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$Ge_3P_6Si_2O_{25}$: A Cage Structure Closely Related to the Intersecting Tunnel Structure $KMo_3P_6Si_2O_{25}$

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A germanosilicophosphate $Ge_3P_6Si_2O_{25}$ has been isolated. Its structure was solved from a single-crystal study in the space group $P\bar{3}1c$. Its cell parameters are $a = b = 7.994(1)$ Å, $c = 16.513(2)$ Å, $Z = 2$. The refinement by full-matrix least-squares calculations leads to $R = 0.043$ with 686 independent reflections. The structure of this oxide is built up from corner-sharing PO_4 and SiO_4 tetrahedra and GeO_6 octahedra. One observes a feature common to several silicophosphates: the presence of the structural unit $P_6Si_2O_{25}$ built up from a disilicate group sharing its corners with six PO_4 tetrahedra. The structural relationships between this oxide and the silicophosphates $AMo_3P_6Si_2O_{25}$ and $Si_3P_6Si_2O_{25}$ (or $Ge_3P_6Ge_2O_{25}$) are described.

Introduction

The recent studies of mixed frameworks involving silicophosphate groups and transition ions in octahedral coordination have shown the possibility of generating new structures closely related to each other. The comparison of the silicophosphates $AM_3P_6Si_2O_{25}$ with A = K, Rb, Tl, Cs and M = Mo, Ti, Sn (*1–3*), MoP_3SiO_{11} (*4*), and $V_3P_5SiO_{19}$ (*5*) shows that their host lattice is characterized by the same structural unit, $P_6Si_2O_{25}$, built up from a Si_2O_7 group linked to six PO_4 tetrahedra. This structural unit has also been observed in the P_2O_5–SiO_2 system for the oxide $Si_5P_6O_{25}$ (*6*) in which a part of the silicon atoms curiously exhibits octahedral coordination, leading to the formulation $Si_3P_6Si_2O_{25}$. The oxide $Ge_3P_6Ge_2O_{25}$ (*7*) which is isostructural with $Si_3P_6Si_2O_{25}$ is less surprising owing to the ability of germanium to take either octahedral or tetrahedral coordination. The similarity between the oxides $AMo_3P_6Si_2O_{25}$ and the oxides $Si_3P_6Si_2O_{25}$ (or $Ge_3P_6Ge_2O_{25}$) is striking: they exhibit closely related frameworks, $M_3P_6Si_2O_{25}$, forming intersecting tunnels which are occupied by A ions in the first compounds and which are empty in the second ones. In order to understand the particular behavior of silicon in $Si_3P_6Si_2O_{25}$ we have studied the replacement of silicon by germanium in that compound. The present work deals with the structure of the oxide $Ge_3P_6Si_2O_{25}$.

Experimental

Single crystals of the composition $Ge_3P_6Si_2O_{25}$ were prepared by heating in a first step mixtures of GeO_2 and SiO_2 oxides and ammonium phosphate $H(NH_4)_2PO_4$ in a

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TABLE I

Atomic Parameters

$Ge_3P_6Si_2O_{25}$				
Atom	X	Y	Z	B_{eq}
Ge(1)	0.33333(0)	−0.33333(0)	0.02428(7)	0.53(1)
Ge(2)	−0.33333(0)	0.33333(0)	0.25000(0)	0.49(2)
P	−0.33737(32)	0.04715(24)	0.39208(9)	0.63(3)
Si	0.00000(0)	0.00000(0)	0.15330(24)	0.39(4)
O(1)	0.42337(75)	−0.11542(80)	0.08972(34)	0.95(13)
O(2)	0.19788(84)	−0.24656(78)	−0.04130(34)	1.06(13)
O(3)	−0.33410(127)	0.13712(93)	0.31159(30)	1.59(17)
O(4)	0.00000(0)	0.00000(0)	0.25000(0)	1.24(27)
O(5)	0.04513(79)	0.20567(78)	0.11759(37)	1.10(13)

platinum crucible in air at 600°C. The resulting product was then added, with traces of molybdenum, to an evacuated silica ampoule and heated at 900°C for 15 days. The presence of molybdenum traces is absolutely necessary for the synthesis of this phase, although the analysis of the crystals, as well as the results of the structure investigation, clearly show that molybdenum has not been trapped in the structure as a major element.

