An investigation of microporous cetineite-type phases $A_6[B_{12}O_{18}][CX_3l_2][D_x(H_2O,OH,O)_{6-y}]$

I. The cetineite structure field

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ABSTRACT.- Hydrothermal syntheses between 120 and 200 °C have been performed to determine the chemical variability of semiconducting microporous materials with cetineite structure. The syntheses were based on the general formula $A_6[B_{12}O_{18}][CX_3][D_x(H_2O,OH,O)_{6-y}]$, ($0 \leq x \leq 2$, $0 \leq y \leq 6$), which was derived from X-ray crystal structure refinements. $A = Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ti^+$, $NH_4^+$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ were introduced as hydroxides, in some cases as carbonates, $B = C = As^{3+}$, $Sb^{3+}$, and $Bi^{3+}$, and $X = S^{2-}$, $Se^{2-}$, and $Te^{2-}$ as elements. Only syntheses with $B = C = Sb^{3+}$ and $X = S^{2-}$ and $Se^{2-}$ were successful. Known cetineite-type phases now include the element combinations $A/Sb^{3+}/S^{2-}$ with $A = Na^+$ and $K^+$, and $A/Sb^{3+}/Se^{2-}$ with $A = Na^+$, $K^+$, $Rb^+$, $Sr^{2+}$, $Ba^{2+}$, and probably $Ti^+$. Variable amounts of $Na^+$, $Sb^{3+}$ and $C^{4+}$ were found to occupy the $D$ position of the cetineite-type structure. The chemical variability can be described by the coupled substitutions $A^+ + H_2O \leftrightarrow A^{2+} + OH^-$, $mH_2O \leftrightarrow D^{m+} + mOH^-$, and $nOH^- \leftrightarrow D^{n+} + nO^{2-}$.

The crystals obtained are orange to dark red, in agreement with their semiconducting properties.

INTRODUCTION

Cetineite is a rare mineral which has only been found as a weathering product of roasted remains of mining operations at the Cetine mine 20 km south-west of Siena, Tuscany, Italy [1]. Its chemical composition $(K,Na)_{3+x}(Sb_2O_3)(SbS_3)(OH)_x(2.8-x)H_2O$ has been determined by electron-microprobe analysis and confirmed by single-crystal structure determination [2].

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Fig. 1  Crystal structure of the cetineite-type
a) projected parallel [001],

b) projected perpendicular to [001].

$Y = H_2O, OH^-$ or $O^{2-}$. 

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Synthetic materials with similar structures and compositions have previously been described [3, 4]. Their structures are schematically shown in Fig.1. Their most characteristic feature is the presence of tube-like structural units of composition Sb2O3. These tubes consist of pyramidal [SbO3] polyhedra which are linked via common oxygen atoms. The two crystallographically non-equivalent trivalent Sb atoms occupy the B1 and B2 positions in Fig.1, respectively. Separate [SbS3]3- pyramids with their Sb atoms on position C and their S atoms on position X are located between the tubes. The electroneutral tubes are held together by strong ionic bonds between alkali ions lining the inner walls of the tubes (position A) and the chalcogen atoms (position X) of the separate [SbS3]3- pyramids. This cohesion is strengthened by weaker secondary bonds between the Sb atoms on B2 and the S atoms of the [SbS3]3- pyramids. The interior of each tube provides space for a column of face-sharing [(H2O, OH)6] octahedra. The centres of the octahedra can statistically, partially or fully, be occupied by Na+ and Sb3+ ions (position D).

The microporous structures of these cetinCite-type phases led us to expect that, in addition to their 1-dimensional hosts of composition Sb2O3, trivalent Sb and chalcogen atoms are able to form porous 2- and 3-dimensional hosts [5]. To get acquainted with the chemical properties of Sb(III) - chalcogen systems, we repeated syntheses of known cetinCite-type phases and synthesised a new one, K4[Sb12O28][SbSe9]6H2O [6]. Single-crystal X-ray structure refinements revealed deviations of the bond valence sums of the Sb atoms of the separate [SbX3] groups of up to 0.8 v.u. from the expected value 3.0 for stoichiometrically trivalent Sb(III) [7]. The degree of such deviations is correlated with the degree of stereoactivity of the lone-electron pair of Sb(III). This together with the observations that these cetinCite-type phases are photo- and conductors [8], and that morphologically idiomorphic crystals of the K, Sb, Se compound are reversibly dehydrated at room temperature under high vacuum [8], led us to systematically explore the chemical variability of the cetinCite-type.

The present paper reports on the syntheses and properties of cetinCite-type phases and the extension of the cetinCite structure field. Detailed structure refinements and discussions of structure variations with chemical composition are reported in part II of this series [9].

