

A Phase-Analytical Study of the Tl-Cu-Se System*

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High-temperature silica-tube syntheses and room-temperature copper extraction experiments of the single phases found with the former technique have established five new ternary phases in the Tl-Cu-Se system. The compositions were determined by microprobe analysis. The new phases have been crystallographically characterized by means of single-crystal and powder diffraction: TlCu_3Se_2 (CsAg₃S₂ type), $a = 15.2128(7) \text{ \AA}$, $b = 4.0115(2) \text{ \AA}$, $c = 8.3944(4) \text{ \AA}$, $\beta = 111.700^\circ(4)$; $\text{Tl}_3\text{Cu}_{14}\text{Se}_{10}$ (new type), $C2/m?$, $a = 18.097(2) \text{ \AA}$, $b = 3.9582(2) \text{ \AA}$, $c = 18.118(2) \text{ \AA}$, $\beta = 116.089^\circ(7)$; TlCu_5Se_3 (new type, $P4n2?$), $a = 12.9023(2) \text{ \AA}$, $c = 3.9905(1) \text{ \AA}$; $\text{TlCu}_{5-x}\text{Se}_3$ (new type, $Pnn2?$), $a = 12.43(1) \text{ \AA}$, $b = 12.80(1) \text{ \AA}$, $c = 3.93(1) \text{ \AA}$; TlCu_7Se_4 (NH₄Cu₇S₄ type), $a = 10.4524(2) \text{ \AA}$, $c = 3.9736(1) \text{ \AA}$. The latter phase may be considered as stoichiometric crookesite. © 1987 Academic Press, Inc.

Introduction

No systematic study of the Tl-Cu-Se system has been performed; the individual phases have sometimes been insufficiently characterized. Elucidation of the TlCu_2Se_2 structure (1) served as an impetus for the study of the physical properties. According to Jellinek, copper is likely to be monovalent in its compounds with the heavier chalcogens. Therefore, TlCu_2Se_2 should contain one hole in the valence band, giving it metallic properties, a hypothesis I had the pleasure to confirm when working in his group at the University of Groningen for a couple of years (2). A similar argument might hold for TlCu_4Se_3 (3), explaining its high electrical conductivity (4). As for the further phases where the structures are claimed to be known, TlCuSe also shows

metallic behavior (4) while TlCuSe_2 is a chalcopyrite-type semiconductor (5).

Additional phases lacking proper characterization ($\text{Tl}_3\text{Cu}_7\text{Se}_5$, TlCu_3Se_2 , $\text{Tl}_2\text{Cu}_8\text{Se}_5$ and TlCu_9Se_5) were reported along the pseudobinary $\text{Tl}_2\text{Se}-\text{Cu}_2\text{Se}$ (6). Therefore, the current investigation was concentrated in this area of the phase diagram. Five new ternary phases were experimentally established and identified on the basis of X-ray diffraction and chemical analysis.

Experimental Techniques

Synthesis

Solid-state reactions. The first synthesis stage encompassed the preparation of single-phase TlSe from the elements at 570 K (2). Beforehand, the elements had been purified where appropriate.

The copper used for making the ternary compounds was added in the form of filings

* Dedicated to Dr. Franz Jellinek.

from massive metal (HCOKOF, Outokumpu Oy, Finland; 4 N purity), etched by nitric acid. The selenium was added as shots (Highways International; 5 N). The mixtures of TlSe, copper and selenium were charged into silica tubes. After evacuation and sealing, these were heated briefly in the torch flame to bring the mixtures to reaction and melting. A temperature of 670 K was chosen for annealing the samples in the solid state. They were kept in a furnace for 4–7 weeks.

Chemical treatment. If metallic copper comes into contact with an aerated ammonia solution, the equilibrium surface concentration of copper ions changes owing to oxidation and complex formation. The ammine complex indicates reaction through its typical color. It was found that the copper content of a selenide powder could be gradually changed by these means even at room temperature, as evidenced by formation of a dark blue solution accompanied by a change in the X-ray powder pattern of the powder.

