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Ge_3O_{10}

IN CRYSTALS

OF COMPOSITION

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CRYSTALLOGRAPHY

1969

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Abstract

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UDC 548.736

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THE GERMANIUM-OXYGEN RADICAL [Ge₃O₁₀] IN CRYSTALS OF COMPOSITION La₂Ge₂O₇

(Presented by Academician N. V. Belov, January 8, 1969)

In recently published works, M. A. Simonov, Yu. K. Egorov-Tismenko, and N. V. Belov described a new silicon-oxygen radical [Si₃O₁₀] in the structures Na₄Cd₂[Si₃O₁₀] and Na₂Cd₃[Si₃O₁₀] [^{1,2}]. A silicon-oxygen radical of the same composition was found by G. Donnay and R. Allmann in determining the structure of the mineral ardennite (³). A germanium-oxygen radical [Ge₃O₁₀], close in structure to [Si₃O₁₀], was found by us in determining the structure of a crystal of composition lanthanum pyrogermanate, La₂Ge₂O₇.

The structure determination was carried out on a crystal grown from a solution-melt in Bi₂O₃. By means of Laue photographs, rotation photographs, and X-ray goniometric scans, it was established that the crystal belongs to the triclinic system. The possible space groups are *P*1, *P* $\bar{1}$. The unit-cell parameters found from scans were then refined on a diffractometer. The following values were obtained: $a = 12.76 \pm 0.01$ Å; $b = 7.070 \pm 0.005$ Å; $c = 7.006 \pm 0.005$ Å; $\alpha = 90^\circ 57' \pm 10'$; $\beta = 90^\circ 21' \pm 10'$; $\gamma = 94^\circ 06' \pm 10'$. The measured density is 5.62 g/cm³; that calculated from 4La₂Ge₂O₇ in the unit cell is 5.64 g/cm³. Measurements of the intensities of X-ray reflections were performed on a single-crystal diffractometer with a scintillation counter according to the perpendicular-beam scheme, by the rotating-crystal-stationary-counter method. Monochromatized by reflection from a crystal-monochromator, Mo *K*α radiation was used. In this way $I(hkl)$ were measured in *l* from 0 to 6 and up to $\sin \theta/\lambda = 1$ Å⁻¹ in each layer. A total of 4100 reflections were measured. The investigated crystal, by the method described in (⁴), was given the shape of a correctly polished sphere 0.22 mm in diameter. The intensities were corrected for polarization, the kinematic factor, and absorption.

The coordinates of the lanthanum atoms in the structure were found by minimizing the three-dimensional Patterson function. It was also thereby established that the heavy atoms are arranged centrosymmetrically, and therefore the space group *P* $\bar{1}$ is probable, which was subsequently confirmed. The positions of the germanium atoms were determined from a three-dimensional difference synthe-

sis (the lanthanum atoms were subtracted). Then the coordinates of the atoms found were refined by the least-squares method ⁽⁵⁾ to an R -factor value of 0.12, and the positions of the oxygen atoms were determined from yet another three-dimensional difference synthesis, in which the heavy atoms with refined parameters had been subtracted.

Next, the coordinates of all atoms were refined by the least-squares method over all 4100 nonzero nonequivalent reflections, using the weighting scheme proposed by Krukshenko ⁽⁶⁾: $w = 1/(a + |F_0| + c|F_0|^2)$, where $a = 2F_{\min}$ and $c = 2/F_{\max}$. In the refinement, atomic scattering functions for neutral atoms were used, calculated from the Dirac-Slater wave functions ⁽⁷⁾ with a dispersion correction for lanthanum and germanium. The final value of the R -factor is 0.059. The refinement results: atomic coordinates, their root-mean-square ...

errors and individual isotropic temperature factors are given in Table 1.