A rectangular plate of 0.084 × 0.096 × 0.024 mm was selected for the structure determination. The Laue patterns showed a trigonal symmetry ($3m$). The cell parameters, initially measured on precession films and later refined by diffractometric techniques with a least-squares refinement based upon 25 reflections, are: $a = b = 7.994(1)$ Å, $c = 16.513(2)$ Å; $Z = 2$ $Ge_3P_6Si_2O_{25}$ formula units. The systematic absences led to $P\bar{3}1c$ or $P31c$ as the space group. The structure refinement was performed in the centrosymmetric group $P\bar{3}1c$. The data were collected on an Enraf–Nonius CAD4 diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 44°$ with a ω–$4/3\theta$ scan of $(1 + 0.35 \tan \theta)°$ and a counter slit aperture of $(1 + \tan \theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane. A periodic check of three control reflections verified the stability of the sample. The 686 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were applied.

Atomic coordinates of the germanium atoms were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Atomic coordinates and their anisotropic thermal motion were refined by full-matrix least-squares with a linear weighting scheme $w = f(\sin \theta/\lambda)$ adjusted by using the program POND (*8*). Final results led to $R = 0.043$ and $R_w = 0.051$ and to the atomic parameters of Table I.[1] Scattering factors for Ge, P, Si, and O were taken from the "International Tables for X-ray Crystallography" (*9*).

Description of the Structure and Discussion

The framework of the oxide $Ge_3P_6Si_2O_{25}$ is built up from corner-sharing GeO_6 octahedra and PO_4 and SiO_4 tetrahedra (Fig. 1).

The Ge–O distances are in agreement with those observed by Mayer and Vollenkle (*7*) in $Ge_3P_6Ge_2O_{25}$. With O–O distances ranging from 2.56 to 2.71 Å the GeO_6 octahedra are rather regular (Table II). Nevertheless, it must be pointed out that Ge(1) is slightly off centered in its octahedron: it exhibits three short Ge–O distances (1.86 Å) and three longer distances (1.89 Å) whereas Ge(2) is characterized by six equal Ge–O bonds (1.87 Å). The geometry of the PO_4 and SiO_4 tetrahedra (Table III) is usual; in each PO_4 tetrahedron the P–O distance involving the oxygen atom common to P and Si is longer than the three other P–O distances. In the same way the Si–O distance belonging to the bridge Si–O–Si of the disilicate group is shorter than the three other Si–O distances as previously observed for the silicophos-

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[1] Lists of structure factors and anisotropic thermal motion parameters are available on request to the authors.

TABLE II

INTERATOMIC DISTANCES AND ANGLES IN THE GeO_6 OCTAHEDRA

Ge(1)	O(1)	$O(1^{i})$	$O(1^{ii})$	O(2)	$O(2^{i})$	$O(2^{ii})$
O(1)	1.862(6)	2.626(9)	2.626(9)	2.672(8)	3.75(1)	2.632(9)
$O(1^{i})$	89.7(3)	1.862(6)	2.626(9)	2.632(9)	2.672(8)	3.75(1)
$O(1^{ii})$	89.7(3)	89.7(3)	1.862(6)	3.75(1)	2.632(9)	2.672(8)
O(2)	90.8(3)	89.1(2)	178.7(3)	1.891(7)	2.69(1)	2.69(1)
$O(2^{i})$	178.7(3)	90.8(3)	89.1(2)	90.5(3)	1.891(7)	2.69(1)
$O(2^{ii})$	89.1(2)	178.7(3)	90.8(3)	90.5(3)	90.5(3)	1.891(7)
Ge(2)	**O(3)**	**$O(3^{iii})$**	**$O(3^{iv})$**	**$O(3^{v})$**	**$O(3^{vi})$**	**$O(3^{vii})$**
O(3)	1.867(8)	2.71(1)	2.71(1)	2.572(8)	3.73(1)	2.56(1)
$O(3^{iii})$	93.1(3)	1.867(8)	2.71(1)	2.56(1)	2.572(8)	3.73(1)
$O(3^{iv})$	93.1(3)	93.1(3)	1.867(8)	3.73(1)	2.56(1)	2.572(8)
$O(3^{v})$	87.1(4)	86.6(3)	179.7(5)	1.867(8)	2.71(1)	2.71(1)
$O(3^{vi})$	179.7(5)	87.1(4)	86.6(3)	93.1(3)	1.867(8)	2.71(1)
$O(3^{vii})$	89.6(3)	179.7(5)	87.1(4)	93.1(3)	93.1(3)	1.867(8)

