



Real-time *in-situ* monitoring of the topotactic transformation of TlCu_3Se_2 into TlCu_2Se_2



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ABSTRACT

The solid state transformation of monoclinic TlCu_3Se_2 into tetragonal TlCu_2Se_2 by oxidative copper leaching in concentrated ammonia solution has been studied *in situ* by the use of synchrotron radiation. The diffraction patterns of parent and daughter phase are both sharp, indicating a strong topotactic relationship between them that effectuates a rapid change by “chimie douce” performed at +19 °C.

The transformation rate is strongly connected to the access of oxygen from the surrounding air. The transformation was followed in a real-time mode, being almost complete after 2.5 h with 1 h incubation due to low oxygen content, as shown from refining the diffraction patterns by Rietveld profile technique.

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1. Introduction

Syntheses of phases containing heavy elements are usually made by high-temperature methods. However, in some very special cases a route based on phase transformations within the solid state may be possible, a route that instead avoids high temperatures. The basis for such a synthesis is a topotactic relationship between a “parent” and “daughter” phase that takes advantage of the fact that most of the parent structure is left intact while a lowered temperature still permits the movement of some of the atoms within the structure to produce the change. This also means that the nucleation step is extremely easy and that the growth of the new phase may occur through shear of whole structure fragments. The phenomenon falls under the concept “chimie douce” (soft chemistry).

In earlier work, some examples were given where the soft chemistry method was applied to the Tl–Cu–Se system. A new form of TlCu_4Se_3 (orthorhombic) was obtained from room-temperature copper extraction from TlCu_5Se_3 [1] and, correspondingly, TlCu_2Se_2 was obtained from TlCu_3Se_2 [1,2], both by oxidative extraction.

The normal form of TlCu_4Se_3 (tetragonal) is made by high-temperature synthesis [3] and that is also the usual way to synthesize TlCu_2Se_2 . The soft-chemistry route is in that case an alternative method, once TlCu_3Se_2 is available (from high-temperature

synthesis). The phase occurrence in the systems Tl–Cu–Se and Tl–Cu S is very similar [4], probably due to the fact that the electronegativity of S and Se is almost the same. Thus, tetragonal TlCu_4X_3 and TlCu_2X_2 have pairwise (X = S or Se) the same structure. This opened the door to preparing TlCu_2S_2 by soft chemistry [5] where ordinary high-temperature methods had failed [3,6]. The explanation for that is that TlCu_2S_2 is not stable above 120 °C and, once made at room temperature, it decomposes into a three-phase mixture on heating.

A topotactic relation was suggested [4] between the structures of TlCu_3X_2 and TlCu_2X_2 (X = S, Se) which was tested both experimentally and theoretically for the sulphide phases [7]. The oxidative copper extraction does not proceed smoothly, and the transformation could therefore be followed to some extent by performing a gradual extraction and intermittent powder neutron diffraction recordings. In the selenide case, however, the transformation occurs much easier, even by using air as oxidizing agent, and the extent of transformation is not tunable in the same way. The use of synchrotron radiation now offered a possibility to follow the transformation more closely in a series of real-time *in-situ* diffraction experiments while the oxidation proceeded. From such an experiment information might be gained as to the mechanism or at least the time scale for the transformation. Thus, no crystal structure gain was expected since both structures are already known.

The essential structural parameters of the parent and daughter structures are collected in Table 1. The two structures are depicted

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in Fig. 1 as projections along a short axis. There, the background model of transformation [4] is also presented.

All atoms occur in two parallel planes shifted apart by half the axis along the direction of the projection, yielding two fixed coordinates of these mirror planes. This fact is illustrated by filled or unfilled symbols. The circles with the smallest radius denote copper atoms and those with the largest radius denote selenium. The thallium atoms are represented by intermediate sized circles. In TlCu_2Se_2 , all atoms are situated in special positions except on the selenium site which carries a free z -parameter. No single crystal study has been made, and its determination from X-ray powder diffraction ($z_{\text{Se}} = 0.36$) is not especially precise. However, the experiments performed aimed at yielding a fair quantitative phase analysis where small structural details do not matter for the outcome. In particular, a refinement of copper occupancies would be futile in the light of the strong scattering of the other atoms. On the other hand, since the dimensions of the short axes are very susceptible to copper content, significant changes in those cell parameters are important indicators of copper deficiency.

2. Experimental

In-situ powder diffraction experiments were performed at the I 711 beamline [8] at the Max II synchrotron of the Max IV laboratory (Lund, Sweden) using a large area Titan CCD detector.

The sample preparation was rather easy: Previously synthesized TlCu_3Se_2 [9], checked by X-ray diffraction to be single-phase material, was finely ground in an agate mortar. A small amount of the powder was placed at the tip of a single-crystal sapphire tube with an inner diameter of 1 mm. Concentrated aqueous ammonia was sucked into it through the capillary force to wet the powder, just before the experiment. The capillary was mounted horizontally and aligned normal to the synchrotron X-ray beam with the temperature held at 19 °C. The sample distance and the radiation wavelength ($\lambda = 0.9866 \text{ \AA}$) were determined using a NIST LaB_6 standard ($a = 4.15689 \text{ \AA}$) [10].

The X-ray beam entered through the sample close to the tip of the capillary and data were taken using an exposure time of 10 s for each recording, with a total duration of nearly 3 h (640 exposures). During the experiment the solution slowly evaporated at the end, and the liquid/gas interface eventually passed the position that was probed by the X-ray beam. The 2d images were reduced to 1d diffractograms using the fit2d software [11].

