. Refinement results at 4 K: $wR_p = 0.0213$, $R_p = 0.0178$, $\chi^2 = 1.46$. No. of variables: 57. Total no. of data points: 3120. CCDC 622639. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614048c

¶ The possibility of the diffraction peaks originating from species inside the broad channel such as solvent molecules such as H_2O trapped during the wash process was eliminated. The neutron scattering length for H is -0.374 , and for O is 0.581, which yields a value of approximately -0.17 for a ‘water center’. This value is substantially different from that of the scattering length of Ge (+0.819).

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