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The Phase Diagrams of Ag_2X–AgY (X = S, Se, Te; Y = Cl, Br, I): Mixtures and the Structure of Ag_5Te_2Cl

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The phase diagrams of Ag_2S–AgI, Ag_2Se–AgI, Ag_2Te–AgI, Ag_2Te–AgBr, and Ag_2Te–AgCl were investigated. The system Ag_2S–AgI shows two broad regions of solid solution which are based on the structure of the high-temperature phases of the constituent compounds. The high-temperature modification of Ag_3SI is part of one of these regions. The system Ag_2Se–AgI resembles the system Ag_2Te–AgI; both contain limited regions of terminal solid solutions. The AgI-based solid solutions decompose peritectically. In the system Ag_2Te–AgBr a compound Ag_3TeBr was found. Ag_3TeBr undergoes a phase transition at 590 ± 20 K. The low-temperature form has hexagonal symmetry with the lattice parameters a = 748.8(1) pm and c = 4357.6(6) pm. The compound Ag_5Te_2Cl was found in the Ag_2Te–AgCl system. In both systems a restricted terminal solid solution, based on the high-temperature form of Ag_2Te, was observed. Ag_5Te_2Cl has a reversible phase transformation at 329 ± 3 K with ΔH_{tr} = 9.82 ± 0.4 kJ mole^{-1}. β-Ag_5TeCl, the low-temperature form probably has the space group $P2_{1/n}$, a = 1365.5(1), b = 1386.1(1), c = 764.23(2), β = 90.201(1)°, and Z = 4. α-Ag_5Te_2Cl has the space group $I4/_{mcm}$ with a = 975.5(3), c = 783.0(1) pm, and Z = 4. The anion sublattice is built of octahedra, which share all their vertices with neighboring octahedra. The Ag^+ ions are distributed over octahedral holes of this network. The phase is similar in behavior to Ag_8GeTe_6 and may be a silver-ion conductor.

Introduction

The phase diagrams of silver chalcogenide–silver halide mixtures have recently been described in the literature. The first investigation into the system Ag_2S–AgI was carried out by Reuter and Hardel (*1*), who determined the phase relations up to the temperature of 620 K and reported the new ternary compound Ag_3SI. However, Takahashi *et al.* (*2*) reported two other phases in this system at 25 and 75 mole% AgI with broad homogeneity regions. The silver chalcogenide–silver chloride (bromide) systems were described by Blachnik and Kudermann (*3*). In contrast with their results Karbanov and Bontschewa–Mladenowa (*4*) observed in the system Ag_2Te–AgBr a broad terminal solid solution at the Ag_2Te corner and a new compound, Ag_6TeBr_4. The latter stoichiometry closely resembles a Tl_6X_4S-class of compounds in the thallous halide–thallous sulfide systems, reported by Blachnik and Dreisbach

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(*5*). The phase diagrams were completed by an investigation of Takahashi *et al.* of the systems Ag_2Se–AgI and Ag_2Te–AgI (*6*).

The present investigation was undertaken as an attempt to clarify the deviations in the reported phase diagrams and to gain some information on the structure type of the compounds.

Experimental

Silver sulfide was prepared from aqueous silver nitrate solutions by precipitation with $(NH_4)_2S$ (*7*). Silver telluride was obtained from the proper amounts of high-purity elemental solids (silver, Degussa 99.999%; tellurium, Preussag 99.999%) by encapsulating them under vacuum in quartz ampoules, then melting in a flame, and annealing at 700 K for about one month. The silver halides AgCl and AgBr (Degussa) were purified by recrystallization. Both were dissolved in the corresponding concentrated acids (HCl and HBr, both Merck suprapur) and precipitated by adding water to the solutions. The products were dried at 400 K and 10^{-2} Torr. The preparative work was carried out under red light. Silver iodide (Degussa) was used after drying without further purification. The purity was tested by difference thermal analyses and X-ray analysis. Ag_2Te was additionally examined by metallographic methods. The powders were mixed in the desired amounts in steps of 2 to 5 mole% and the mixtures sealed under vacuum in quartz ampoules. The mixtures were molten, homogenized by shaking, and then annealed for periods between 1 week and 3 months. The annealing temperatures were chosen from preliminary experiments in the systems Ag_2Te–AgCl and Ag_2Te–AgBr, usually at about 20–30 K below the solidus temperatures. In the system AgI–Ag_2S, the samples were first annealed at 700 K for about 1 month and then at 380 K for 2 weeks. This procedure was necessary to clarify the phase diagram, because on quenching from 700 K to ambient temperatures, mixtures of the low-temperature phase Ag_3SI and the high-temperature solid solutions were obtained. These mixtures lead to rather confusing results in the X-ray and differential scanning calorimeter (DSC) experiments.