The structure determined in this way is shown in Fig. 1 as a projection onto the plane (001). The circles show the z -coordinates of the atoms in hundredths of the period. As can be seen from the figure, the structure, while formally corresponding to the composition $\text{La}_2\text{Ge}_2\text{O}_7$, contains two types of germanium-oxygen radicals: the triorthogroup $[\text{Ge}_3\text{O}_{10}]$, consisting of three tetrahedra arranged in a chain, and an isolated tetrahedron $[\text{GeO}_4]$. The chemical formula

Table 1

Atomic coordinates, root-mean-square errors, and temperature factors

Atoms	x/a	σ_x/a	y/b	σ_y/b	z/c	σ_z/c	$B, \text{\AA}^2$
La ₁	0.11760	0.00004	0.33317	0.00007	0.04991	0.00012	0.443
La ₂	0.36147	0.00004	0.08655	0.00007	0.11954	0.00012	0.452
La ₃	0.37147	0.00004	0.76274	0.00008	0.63368	0.00012	0.544
La ₄	0.10573	0.00004	0.82812	0.00007	0.33715	0.00012	0.477
Ge ₁	0.11694	0.00008	0.85140	0.00014	0.84472	0.00022	0.488
Ge ₂	0.17307	0.00008	0.32823	0.00014	0.51091	0.00022	0.449
Ge ₃	0.40248	0.00007	0.26510	0.00014	0.62438	0.00022	0.436
Ge ₄	0.61433	0.00008	0.37764	0.00014	0.85236	0.00022	0.475
O ₁	0.1264	0.0006	0.4889	0.0011	0.3568	0.0016	0.823
O ₂	0.2106	0.0006	0.1394	0.0011	0.3683	0.0016	0.891
O ₃	0.0906	0.0006	0.2819	0.0011	0.6995	0.0016	0.736
O ₄	0.3010	0.0005	0.4209	0.0010	0.6036	0.0015	0.657
O ₅	0.4445	0.0006	0.1642	0.0011	0.4436	0.0016	0.763
O ₆	0.3783	0.0006	0.0785	0.0012	0.7761	0.0017	1.061
O ₇	0.5058	0.0006	0.4307	0.0012	0.7033	0.0016	0.934
O ₈	0.6836	0.0005	0.2226	0.0010	0.7068	0.0015	0.582
O ₉	0.5660	0.0006	0.2296	0.0011	0.0333	0.0016	0.857
O ₁₀	0.6831	0.0006	0.5856	0.0011	0.9300	0.0016	0.794

Fig. 1. Structure of $\text{La}_4 \cdot [\text{Ge}_3\text{O}_{10}][\text{GeO}_4]$, projected along the c axis. The circles indicate the z -coordinates of the atoms, in hundredths of the period.

Figure 1: Fig. 1. Structure of $\text{La}_4 \cdot [\text{Ge}_3\text{O}_{10}][\text{GeO}_4]$, projected along the c axis. The circles indicate the z -coordinates of the atoms, in hundredths of the period.

Atoms	x/a	σ_x/a	y/b	σ_y/b	z/c	σ_z/c	$B, \text{Å}^2$
O ₁₁	−0.0030	0.0006	0.9036	0.0011	0.7481	0.0016	0.741
O ₁₂	0.1923	0.0006	0.7818	0.0012	0.6573	0.0017	1.036
O ₁₃	0.0789	0.0006	0.6676	0.0010	0.0067	0.0015	0.697
O ₁₄	0.1835	0.0006	0.0124	0.0011	0.0029	0.0016	0.855

of this compound, taking account of the structural features, should evidently be written as $\text{La}_4[\text{Ge}_3\text{O}_{10}][\text{GeO}_4]$. The coordination number with respect to oxygen for all four La atoms, not related by symmetry, is equal to eight; moreover, not only terminal oxygens (of the triorthogroup and tetrahedron), but also bridging oxygens of the triorthogroup participate in the formation of the lanthanum coordination polyhedra (see Fig. 1).

Table 2 gives the interatomic distances and angles in the triorthogroup and in the tetrahedron.

