
Literatur

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Crystal data and structural relation between Pb₆GeO₈, Pb₁₁Ge₃O₁₇ and PbO. By H. H. Otto, Fachbereich Physik der Universit/ität Regensburg, Postfach 397, D 8400 Regensburg 2, Federal Republic of Germany

(Received 7 November 1979; accepted 1 December 1979)

Abstract

Transparent yellow-greenish single crystals of Pb₆GeO₈ were obtained by spontaneous crystallization from a melt with a molar ratio of PbO·GeO₂= 4:7:1. The compound is monoclinic, probable space group P2₁/a, a = 52,665 (12), b = 15,063 (4), c = 23,949 (6) Å and β = 111,03 (5)°; D₄ (293 K) = 8,653 (3), D₄ = 8,653 Mg m⁻³ for Z = 64 formula units. Pb₁₁Ge₃O₁₇ was synthesized by sintering high-purity oxides PbO and GeO₂ of molar ratio 3:6:1 at 990 K. The compound is also monoclinic, probable space groups C2/c or Cc, a = 25,117 (5), b = 15,440 (2), c = 45,529 (13) Å and β = 103,20 (4); D₄ (293 K) = 8,55 (2), D₄ = 8,560 Mg m⁻³ for Z = 32. The crystal structural relation between both compounds and PbO is discussed. Indexed X-ray powder data are given.

0021-8898/80/030307-04$01.00 © 1980 International Union of Crystallography
Introduction

A phase of composition Pb₆GeO₈ was first proposed by Speranskaya (1959) and later questioned several times by different authors. It has now become evident that she did not really study Pb₆GeO₈ but rather Pb₃GeO₅, which was recently described by Hirota & Sekine (1979) and by Otto (1979a) in detail and confirmed by Kato (1979). The present work shows, however, that a phase of composition Pb₆GeO₈ exists nevertheless. Moreover, structural similarities between Pb₆O₈, Pb₃GeO₅ and Pb₁₁Ge₃O₁₇ were found. Pb₁₁Ge₃O₁₇ was confirmed to be stable below 1001 K by Hirota & Sekine (1979).

Origin of specimens

Starting materials for the lead germanate synthesis were Optipur-quality red PbO from Merck Chemical Corp. and Specpure-quality GeO₂ (quartz modification) from Johnson Matthey Chemicals Ltd. The oxides were well mixed and sintered in a gold crucible at 990 K in air to prevent their reaction. The calcining product was reground and the sintering procedure repeated since the oxides react sluggishly. Following this procedure, equilibrium was reached after 50 h. With a molar ratio of PbO:GeO₂ = 5.9:1, the X-ray powder diagram of the material obtained shows no evidence for the existence of a Pb₆GeO₈ phase of composition Pb₄GeO₆ proposed by Phillips & Scroger (1965), Bush & Venevtsev (1978) and Breuer (1978). Starting materials for the lead germanate synthesis were Optipur-quality red PbO from Merck Chemical Corp. and Specpure-quality GeO₂ (quartz modification) from Johnson Matthey Chemicals Ltd. The oxides were well mixed and sintered in a gold crucible at 990 K in air to prevent their reaction. The calcining product was reground and the sintering procedure repeated since the oxides react sluggishly. Following this procedure, equilibrium was reached after 50 h. With a molar ratio of PbO:GeO₂ = 5.9:1, the X-ray powder diagram of the material obtained shows no evidence for the existence of a Pb₆GeO₈ phase of composition Pb₄GeO₆ proposed by Phillips & Scroger (1965), Bush & Venevtsev (1978) and Breuer (1978).

Pb₁₁Ge₃O₁₇ is also monoclinic. The probable space groups are C2/c (C₆h) or Cc (C₆). Its unit cell has about the same volume but the lattice constants are altered so that a is halved and c is doubled compared with Pb₆GeO₈. The measured density Dₚ = 8.55 (2) Mg m⁻³ yields Z = 32 formula units. From this the calculated density is Dc = 8.560 Mg m⁻³. The crystal data of Pb₁₁Ge₃O₁₇ are given in Table 2.

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Unit-cell data

Pb₆GeO₈ is monoclinic. The lattice constants were determined from precession records and refined by least-squares methods using indexed Guinier counter diffractometer data as presented in Table 3. The probable space group is P2₁/a (C₅h). The density of Pb₆GeO₈ was calculated from that of the mixture containing Pb₆GeO₈ and Pb₃GeO₅. Its density measured by toluene displacement in a pycnometer at 293 K was Dₚ = 8.614 (15) Mg m⁻³. Using Dₚ = 8.52 (5) Mg m⁻³ for Pb₃GeO₅ (Otto, 1979b), one obtains Dₚ = 8.65 (3) Mg m⁻³ for Pb₆GeO₈. The calculated density is Dc = 8.653 Mg m⁻³ for Z = 64 formula units. The crystal data are summarized in Table 1.

