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Time-of-Flight Neutron Diffraction Study of Germanium Nitride Oxide, Ge_2N_2O*

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Abstract. Ge_2N_2O, orthorhombic, $Cmc2_1$, $a = 9{\cdot}312\,(1)$, $b = 5{\cdot}755\,(1)$, $c = 5{\cdot}105\,(1)$ Å, $Z = 4$. The structure was solved using multicomponent profile analysis of time-of-flight neutron diffraction data from powdered Ge_2N_2O. It was shown that Ge_2N_2O is isostructural with Si_2N_2O but has larger unit-cell dimensions, and Ge—O—Ge linking angles equal to those in GeO_2. The Ge—O distance is 1·77 (1) Å, the mean Ge—N distance is 1·83 Å, and the Ge—O—Ge angle is 131·5 (5)°.

Introduction. White granular Ge_2N_2O powder was prepared by techniques described by Labbe & Billy (1973). The sample used in this study contained a small amount of GeO_2 (rutile phase) as an impurity, due to the nature of the chemical reaction by nitriding GeO_2. Labbe & Billy (1973) indexed their X-ray powder pattern as orthorhombic and suggested that Ge_2N_2O was isostructural with Si_2N_2O. However, the structure of Ge_2N_2O has not been reported in the literature.

Using the neutron time-of-flight diffractometer at Argonne's CP-5 research reactor, the diffraction data were collected with the sample in a vanadium tube. About 24 h were required to collect the data using time-focused BF_3 detectors at a scattering angle of $2\theta = 90°$, with a total flight path of 3·7 m. The diffractometer resolution is about 1% (FWHM) for *d*-spacings of 1·0 Å. It was calibrated by taking a diffraction pattern of Si (lattice parameter was taken to be 5·4307 Å) in the sample position. The data were analyzed using the multicomponent-profile-analysis technique previously described by Worlton, Jorgensen, Beyerlein & Decker (1976). In this technique the structural parameters are the variables in a least-squares minimization which fits a calculated diffraction profile directly to the raw time-of-flight data.

The study was carried out at the same time at CEN Grenoble using a fixed-wavelength neutron diffractometer at the Melusine Reactor. The results were in close agreement and it was decided to continue the structural study at ANL where the profile-analysis program was available. It is also worth noting that a small non-stoichiometry was believed to be present in the specimen studied at CENG (Labbe & Billy, 1977).

The atomic positions for Ge_2N_2O were refined based on the orthorhombic space group $Cmc2_1$, No. 36. Positional parameters obtained by Idrestedt & Brosset (1964) for Si_2N_2O were used as initial values in the refinement. Additional peaks representing GeO_2 (rutile phase) reflections were included in the calculated spectra. The fitted region included 131 Ge_2N_2O reflections and 32 GeO_2 (rutile phase) reflections with *d*-spacings from 0·85 to 2·27 Å. The parameters refined included 13 background parameters, three lattice parameters for Ge_2N_2O, two lattice parameters for GeO_2 (rutile phase), seven atomic position parameters for Ge_2N_2O, isotropic Debye–Waller factors for Ge, N, and O in Ge_2N_2O and overall scale factors for Ge_2N_2O and GeO_2. The refined scale factors indicated that the sample contained 5·8% GeO_2 by weight. The Ge_2N_2O peaks were found to be slightly broadened beyond the known instrumental resolution. Profile refinements were performed using line-broadening models based on both small particle size and strain. The model based on strain gave a slightly better fit to the data; however, the observed broadening was sufficiently small that the Ge_2N_2O structural parameters were essentially insensitive to whether or not a line-broadening model was included in the refinement. Fig. 1 shows the raw data and the calculated profile including strain broadening. The *R*(profile) for this fit was 0·039. [The *R*(profile) for time-of-flight profile refinement is not exactly equivalent to the conventional *R* value; see Worlton *et al.* (1976).]

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Discussion. The lattice parameters obtained in this study are in good agreement with the X-ray results of Labbe & Billy (1973). The positional parameters and temperature factors for Ge_2N_2O are given in Table 1. The anomalously low temperature factor for O could be a result of non-stoichiometry, which is common in these samples. However, attempts to refine occupation numbers typically gave values within one standard deviation of unity, and were therefore inconclusive.

