Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1968). B24, 459

The crystal structures of LaC_2.*

By A. L. Bowman, N. H. Krikorian, G. P. Arnold, T. C. Wallace and N. G. Nereson, *Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico* 87544, *U.S.A.*

(*Received* 26 *October* 1967)

Lanthanum dicarbide has been examined by high-temperature neutron diffraction and by thermal analysis. A tetragonal to cubic transformation has been observed at 1060°C, with lattice parameters $a_0 = 4{\cdot}00$, $c_0 = 6{\cdot}58$ Å at 900°C and $a_0 = 6{\cdot}02$ Å at 1150°. The structure of the tetragonal phase was found to be the *C*11*a* calcium carbide-type, in agreement with previous room temperature results. The structure of the cubic phase is the KCN type. Both phases are isomorphous with the corresponding uranium dicarbide phases.

The existence of the rare earth dicarbides (including yttrium) is well established. The crystal structures of LaC_2, CeC_2, TbC_2, YC_2, YbC_2 and LuC_2 have been described from room temperature neutron diffraction studies (Atoji, 1961) as the *C*11*a* calcium carbide structure: tetragonal, space group $I4/mmm$, with metal atoms in (0,0,0) and carbon atoms in $(0,0,z)$, $z \sim 0{\cdot}40$. A systematic investigation of these dicarbides by thermal analysis, X-ray diffraction and high-temperature neutron diffraction has shown that they transform to cubic phases at high temperatures. Possible exceptions are YbC_2 and EuC_2. The existence of EuC_2 could not be confirmed. In addition, the tetragonal structure of LuC_2 could not be obtained except through the addition of erbium as an impurity. The details of the neutron diffraction experiments are described in this paper. The remainder of this work has been described previously (Krikorian, Wallace & Bowman, 1967).

A sample of lanthanum dicarbide was prepared from the high-purity elements by arc-melting and pulverizing. The composition by chemical analysis was $LaC_{2{\cdot}0}$ with < 500 ppm oxygen and free carbon. The sample was examined by high-temperature neutron diffraction (Bowman, Hull, Witteman, Arnold & Bowman, 1966) in a graphite holder under an atmosphere of flowing helium. The diffraction data were obtained from $2\theta = 25$ to 70° at a wavelength of 1·3926 Å, and were corrected by subtracting a blank run on the graphite sample holder. The corrected patterns are shown in Fig. 1. Additional scans were taken at $2\theta = 25$–30° in order to determine the transition temperatures. Observed intensities were determined by least-squares analysis of the diffraction data (Bowman, Wallace, Yarnell, Wenzel & Storms, 1965), and were fitted to trial structures by least-squares solution of the equation (Bacon, 1962)

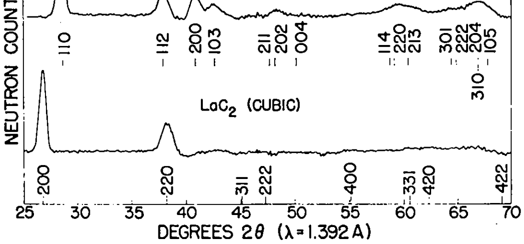

Fig. 1. Neutron diffraction patterns of lanthanum dicarbide.

Table 1. *Neutron diffraction data*

$LaC_2(t)$

d	hkl	I_o	I_c
2·83	110	56·0	55·7
2·15	112	24·0	21·1
2·00	200	20·5	24·2
1·92	103	13·4	12·5
1·73	211	0·0	0·9
1·71	202	7·9	11·5
1·64	004	0·0	0·0
1·42	114	0·0	0·1
1·41	220	12·5	9·4
1·39	213	9·4	10·0
1·31	301	7·9	5·5
1·30	222		
1·27	204	24·5	25·7
1·26	310		
1·25	105		

$LaC_2(c)$

d	hkl	I_o	I_c
3·01	200	55·1	55·1
2·13	220	30·8	30·8
1·82	311	0·0	2·3
1·78	222	1·3	8·1
1·50	400	5·3	1·5
1·38	331	5·6	2·3
1·34	420	2·7	3·8

$$I = K\frac{\exp\left(-\mu t \sec\theta\right)}{\sin^2 2\theta}\exp\left(\frac{-2B\sin^2\theta}{\lambda^2}\right)jF^2 \,. \qquad (1)$$

Scattering amplitudes of 0·83 for lanthanum and 0·661 for carbon (both $\times 10^{-12}$ cm) were used.

A tetragonal to cubic transition was observed at 1060°, in excellent agreement with the value determined by ther-

---

[*] Work done under the auspices of the U.S. Atomic Energy Commission.

mal analysis. The structure of the tetragonal phase was found to be the $C11a$ type, in agreement with the previous room-temperature results. The LaC_2 pattern at 900°C gave $K=0\cdot24\pm0\cdot01$, $B=3\cdot1\pm0\cdot6$, $z=0\cdot404\pm0\cdot002$, $R=0\cdot08$, where $R=\Sigma w|I_o-I_c|/\Sigma wI_o$. Lattice parameters were $a_0=4\cdot000$, $c_0=6\cdot58$, giving a C–C distance of $1\cdot26\pm0\cdot03$ Å. The structure of the cubic phase was found to be the KCN type, isomorphous with cubic uranium dicarbide (Bowman, Arnold, Witteman, Wallace & Nereson 1966). This structure is face-centered, space group $Fm3m$, with metal atoms in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and C_2 groups with centers at (0,0,0) randomly oriented along [111] directions. Intensities were calculated on the basis of one-fourth of a carbon atom in (x,x,x). The C_2 groups may also be described by a free rotator model. There seems to be no significant difference between the two models. The LaC_2 pattern at 1100° gave $K=0\cdot06\pm0\cdot01$, $B=5\cdot6\pm2\cdot0$, $x=0\cdot061\pm0\cdot012$, $R=0\cdot02$. With $a_0=6\cdot022$, $d_{\text{C–C}}=1\cdot27\pm0\cdot06$ Å. The observed C–C distances are in reasonable agreement with the room temperature value of 1·30 Å (Atoji, 1961). The actual values may be somewhat larger, however, owing to the effect of thermal motion of the carbon atoms.

