Unit-cell data

Precession photographs taken with Cu Kα radiation showed that the unit cell is orthorhombic with the lattice constants given in Table 1, which were refined from the indexed powder data given in Table 2. The refinement was carried out with the program PULVER (Weber, unpublished). Systematic absences hk0 for k odd, 0kl for l odd, h0l for h odd, and h00, 0k0, 00l for h,k,l odd were found. The probable space group is therefore Pcab (D16). The density measured by toluene displacement in a pycnometer was D293 = 5.94 (4) g cm⁻³. The calculated density is Dx = 5.985 g cm⁻³ for eight formula units. The cell contents agree with the space-group requirements because all equipoints have a multiplicity of four.

The relatively high density indicates octahedral coordination for some of the Ge⁴⁺ ions.

The crystal data are summarized in Table 1. The 3σ errors associated with the final digit of the lattice constants are given in parentheses.

X-ray powder data

The powder data were obtained with a Guinier counter diffractometer using Cu Kα₁ radiation (λ = 1.54051 Å). Intensities represent relative peak heights. The mean angle error for the lines listed in Table 2 is σ(2θ) = 0.008°.

Comparison with other results

In the phase diagram of the PbO–GeO₂ system proposed by Speranskaya (1958) the existence of a phase PbGe₃O₇ is supposed. A phase of composition PbGe₂O₅ reported by Eulenberger, Wittmann & Nowotny (1962) and Phillips & Scroger (1965) does not exist and was identified as a mixture of PbGeO₃ and α-PbGeO₃. Finally, we may remark that PbGe₂O₅ or a similar phase was obtained by thermal decomposition of fleischerite, Pb₃Ge[(OH)₆)(SO₄)₂].3H₂O, together with PbSO₄ and α-PbGeO₃. From the reported powder data of the mixture (Otto, 1975) lattice constants are calculated to be a = 5.270 (2), b = 14.086 (5), c = 16.040 (5) Å, and α(2θ) = 0.006°.

References


Crystal data for Pb₃Bi₂[□(GeO₄)₃]. By H. H. OTTO and W. MÜLLER-LIERHEIM, Fachbereich Physik der Universität Regensburg, Postfach 397, D-8400 Regensburg, Federal Republic of Germany


Single crystals of Pb₃Bi₂[□(GeO₄)₃]  were grown from the melt. The unit-cell parameters are a = 10.034 (1) and c = 7.267 (2) Å, Z = 2, Dx = 7.60 g cm⁻³. Indexed powder data are given. The possibility of a ferroic phase transformation is discussed.

Introduction

The asymmetric electron configuration of the cations Pb²⁺ and Bi³⁺ with a lone electron pair, which can be observed mainly at low temperatures, frequently leads to pyramidal coordination with respect to O and, as a consequence of the electric dipole moment, to ferroelectric properties of corresponding compounds, which are also assumed for the compound described here.

Origin of specimens

A melt of the composition 3PbO·Bi₂O₃·3GeO₂ was homogenized in a Pt crucible at 1100 K and then the temperature was decreased linearly 5 K h⁻¹ in a programmed tubular furnace; long prismatic and completely transparent slightly brownish single crystals of centimeter size were grown by spontaneous crystallization.

Unit-cell data

The symmetry and the metric of the unit cell were determined by means of precession photographs taken with Cu Kα radiation. The lattice constants were refined from the indexed powder data given in Table 2. The density was measured with a pycnometer at 293 K. Crystal data are summarized in Table 1.

Table 1. Crystal data

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<th>Pb₃Bi₂[□(GeO₄)₃]</th>
<th>FW 1449.33</th>
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<tr>
<td>Space group: P6₃/m or P6₃</td>
<td>D₂₉₃ = 7.51 g cm⁻³</td>
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<td>a = 10.034 (1) Å</td>
<td>Dₓ = 7.60</td>
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<tr>
<td>c = 7.267 (2) Å</td>
<td>Z = 2</td>
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<td>V = 633.60 Å³</td>
<td>Morphology: {1010} determines the long-prismatic habit</td>
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Powder data

The powder data were collected with Guinier counter diffractometer equipment using Cu Kα₁ radiation (λ = 1.54051 Å) and were indexed out to 2θ = 60°. The mean angle error for the lines listed in Table 2 is σ(2θ) = 0.010°.

Crystal chemistry

The crystal data confirm an apatite-like crystal structure. The introduction of a modified crystal chemical formula ex-
presses that channels along [001], which are occupied by F-
anions in the crystal structure of the prototype apatite,  

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Comparison with other results

It is probable that Pb₂Bi₂[GeO₄]₃ is identical with a phase of the same chemical composition found by Riebling (1975) at the surface of solidified Pb-Bi germanate melts, which has not yet been further identified.

References