As can be seen from the values given, the largest germanium–oxygen distances are characteristic of the bridging bonds Ge—O—Ge. This circumstance is apparently connected with the fact that the bridging oxygens, forming two bonds with germaniums, additionally also enter into the coordination polyhedra of the lanthanums (see Fig. 1). The influence of the cation field can also explain some differences in the lengths of the terminal Ge—O bonds. The terminal oxygens of the $[\text{GeO}_4]$ tetrahedra, as can be seen from Table 3, have different coordination with respect to lanthanum.

Seven of the terminal oxygens of the GeO_4 tetrahedra have double coordination with respect to lanthanum, and the remaining five have triple coordination. An increase in the coordination number of a terminal oxygen from two to three is apparently accompanied by an increase in the polarization of the O—Ge bonds and a decrease in their order. Thus, the germanium–oxygen bond lengths for oxygens with coordination 2 with respect to lanthanum vary in the structure from 1.715 to 1.736 Å at

Fig. 1. Structure of $\text{La}_4 \cdot [\text{Ge}_3\text{O}_{10}][\text{GeO}_4]$, projected along the c axis. The circles indicate the z -coordinates of the atoms, in hundredths of the period.

Legend:

La
Ge
O

Table 2
Interatomic distances in Å and angles in the triorthogroup [Ge₃O₁₀]

Ge ₂ —O ₁ 1.715 ± 0.010	O ₃ —O ₄ 2.879 ± 0.010	∠O ₄ —Ge ₃ —O ₆ 115°46′
Ge ₂ —O ₂ 1.750 ± 0.009	O ₄ —O ₅ 2.973 ± 0.012	∠O ₄ —Ge ₃ —O ₇ 99°04′
Ge ₂ —O ₃ 1.715 ± 0.010	O ₄ —O ₆ 2.952 ± 0.013	∠O ₅ —Ge ₃ —O ₆ 105°16′
Ge ₂ —O ₄ 1.826 ± 0.007	O ₄ —O ₇ 2.697 ± 0.011	∠O ₅ —Ge ₃ —O ₇ 106°32′
Ge ₃ —O ₄ 1.765 ± 0.008	O ₅ —O ₆ 2.745 ± 0.016	∠O ₆ —Ge ₃ —O ₇ 113°40′
Ge ₃ —O ₅ 1.734 ± 0.010	O ₅ —O ₇ 2.815 ± 0.013	∠O ₇ —Ge ₄ —O ₈ 103°03′
Ge ₃ —O ₆ 1.720 ± 0.010	O ₆ —O ₇ 2.929 ± 0.012	∠O ₇ —Ge ₄ —O ₉ 108°01′
Ge ₃ —O ₇ 1.779 ± 0.008	O ₇ —O ₈ 2.790 ± 0.011	∠O ₇ —Ge ₄ —O ₁₀ 110°14′
Ge ₄ —O ₇ 1.793 ± 0.009	O ₇ —O ₉ 2.863 ± 0.015	∠O ₈ —Ge ₄ —O ₉ 102°40′
Ge ₄ —O ₈ 1.770 ± 0.008	O ₇ —O ₁₀ 2.895 ± 0.012	∠O ₈ —Ge ₄ —O ₁₀ 116°38′
Ge ₄ —O ₉ 1.745 ± 0.010	O ₈ —O ₉ 2.745 ± 0.014	∠O ₉ —Ge ₄ —O ₁₀ 115°09′
Ge ₄ —O ₁₀ 1.735 ± 0.008	O ₈ —O ₁₀ 2.983 ± 0.012	∠Ge ₂ —O ₄ —Ge ₃ 118°53′
O ₁ —O ₂ 2.766 ± 0.012	O ₉ —O ₁₀ 2.938 ± 0.011	∠Ge ₃ —O ₇ —Ge ₄ 125°30′
O ₁ —O ₃ 2.856 ± 0.015	∠O ₁ —Ge ₂ —O ₂ 105°57′	
O ₁ —O ₄ 2.884 ± 0.012	∠O ₁ —Ge ₂ —O ₃ 112°39′	
O ₂ —O ₃ 2.988 ± 0.014	∠O ₁ —Ge ₂ —O ₄ 109°01′	
O ₂ —O ₄ 2.747 ± 0.012	∠O ₂ —Ge ₂ —O ₃ 119°08′	
	∠O ₂ —Ge ₂ —O ₄ 100°22′	
	∠O ₃ —Ge ₂ —O ₄ 108°44′	
	∠O ₄ —Ge ₃ —O ₅ 116°19′	