No attempts were made to chemically analyze the solutions quantitatively to determine the degree of copper extraction. The chemical treatment was stopped at an arbitrary stage, at which the reagent was decanted and the powder washed with distilled water, alcohol, and acetone before a sample was withdrawn for diffraction analysis.

X-ray Diffraction

The synthesis products from the high-temperature or room-temperature treatments were investigated by X-ray powder diffraction using a Guinier–Hägg focusing camera equipped with $\text{CuK}\alpha_1$ radiation [$\lambda = 1.540596 \text{ \AA}$ (7, 8)]. The high angular resolution (at least 0.015°), paired with a low background, enabled minute line splittings to be detected, essential for the interpretation of unknown powder patterns. Silicon or germanium ($a = 5.431028 \text{ \AA}$ (8, 9)

and $a = 5.657805 \text{ \AA}$ (7, 10), respectively, both at 295.6 K) were used as internal calibration standards.

Where single crystals could be found, they were studied with a Weissenberg camera. The symmetry and systematic extinctions for allotting the space groups were judged from three consecutive reciprocal layers on rotation about the unique axis, in some cases supplemented with a zero-layer film taken in a different setting.

The ultimate cell parameters were obtained from a least-squares procedure based on the Q values (powder data) and the Miller indices, proper account being taken of the individual errors of the Bragg angle measurement and their nonlinear propagation to the weights of the Q values in the refinement (11).

The line positions were measured either by hand (film projection, typical error $\pm 0.003^\circ$) or in an automated film-scanner system (12). The latter procedure also permitted the intensities of the powder lines to be established. In some cases, the observed intensity data were compared with calculated values based on proposed structure models as input into the LAZY-PULVERIX program (13).

Chemical Analysis

The elemental contents for each phase found in this study were quantitatively analyzed with an electron microprobe (ARL-SEM-Q). Point analyses ($0.5\text{-}\mu\text{m}$ beam) were performed on different parts of metallographically polished samples (Epo-fix; alumina and magnesia powder) to ascertain homogeneity. At least three points were taken for each phase, the mass percentages of the elements adding up to 99.2–100.4%. When taking the average of the contents, each element value was normalized to give a sum of 100%. A single crystal of TlCu_3Se_2 , coated with graphite, was used as internal standard; $\text{CuK}\alpha$, $\text{TlL}\alpha$, and $\text{SeK}\alpha$ radiations were recorded. The neces-

sary calculations and corrections were made by computer using the MAGIC IV program (14).

Results: Phase Characterization and Relationships

In Table I, the crystallographic characteristics of the thallium copper selenides found so far are presented, supplemented with chemical analysis data on, preferentially, the new phases evidenced in the current study.

As can be seen from the analysis data, the agreement with expectation is very good. The errors given correspond with counting statistics only. The actual errors might therefore be somewhat greater. The space group and structure type assignments were based on diffraction data, including intensity calculations.

Stability relationships have as yet not been studied in detail, and no claim is made that Table I covers all ternary phases in the system. In particular, the phase relationships near TlCu_5Se_3 and TlCu_7Se_4 are complicated owing to homogeneity ranges (variable copper content) and vacancy ordering phenomena in that context.

The only previous study of the phase relationships concerns the section $\text{Tl}_2\text{Se}-\text{Cu}_2\text{Se}$ (6). A pseudobinary diagram was presented based on DTA, EMF and microhardness measurements, and X-ray powder diffraction. The present study confirms the existence of TlCuSe and TlCu_3Se_2 (4, 6). The proposed phases $\text{Tl}_2\text{Cu}_8\text{Se}_5$ and TlCu_9Se_5 (6) are to be identified with respectively TlCu_5Se_3 and TlCu_7Se_4 . From the available data it cannot be concluded whether the proposed phase $\text{Tl}_3\text{Cu}_7\text{Se}_5$ would be identical with $\text{Tl}_5\text{Cu}_{14}\text{Se}_{10}$, although the latter lies slightly off the tie line. The exact stoichiometry of the starting materials for that study (Tl_2Se and Cu_2Se) is unknown. Both Tl_2Se (15) and Cu_2Se appear with appreciable homogeneity ranges. In fact, a tie-line

$\text{Tl}_5\text{Se}_3-\text{Cu}_2\text{Se}$ would contain $\text{Tl}_5\text{Cu}_{14}\text{Se}_{10}$. According to the X-ray line diagram published, the Cu_2Se does not differ significantly from the strictly stoichiometric composition.

