5. We thank C. A. Burk, B. H. Erickson, E. L. Hamilton, R. J. Hurley, T. V. Ryan, and H. B. Stewart, Jr., for discussions about the channel. The navigational skill of the officers and crew of the *Pioneer*, *Surveyor*, and *Oceanographer* made this study possible.

13 September 1968; revised 22 November 1968

Garnet-Like Structures of High-Pressure Cadmium Germanate and Calcium Germanate

Abstract. *Crystals of* CdGeO$_3$ *grown at a pressure of 65 kilobars are tetragonal and have an ordered, garnet-like crystal structure with cadmium occupying the dodecahedral and octahedral sites, and germanium the octahedral and tetrahedral sites. The crystal structure* (a = *12.406* ± *1 angstroms,* c = *12.256* ± *1 angstroms, and space group* $I4_1/a$) *has been refined by least-squares analysis to an* R *(discrepancy index) of 0.073. Two high-pressure phases of* CaGeO$_3$ *were synthesized, one isotypic with tetragonal* CdGeO$_3$ (a = *12.514* ± *3 angstroms,* c = *12.358* ± *3 angstroms), and the other isotypic with perovskite.*

In 1963 Ringwood and Seabrook (*1*) reported the synthesis of a high-pressure phase of CaGeO$_3$ which apparently had the garnet structure. They also synthesized CdGeO$_3$, which had an x-ray powder pattern similar to that of garnet except that the reflections were split; this indicated that the symmetry was lower than cubic. Ringwood and Seabrook proposed the formula Cd$_3^{\mathrm{VIII}}$(CdGe)$^{\mathrm{VI}}$Ge$_3^{\mathrm{IV}}$O$_{12}$. However, CaGeO$_3$ also has the lower symmetry, and its x-ray powder patterns can be indexed on a tetragonal cell with a = 12.51 Å, c = 12.36 Å (*2*). Because there has been considerable comment about anisotropic optical properties of garnet (*3*) and because, to our knowledge, no other modifications of garnet with symmetry lower than cubic have been reported, we have investigated the high-pressure CdGeO$_3$ and CaGeO$_3$ phases to determine the actual symmetry and have refined the crystal structure of CdGeO$_3$ because we could prepare better crystals of this phase.

High-purity CdO and GeO$_2$ in a 1:1 molar ratio were thoroughly mixed. The mixture was subjected to a pressure of 65 kb at 1200° to 1400°C for about 4 hours and then quenched. Two CaGeO$_3$ phases were prepared by analogous high-pressure methods, except that the starting material was CaGeO$_3$ with the wollastonite structure. One of these phases has the garnet-like structure (*1*, *2*), and the other is isotypic with perovskite. The tetrahedral anvil used for these high-pressure experiments has been described by Bither *et al.* (*4*).

A Hägg-Guinier photograph was initially taken of the CdGeO$_3$ sample. We assumed that the cell was tetragonal with $a \sim c \sim 12.40$ Å; using a computer program for the assignment of indices and refining by least-squares analysis, we were able to index the pattern and to refine the cell. These results were confirmed with precession photographs of a single crystal, and the space group was identified as $I4_1/a$-C^6_{4h} [absences: for hkl, $h + k + l \neq 2n$ and for $hk0$, $h(k) \neq 2n$]. Other cell data are a = 12.406 ± 1 Å, c = 12.256 ± 1 Å, cell volume (V) = 1.886.3 Å^3, number of formula units per cell (Z) = 32, calculated density (D_x) = 6.56 g cm^{-3}, and absorption coefficient μ = 115.0 cm^{-1} (AgKα radiation). The cell for tetragonal CaGeO$_3$ has a = 12.514 ± 3 Å, c = 12.358 ± 3 Å; we have assumed that CaGeO$_3$ has the same space group as CdGeO$_3$, although no crystals large enough for single-crystal examination have been synthesized. The observed and calculated powder patterns for CdGeO$_3$ and CaGeO$_3$ have been submitted to the powder data file of the American Society for Testing and Materials.

Ringwood and Major (*5*) reported the synthesis of a perovskite form of CaGeO$_3$ at 120 kb and 900°C. This compound appeared to be cubic with a = 3.723 Å. Although one of the phases in our samples of CaGeO$_3$ is also the perovskite type, it would be necessary to double the cell parameter (7.448 ± 2 Å) to account for weak reflections on both the Guinier and precession photographs.

Using a Picker diffractometer with Pd-filtered AgKα radiation, a takeoff angle of 3°, pulse-height analysis, and a scan range for each reflection of 1.5° plus the ($\alpha_1 - \alpha_2$) dispersion, we measured three-dimensional diffraction data (740 nonequivalent reflections). These data were corrected for absorption, and provision was later made for secondary extinction correction during least-squares refinement.