Note. The diagonal through the cation indicates the cation–oxygen bond length. The values above this diagonal are the O . . . O lengths and the values below it are the O . . . M . . . O angles. See Table III for symmetry operators.

phates $AMo_3P_6Ge_2O_{25}$ (*1–3*), MoP_3SiO_{11} (*4*), and $V_3P_5SiO_{19}$ (*5*).

The structure of $Ge_3P_6Si_2O_{25}$ exhibits a great similarity with the framework of $AMo_3P_6Si_2O_{25}$ and the structure of $Si_3P_6Si_2O_{25}$. The existence in those three structures of the units $P_6Si_2O_{25}$ (Fig. 2) confirms the ability of the PO_4 and SiO_4 tetrahedra to form disilicate groups linked to six PO_4 tetrahedra. In those three structures the $P_6Si_2O_{25}$ units are linked to each other through octahedra in such a way that the MoO_6,

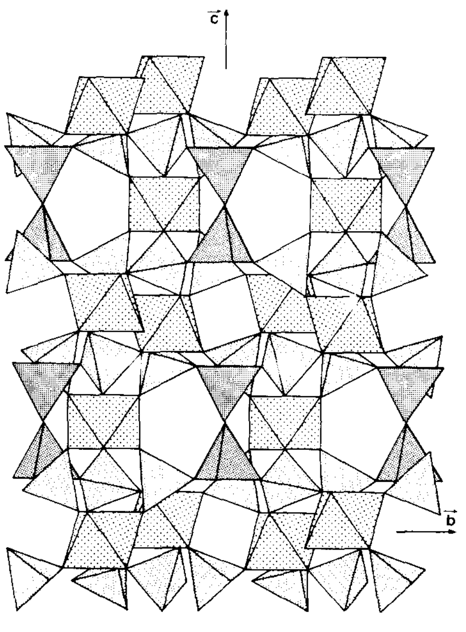

FIG. 1. Projection of the $Ge_3P_6Si_2O_{25}$ structure along *a* onto the (2–10) plane.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE PO_4 AND SiO_4 TETRAHEDRA

P	$O(1^{viii})$	$O(2^{ix})$	O(3)	$O(5^{v})$
$O(1^{viii})$	1.510(8)	2.553(8)	2.473(8)	2.47(1)
$O(2^{ix})$	114.8(3)	1.521(6)	2.507(8)	2.47(1)
O(3)	110.1(4)	111.9(4)	1.505(6)	2.46(1)
$O(5^{v})$	107.1(3)	106.3(4)	106.2(5)	1.567(8)
Si	**O(4)**	**O(5)**	**$O(5^{x})$**	**$O(5^{xi})$**
O(4)	1.597(4)	2.650(6)	2.650(6)	2.650(6)
O(5)	111.5(2)	1.609(7)	2.592(9)	2.592(9)
$O(5^{x})$	111.5(2)	107.4(3)	1.609(7)	2.592(9)
$O(5^{xi})$	111.5(2)	107.4(3)	107.4(3)	1.609(7)

Note. Symmetry operators: i, $-y, x-y-1, z$; ii, $1-x+y, -x, z$; iii, $-y, 1+x-y, z$; iv, $-x+y-1, -x, z$; v, $-y, -x, 0.5-z$; vi, $x, 1+x-y, 0.5-z$; vii, $-x+y-1, y, 0.5-z$; viii, $-x+y, y, 0.5-z$; ix, $y, x, 0.5-z$; x, $-y, x-y, z$; xi, $-x+y, -x, z$.