Table 1. Crystal data for Pb₆GeO₈

| Space group: | P₂₁/a (C₅h) | V = 17733 Å³ |
| a = 52.665 (12) Å | Dₚ(293 K) = 8.65 (3) Mg m⁻³ |
| b = 15.063 (4) | Dc = 8.653 |
| c = 23.949 (6) | Z = 64 |
| β = 111.03 (5)° | Twinning on (001) |

Pb₁₁Ge₃O₁₇ is also monoclinic. The probable space groups are C2/c (C₆h) or Cc (C₆). Its unit cell has about the same volume but the lattice constants are altered so that a is halved and c is doubled compared with Pb₆GeO₈. The measured density Dₚ = 8.55 (2) Mg m⁻³ yields Z = 32 formula units. From this the calculated density is Dc = 8.560 Mg m⁻³. The crystal data of Pb₁₁Ge₃O₁₇ are given in Table 2.

Table 2. Crystal data for Pb₁₁Ge₃O₁₇

| Space group: | C2/c (C₆h) | V = 17190 Å³ |
| a = 25.117 (5) Å | Dₚ(293 K) = 8.55 (2) Mg m⁻³ |
| b = 15.440 (2) | Dc = 8.560 |
| c = 41.560 (13) | Z = 32 |
| β = 103.20 (4)° |

Table 3. Guinier diagram of Pb₆GeO₈

<table>
<thead>
<tr>
<th>I/I₀</th>
<th>2θa</th>
<th>2θc</th>
<th>dₐ</th>
<th>dₜ</th>
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<tr>
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<td>5.5500</td>
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<td>3.2526</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>2.9452</td>
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<td>2.9062</td>
<td>2.9062</td>
<td>16 0 1</td>
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</tr>
</tbody>
</table>

d = diffuse or broad.
X-ray powder data

The powder data of Pb₆GeO₈ (Table 3) and Pb₁₁Ge₃O₁₇ (Table 4) were obtained with a Guinier counter diffractometer using Ge monochromated Cu Kα radiation (λ = 1.54051 Å) and Si as internal standard. Intensities represent relative peak heights. The indexing was checked using the strong reflections from single-crystal records. Only reflections from the intense heights. The indexing was checked using the strong reflections (Table 4) were obtained with a Guinier counter diffractometer. Moreover, the k=4n + 1 layers are not only very weak but also diffuse, indicating disorder effects. They were ignored on deriving the space group. In addition, the h0l (00l) reflections are very intense for l=7n, whereas the hkl reflections, for example, are intense for l=(7±1)/2. The strong reflections form a pseudo-tetragonal subcell in direct space with a' = 3.799 Å, b' = 3.766 Å, c'= 5.530 Å and β' = 87.6°, which can be related to the unit cell of tetragonal α-PbO. The transformation to the large unit-cell of Pb₆GeO₈ can be conveniently written down in matrix notation.

\[
\begin{pmatrix}
\alpha' \\
\beta' \\
\gamma'
\end{pmatrix} = \begin{pmatrix}
8 & 0 & -8 \\
0 & 4 & 0 \\
0 & 0 & 2
\end{pmatrix} \begin{pmatrix}
\alpha \\
\beta \\
\gamma
\end{pmatrix}.
\]

As in the case of α-PbO there are two metal atoms in the subcell. Since the oxygen coordination of Pb and Ge is quite different, the altered sequence of 6Pb + 1Ge in Pb₆GeO₈ compared with PbO has the obvious effect of enlarging the unit cell by a factor of 3/2 in one direction. The resulting cell volume then contains 2 × 3 = 7 metal atoms corresponding to one formula unit. Moreover, the oxygen atoms extending the number of metal atoms according to (Pb₂Ge₄O₈) may give rise to a further complicated crystal structure of the observed very large monoclinic unit cell and to disorder effects. In this way the crystal structure of Pb₆GeO₈ can be thought of as a distorted cubic close packing of metal atoms with oxygen atoms in the tetrahedral and octahedral holes. Ge⁴⁺ forms the [GeO₄]²⁻ tetrahedral anion with the bonded O atoms in tetrahedral holes. This means that three of the octahedral holes in the immediate neighbourhood of that anion are not allowed to be filled with O atoms. For formula unit 7 – 3 = 4 octahedral holes remain and they may be occupied out of centre with oxygen according to Pb₆[O₂Ge₄O₆]. However, the occupation of tetrahedral holes near these positions is also possible.

