# CRYSTAL STRUCTURE OF Na-TITANOGERMANATE

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## Abstract

## Full Text

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# CRYSTAL STRUCTURE OF Na-TITANOGERMANATE

# $Na_2(TiO)[GeO_4]$

The negligible amount of germanium minerals proper in nature should be regarded as a consequence of a low Clarke value, not at all connected with the "quality" of the element itself, since its position at the center of the Mendeleev table allows germanium to play a dual role in compounds—cationic (Ge is localized in octahedra) and anionic (Ge in tetrahedra). This crystal-chemical prerequisite, against the background of an artificial increase of the Clarke value in laboratories (hydrothermal autoclave synthesis), opens up great possibilities for obtaining stable Ge compounds, the number of which may increase sharply in comparison with silicates, if one takes into account that there is no prohibition on the realization of Ge in tetrahedra and octahedra within one structure ([1,2]).

**Fig. 1**

**Fig. 2**

Fig. 1. $Na_2TiGeO_5$. Projection of the structure onto the $xy$ plane in polyhedra. Ti atoms in (semi-)octahedra, Ge atoms in tetrahedra, circles—Na cations

Fig. 2. $Na_2TiGeO_5$. Projection of the structure onto the $xz$ plane in polyhedra. Two layers of the structure are distinguished: $a$—lighter polyhedra at the level $x = 0$ and $b$—darker ones at the level $x = a/2$. By a dashed line the Ti five-vertex polyhedron is completed to an octahedron

Despite the broadly noted crystal-chemical affinity of Ge and Si, one cannot *a priori* assert a complete analogy of Si and Ge compounds, even when these elements are in a tetrahedron, and indeed, one of the pos-

recent structure determinations of the TR-germanate with Ge in tetrahedra ([3]) effectively showed its non-isostructural character with the corresponding silicate.

The Na-titanogermanate investigated by us, $Na_2(TiO)[GeO_4]$, was synthesized under hydrothermal conditions in the system $Na_2O$–$GeO_2$–$H_2O$ (only in titanium inserts) at NaOH concentrations above 20% ([4]).

Transparent, colorless crystals of platy habit (principal forms {001}, {201}, {111}) possessed large internal stresses, and a sufficiently regular single-crystal fragment suitable for X-ray studies could be cut from a large crystal.

**Table 1**

**Structure of $Na_2(TiO)[GeO_4]$. Coordinates of the basis atoms and thermal corrections $B_j$**

| Atoms | $x/a$ | $y/b$ | $z/c$ | $B_j = B + u_j$ |
|---|---|---|---|---|
| Ti | 0.500 | 0 | 0.924 | −0.35 |
| Ge | 0 | 0 | 0 | −0.49 |
| Na | 0.250 | 0.250 | 0.500 | −1.51 |
| $O_1$ | 0.213 | 0 | 0.88 | −0.74 |
| $O_2$ | 0.500 | 0 | 0.257 | −0.92 |

The parameters of the tetragonal cell are: $a = 6.67$ Å, $c = 5.16$ Å, $Z = 2$; the Fedorov group $D_{4h}^7 = P\frac{4}{n}mm$ is determined unambiguously from the extinctions. The three-dimensional experimental material comprised 300 nonzero reflections $0kl$—$4kl$ and $hk0$—$hk1$ (Mo$K_\alpha$ radiation, $\sin\theta/\lambda \leq 0.9\,\text{Å}^{-1}$).

Analysis of the three-dimensional Patterson function $P(xyz)$ localized all atoms of the structure: Ti, Ge, Na, and O, occupying, respectively, special twofold, fourfold, and eightfold positions. Refinement of the positional and thermal parameters led to $R_{hkl} = 12.8\%$. The final coordinates of the atoms of the structure are collected in Table 1, and the interatomic distances calculated from them are in Table 2.

Direct determination of the structure of $Na_2(TiO)[GeO_4]$ showed that Na-titanogermanate is yet another example of complete isomorphous substitution of Si by Ge in the quaternary system $Na_2O$–$B_xO_y$–$\left\{\begin{matrix}SiO_2\\GeO_2\end{matrix}\right\}$–$H_2O$ (according to [5]), it is precisely in quaternary systems that pure isomorphism of Si and Ge is observed). The Ge cation, isomorphously replacing equicharged Si, is located in a very regular tetrahedron: Ge—O = 1.74 Å with O—O = 2.82 Å. The large Na is situated in a somewhat distorted (flattened) octahedron: the Na—O distances lie within narrow limits: Na—$O_1$ = 2.32 Å (4) and Na—$O_2$ = 2.67 Å (2).

**Table 2**

**Structure of $Na_2(TiO)[GeO_4]$. Interatomic distances in Å**

| Ge-tetrahedron | Na-octahedron | Ti-polyhedron |
|---|---|---|
| Ge—O = 1.74 | Na—$O_1$ = 2.32 | Ti = $O_1$ = 2.00 |

| Ge-tetrahedron | Na-octahedron | Ti-polyhedron |
|---|---|---|
| $O_1' = 1.74$ | $O_1' = 2.32$ | $O_1' = 2.00$ |
| $O_1'' = 1.74$ | $O_1'' = 2.32$ | $O_1'' = 2.0$ |
| $O_1''' = 1.74$ | $O_1''' = 2.32$ | $O_1''' = 2.0$ |
| $O_1$—$O_1 = 2.82$ | $O_2' = 2.67$ | $O_2 = 1.72$ |
| | $O_2 = 2.67$ | $O_2' = 3.44$ |
| | | $O_1$—$O_2' = 3.42$ |
| | | $O_1 = 2.70$ |
| | | $O_2 = 3.00$ |

Despite the increased ionic radius of Ge in comparison with Si, the general motif of the structure of $Na_2(TiO)[GeO_4]$ has not changed in comparison with

$Na_2(TiO)[SiO_4]$. The fivefold coordination, unusual for Ti, was also retained: four Ti–O distances are 2.00 Å, the fifth is very short–1.72 Å, while the sixth is 3.44 Å (in the corresponding silicate: 1.67 and 3.41 Å). Thus, the earlier proposed[6] assumption concerning the existence in silicate (germanate) structures of a titanyl group, the ion Ti = O (double bond), is once again confirmed. It may be supposed that Ti in such compounds plays a dual role: "semicationic" – "semianionic," i.e., along with Ge, which is equivalent (in charge and ionic radius), it participates in the construction of a three-dimensional framework structure made up of alternating Ge tetrahedra and Ti pentagonal bipyramids (semioctahedra).

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