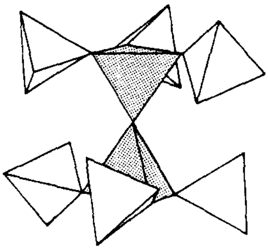

FIG. 2. The $P_6Si_2O_{25}$ unit.

SiO_6, and GeO_6 octahedra have the same orientation, as shown from the view along [001] (Fig. 3). One can also describe those structures as an assemblage of $M_3P_6O_{30}$ columns (Fig. 4) sharing the corners of their polyhedra along [001] and connected to each other through Si_2O_7 groups laterally in (001) planes.

The comparison of the three structures $AMo_3P_6Si_2O_{25}$ (Fig. 5), $Si_3P_6Si_2O_{25}$ (Fig. 6), and $Ge_3P_6Si_2O_{25}$ (Fig. 1) shows that they exhibit appreciable differences in spite of their similarity. Both $AMo_3P_6Si_2O_{25}$ and $Si_3P_6Si_2O_{25}$ exhibit very similar dense layers of $Mo_2P_6Si_2O_{25}$ (or $Si_2P_6Si_2O_{25}$) polyhedra parallel to the (001) plane. Such layers are built up from $P_6Si_2O_{25}$ units linked through the MoO_6 or SiO_6 octahedra. In the two oxides, the $M_2P_6Si_2O_{25}$ layers are linked through MoO_6 or SiO_6 octahedra whose ternary axis is parallel to c.

Both compounds can be described as having intersecting tunnels running along the [100] direction. The difference between the two structures deals with the occupancy of the tunnels which are empty in the case of $Si_3P_6Si_2O_{25}$ and fully occupied by univalent cations (A = K, Rb, Tl, or Cs) in the case of $AMo_3P_6Si_2O_{25}$. Another important difference between the two structures deals with the stacking of the $M_2P_6Si_2O_{25}$ layers along c: two successive layers are deduced one from the other by a binary axis in $AMo_3P_6Si_2O_{25}$ whereas they are displaced of $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$ corresponding to the R lattice in $Si_3P_6Si_2O_{25}$.

The structure of $Ge_3P_6Si_2O_{25}$ differs from the other two compounds by the composition of the dense layers parallel to (001), which do not contain the disilicate group any more, leading to the formulation $[Ge_2P_6Si_2O_{24}]$. Those layers of corner-sharing PO_4 and GeO_6 polyhedra are linked to each other through GeO_6 octahedra as in the two other oxides. Moreover the Si_2O_7 groups ensure the connection between two successive layers, so that the structural

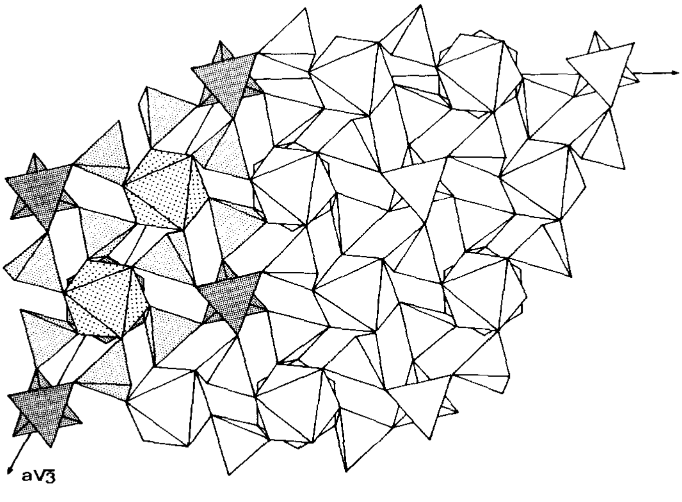

FIG. 3. View along c of the $M_2P_6Si_2O_{25}$ layer.