The apparatus and the method (*8*) used in the difference thermal analysis have already been described. The heating rate was usually 5 or 10 K min^{-1}; the accuracy of the liquidus temperatures is ±5 K, that of three-phase equilibria lines ±2 K. In some cases, especially with low heating rates (0.5 K min^{-1}), a DSC (990 thermal analyser, Du Pont) was used. X-Ray data of the powders were obtained with a Guinier-4 (radiation Cu$K_{\alpha 1}$) or a Huber–Guinier camera (radiation Cr$K_{\alpha 1}$), using low quartz as internal standard. Single crystal data were collected by a precession camera (Huber, radiation Mo$K_{\alpha 1}$). High-temperature X-ray data were obtained by a Simon–Guinier camera (radiation Cu$K_{\alpha 1}$). In these experiments, a heating rate of 2 K h^{-1} was used. Metallographic and quantitative analyses were carried out with a microprobe (Superprobe 733, Jeol). All samples in the systems were subjected to thermal analyses, X-ray and metallographic studies.

Single crystals of Ag_5Te_2Cl (tetragonal columns or rectangular platelets) were grown by recrystallization in a salt melt. A total of 0.1–0.5 g of finely ground Ag_5Te_2Cl powder was mixed with 50 g of a 40 mole% AgCl–60 mole% $ZnCl_2$ salt mixture. The mixture was encapsulated in an evacuated quartz ampoule, heated at 10 K h^{-1} to 720 K and kept at this temperature for 24 h. Thereafter, the melt was slowly cooled (1 K h^{-1}) to ambient temperature. The flux was dissolved in concentrated ammonia, in which the crystals are insoluble. In the same manner single crystals of Ag_3TeBr were grown in a salt melt (at 680 K), composed of 50 mole% AgBr and 50 mole%

$ZnBr_2$. These crystals were obtained in form of thin hexagonal plates.

Results

The System Ag_2S–AgI

The phase diagram, reported by Reuter and Hardel (*1*), contains the ternary phase Ag_3SI, which transforms at 508 K into the high-temperature modification. According to these authors the α-phase is an isolated compound and not part of a continuous solid solution. This is surprising, because α-AgI (*9*), α-Ag_3SI (*10*), and α-Ag_2S (*11*) form identical anion lattices. The Ag^+ sites are occupied statistically in AgI by two, in Ag_3SI, by three, and in Ag_2S, by four Ag^+ ions per elementary cell. The phase diagram, reported by Takahashi *et al.* (*2*), differs considerably, because the authors encountered two additional phases. Our interpretation of the results, gained with the different methods, used in this investigation, are displayed in Fig. 1.

The agreement between the data of Reuter and Hardel and our low-temperature data is very good. β-AgI and β-Ag_2S show limited terminal solid solutions. Between these regions the compound β-Ag_3SI with a homogeneity range of approximately 10 mole% was observed. This range broadens with increasing temperature.

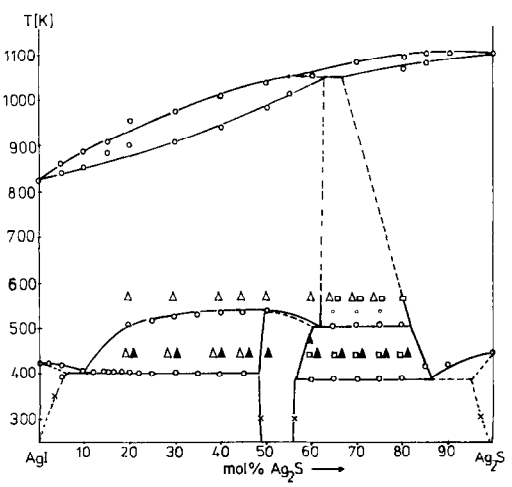

FIG. 1. The phase diagram Ag_2S–AgI: △–α-AgI-based; □—α-Ag_2S-based solid solution; ▲—Ag_3SI; ×—concentration data from Reuter (*1*).

