Structure Studies and Thermal Analysis of Transition Metal Diarsenates(V) $M_2\text{As}_2\text{O}_7$ ($M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$)

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Introduction

Structural data of transition metal diarsenates $M_2\text{As}_2\text{O}_7$ are restricted to $\text{Mn}$, $\text{As}_2\text{O}_7$, and the high-temperature modifications ($\beta$-forms) of $\text{Cu}_2\text{As}_2\text{O}_7$ and $\text{Ni}_2\text{As}_2\text{O}_7$. Their structures have been determined from powder neutron data [1, 2]. No reliable structural data on the corresponding low-temperature phases have been published so far. This motivated us to grow single crystals of all $M_2\text{As}_2\text{O}_7$ phases by chemical transport reactions for subsequent structure analyses and to re-investigate the thermal behaviour of the compounds.

Experimental

Preparation

Single crystals of the $M_2\text{As}_2\text{O}_7$ phases (Fig. 1a–c) were prepared in sealed and evacuated silica tubes in a temperature gradient 880 °C to 800°C, starting from stoichiometric mixtures of the component oxides $M_2\text{O}_3$, $\text{As}_2\text{O}_3$, and $\text{Cu}_2\text{O}$ as transport agent. After the reaction period of one week, no solids were left in the source region of the ampoule.

Thermal analysis

DSC (Differential Scanning Calorimetry) measurements (Fig. 2) of the $M_2\text{As}_2\text{O}_7$ phases were performed employing a NETZSCH DSC 204 Phoenix3 (temperature range: -50 to 500°C, aluminium crucible with paraffin lid, N$_2$ atmosphere: 20 ml/min, heating/cooling rate: 10 °C/min).

$\beta$-ray diffraction

Single crystal diffraction data were measured on a SMART CCD system (Siemens). The structure of $\text{Cu}_2\text{As}_2\text{O}_7$ was solved and refined with the SHELXTL programs [5]. High-temperature $\beta$-ray powder diffraction (Fig. 4) was performed on a PHILIPS PW 3050/60 $\beta$-ray diffractometer in Derksen-Scherrer geometry with an home-built heating device which was calibrated up to 500°C. The structural refinement of $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ was carried out using the program PC-Rietveld Plus [6].

Table 1. $\alpha$- and $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ Crystallographic data and details of data collection, structure solution and refinement

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Space group</th>
<th>$a$ [Å]</th>
<th>$b$ [Å]</th>
<th>$c$ [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
<th>$V$ [Å$^3$]</th>
<th>$Z$</th>
<th>$\rho$ (calc.) [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$</td>
<td>single crystal</td>
<td>C2/c (No. 15)</td>
<td>7.273(3)</td>
<td>13.703(6)</td>
<td>14.938(7)</td>
<td>90</td>
<td>120</td>
<td>90</td>
<td>2191(3)</td>
<td>4</td>
<td>3.794</td>
</tr>
<tr>
<td>$\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$</td>
<td>powder</td>
<td>C2 (No. 12)</td>
<td>7.087(3)</td>
<td>13.603(6)</td>
<td>14.827(7)</td>
<td>90</td>
<td>120</td>
<td>90</td>
<td>2186(3)</td>
<td>4</td>
<td>3.794</td>
</tr>
</tbody>
</table>

Results

Except for $\text{Mn}_2\text{As}_2\text{O}_7$ (orthorhombic) all other $M_2\text{As}_2\text{O}_7$ compounds are dimorphous and show $\alpha$- and $\beta$-phase transitions with transition temperatures of 183°C (Cu$_2$O$_3$), 422°C (Ni$_2$O$_3$), 356°C (CuO) and 9°C (ZnO) with only slight hysteresis (Fig. 2). The values for the Cu and Ni compounds are in good agreement with limited data [2]. Values for the Cu and Zn compounds are reported here for the first time.

$\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$ crystallizes isomorphically with the phosphate analogue $\alpha$-$\text{Cu}_2\text{P}_2\text{O}_7$ [7] and the mineral ziesite, $\beta$-$\text{Cu}_2\text{O}_3$ [8], whereas $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ adopts the thortveitite structure type [9]. The crystal structures of both polymorphs are closely related and consist of infinite sheets of $[\text{CuO}_2]$ polyhedra ($\alpha$: $z = 5$, $\beta$: $z = 6$) and interlayer $\text{As}_2\text{O}_7$ anions which occur either in a bent (As-O-As) configuration (both polymorphs are dimorphous and show reversible $\alpha$-$\beta$ phase transitions with transition temperatures of 183°C (Cu$_2$O$_3$), 422°C (Ni$_2$O$_3$), 356°C (CuO) and 9°C (ZnO) with only slight hysteresis (Fig. 2)). The values for the Cu and Ni compounds are in good agreement with limited data [2]. Values for the Cu and Zn compounds are reported here for the first time.

Structure determinations of $\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$ and $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ and both $\alpha$- and $\beta$-$\text{Zn}_2\text{As}_2\text{O}_7$ were hampered by multiple twinning of the crystals (see Fig. 1b). Preliminary results from combined single crystal and powder diffraction revealed a close relation of all these phases to the thortveitite sub-cell. For both temperature phases $\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$ and $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ lattice parameters of $a = 5.33(1)$, $b = 8.67(1)$, $c = 16.64(1)$ $\AA$, $\alpha = 82.92(1)$, $\beta = 84.71(1)$, $\gamma = 72.87(1)$, $z = 5$, and $\alpha = 5.29(1)$, $\beta = 5.74(1)$, $\gamma = 10.16(1)$, $\alpha = 72.870$, $\beta = 75.750$, $\gamma = 85.150$, and $z = 1$, respectively, were determined. An reliable indexing for both $\text{Zn}_2\text{As}_2\text{O}_7$ phases was not possible up to now.

Table 2. $\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$ and $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$. Selected interatomic distances (Å).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha$-Cu$_2$As$_2$O$_7$</th>
<th>$\beta$-Cu$_2$As$_2$O$_7$</th>
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<tbody>
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<td>$\alpha$-Cu$_2$As$_2$O$_7$</td>
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<td>$\beta$-Cu$_2$As$_2$O$_7$</td>
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Fig. 5. The crystal structures of $\alpha$-$\text{Cu}_2\text{As}_2\text{O}_7$ (left) and $\beta$-$\text{Cu}_2\text{As}_2\text{O}_7$ (right). Anisotropic displacement parameters are given on the 90% probability level.

References