Refinements of the diffraction pattern parameters were performed using the Rietveld method [12] as implemented in the Fullprof program [13]. As an improvement of the statistics and at the same time reducing the number of refinements, the number of patterns was reduced from 640 to 160 by adding every 4 of them. Out of these patterns, a still more limited number of data sets were selected so as to yield a fair picture of the copper extraction process from start of the transformation to finish. The data sets were cut to cover the 2θ range of 6.0–31.5°. The high-angle cut from 45° was motivated by the fact that the diffraction rings of the 2d diffractograms were so incomplete that the reduction to 1d introduced erroneous intensities.

Because of a very complicated background for the first sets of data (*vide infra*, Fig. 5), that was determined largely manually with additional refinements of points within the program. The cell parameters of the phases were in excellent agreement with the published values and hardly needed any refinement, but the position of the selenium atom in TlCu_2Se_2 was found to give the best refinement for $z = 0.357$, and that value was further fixed in all refinements. The scale factor and the peak profile width w were refined for each phase. The profile form chosen was that of Thomson-Cox-Hastings pseudo-Voigt. At each selected data set of the refinements, the relative mass amounts of the phases were calculated in the program, using the proper cell contents and volumes. These values were quite insensitive to profile parameters. In the beginning, only the two phases of the transformation occurred, but at the end of the experiment small extra peaks appeared, interpreted as belonging to $\text{Cu}(\text{OH})_2$ [14].

Table 1
Selected structural data for monoclinic TlCu_3Se_2 and tetragonal TlCu_2Se_2 .

Phase	Space group	Cell parameters	Refs.
TlCu_3Se_2	C 2/m	$a = 15.2128 \text{ \AA}$; $b = 4.0115 \text{ \AA}$; $c = 8.3944 \text{ \AA}$; $\beta = 111.70^\circ$	[9]
TlCu_2Se_2	I 4/mmm	$a = b = 3.8572 \text{ \AA}$; $c = 14.038 \text{ \AA}$	[3,16]

3. Results and discussion

Fig. 2 gives an overview of the process, starting with the diffraction pattern of single-phase TlCu_3Se_2 at the top ($t = 0$). The powder diffraction lines appear as white streaks towards a dark background. The brighter the streaks are the stronger is the scattering. Thus, the growing and waning as a function of time (*i.e.* downwards along the vertical axis) show how the parent phase gradually disappears while new lines appear, the main change occurring after slightly more than 1 h. These new lines belong to TlCu_2Se_2 . During the experiment the liquid evaporates slowly, so that the interface facing air at the end of the capillary moves inwards. The growth of the new phase accelerates at a point of time at which the meniscus approaches the position of the X-ray beam. At the same time there is a radical change of background when the interface air/liquid has passed so that the main liquid phase is no longer in the beam. Still, the powder is in contact with the ammonia solution that is trapped by capillary forces, and air is henceforth highly available. The transformation process is also depicted in Fig. 3 which in a qualitative way shows the increasing amount of the new tetragonal phase by time. The data are the same as in Fig. 2, only being cut – both in time and in angle. Fig. 4 is a diagram based on the refinements of selected data sets to show in more detail what relative amount the mother phase takes during the process. The degradation of the mother phase is slow in the beginning until oxygen is easily available. No proper analysis can be made from the oxidation process since parallel mechanisms are at play simultaneously. Only a few representative refinements in the form of X-ray powder patterns are shown in Fig. 5. Towards the end, very small amounts of copper(II) hydroxide are seen (Figs. 2 and 5) which was included in the refinements, now in a three-phase mixture.

The transformation is too fast to be analysed in detail as to the local changes of the parent structure, and the much distorted background in the beginning precludes an adequate analysis because the refinement would be too susceptible to the manual setting of the background in an angular range covered by diffraction peaks. The structural change is very likely to proceed in the same way as that of the sulphide analogue, *i.e.* 50% of those copper atoms that carry a trigonal chalcogen environment are vulnerable for chemical attack and leave the solid. The model applied to the isostructural sulphides [4] was supported by neutron powder diffraction and electronic calculation [7] and is illustrated in Fig. 1. The parent structure is expressed by a slab sequence ABA'B'ABA'B'. The primes denote a difference in projection height only. The B-type slabs have a composition TlCu_4Se_2 and lose half of the copper atoms on leaching from which their average composition changes into TlCu_2Se_2 . A diffusion train of copper atoms along a slab is started, and in the next mechanistic step of the transformation a whole slab is moved by crystal shear and connects again to an adjacent slab. Only minor rearrangements transform them all into A-type slabs, *i.e.* into a sequence AAA... Hence, the new composition and structure is identical to what is found for TlCu_2Se_2 .

From the diffraction result it is seen that there is no apparent change of the parent compound until a certain time has passed. However, even if no occupancy parameters may be refined, the removal of copper should be revealed by a subtle change in metrics of the cell. For the corresponding sulphide there was a 1% decrease of the b -axis during a slow leaching process, illustrating a very high sensitivity to copper content. For TlCu_3Se_2 , the change is hardly significant, only a decrease from 4.0115 Å to 4.0089 Å at the beginning of the copper leaching according to refinement.

The rate of the transformation is probably closely connected to the access of oxidant, the macroscopic reaction occurring according to the formula:

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