Above the temperature of 401 K β-AgI and β-Ag_3SI combine by a eutectoid reaction to a solid solution with a structure which is based on the α-AgI lattice. The stability field of this solid solution ends at 1048 K in a peritectic reaction at a peritectic composition of 40 mole% AgI.

The high-temperature form, α-Ag_3SI, is part of this solution; β-Ag_3SI transforms at 508 K into this mixed crystal. We have found no indications of a two-phase region between the α-AgI solid solution and α-Ag_3SI. All high-temperature X-ray photographs in the concentration range between 10 and 40 mole% AgI revealed a transformation into a continuous region of solid solution. As for α-AgI, no metastable solid solutions can be obtained at ambient temperature by quenching. However, near the composition Ag_3SI metastable solid solutions were found after quenching, because the transition from the mixed crystal to β-Ag_3SI is associated with an order–disorder transformation in the anion sublattice. This effect complicated the interpretation of the results since in quenched α-Ag_3SI the solid solutions of β-AgI, α-Ag_3SI and β-Ag_3SI were found. This observation was taken by Reuter and Hardel as evidence for a two-phase region between α-AgI and α-Ag_3SI. The metallographic examination of the samples confirmed the eutectoid decomposition of the solid solutions.

The homogeneity range of α-Ag_2S solid solution increases with increasing temperatures (540 K, 20–25 mole% AgI; 1000 K, 30–35 mole% AgI). In agreement with Reuter und Hardel a two-phase field was observed between the AgI-based and the Ag_2S-based solid solution.

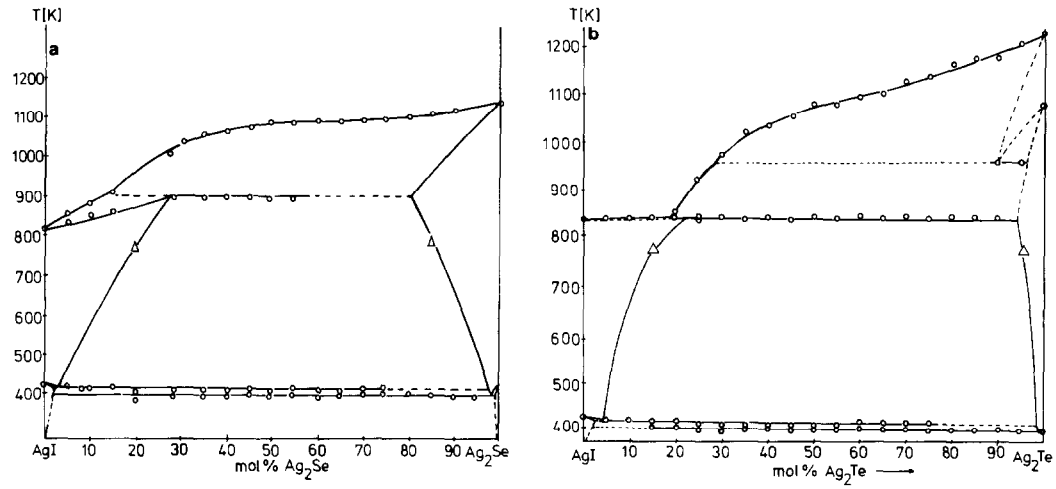

FIG. 2. The phase diagrams Ag_2Se–AgI (a) and Ag_2Te–AgI (b); △ obtained from microprobe analyses.

The Systems Ag_2Se–AgI and Ag_2Te–AgI

Both systems, depicted in Fig. 2, are in good agreement with previous results (*6*). In the phase diagrams limited regions of solid solubility, broadening with increasing temperature, were observed. The α-AgI-based solid solution decomposes peritectically at 902 ± 3 K in the Ag_2Se–AgI system and at 833 ± 3 K in the Ag_2Te–AgI system. At lower temperatures both undergo a eutectoid decomposition at 406 K. The phase borders were obtained from quantitative microprobe analyses.