Fig. 2 shows a projection of the structure along the *b* axis. The basic structural units are identical GeN_3O tetrahedra sharing either N or O corners. Each N is three-coordinated, while each O is two-coordinated. The tetrahedra are oriented such that the Ge and N atoms are in layers, with adjacent layers being connected through Ge—O—Ge bonds.

Bond lengths and angles are listed in Table 2. The mean Ge—N distance is 1·83 Å compared to a mean Si—N distance of 1·72 Å in Si_2N_2O (Idrestedt & Brosset, 1964). Likewise, the Ge—O distance is 1·77 (1) Å, compared to an Si—O distance of 1·62 Å in Si_2N_2O and the Ge—O—Ge angle is substantially smaller, 131·5 (5)°, than the corresponding Si—O—Si angle, 147·7°. These Ge—O bond lengths and angles are very similar to those found in α-quartz GeO_2 which has a mean Ge—O bond length of 1·74 Å and a Ge—O—Ge angle of 130·1 (1)° (Smith & Isaacs, 1964). In general, the GeN_3O tetrahedra are fairly regular, with the largest distortions occurring in the O—Ge—N angles. The differences between Ge_2N_2O and Si_2N_2O undoubtedly arise from the larger effective radius of Ge, giving rise to the longer bonds and, therefore, less rigid tetrahedra.

Table 1. *Atomic positional parameters for* Ge_2N_2O

	Position	*x*	*y*	*z*	*B* (Å^2)
Ge	8(*b*)	0·173 (1)	0·149 (2)	0·321 (2)	1·0 (1)
N	8(*b*)	0·205 (1)	0·136 (1)	0·666 (2)	0·6 (1)
O	4(*a*)	0·0	0·246 (2)	0·230	0·0 (2)

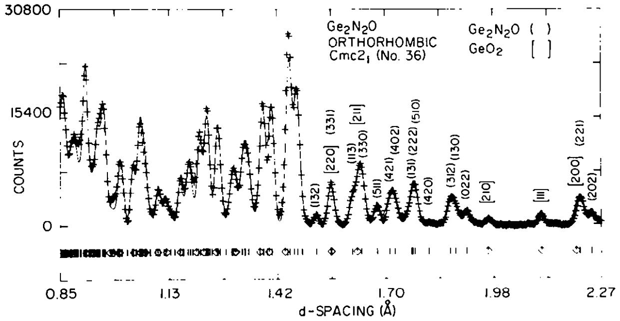

Fig. 1. Neutron time-of-flight diffraction spectra of Ge_2N_2O (2θ = 90°). The solid curve is the calculated profile and the plus marks are the raw data; background has been subtracted in both cases. Tick marks below the profile indicate the calculated line positions. Where space permits, the indexing has been indicated in parentheses above the profile.

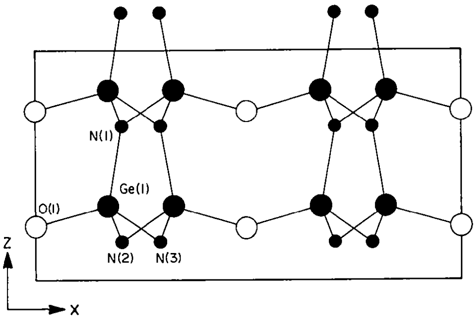

Fig. 2. Projection of the Ge_2N_2O structure along the *b* axis. Large shaded circles are Ge, small shaded circles are N and open circles are O.

Table 2. *Bond distances* (Å) *and angles* (°) *in* Ge_2N_2O

Ge—O	1·77 (1)	Ge(1)—N(2)	1·85 (1)
Ge(1)—N(1)	1·79 (1)	Ge(1)—N(3)	1·86 (1)
Ge—O—Ge	130·5 (5)	N(1)—Ge(1)—N(2)	111·0 (6)
O(1)—Ge(1)—N(1)	115·1 (6)	N(1)—Ge(1)—N(3)	110·2 (6)
O(1)—Ge(1)—N(2)	108·4 (6)	N(2)—Ge(1)—N(3)	108·1 (6)
O(1)—Ge(1)—N(3)	103·6 (6)		

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