We devised a model for the structure by comparing possible locations in space group $I4_1/a$ with those of the garnet structure in $Ia3d$. In doing this, it was necessary to shift the origin of $I4_1/a$ by ½,¼,⅛ from that given in *International Tables for X-Ray Crystallography* (origin at $\bar{4}$) (*6*). This orients the symmetry elements of $I4_1/a$ in a manner similar to those for $Ia3d$ (*6*). Table 1

Table 1. Relations between equivalent positions in the garnet and CdGeO$_3$ structures and the refined CdGeO$_3$ atom coordinates and isotropic temperature factors.

Garnet space group $Ia3d$				CdGeO$_3$ space group $I4_1/a$						
Site	Equipoint	Symmetry	Coordinates	Atom	Equipoint	Symmetry	Refined coordinates			B (Å^2)
							x	y	z	
Dodecahedral	24c	222	⅛,0,¼	Cd(1)	16f	1	0.1256 ± 1	0.0052 ± 1	0.2564 ± 1	0.64 ± 5
				Cd(2)	8e	2	0	¼	.6236 ± 2	.61 ± 6
Octahedral	16a	$\bar{3}$	0,0,0	Cd(3)	8d	$\bar{1}$	0	0	½	.63 ± 6
				Ge(1)	8c	$\bar{1}$	0	0	0	.43 ± 7
Tetrahedral	24d	$\bar{4}$	⅛,0,¾	Ge(2)	4b	$\bar{4}$	0	¼	⅜	.50 ± 9
				Ge(3)	4a	$\bar{4}$	0	¼	⅞	.36 ± 9
				Ge(4)	16f	1	.1267 ± 2	.0166 ± 2	.7599 ± 2	.37 ± 6
Oxygen	96h	1	x,y,z	O(1)	16f	1	.0251 ± 11	.0672 ± 11	.6718 ± 12	.41 ± 27
				O(2)	16f	1	.0478 ± 11	.0500 ± 11	.8621 ± 11	.36 ± 28
				O(3)	16f	1	.2260 ± 11	.1117 ± 12	.8101 ± 11	.41 ± 27
				O(4)	16f	1	.2148 ± 11	−.0823 ± 11	.7023 ± 12	.28 ± 26
				O(5)	16f	1	−.0653 ± 11	.1636 ± 12	.4696 ± 12	.63 ± 28
				O(6)	16f	1	−.1051 ± 11	.2128 ± 12	.7840 ± 12	.59 ± 28

Table 2. Interatomic distances in the $CdGeO_3$ structure. Standard errors for all distances are ± 0.01 Å.

Atom	Neighboring atom	Distance (Å)
Cd(1)	O(1)	2.25
	O(2)	2.65
	O(3)	2.44
	O(3)	2.44
	O(4)	2.49
	O(4)	2.30
	O(5)	2.30
	O(6)	2.76
	O(av.)	2.45
Cd(2)	2O(1)	2.36
	2O(2)	2.56
	2O(5)	2.32
	2O(6)	2.40
	O(av.)	2.41
Cd(3)	2O(1)	2.29
	2O(4)	2.21
	2O(5)	2.22
	O(av.)	2.24
Ge(1)	2O(2)	1.90
	2O(3)	1.89
	2O(6)	1.90
	O(av.)	1.90
Ge(2)	4O(5)	1.78
Ge(3)	4O(6)	1.78
Ge(4)	O(1)	1.77
	O(2)	1.79
	O(3)	1.82
	O(4)	1.79
	O(av.)	1.79

gives the equipoints (equivalent positions), based on this new orientation, of *Ia*3*d* occupied in the garnet structure and the related equipoints of $I4_1/a$ occupied in the $CdGeO_3$ structure. In $CdGeO_3$, Cd(1) and Cd(2) occupy dodecahedral sites, Cd(3) and Ge(1) octahedral sites, and Ge(2), Ge(3), and Ge(4) tetrahedral sites; there are six oxygen sites. The oxygen sites in $CdGeO_3$ are related to the oxygen site in garnet by the following transformations: x,y,z; $x,\bar{y},3/2-z$; $1/4-x,3/4-z,3/4+y$; $1/4-x,-3/4+z,3/4-y$; $\bar{y},-1/2+z,1/2-x$; $-3/4+z,1/4-y,3/4+x$.

Full-matrix least-squares refinement reduced R ($R = \Sigma|\,|F_{obs}|-|F_{calc}|\,| \div \Sigma|F_{obs}|$, where F is the structure factor) to 0.073 for all the observed reflections. The weighted R was 0.080. In the final cycle of refinement, the scale factor, secondary extinction parameter (C), appropriate atom coordinates, and isotropic temperature factors (B) were varied. The final isotropic temperature factors (Table 1) are all reasonable, although the calculated errors for the B values for oxygen are rather large. This may reflect a somewhat poorer agreement for weak reflections where $l \neq 2n$.