The System Ag_2Te–AgCl

The results (Fig. 3) are in close agreement with the data, published recently by Blachnik and Kudermann (*3*) and Bontschewa-Mladenowa *et al.* (*12*). The system is quasibinary. The eutectic temperature was found to be 660 ± 3 K and the eutectic composition was 20 ± 2 mole% Ag_2Te. The compound Ag_5Te_2Cl, which decomposes peritectically at 790 ± 3 K, has no observable composition field. A phase transformation was detected at 329 ± 3 K. The thermodynamic data of the transition, measured in a DSC on single crystals, are $\Delta H_{tr} = 9.82 \pm 0.4$ kJ mole^{-1} and $\Delta S_{tr} = 29.85 \pm 1.5$ kJ mole^{-1} K^{-1}.

The System Ag_2Te–AgBr

The system Ag_2Te–AgBr is displayed in Fig. 4. It contains three-phase equilibria, especially a eutectic one at 643 ± 3 K and 82 mole% AgBr and a peritectic at 710 ± 3 K, connected with the decomposition of the

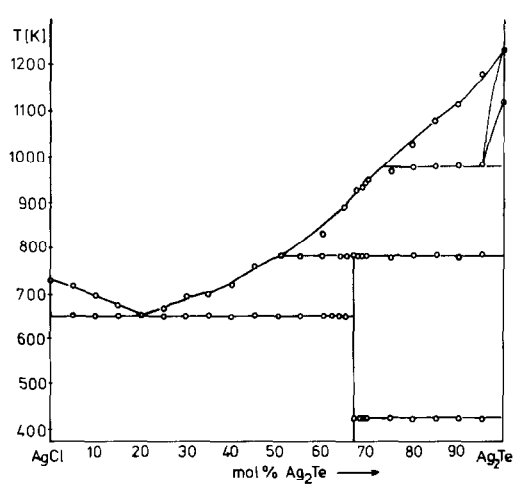

FIG. 3. The phase diagram AgCl–Ag_2Te.

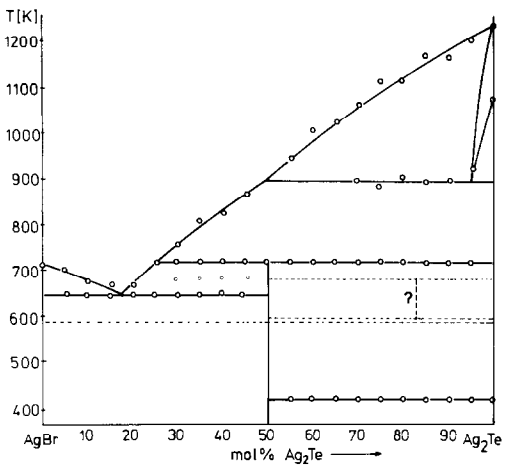

FIG. 4. The phase diagram AgBr–Ag_2Te.

compound Ag_3TeBr. Neither the broad region of solid solubility of AgBr in Ag_2Te (40 mole% (*4*)) nor the phase Ag_6TeBr_4 could be observed. These results were confirmed by quantitative analyses with a microprobe. However, the X-ray data revealed that the phase diagrams, obtained from DTA- and DSC investigations are not well established. Samples of identical compositions which were subjected to different thermal treatment showed characteristic deviations in their X-ray pattern. In the concentration range from 20 to 45 mole% AgBr, all samples annealed above 600 K showed an X-ray pattern with unidentified reflections. Both series also showed deviations in their thermal behavior. In the samples annealed between 600 and 660 K the β–α transition of Ag_2Te was not observed. In specimens cooled from the melt or annealed at lower temperatures this effect was recorded in the DSC. We tentatively explain these effects by the possible existence of a currently unidentified high-temperature compound.

When the compound Ag_3TeBr is quenched from temperatures above 590 K, a complicated pattern appears, instead of the simple X-ray pattern of the low-temperature modification. Ag_3TeBr thereafter undergoes a phase transformation with a transition temperature of 590 ± 20 K, which is not detectable in the DSC.

X-Ray Results

Laue and precession photographs of a single crystal of the low-temperature β-Ag_3TeBr showed hexagonal symmetry with the lattice parameters a = 784.8(1) pm and c = 4357.6(6) pm. The data are given in Table I.

