Crystallization from High-Temperature Solutions in the K₂O–P₂O₅–V₂O₅–Bi₂O₃ System

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INTRODUCTION

Oxide compounds, in particular phosphates and vanadates, are currently among the most promising basic systems for advanced functional materials, which are successfully used in many technological applications. This is due to the diversity of their valuable physical properties, such as ionic conductivity, selective catalytic activity, optical nonlinearity, and anisotropic electrical and magnetic properties [1–10]. The structure–composition relations found for mixed oxides enable targeted synthesis of materials with tailored properties [9, 10]. Accordingly, there is high current interest in understanding the conditions and general trends of the formation of phosphate–vanadate matrices, which would offer greater possibilities for creating advanced functional materials.

This paper examines the phase relations, general trends of crystallization, and crystal structure of compounds in the pseudoquaternary system K₂O–P₂O₅–V₂O₅–Bi₂O₃.

EXPERIMENTAL

We studied phosphate–vanadate high-temperature solutions with P/V = 0.5, 1.0, and 2.0 and K/(P + V) = 0.7, 1.0, 1.2, and 1.4. The Bi₂O₃ content was varied from 25 to 50 wt %. The starting chemicals used were KPO₃, K₂CO₃, KVO₃, V₂O₅, and Bi₂O₃ (analytical grade or higher purity). Crystalline phases were prepared as follows: Weighed amounts of the starting reagents were ground, placed in a platinum crucible, slowly heated to 950–1000°C, and held at temperature for 1–2 h. The resultant homogeneous melt was cooled to 700°C at a rate of 20–50°C/h with periodic stirring. Next, the melt was decanted, and the crystalline phases were cooled to room temperature and washed with hot water, dilute mineral acids (0.1 N HCl or H₂SO₄), or EDTA in order to remove the residual flux.

The composition of the synthesized compounds was determined by X-ray fluorescence analysis (Elvax Light spectrometer) and in a number of cases by atomic emission spectroscopy (ICAP 6500 DUO spectrometer).

X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 powder diffractometer (CuKα radiation, λ = 1.54178 Å, diffracted-beam monochromator) in a continuous 20 scan mode at a rate of 0.5°/min in the range 20 5.0°–90.0°.

IR spectra were measured on a PerkinElmer Spectrum BX FTIR spectrometer in the frequency range 400–4400 cm⁻¹ using samples pressed with KBr.

X-ray crystal structure analyses were carried out with an Oxford-Diffraction XCalibur 3 diffractometer equipped with a 2048 × 2048 (4 Mpixel) CCD detector. The structures were solved by the direct method and refined by a full-matrix least squares technique with anisotropic thermal parameters using SHELXS-97 [7] and SHELXL-97 [8]. The intensity data collection conditions, crystal data, and refinement statistics for K₃Bi₂(PO₄)₂(VO₄) and K₃Bi₂(PO₄)₁.₂₅(VO₄)₁.₇₅ are presented in Table 1. The atomic position coordinates and thermal parameters in their structures are given in Table 2, and the bond distances are listed in Table 3. Detailed data on the crystal structures and refinement can be obtained from the ICSD database: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany; depository numbers CSD-421363 for K₃Bi₂(PO₄)₂(VO₄) and CSD-421362 for K₃Bi₂(PO₄)₁.₂₅(VO₄)₁.₇₅.
Table 1. Intensity data collection conditions, crystal data, and agreement factors for $K_3Bi_2(PO_4)_2(VO_4)$ and $K_3Bi_2(PO_4)_{1.25}(VO_4)_{1.75}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_3Bi_2(PO_4)_2(VO_4)$</th>
<th>$K_3Bi_2(PO_4)<em>{1.25}(VO_4)</em>{1.75}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system (sp. gr.)</td>
<td>Monoclinic (C2/c)</td>
<td>Monoclinic (C2/c)</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>13.8857(8)</td>
<td>13.907(4)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>13.5432(5)</td>
<td>13.6154(9)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>6.8679(4)</td>
<td>6.9562(2)</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>114.031(7)</td>
<td>113.52(4)</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>1179.61(11)</td>
<td>1207.6(5)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$, g/cm$^3$</td>
<td>4.73</td>
<td>4.70</td>
</tr>
<tr>
<td>Crystal dimensions, mm</td>
<td>$0.18 \times 0.04 \times 0.03$</td>
<td>$0.15 \times 0.03 \times 0.02$</td>
</tr>
</tbody>
</table>

Data collection conditions

- Wavelength, Å: 0.71073, 0.71073
- Monochromator: Graphite, Graphite
- Temperature, K: 293(2), 293(2)
- Mode: $\phi$ and $\omega$ scans, $\phi$ and $\omega$ scans
- $\mu$, mm$^{-1}$: 31.93, 31.93
- $T_{\text{min}}, T_{\text{max}}$: 0.0690, 0.4476, 0.0876, 0.5703
- Measured reflections: 5048, 8460
- Independent reflections: 1717, 1758
- Observed reflections ($I > 2\sigma(I)$): 1452, 1446
- $R_{\text{int}}$: 0.061, 0.082
- $\theta$ range, deg: 3.0–30.0, 3.0–30.0
- $h, k, l$: $-19 \rightarrow 19, -19$ $17, -9 \rightarrow 9$ $-19 \rightarrow 19, -19$ $19, -9 \rightarrow 9$
- $F(000)$: 1488, 1512

Structure refinement results

- Method: Direct, Direct
- Weighting scheme: $w = 1/\left[\sigma^2(F_0^2) + (0.0497P)^2\right]$, $w = 1/\left[\sigma^2(F_0^2) + (0.0475P)^2\right]$
- where $P = (F_0^2 + 2F_c^2)/3$, $P = (F_0^2 + 2F_c^2)/3$
- $R_1$(all): 0.049, 0.068
- $wR_2$: 0.090, 0.096
- $S$: 1.06, 1.08
- Refinement parameters: 98, 98
- $(\Delta\rho)_{\text{max, min}}$, $e$/Å$^3$: 3.23, -3.15, 3.72, -2.51
- ICSD number: 421363

RESULTS AND DISCUSSION

Phase relations. As shown in studies of crystallization processes in bismuth-containing alkali phosphate molybdate (tungstate) polyanionic melts [7, 8], the preparation of monoanionic compounds (phosphates, molybdates, or tungstates) or mixed-anion compounds and their composition are highly dependent on both the initial relationship between the anion components in the solvent and the “acidity” of the melt. Accordingly, to obtain a general pattern of phase relations in the $K_2O$–$P_2O_5$–$V_2O_5$–$Bi_2O_3$ system, we examined melts with discrete $P/V$ values for particular $K/(P + V)$ ratios. The compositions of the crystallization products are listed in Table 4.

In acid melts ($K/(P + V) = 0.7$) with an appreciable vanadium content ($P/V = 0.5$), we observe $V_2O_5$ crystallization independent of $Bi_2O_3$ content. In this section,