SYNTHESSES

Synthesis methods

The general structural formula of cetinCite-type phases can be written as

\[ A_x[B_{12}O_{18}][CX_3y][D_{y}(H_2O,OH,O)]_{x-y} \]

(Fig.1) with \( 0 \leq x \leq 2 \) and \( 0 \leq y \leq 6 \). Here A are electropositive mono- and divalent cations, B and C are trivalent cations having one lone-electron pair, and D can
TABLE I  Element combinations A/B/X for which synthesis experiments have been performed.

<table>
<thead>
<tr>
<th>X</th>
<th>A</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
<th>Tl⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Sr²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>S²⁻</td>
<td>Sb</td>
<td>As, Sb</td>
<td>As, Sb, Bi</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
</tr>
<tr>
<td>Se²⁻</td>
<td>Sb</td>
<td>As, Sb</td>
<td>As, Sb, Bi</td>
<td>Sb</td>
<td>Sb, Bi</td>
<td>Sb, Bi</td>
<td>Sb, Bi</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td></td>
</tr>
<tr>
<td>Te²⁻</td>
<td>Sb</td>
<td>As, Sb</td>
<td>As, Sb, Bi</td>
<td>Sb</td>
<td>Sb, Bi</td>
<td>Sb, Bi</td>
<td>Sb, Bi</td>
<td>Sb</td>
<td>Sb</td>
<td>Sb</td>
<td></td>
</tr>
</tbody>
</table>

be atoms of the elements occupying the A, B and C positions. In the present study, only syntheses with B = C have been performed. The element combinations A/B/X applied are summarised in Table I.

The component A was introduced as an aqueous solution of AOH or A(OH)₂ or as A₂CO₃ or ACO₃, B as elemental As, Sb and Bi, and X as elemental S, Se and Te, respectively. For syntheses with A = Na⁺ and K⁺, B = Sb, and X = S, the molar ratio S:Sb was varied between 0.5 and 1.55, all other syntheses were performed with X:B = 1.50. In some experiments, amines such as methylamine, pentylamine, diethylamine, tripropylamine and piperidine were added to the reaction mixture.

The mixtures were filled into teflon-coated steel autoclaves of 25, 50 and 100 ml reaction volume and water was added up to 10% or less of the volume. The autoclaves were heated for 2-7 days at 120 to 220°C. The reaction products were washed with water and/or methanol and dried at room temperature in air.

In a typical experiment, 6 mmol Sb, 9 mmol Se and 14 mmol KOH were mixed with 2.5 ml H₂O and 0.5 ml 2-aminopentane. The mixture was transferred into a teflon-coated autoclave with a 100 ml inner volume, and heated at 200°C for 4 days.

Product characterisation

Only in some cases was the synthesis product a pure cetineite-type phase based on X-ray powder diffraction.

The powder diffractogram of K₆[Sb₁₂O₁₈][SbSe₃]₂·6H₂O is shown in Fig.2. In most experiments the synthesis product was a mixture of several phases. In these cases selected crystals have been identified as cetineite-type phases by X-ray diffraction (Gandolfi and Weissenberg methods, and four circle diffractometry) followed by structure refinement.
In some cases the chemical composition of carefully selected crystals was determined by electron microprobe analysis (EMA) with a Cameca CAMEBAX MICROBEAM, using as standards Sb$_2$S$_3$ for Sb and S, elemental Se for Se, synthetic glass $K_{0.35}Mg_{0.65}Ca_{0.65}Al_{0.35}Si_2O_6$ for K, jadeite NaAlSi$_2$O$_6$ for Na, and synthetic glass ‘X’ from A. A. Chodos, Cal Tech, Pasadena, for Rb. Probably due to a strongly varying dehydration tendency of the crystals and a considerable tendency of Sb, S and, to a lesser extent, Se to change their oxidation state, crystals of $A_S$-cetineites were unstable in the electron beam preventing microbeam analysis. Although $A_S$-Se crystals were more stable in the electron beam, the accuracy of the EMA results is considered not better than 4%.