Similar photographs of the low temperature β-Ag_5Te_2Cl showed the systematic extinctions $h0l$ with $h + l = 2n$ and $0k0$ with $k = 2n$, in the space group $P2_{1/n}$. The refined lattice parameters, obtained by a least-squares treatment of the powder data, are a = 1365.5(1), b = 1386.1(1), c = 764.23(2) pm, β = 90.201(1), and Z = 8, the latter calculated with an estimated density of 7.5

TABLE I

X-RAY POWDER DATA OF Ag_3TeBr

β-Ag_3TeBr						α-Ag_3TeBr (635 K)	
d_{obs} (pm)	d_{calc} (pm)	h	k	l	I/I_0 estim.	d_{obs} (pm)	I/I_0 estim.
726.2	726.3	0	0	6	3	1416	1
665.0	671.6				2	751	2
575.5	576.7	1	0	4	1	710	2
390.8	390.8	1	1	1	2	692	3
344.6	345.2	1	1	6	4	568	1
324.3	324.4	2	0	4	2	376	3
316.6	316.3	2	0	5	2	369	3
305.4	304.9	1	1	9	3	358	2
298.7	298.2	2	0	7	3	345	1
226.6	226.6	3	0	0	2	329	3
221.9	221.8	3	0	4	4	318	1
216.3	216.3	3	0	6	4	310	2
207.5	207.5	0	0	21	3	303	2
197.1	197.2	2	0	18	4	298	3
						297	2
						289	1
						285	2
						280	2
						244	1
						227	3
						223	2
						222	1

TABLE II

X-RAY POWDER DATA OF Ag_5Te_2Cl

β-Ag_5Te_2Cl					
d_{calc} (pm)	d_{obs} (pm)	h	k	l	I/I_0 est.
693.1	690	0	2	0	3
682.7	678	2	0	0	3
665.9	665.9	1	0	1	3
486.4	485.7	2	2	0	4
382.1	382.3	0	0	2	3
375.8	375.8	3	1	1	2
368.3	368.0	0	1	$\bar{2}$	3
355.9	355.9	1	1	$\bar{2}$	2
346.5	346.5	0	4	0	2
341.0	341.1	3	2	$\bar{1}$	3
324.7	324.7	1	2	$\bar{2}$	3
312.1	311.8	4	0	$\bar{1}$	1
309.0	308.9	2	4	0	1
306.3	306.4	4	2	0	1
303.7	303.8	4	1	1	2
300.9	300.8	2	2	$\bar{2}$	3
288.3	288.0	1	3	$\bar{2}$	2
286.4	286.3	2	4	1	3
269.9	270.1	2	3	$\bar{2}$	5
259.8	259.5	3	4	$\bar{1}$	2

g cm^{-1}. All crystals with the low-temperature structure were twinned and appeared to be of tetragonal symmetry. The X-ray data are given in Table II.

The twins vanished during the β–α phase transformation; therefore, the structure of the α-phase was investigated at 338 K. High-temperature α-Ag_5Te_2Cl crystallizes with a tetragonal body-centered lattice and the lattice parameters of a = 975.5(3) and c = 783.0(1) pm, obtained from the Guinier powder data. From the precession data we obtained the systematic extinctions $h + k + l = 2n$ and $0kl$ with $k = 2n$, $l = 2n$, which agree with the space group $I4/_{mcm}$ with Z = 4. A 0.15 × 0.15 × 0.25-single crystal of the α-modification was used to collect the intensities on a four-circle diffractometer (Enraf–Nonius, CAD-4, MoK_α radiation, λ = 71.07 pm, graphite monochromator, SDP-program package (*13*), 338 ± 5 K). The $\omega - 2\theta$ scan was used to collect 570 symmetry independent reflections up to θ = 35°. A total of 233 reflections with $I \leqq 2\sigma_I$ were used to solve the structure. Lorentz polarization and absorption corrections (*14*) were applied. Scattering factors for Ag, Te, and Cl were taken from the "International Tables" (*15*). The atomic coordinates of the Te and Cl atoms were determined by direct methods (Multan 80 (*16*)). A first isotropic refinement of the atomic coordinates converged at R = 0.25. From these data the atomic positions of Ag were calculated by successive Fourier and difference-Fourier syntheses. The thermal and

TABLE III

ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE COEFFICIENTS[a]