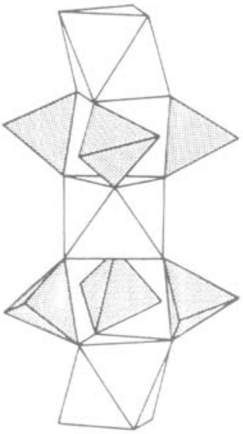

FIG. 4. $AM_3P_6O_{30}$ columns.

units $P_6Si_2O_{25}$ are shared between two $[Ge_2P_6O_{24}]$ layers. In fact paradoxically, the structure of $Ge_3P_6Si_2O_{25}$ is more closely related to that of $AMo_3P_6Si_2O_{25}$. Comparison of Figs. 1 and 5 shows that the $[Mo_2P_6Si_2O_{25}]$ and $[Ge_2P_6O_{24}]$ layers are almost superposable and exhibit the same stacking sequence along *c*. Thus, it appears that the structure of $Ge_3P_6Si_2O_{25}$ can be deduced from that of $AMo_3P_6Si_2O_{25}$ by a simple migration of the "Si_2O" groups of the $[Mo_2P_6Si_2O_{25}]$ layers along *c* by about the height of a tetrahedron. This migration leads to the formation of cages in the $[Ge_2P_6O_{24}]$ layers and stops the extension of the tunnels, which are blocked by the Si_2O_7 groups, leading to the formation of cages between the $[Ge_2P_6O_{24}]$ layers.

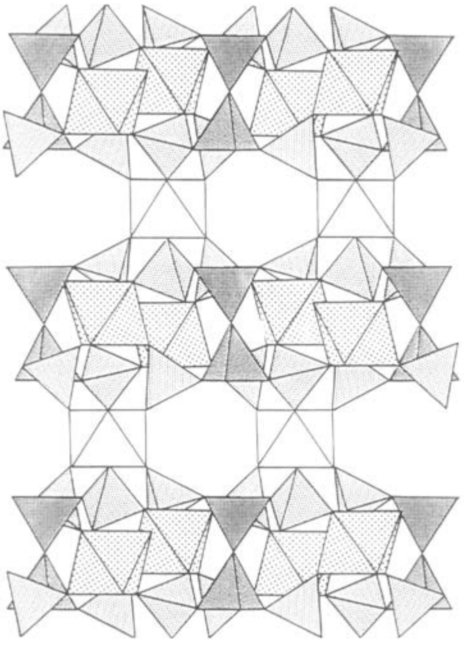

FIG. 5. Projection of the $AM_3P_6Si_2O_{25}$ framework along *a* onto the (2–10) plane.

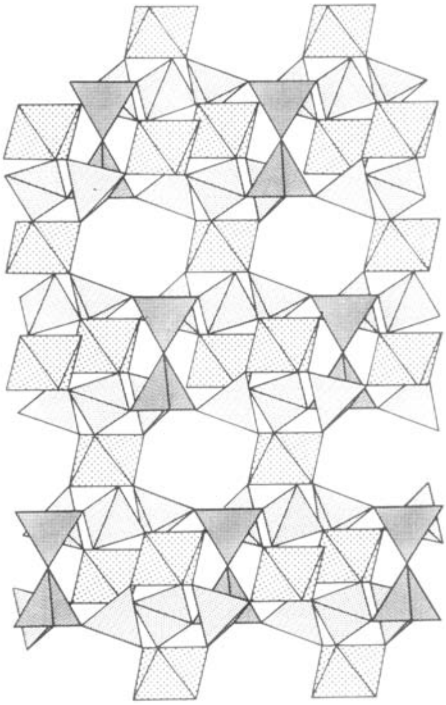

FIG. 6. Projection of the $Si_3P_6Si_2O_{25}$ structure along *a* onto the (2–10) plane.

The crystallographic study of the silicophosphates shows a common feature to these oxides, the structural unit $P_6Si_2O_{25}$. The great similarity between these structures suggests the possibility of a wide field of nonstoichiometry, involving insertion of cations and also a possible intergrowth of these frameworks.

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