<table>
<thead>
<tr>
<th>$A_S$X</th>
<th>A</th>
<th>Sb</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_S$Se</td>
<td>3.02</td>
<td>6.88</td>
<td>3.00</td>
</tr>
<tr>
<td>$C-Ba_S$Se</td>
<td>3.03</td>
<td>7.01</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Results of the microprobe analyses are given in Table II; they are confirmed by crystal structure refinements [9]. For the other phases reported in this paper the chemical composition is that obtained by single-crystal structure refinements.
RESULTS

Cetineite-type phases

Of all the element combinations listed in Table I only syntheses with \( B = \) Sb(III) produced cetineite-type phases. This allows one to use, henceforth, the short-hand notation \( A;X \) as, for example, \( K;Se \) for \( K_6[Sb_{12}O_{18}][SbSe_3]_2 \cdot 6H_2O [6] \) and \( Na;S \) for \( Na_2[Sb_{12}O_{18}][SbS_3]_2 \cdot [Na_{1.2}(H_2O)_{4.8}(OH)_{1.2}] \) as synthesised by Sabeli et al. [2].

<table>
<thead>
<tr>
<th>TABLE III</th>
<th>Element combinations ( A/Sb/X ) for which cetineite-type phases have definitely (+) or very probably (?) been obtained.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X )</td>
<td>( A )</td>
</tr>
<tr>
<td>( S^2- )</td>
<td>+</td>
</tr>
<tr>
<td>( Se^{2-} )</td>
<td>+</td>
</tr>
</tbody>
</table>

In Table III the element combinations \( A/Sb/X \), for which cetineite-type phases have successfully been synthesised, are indicated by crosses (+). Comparison of Table III with Table I reveals that such phases were neither obtained with \( B = As(III) \) and \( Bi(III) \) instead of \( Sb(III) \) nor with \( X = O^2- \) and \( Te^{2-} \).

\( K;S \)-cetineite was obtained as pure phase from syntheses with molar ratios \( S:Sb = 1.5 \); the best crystals formed below 200°C. Reaction mixtures with \( S:Sb > 1.5 \) yielded phases richer in sulphur, such as \( K_2Sb_5S_7 \cdot H_2O \); mixtures with \( S:Sb < 1.5 \) contained recrystallised \( Sb \) in addition to the cetineite-type phase.

\( Na;S \)-cetineite has always been contaminated with crystalline \( Sb \) and \( Sb_2O_3 \). Syntheses in the presence of amines yielded always amorphous phases.

\( Na;Se- \) and \( K;Se \)-cetineite were obtained phase-pure only when amines were added to the reaction mixture. The best crystals formed in the presence of methylamine or 2-amino pentane. In the absence of amines the cetineite-type phase was always contaminated with crystalline \( Sb_2O_3 \) and non-identified brown amorphous particles.

\( Rb;Se \)-cetineite was always mixed with other phases.

\( Sr;Se \)-cetineite was only obtained when \( LiOH \) was added to the reaction mixture in order to increase its basicity. If \( Sr^{2+} \) was provided in the form of \( Sr(OH)_2 \), the cetineite-type crystals became amorphous in air within several days to
a few weeks. If, instead, SrCO₃ was used in the synthesis, no cetineite-type phase was obtained.

**Ba**₃**Se-cetineite**, like Sr₃Se, formed only when LiOH was added to the reaction mixture. Introducing Ba²⁺ as Ba(OH)₂ yielded cetineite-type crystals which became X-ray amorphous within several hours. Using BaCO₃ instead, the resulting crystals were stable in air. With powder and single-crystal X-ray diffraction it has been proven that both phases have a cetineite-type structure.

**Tl(I)₃**Se-cetineite: When Tl₂CO₃ was used for synthesis some very small (<5μm), dark red needles were obtained which were very similar to the other cetineite-type phases with regard to colour and morphology. The small crystal size and very small amount of these crystals prevented reliable identification as a cetineite-type phase.

**Crystal morphology and colour**

In almost all cases the cetineite-type crystals were of acicular to columnar habit, elongated along the hexagonal [001] axis. Most of them show very prominent prisms {100} or {110} and small dipyramids {301} or {331} as the only forms. In contrast, the less stable crystals obtained from syntheses with Sr(OH)₂ or Ba(OH)₂ exhibited a more platy habit with {301} or {001} as the prominent forms, respectively.

The difference in morphology and, in particular, the remarkable differences in stability in air of the cetineite-type phases of Sr²⁺ and Ba²⁺ synthesised with their corresponding hydroxides A(OH)₂ on the one hand and with their carbonates ACO₃ on the other, suggest substantial differences of the two variants. They are, therefore, referred to as H-Sr₃Se and H-Ba₃Se to distinguish them from C-Ba₃Se.

Independent of their morphology, single crystals of all the described cetineite-type phases have an orange to dark red colour.

