

OLIVINE STRUCTURE OF CADMIUM ORTHO-GERMANATE

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Abstract— Cd_2GeO_4 is orthorhombic, space group $Pbnm$ with:

$$a_0 = 5.20 \quad b_0 = 11.13 \quad c_0 = 6.57 \text{ \AA}$$

Simultaneous use of infra-red spectroscopy and X-ray powder diffractometry prove it possesses the olivine structure.

CADMIUM ortho-germanate has been synthesized by LUDEKENS,⁽¹⁾ who also gave an unindexed powder diffraction diagram, but no structural study of this substance has been reported so far.

This paper describes infra-red absorption and X-ray powder diffraction data which prove the olivine structure of Cd_2GeO_4 .

RESULTS

Infra-red absorption spectra

a. *Pure compound.* It has been shown by the author that isomorphic or isotypic substances of the same chemical type generally give fairly similar infra-red absorption spectra,⁽²⁾ at least in the high frequency region, and a detailed study of the relationships between infra-red spectrum and structure has been made for silicates and germanates possessing the olivine structure.⁽³⁾

On the other hand, structurally different compounds always give different absorption patterns. Thus, if two compounds of the same chemical type give very similar infra-red patterns, it is highly probable that these compounds are isotypic (or at least are structurally related).

The infra-red spectra of Mn_2GeO_4 (which belongs to the olivine group)⁽⁴⁾ and Cd_2GeO_4 are given in Fig. 1. The spectra are nearly identical, and it may be inferred that these compounds most probably are isotypic, and thus that Cd_2GeO_4 has the olivine structure.

b. *Dilute solid solution* $\text{Cd}_2(\text{Ge}_{0.99}\text{Si}_{0.01})\text{O}_4$. Dilute solid solutions may give highly characteristic infra-red patterns.⁽²⁾ In the case of germanates of the olivine type, the occurrence of a small quantity (1 mole %) of SiO_4 ions in solid solution is characterized by three narrow peaks in the 1000–800 cm^{-1} region.⁽³⁾ The results given by $\text{Mn}_2(\text{Ge}_{0.99}\text{Si}_{0.01})\text{O}_4$ and $\text{Cd}_2(\text{Ge}_{0.99}\text{Si}_{0.01})\text{O}_4$ solid solutions are illustrated by Fig. 2.

Here again, the striking similarity of the infra-red patterns strongly supports the structural analogy of Mn_2GeO_4 and Cd_2GeO_4 .

⁽¹⁾ W. L. W. LUDEKENS, *J. Inorg. Nucl. Chem.* **3**, 281 (1956).

⁽²⁾ P. TARTE, *Mém. Acad. Roy. Belg.* in press.

⁽³⁾ P. TARTE, *Spectrochim. Acta* **19**, 25 (1963).

⁽⁴⁾ A. DURIF-VARAMBON, Thèse de Doctorat, Grenoble (1958).

A detailed discussion of the observed effects and of their theoretical interpretation is out of place here and has been presented elsewhere.⁽⁵⁾ It is worth while to mention, however, that the occurrence of three widely separated peaks points to a fairly important deformation of the SiO_4 and GeO_4 tetrahedra.⁽³⁾

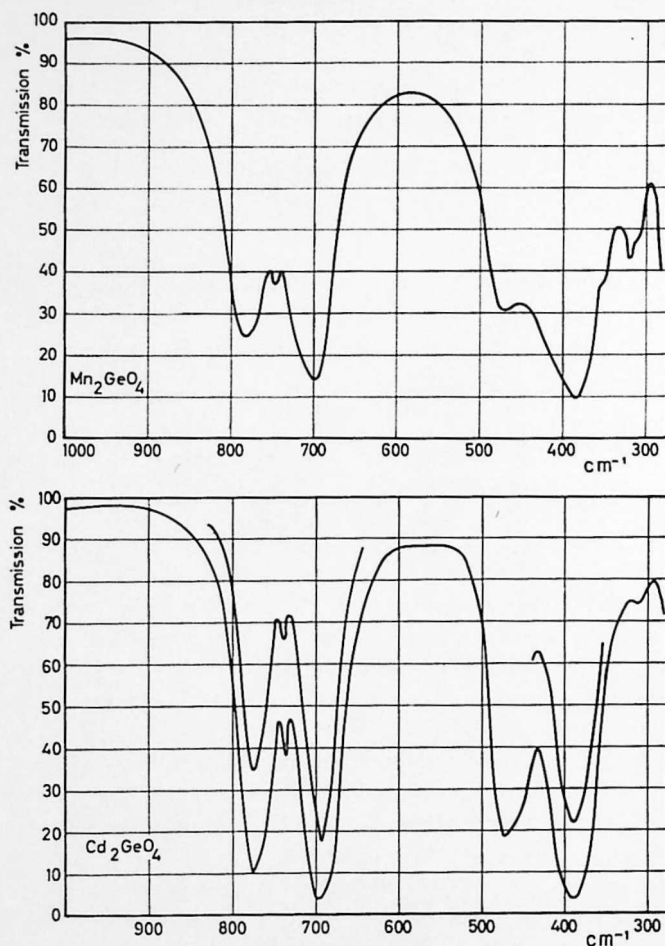


FIG. 1.—Infra-red absorption spectra of Mn_2GeO_4 and Cd_2GeO_4 .