Some phase relationships are indicated from the results of copper extraction where the neighboring two-phase area may eventually be entered. Powder diffraction on TlCu_3Se_2 treated with an aerated ammonia solution showed that besides TlCu_3Se_2 , tetragonal TlCu_2Se_2 was formed. On further extraction, single-phase TlCu_2Se_2 was eventually obtained. The coexistence of these two phases was also established in one of the microprobe samples where a microstructure indicative of a crystallographically related intergrowth was observed. The absence of monoclinic $\text{Tl}_5\text{Cu}_{14}\text{Se}_{10}$ as a possible product of copper leaching indicates that this is a high-temperature phase or it does not nucleate as easily as TlCu_2Se_2 . TlCu_3Se_2 grains were also found embedded in TlCuSe which supports the suggestion that no phase exists between those two.

Copper extraction in a phase mixture $\text{TlCu}_7\text{Se}_4/\text{Cu}_2\text{Se}$ gave interesting results. Both phases released copper, the latter so that the initially monoclinic(?) phase (16) was subsequently transformed into cubic berzelianite, Cu_7Se_4 (17), tetragonal umangite, Cu_3Se_2 (18), and eventually hexagonal klockmannite, CuSe (19). The TlCu_7Se_4 phase changed practically only its tetragonal c axis in the process. Thereby, the initial small line splittings disappeared at the stage where $a/c = \sqrt{7} \approx 2.65$ —yielding a "cubic appearance" for the powder pattern—to occur again in a displaced manner when c had decreased further. The reaction could be enhanced by using H_2O_2 rather than air, but the neighboring three-phase area was virtually not entered. The cell volume decreased up to 1% in the process, the powder lines remaining sharp.

TlCu_5Se_3 reacted similarly to ammonia with a decrease in its tetragonal c axis at the

TABLE I
CHARACTERISTICS OF THE TERNARY PHASES IN THE Tl-Cu-Se SYSTEM

Compound	Composition (wt%)		Structure type	Cell parameters (Å)	Space group ^a
	Theory	Found			
TlCuSe ₂	Tl 48.0 Cu 14.9 Se 37.1		CuFeS ₂	5.8 11.6 (5)	$\bar{I}42d$
TlCuSe	Tl 58.9 Cu 18.3 Se 22.8	59.2(6) 18.1(1) 22.8(2)	PbFCl	4.08(1) 8.16(1) (21)	$P4/nmm$
TlCu ₂ Se ₂	Tl 41.8 Cu 26.0 Se 32.2	41.5(4) 26.5(2) 32.0(3)	ThCr ₂ Si ₂	3.8572(2) 14.038(1) (2)	$I4/mmm$
TlCu ₄ Se ₃	Tl 29.4 Cu 36.5 Se 34.1	29.8(4) 36.5(2) 33.7(3)	KCu ₄ Se ₃	3.975(1) 9.834(1)	$P4/mmm$
Tl ₅ Cu ₁₄ Se ₁₀	Tl 37.8 Cu 32.9 Se 29.2	38.1(4) 32.8(2) 29.1(2)	New	18.097(2) 3.9582(2) 18.118(2) 116.089°(7)	$C2/m^*$
TlCu ₃ Se ₂	Tl 37.0 Cu 34.5 Se 28.5	37.2(4) 34.2(2) 28.6(2)	CsAg ₃ S ₂ (22)	15.2128(7) 4.0115(2) 8.3944(4) 111.700°(4)	$C2/m$
TlCu ₅ Se ₃	Tl 26.9 Cu 41.9 Se 31.2	27.5(4) ^b 41.2(2) 31.3(3)	New	12.9023(2) 3.9905(1)	$P\bar{4}n2^*$
TlCu ₅₋₁ Se ₃ ^c			New	12.43(1) 12.80(1) 3.93(1)	$Pnn2^*$
TlCu ₇ Se ₄	Tl 21.2 Cu 46.1 Se 32.7	21.3(3) 46.1(2) 32.7(2)	NH ₄ Cu ₇ S ₄ (23)	10.4524(2) 3.9736(1)	$\bar{I}\bar{4}$