**Crystal structures**

With the exception of Tl(I)₃Se and H-Ba₃Se structure refinements of the other synthesised phases with single-crystal X-ray diffraction methods have been carried out. Their results are described in detail in part II of this series [9]. Here it should only be pointed out that, in addition to the electron density maxima of the D cations and the six crystallographically equivalent Y maxima, in none of the refined structures have maxima been found within the tubes, that can be interpreted as representing amine molecules or ions incorporated during synthesis.
DISCUSSION

The cetineite structure field map

Muller and Roy [10] have extensively demonstrated that families of isotypic inorganic ternary phases, $A_mB_nX_m$, constitute continuous regions if, for a given anion type $X$, their ionic radii, $r_A$, are plotted versus their corresponding $r_B$. For these 2-dimensional regions they introduced the term 'structure field'. This concept can easily be extended by taking, in addition, into account the anion radius, $r_X$, as a third dimension.

Neglecting the $[D_x(H_2O,OH,O)_{6}]$ octahedra, the cetineite family forms a narrow 3-dimensional region in the structure field map shown in Fig.3. It is evident that the cetineite structure field extends considerably along $r_A$ (1.02 Å - 1.52 Å) and much less along $r_X$ (1.84 Å - 1.98 Å) and $r_B$ ((0.76 ± 0.8) Å). This clearly reflects the flexibility of the ionic (A) and the rigidity of the covalent (B, C) components of the structures.

Fig.3 Three-dimensional structure field map for cetineite-type phases.
(Atomic radii are given in Å.)

\[1\] Since structures are dominantly controlled by the radius ratios of their atoms, it seems sufficient to use relative radii. In the structure field map of Fig.3, therefore, Ahrens radii [11] are used rather than Shannon-Prewitt radii [12].
Atomic substitutions

As will be discussed in part II of this series [9], K₂Se is the only known cetineite-type phase which has a stoichiometrical composition and is crystallographically ordered. It is, therefore, considered to be the energetically most favourable of these compounds. We, therefore, start from K₆[Sb₁₂O₁₈][SbSe₃]₂·6H₂O to describe the various substitutions observed.

Replacement of monovalent cations A⁺ by divalent A²⁺ takes place according to the coupled substitution

\[ A^+ + H_2O \rightleftharpoons A^{2+} + OH^- \]  

The corresponding end members of this series are

A⁺₆[Sb₁₂O₁₈][SbX₃]₂·6H₂O \quad \text{E1}

and

A^{2+}₆[Sb₁₂O₁₈][SbX₃]₂·(OH)₆ \quad \text{E2}

In natural cetineite and in most of the synthetic isotypes there is partial to complete occupation of D positions on the tube axes by either Na⁺ or Sb³⁺. The necessary charge compensation is described by the corresponding substitutions

\[ H_2O \rightleftharpoons Na^+D + OH^- \] \quad \text{S2}

\[ 3H_2O \rightleftharpoons Sb^{3+}D + 3OH^- \] \quad \text{S3}

Starting from E1, substitution S2 leads to the end member

A⁺₆[Sb₁₂O₁₈][SbX₃]₂[D⁺₂(H₂O)₄(OH)₂], \quad \text{E3}

substitution S3 to

A⁺₆[Sb₁₂O₁₈][SbX₃]₂[D⁺₂⁺(OH)₆]. \quad \text{E4}

Starting, instead, from end member E2, the substitution

\[ 3OH^- \rightleftharpoons Sb^{3+}D + 3O²⁻ \] \quad \text{S4}

is expected. The corresponding theoretical end member is

A^{2+}₆[Sb₁₂O₁₈][SbX₃]₂[D⁺₂⁺O₆]. \quad \text{E5}

The two synthetic phases K₆[Sb₁₂O₁₈][SbSe₃]₂·6H₂O and Sr₆[Sb₁₂O₁₈][SbSe₃]₂·(OH)₆ can be considered as examples of the end members E₁ and E₂. In contrast, no way has yet been found to control the kind and degree of occupation of the D position. As a consequence, no cetineite-type phases with theoretical end member compositions E₃ to E₅ have been obtained. Whenever phases containing cations in D positions have been obtained, either the two equivalent D positions per unit cell were not fully occupied or they were partly occupied by Na⁺ and partly by Sb³⁺ (see Table IV).