The symmetry of the $CdGeO_3$ structure is lower than that of garnet because all the cadmium and germanium atoms are ordered into distinct crystallographic sites. Examination of the garnet structure shows that this is not the only possible ordering. For example, atoms in the octahedral sites (16*a*) in the space group *Ia*3*d* could order so as to occupy equipoints 8*a* and 8*b* *Ia*3. The dodecahedral and tetrahedral sites would be 24*d* in *Ia*3, and there would be two oxygen atoms in 48*e*. This would require that additional reflections be present because of the loss of the *d* glide plane. To our knowledge, no such ordering has been observed, but possibly this or some other scheme might be as probable as the one observed for $CdGeO_3$.

Reports of noncubic garnets are not restricted to $CdGeO_3$ and $CaGeO_3$ (*3*). Apparently garnets such as uvarovite ($Ca_3Cr_2Si_3O_{12}$), grossularite ($Ca_3Al_2Si_3O_{12}$), and andradite ($Ca_3Fe_2Si_3O_{12}$) are often optically anisotropic, whereas those such as pyrope ($Mg_3Al_2Si_3O_{12}$), almandite ($Fe_3Al_2Si_3O_{12}$), and spessartite ($Mn_3Al_2Si_3O_{12}$) are not. Furthermore, although the external form of anisotropic garnets is usually cubic, the crystals are actually twinned composites of either uniaxial or biaxial individuals. Birefringence disappears at about 800°C and may or may not reappear upon cooling. Although anisotropic character seems to be associated with a large cation in the dodecahedral site, structure refinements of pyrope also raise questions about small cations in the dodecahedral site. Zemann and Zemann (*7*) suggested that magnesium is not actually in the center of the dodecahedron but rather is statistically distributed on either side of the center. Gibbs and Smith (*8*), however, thought that this was due to thermal anisotropy and was not a static displacement.

Table 2 lists the interatomic distances for the $CdGeO_3$ structure. Cd(1) and Cd(2) are each surrounded by eight oxygen atoms in a distorted triangular dodecahedron at average distances of 2.45 Å and 2.41 Å, respectively; the distance between ^{VIII}Cd and ^{IV}O, predicted on the basis of the Shannon and Prewitt (*9*) table of effective ionic radii, is 2.45 Å. Some difficulty exists with Cd(3), however, because it is octahedrally coordinated with an average distance of 2.24 Å, whereas the predicted value for the distance between ^{VI}Cd and ^{IV}O is 2.33 Å. It is difficult to explain this large difference because it seems unlikely that there could be a mixing of Ge and Cd in the octahedral sites. The average observed distance between Ge(1) and oxygen is 1.90 Å; the predicted value is 1.92 Å, thus effectively eliminating the possibility that Cd might be substituting for Ge here. The anomaly might be a real feature since unusual interatomic distances are often found in garnet structures. The tetrahedral Ge-O distances of 1.77 Å, 1.78 Å, and 1.79 Å are in good agreement with the predicted value of 1.78 Å (Table 2).

C. T. PREWITT
A. W. SLEIGHT

Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

References and Notes

1. A. E. Ringwood and M. Seabrook, *J. Geophys. Res.* **68**, 4601 (1963).
2. S. Geller, *Z. Krist.* **125**, 1 (1967).
3. A. N. Winchell and H. Winchell, *Elements of Optical Mineralogy* (Wiley, New York, 1961), part 2.
4. T. A. Bither, J. L. Gillson, H. S. Young, *Inorg. Chem.* **5**, 1559 (1966).
5. A. E. Ringwood and A. Major, *Earth Planet. Sci. Lett.* **2**, 106 (1967).
6. *International Tables for X-Ray Crystallography* (Kynoch Press, Birmingham, England, 1952), vol. 1.
7. A. Zemann and J. Zemann, *Acta Cryst.* **14**, 835 (1961).
8. G. V. Gibbs and J. V. Smith, *Amer. Mineral.* **50**, 2023 (1965).
9. R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, in press.
10. Contribution No. 1499 from the Central Research Department.

1 November 1968

Bird Energetics: Effects of Artificial Radiation

Abstract. *Radiant energy reduces oxygen consumption in birds; this reduction is correlated with feather color, being greater in dark birds (26 percent reduction) than in white ones (6 percent reduction). With radiant energy (basking), the cowbird effectively increased its insulation, thus shifting the lower end of the zone of thermal neutrality down by as much as 10°C (35° to 25°C).*

Some birds sunbathe (*1*) and Lanyon (*2*) has suggested that the stimulus which initiates sunbathing behavior is heat. As early as 1925, Cartwright and Harrold (*3*) set forth the hypothesis that a governing principle of avian metabolism is radiant energy and that the absorption of this radiation is dependent upon the coloration of the plumage. Morton (*4*) showed that at low air temperatures, white-crowned sparrows (*Zonotrichia leucophrys*) that received radiant energy