Note. The italic numbers within parentheses denote references that may be consulted for information on either the structure type or the cell parameters. Data not followed by a reference number are the results of this work. The figures within parentheses are the estimated standard deviations based on statistics. Cell parameters are given in the order *a*, (*b*), *c*, (β).

^a Asterisks indicate that the space group assignments are only tentative, based on extinction rules and structural considerations.

^b The chemical analysis refers to a sample from the three-phase area also containing TlCu₄Se₃ and Cu₇Se₄. The cell parameters of this phase were *a* = 12.9034(4) Å and *c* = 3.9776(2) Å, the shortened *c* axis indicating copper deficiency. The analysis results rather correspond to TlCu_{4.9}Se₃.

^c No large-grained material suitable for a microprobe analysis was obtained. This orthorhombic phase occurs on copper extraction of the tetragonal TlCu₅Se₃.

initial stage, but continued copper extraction led to the appearance of a new pattern. That could be indexed on an orthorhombic cell (o) which bears a simple metric relationship with the original tetragonal cell (t), such that $a_o \approx b_o \approx a_t$, $c_o \approx c_t$ (see Table I). This new phase might be a vacancy ordered variation of the structural theme assigned to TiCu_5Se_3 . Its composition obviously lies somewhere between those of TiCu_5Se_3 and TiCu_4Se_3 . Density considerations would suggest $\text{TiCu}_{4.3}\text{Se}_3$. The composition $\text{TiCu}_{4.6}\text{Se}_3$ was obtained from microprobe analysis on powder.

Conclusions

Syntheses in the TI-Cu-SE system have shown that there are more phases than previously anticipated. In particular, the method of copper extraction introduced in this work presents a very convenient way of making subtle composition changes and is also a means of investigating phase relationships. It is very striking how easily the compositions of TiCu_7Se_4 and TiCu_5Se_3 may be changed without disrupting the structures. It is possible that copper deficiency is paired with valence-band hole formation. Preliminary measurements of the thermoelectric effect of $\text{TiCu}_{7-x}\text{Se}_4$ indicate metallic behavior and a decreasing positive slope of S vs temperature (S being the Seebeck coefficient) for increasing x . This hypothesis might explain why neither TiCuSe nor TiCu_2Se_2 is affected by the ammonia solution. The latter compound has one hole in the valence band per formula unit and tolerates no more. In the near future a more extensive study of the physical properties of the various phases is intended, preferably on single-crystal material. In that context, the microprobe analysis method has proved a very excellent tool with which to correlate composition with other properties.

In Table I suggestions are given as to the

structural identity of the new phases. Single-crystal diffractometry must establish the structural parameters. Intensity calculations have proved the structure types of TiCu_7Se_4 and TiCu_3Se_2 . According to preliminary suggestions based on a consistent crystal chemistry of the phases, the structure of $\text{Ti}_5\text{Cu}_{14}\text{Se}_{10}$ is intimately related to the structure of TiCu_3Se_2 , and the structures of TiCu_5Se_3 and its copper-deficient orthorhombic variety are related to that of TiCu_7Se_4 . Such structural hypotheses have given a good qualitative agreement when comparing powder intensities. Single-crystal diffractometry work will be started shortly and reported in a forthcoming paper.

Finally, this study has also led to mineralogical offspring. Two TI-Cu-SE minerals have been reported, crookesite and sabatierite. Their compositions in relation to the current studies are discussed elsewhere (20).

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