Since IR spectra gave no indication of amines [8] and the presence of amines in the interior of the tubes has been excluded by structure refinements [9], incorporation of other cations in D positions of cetineite-type phases with divalent A²⁺ cations according to substitution S₄ requires incorporation of O²⁻ ions which have, at least formally, two negative charges. It is well known that O²⁻ ions which are ionically bonded are very unstable. It is, therefore, not surprising that crystalline
H-Sr;Se and H-Ba;Se, which have been synthesised from mixtures containing Sr(OH)\(_2\) or Ba(OH)\(_2\) as sources of A\(^{2+}\), turned amorphous in air. The higher stability of C-Ba;Se synthesised with BaCO\(_3\) instead of Ba(OH)\(_2\) can be explained by replacing substitution 54 formally by

\[
4\text{OH}^- \leftrightarrow [\text{C}^{4+} + 4\text{O}^{2-}] \leftrightarrow \text{CO}_3^{2-} + \text{O}^{2-}
\]

thus reducing considerably the number of unstable O\(^2-\) ions by introducing stable carbonate ions. The theoretical end member resulting from this substitution is

\[
\text{A}^{2+}_6 [\text{Sb}_12\text{O}_{18}] [\text{SbX}_3]^2 [\text{CO}_3]_{1.5} \text{O}_{1.5}.
\]

The presence of carbonate groups in C-Ba;Se is in good agreement with results of the structure refinement of this phase [9].

No attempt has been made to study the solid solubility between the various theoretical end members.

**TABLE IV** Approximate chemical composition of known cetineite-type phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Approximate chemical composition</th>
<th>Analytical method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na;S</td>
<td>Na(<em>6)[Sb(</em>{12})O(_{18})][SbS(<em>3)](<em>2)[Na(</em>{1.2})(H(<em>2)O)(</em>{4.8})(OH)(</em>{1.2})]</td>
<td>X</td>
<td>[1]</td>
</tr>
<tr>
<td>(K,Na);S</td>
<td>(K(<em>{3.5})Na(</em>{2.5})))[Sb(<em>{12})O(</em>{18})][SbS(<em>3)](<em>2)[Na(</em>{6.7})(H(<em>2)O)(</em>{5.3})(OH)(</em>{0.7})]</td>
<td>EMA, X</td>
<td>[1]</td>
</tr>
<tr>
<td>K;S</td>
<td>K(<em>6) [Sb(</em>{12})O(_{18})][SbS(<em>3)](<em>2)[Sb(</em>{1.24})(H(<em>2)O)(</em>{2.28})(OH)(</em>{3.72})]</td>
<td>X</td>
<td>[9]</td>
</tr>
<tr>
<td>Na;Se</td>
<td>Na(<em>6)[Sb(</em>{12})O(<em>{18})][SbSe(<em>3)](<em>2) [(Na(</em>{1.86})Sb(</em>{0.14}))(H(<em>2)O)(</em>{3.72})(OH)(</em>{2.28})]</td>
<td>X</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>Na(<em>6)[Sb(</em>{12})O(<em>{18})][SbSe(<em>3)](<em>2) [(Na(</em>{1.60})Sb(</em>{0.9}))(H(<em>2)O)(</em>{2.3})(OH)(</em>{3.7})]</td>
<td>EMA</td>
<td>[4]</td>
</tr>
<tr>
<td>K;Se</td>
<td>K(<em>6) [Sb(</em>{12})O(_{18})][SbSe(_3)](_2) -6H(_2)O</td>
<td>EMA, X</td>
<td>WL, [9]</td>
</tr>
<tr>
<td>Rb;Se</td>
<td>Rb(<em>6) [Sb(</em>{12})O(_{18})][SbSe(<em>3)](<em>2) [Sb(</em>{0.22})(H(<em>2)O)(</em>{3.34})(OH)(</em>{0.66})]</td>
<td>X</td>
<td>[9]</td>
</tr>
<tr>
<td>H-Sr;Se</td>
<td>Sr(<em>6) [Sb(</em>{12})O(_{18})][SbSe(_3)](_2) (OH)(_6)</td>
<td>X</td>
<td>[9]</td>
</tr>
<tr>
<td>C-Ba;Se</td>
<td>Ba(<em>6) [Sb(</em>{12})O(_{18})][SbSe(<em>3)](<em>2) [(OH)(</em>{3.6})(CO(<em>3))(</em>{0.6})O(</em>{0.8})]</td>
<td>EMA, X</td>
<td>WL, [9]</td>
</tr>
</tbody>
</table>

**Thermal properties**

Morphologically well developed single crystals of synthetic K\(_6\)[Sb\(_{12}\)O\(_{18}\)][SbSe\(_3\)]\(_2\) -6H\(_2\)O can readily and reversibly be dehydrated within a few seconds at room temperature and 10\(^{-3}\) Torr [8], because the water molecules occluded in the tubes are only weakly bonded to the K\(^+\) ions in A positions and by
hydrogen bonds between each other. Dehydration is strongly retarded by even minor replacement of H$_2$O by OH$^-$ according to substitutions S1 to S3, due to the stronger bonds between OH$^-$ and the A and D cations.

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References