Interatomic distances in Å and angles in the tetrahedron [GeO₄]

Ge ₁ —O ₁₁ 1.736 ± 0.008	O ₁₁ —O ₁₃ 2.736 ± 0.013	∠O ₁₁ —Ge ₁ —O ₁₂ 106°32′
Ge ₁ —O ₁₂ 1.718 ± 0.011	O ₁₁ —O ₁₄ 3.013 ± 0.012	∠O ₁₁ —Ge ₁ —O ₁₃ 102°04′
Ge ₁ —O ₁₃ 1.782 ± 0.009	O ₁₂ —O ₁₃ 2.945 ± 0.014	∠O ₁₁ —Ge ₁ —O ₁₄ 119°47′
Ge ₁ —O ₁₄ 1.748 ± 0.008	O ₁₂ —O ₁₄ 2.904 ± 0.015	∠O ₁₂ —Ge ₁ —O ₁₃ 114°35′
O ₁₁ —O ₁₂ 2.768 ± 0.012	O ₁₃ —O ₁₄ 2.695 ± 0.010	∠O ₁₂ —Ge ₁ —O ₁₄ 113°51′
		∠O ₁₃ —Ge ₁ —O ₁₄ 99°30′

Table 3
Interatomic La–O distances in Å

La ₁ —O ₁	2.393 ± 0.011	La ₃ —O ₇	3.048 ± 0.011	La ₂ —O ₁₀	2.455 ± 0.008
La ₁ —O ₂	2.926 ± 0.010	La ₃ —O ₇ '	3.184 ± 0.009	La ₂ —O ₁₄	2.427 ± 0.008
La ₁ —O ₃	2.494 ± 0.011	La ₃ —O ₈	2.488 ± 0.010	La ₄ —O ₁	2.437 ± 0.009
La ₁ —O ₁₀	2.563 ± 0.007	La ₃ —O ₉	2.460 ± 0.011	La ₄ —O ₂	2.497 ± 0.008
La ₁ —O ₁₁	2.587 ± 0.009	La ₃ —O ₁₂	2.307 ± 0.008	La ₄ —O ₃	2.579 ± 0.007
La ₁ —O ₁₃	2.473 ± 0.007	La ₂ —O ₂	2.647 ± 0.009	La ₄ —O ₈	2.755 ± 0.007
La ₁ —O ₁₃ '	2.535 ± 0.007	La ₂ —O ₃	2.349 ± 0.010	La ₄ —O ₁₁	2.461 ± 0.008
La ₁ —O ₁₄	2.492 ± 0.008	La ₂ —O ₆	2.417 ± 0.012	La ₄ —O ₁₂	2.531 ± 0.011
La ₃ —O ₄	2.523 ± 0.007	La ₂ —O ₈	2.551 ± 0.010	La ₄ —O ₁₃	2.571 ± 0.010
La ₃ —O ₅	3.329 ± 0.007	La ₂ —O ₉	2.633 ± 0.009	La ₄ —O ₁₄	2.847 ± 0.010
La ₃ —O ₆	2.426 ± 0.009	La ₂ —O ₉ '	2.803 ± 0.008		

with an average value of 1.725 Å; the lengths of the Ge–O bonds for oxygens in triple coordination vary from 1.745 to 1.782 Å, with an average of 1.759 Å.

In conclusion, the authors express their gratitude to I. A. Bondar, who supplied the crystals investigated.

Institute of Silicate Chemistry named after I. V. Grebenshchikov
Academy of Sciences of the USSR

Received
1 XII 1968

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