X-ray powder diffraction data

On the hypothesis of an olivine structure, the X-ray powder diagram (Table 1) can be immediately indexed on the basis of an orthorhombic cell, space group $Pbnm$, with:

$$a_0 = 5.20 \quad b_0 = 11.13 \quad c_0 = 6.57 \text{ \AA}$$

Moreover, this powder diagram is very similar to those given by Mg_2GeO_4 , Mn_2GeO_4 and Ca_2GeO_4 . These data definitely confirm the olivine structure suggested by the infra-red spectra.

⁽⁵⁾ P. TARTE, *Spectrochim. Acta* **18**, 467 (1962).

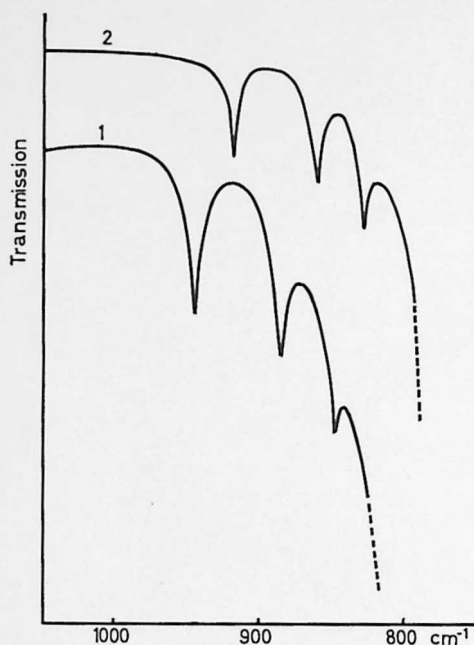


FIG. 2.—Infrared absorption pattern of SiO_4 tetrahedra in the dilute solid solutions $\text{Mn}_2(\text{Ge}_{0.99}\text{Si}_{0.01})\text{O}_4$ (curve 1) and $\text{Cd}_2(\text{Ge}_{0.99}\text{Si}_{0.01})\text{O}_4$ (curve 2). The strong absorption near and below 800 cm^{-1} is due to GeO_4 tetrahedra.

DISCUSSION

Cell dimensions and ionic radii

The cell dimensions of the different germanates having the olivine structure are collected in Table 2.

The experimental data related to Cd_2GeO_4 fit very well the general increase of the unit cell dimensions with increasing ionic radius of the cation. It should be noticed, however, that no linear relationship can be found between r_{ion} and a_0 , b_0 or c_0 (Fig. 3). Clearly, the unit cell dimensions of Cd_2GeO_4 are smaller than could be expected from the data related to Ca_2GeO_4 . This effect is also observed with Goldschmidt's scale of ionic radii, and thus is likely to be real. It is most probably related to differences in the electronic structures of Cd and Ca. In fact, if the electronic structures of the cations are taken into account, all the points related to the cations with d electrons (Mn and Cd) lie above the straight line joining the cations free from d electrons (Mg and Ca). In other words, the cations with d electrons lead to comparatively smaller cell dimensions than those cations free from d electrons.

Structure of corresponding silicates and germanates

It is fairly frequently found that corresponding silicates and germanates are isostructural. This rule is poorly verified for the olivine structure, since out of seven cations, three only give isostructural silicates and germanates (Table 3).