References

ATOJI, M. (1961). *J. Chem. Phys.* **35**, 1950.

BACON, G. E. (1962). *Neutron Diffraction*. Oxford: Clarendon Press.

BOWMAN, A. L., WALLACE, T. C., YARNELL, J. L., WENZEL, R. G. & STORMS, E. K. (1965). *Acta Cryst.* **19**, 6.

BOWMAN, A. L., ARNOLD, G. P., WITTEMAN, W. G., WALLACE, T. C. & NERESON, N. G. (1966). *Acta Cryst.* **21**, 670.

BOWMAN, M. G., HULL, D. E., WITTEMAN, W. G., ARNOLD, G. P. & BOWMAN, A. L. (1966). *Rev. Sci. Instrum.* **37**, 1543.

KRIKORIAN, N. H., WALLACE, T. C. & BOWMAN, M. G. (1967). *Propriétés Thermodynamiques, Physiques et Structurales des Dérivés Semi-Métalliques*, p.489–94. Paris: Centre National de la Recherche Scientifique.

Acta Cryst. (1968). B**24**, 460

Crystal data for sodium tetragermanate

By J. H. JOLLY and R. L. MYKLEBUST, *College Park Metallurgy Research Center, Bureau of Mines, College Park, Maryland, U.S.A.*

(*Received* 11 *July* 1967)

Single-crystal X-ray studies on sodium tetragermanate, $Na_2Ge_4O_9$, gave $a_0=11\cdot335$ $c_0=9\cdot697$, space group $P6_3/m$, $Z=6$. This colorless transparent compound with $\omega=1\cdot731$ and $\varepsilon=1\cdot773$ has a measured density of 4·41 g.cm^{-3} (27°C). Indexed powder data are listed.

Small single crystals of sodium tetragermanate ($Na_2Ge_4O_9$) were grown in slowly cooled 1:4 Na_2O–GeO_2 melts. The crystal data for the compound have not been published although Schwarz & Heinrich (1932) and Tresvyats'kii (1958) reported $Na_2Ge_4O_9$ in their studies of the Na_2O–GeO_2 phase system. Nowotny & Wittmann (1954) reported a $Na_2Ge_4O_9$ modification isotypic with $K_2Ge_4O_9$ and Shaw, Corwin & Edwards (1958) grew from a 1:4 Na_2CO_3–GeO_2 melt, a crystalline compound having indices of refraction very similar to those found in this study. A more recent investigation of the Na_2O–GeO_2 phase system by Murthy & Aguayo (1964) questioned the existence of sodium tetragermanate; however, chemical analysis and crystallographic data confirm $Na_2Ge_4O_9$ as a valid compound.

The crystals are colorless, transparent with a vitreous luster and have no apparent cleavage. The only crystal form present is the first order hexagonal prism $(10\bar{1}0)$; the terminating faces are not developed or interfered with by other crystal growth. The refractive indices of the crystal, measured by immersion oils for sodium light ($\lambda=589\cdot2$ mμ) at 25°C, are $\varepsilon=1\cdot773\pm0\cdot001$ and $\omega=1\cdot731\pm0\cdot001$.

Since the only systematic extinctions observed in Weissenberg and precession photographs were for $000l$, where l is odd, the crystals are in hexagonal crystal class 6 or $6/m$. A thin section (0·2 mm thick) containing crystals oriented normal to the c axis was examined under the petrographic microscope using sodium light. No optical activity was observed and, therefore, it is concluded that the crystal class is probably $6/m$ and the space group is $P6_3/m$.

The X-ray diffraction data of a powdered sample (Table 2) were measured on a calibrated Norelco diffractometer at $\frac{1}{4}°\,2\theta$ per minute using filtered copper radiation. A least-squares refinement program of these data on an IBM 7094 computer yielded the lattice constants with e.s.d.'s listed in Table 1.

Table 1. *Crystal data for* $Na_2Ge_4O_9$

$a\ =11\cdot335\pm0\cdot001$ Å (25°C)
$c\ =\ 9\cdot697\pm0\cdot001$ Å (25°C)
$c/a=0\cdot8555$
$V\ =1245\cdot9$ Å^3
$D_m=4\cdot41\pm0\cdot02$ g.cm^{-3} (27°C)
$D_x\ =4\cdot435$ g.cm^{-3}
$Z\ =6$

Table 2. *Diffraction data for* $Na_2Ge_4O_9$

hkl	$d(hkl)$	$10^4 \sin^2\theta_o$	$10^4 \sin^2\theta_c$	I_o
110	5·66 Å	185	185	65
111	4·89	249	248	53
002	4·84	254	253	44
102	4·34	316	314	5
112	3·68	439	438	20
211	3·45	498	495	20
202	3·44	501	499	6
300	3·26	559	556	2
301	3·105	615	618	1
212	2·943	685	684	35
220	2·830	740	740	6
113	2·802	755	754	37