Some details in the intensity distribution of the reflections Pb₆GeO₈ are very similar to Pb₁₁Ge₃O₁₇. In the case of Pb₁₁Ge₃O₁₇ the subcell relation holds as well, when taking into consideration the modified lattice constants a and c. The transformation matrix is then

\[
\begin{pmatrix}
\alpha' \\
\beta' \\
\gamma'
\end{pmatrix} = \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
7 & 0 & 0
\end{pmatrix} \begin{pmatrix}
\alpha \\
\beta \\
\gamma
\end{pmatrix}.
\]

This compound also shows disorder effects. Diffuse streaks extending in the c* direction are observed on the weak hkl layers with k ≠ 4n.

Solving the crystal structures directly is more difficult than we had hoped it would be. Therefore, the concept of the subcell relation may be helpful in cases like Pb₆GeO₈ and Pb₁₁Ge₃O₁₇, where structures of high complexity with numerous atoms in the unit cell are being studied.

Morphology

Crystals of Pb₆GeO₈ were obtained several mm in size and most of them were tabularly developed on (001) and [010] was elongated due to the relatively strong periodic bond of short metal separation, b = 3.766 Å. Twinning was observed on (001). The morphologically determined monoclinic angle was β = 111.03°. The perfect cleavage observed in PbO disappears in Pb₆GeO₈ as well as in Pb₁₁Ge₃O₁₇. Crystals of Pb₁₁Ge₃O₁₇ could only be obtained smaller in size but their size increased when some Ge⁴⁺ was replaced by Si⁴⁺.
Unit-cell dimensions and space group of cholesteryl ethyl carbonate. By N. C. Shivaparakash, P. K. Rajalakshmi and J. Shashidhara Prasad, Department of Physics, University of Mysore, Mysore 570 006, India

(Received 3 November 1979; accepted 3 December 1979)

Abstract
Unit-cell dimensions and space group of cholesteryl ethyl carbonate (C₃₀H₅₀O₃) are: monoclinic P2₁, \( Z = 4 \), \( a = 17.89 \) Å, \( b = 11.34 \) Å, \( c = 13.11 \) Å, \( \beta = 105.2 \)°.

It is well established that the molecular structural studies of liquid crystalline materials in the crystalline state provides a better understanding of the physical properties. It is also quite well known that the molecular structure of mesogenic materials in the solid state prefigures the orientation of molecules in the liquid crystalline state. An integrated study of the physical properties of liquid crystalline materials related to the molecular structure provides deeper understanding of the changes in physical properties with molecular structure variation, which enable us to synthesize liquid crystals to suit our applications. In particular, the study of molecular structure and physical properties of cholesteric liquid crystals are of very great importance owing to the involvement of these compounds in a myriad of industrial and biological research areas such as thermography, display devices and the formation of atherosclerosis of arterial deposits containing cholesteryl esters and have unique optical properties. A proper understanding of the physical properties requires a knowledge of the molecular structure. As such, we communicate here the preliminary crystallographic data for the mesogenic material cholesteryl ethyl carbonate, the detailed structure analysis of which has been taken up.

Origin of specimen
The chemical was purchased from Eastman Kodak Company, USA. Crystals of cholesteryl ethyl carbonate were grown by successive recrystallization in acetone.

Crystal geometry
The preliminary crystallographic data have been obtained from oscillation and Weissenberg photographs taken about \( b \) and \( c \) axes of the crystal using Cu Kα radiation (\( \lambda = 1.5418 \) Å). The density was measured by flotation in a solution of potassium iodide. The systematic absence \( 0k0 \), \( k = 2n + 1 \) indicates a monoclinic cell with space group \( P2_1 \).

Crystal data
The crystal data are: \( a = 17.89 \) Å, \( b = 11.34 \) Å, \( c = 13.11 \) Å; \( \beta = 105.2 \)°; \( V = 2566-62 \) Å³; \( Z = 4 \); \( D_n = 1.143 \); \( D_r = 1.187 \) Mg m⁻³; \( MW = 458.73 \).

Two of the authors (NCS and PKR) thank CSIR, New Delhi for the award of research fellowships.

0021-8898/80/030310-01 $01.00 © 1980 International Union of Crystallography