TABLE 1.—X-RAY POWDER DIAGRAM OF Cd_2GeO_4

Relative intensity	$d_{\text{obs.}}$	h	k	l	$d_{\text{calc.}}$	$d_{\text{calc.}} - d_{\text{obs.}}$
3	5.553	0	2	0	5.565	+0.012
4	4.701	1	1	0	4.714	+0.013
6	4.243	0	2	1	4.246	+0.003
2	4.074	1	0	1	4.079	+0.005
37	3.826	1	1	1	3.830	+0.004
11	3.289	0	0	2	3.285	-0.004
		1	2	1	3.289	0.000
88	3.020	1	3	0	3.021	+0.001
50	2.827	0	2	2	2.829	+0.002
10	2.782	0	4	0	2.782	0.000
90	2.744	1	3	1	2.745	+0.001
>100	2.692	1	1	2	2.694	+0.002
33	2.599	2	0	0	2.601	+0.002
20	2.563	0	4	1	2.562	-0.001
3	2.531	2	1	0	2.533	+0.002
3	2.452	1	4	0	2.453	+0.001
8	2.360	2	1	1	2.363	+0.003
		2	2	0	2.357	-0.003
4	2.221	1	3	2	2.224	+0.003
		2	2	1	2.218	-0.003
7	2.122	0	4	2	2.123	+0.001
6	2.046	1	5	0	2.046	0.000
2	2.005	2	1	2	2.006	+0.001
11	1.985	1	1	3	1.986	+0.001
7	1.954	1	5	1	1.954	0.000
74	1.913	2	2	2	1.915	+0.002
26	1.899	2	4	0	1.900	+0.001
		1	2	3	1.897	-0.002
17	1.824	2	4	1	1.825	+0.001
18	1.786	2	3	2	1.787	+0.001
		0	6	1	1.786	0.000
27	1.773	1	3	3	1.773	0.000
20	1.737	1	5	2	1.737	0.000
12	1.721	0	4	3	1.721	0.000
?	1.714	3	1	0	1.713	-0.001
1	1.675	3	0	1	1.677	+0.002
11	1.656	3	1	1	1.658	+0.002
		3	2	0	1.655	-0.001
		2	1	3	1.657	+0.001
27	1.643	0	0	4	1.642	-0.001
		2	4	2	1.645	+0.002
27	1.616	0	6	2	1.615	-0.001
1	1.605	2	2	3	1.605	0.000
		3	2	1	1.606	+0.001
11	1.570	3	3	0	1.571	+0.001
5	1.527	3	3	1	1.528	+0.001
		2	3	3	1.526	-0.001
30	1.520	1	7	0	1.520	0.000
		3	1	2	1.519	-0.001
3	1.496	1	5	3	1.495	-0.001
5	1.478	3	2	2	1.478	0.000

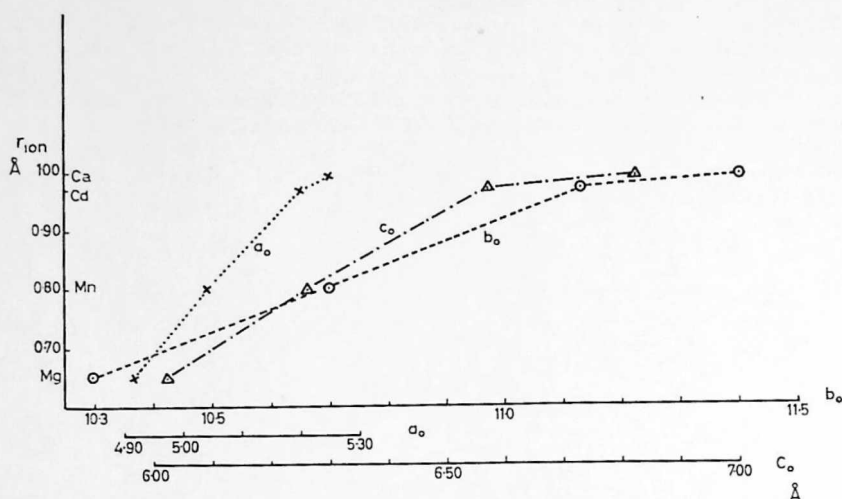


FIG. 3.—Relationship between the cell dimensions and the ionic radius (Pauling scale) of the cation for the olivine germanates X_2GeO_4 ($X = Mg, Mn, Cd$ and Ca).

TABLE 2

Substance	Ionic radius of the cation (Pauling scale)	a_0	b_0	c_0	Ref.
Mg_2GeO_4	0.65	4.915	10.295	6.020	4
Mn_2GeO_4	0.80	5.04	10.7	6.26	4
Cd_2GeO_4	0.97	5.20	11.13	6.57	this work
Ca_2GeO_4	0.99	5.25 5.14	11.4 11.55	6.82 6.88	4 6

TABLE 3

Cation	Type of structure	
	Silicate	Germanate
Mg	Olivine	Olivine and spinel
Ni	Olivine	Spinel
Co	Olivine	Spinel
Fe	Olivine	Spinel
Mn	Olivine	Olivine
Cd	Peculiar structure	Olivine
Ca	Olivine (γ form)	Olivine

EXPERIMENTAL

Cadmium ortho-germanate has been synthesized by solid state reaction between CdO and GeO_2 of analytical purity. Stoichiometric quantities of the 2 oxides are thoroughly ground and mixed under petroleum ether, the mixture is slowly heated in a covered platinum crucible up to $900^\circ C$,

(6) H. STRUNZ and P. JACOB, *N. Jb. Mineral., Mh.* 78 (1960).

and this temperature is maintained for 5 hr. The infra-red spectrum and the X-ray powder diffraction diagram of the resulting product show no detectable amount of CdO, GeO₂ or CdGeO₃.

Samples for infra-red spectroscopy were prepared in the form of KBr discs. The spectra were scanned with Perkin-Elmer spectrometers equipped with NaCl, KBr and CsBr prisms. The X-ray powder diffraction diagram was obtained with a C.G.R. diffractometer, using Cu K α radiation.

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