Atom		x	y	z	n	U_{11}	U_{22}	U_{33}	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Te	8h	0.3386	0.1614	0	0.250	54.6(6)	54.6(6)	56.8(9)	3(1)	0	0
Cl	4a	0	0	0.25	0.125	52(3)	52(3)	49(5)	0	0	0
Ag(1)	16k	0.3006	0.4266	0	0.067	61(7)	27(5)	92(8)	7(4)	0	0
Ag(2)	32m	0.4134	0.7631	0.1635	0.231	76(3)	107(5)	93(4)	−9(3)	27(9)	2(3)
Ag(3)	16l	0.0508	0.4492	0.2063	0.071	140(10)	140(10)	58(9)	10(9)	10(9)	10(6)
Ag(4)	16j	0.2732	0	0.25	0.041	120(10)	80(10)	120(10)	−49(9)	50(30)	49(9)
Ag(5)	16l	0.1315	0.3685	0.1378	0.055	77(6)	77(6)	130(20)	24(9)	15(9)	15(9)
Ag(6)	32m	0.2731	0.4225	0.0829	0.038	60(10)	15(6)	30(8)	13(8)	−10(10)	6(8)
Ag(7)	16k	0.3020	0.4531	0	0.059	140(20)	90(10)	75(9)	30(10)	0	0

[a] $\left(T = \exp\left[-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} U(i,j)h_ih_j/a_i^x/\!/a_j^x/\right]\right)$ in $pm^2 \times 10^{-1}$.

X-ray investigations of the phase transformation as well as the observation that the electron density at the silver positions was less than that at the chlorine position allowed the conclusion that the possible atomic sites of silver are only partially occupied. Thus the occupation number and the isotropic temperature factor of each position were refined in alternation until the calculations converged to a final $R = 0.057$. A difference Fourier synthesis with the parameters obtained from this calculation still revealed electron density at some silver positions. However, the occupation probability of these positions is very low. Therefore we introduced only those positions into the structure determination which had a statistically significant occupation by silver atoms. Listed in Table III are the atomic coordinates and the thermal parameters. The observed cation–anion distances are similar to those of the binary compounds Ag_2Te, resp., AgCl ($d_{Ag-Te}(\alpha\text{-}Ag_5Te_2Cl)$ 266 to 296.6 pm, d_{Ag-Te} (Ag_2Te–hessite) 287 to 304 pm (*17*); $d_{AgCl}(\alpha\text{-}Ag_5Te_2Cl)$ 278.2 to 285.8 pm, d_{Ag-Cl}(AgCl) 278 pm (*18*)). The silver–silver distances are extremely short and the temperature factors unusually high. These results may be explained on the assumption that the silver atoms are not localized. Thus in the elementary cell of α-Ag_5Te_2Cl (Fig. 5) only the localized anion positions are shown. The anion sublattice consists of a network of vertex-sharing Te_4Cl_2 octahedra. The silver atoms occupy the holes of the network except the one in the middle of the Te_4Cl_2 octahedron. The distribution over all possible positions is not statistical. Some positions are preferred as shown by the different occupation numbers. The cations are positioned outside the centers of the holes in the direction of octahedra faces or edges. The results very closely resemble those reported by Rysanek *et al.* of the high-temperature phase of Ag_8GeTe_6 (*19*). We assume, that by analogy to this phase Ag_5Te_2Cl becomes a silver-ion conductor by the β–α transformation.

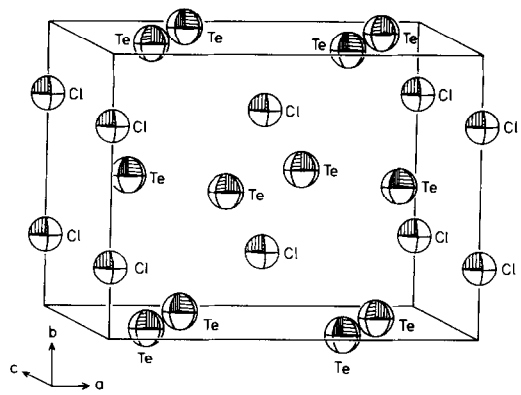

FIG. 5. The anion positions in the elementary cell of α-Ag_5Te_2Cl.

The composition, the axis ratios, and the space group of α-Ag_5Te_2Cl indicate that this compound might be related to the Tl_5X_2Y class of compounds (*20*), which is isopuntal to the Cr_5B_3 type. In fact, the anion lattices of both compounds are isotypic, in the thallous compounds the metal atoms are in fixed positions, while in the silver compound they are distributed in a nonrandom manner over all positions.

Acknowledgments

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