Synthesis and Crystal Structure of Disilvertitanate-(IV), Ag_2TiO_3

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Ag_2TiO_3 was synthesized by solid state reaction of K_2TiO_x $(OH)_{6-2x}$ ($x \cong 1$), as prepared by sol–gel methods, and Ag powder. During the reaction at 630°C an oxygen pressure of 0.14 GPa was maintained. Crystals of Ag_2TiO_3 (monoclinic, $C/2c$, $a = 16.813(4)$ Å, $b = 7.612(1)$ Å, $c = 5.054(1)$ Å, $\beta = 101.95$ (2)°, $Z = 8$, ω/θ scan, data collection excluding daylight, numerical absorption correction, $R_1 = 0.035$, $wR_2 = 0.074$) are yellow, of flat prismatic shape, and stable against air and moisture. The crystal structure exhibits the novel polymeric titanate anion $^1_\infty[TiO_3]_n^{2n-}$: TiO_6 octahedra are connected by common edges to form one-dimensionally extended chains. The silver atoms are arranged to an extended homoatomic structural unit with rather short silver–silver contacts, which are indicative for weak bonding interactions between the d^{10} configured silver cations. © 1997 Academic Press

1. INTRODUCTION

A general topological feature of ternary silver oxides is the tendency to form cluster-like arrangements of silver cations, which segregate from the anionic part of the structure (1, 2). These agglomerates show impressive topological similarities even in very different compounds (2). The silver–silver distances within such aggregates are significantly shorter than the van der Waals distance of 3.40 Å (3) and sometimes even fall short of those in silver metal (2.89 Å) (4). Such metal–metal contacts have been perceived as evidence for weak bonding interactions between the d^{10} configured silver cations (1,2). To get a broader experimental basis for the understanding of the nature of the peculiar d^{10}–d^{10} interactions, we have extended our investigations to ternary silver oxides of the early transition elements. As a first result we present here the synthesis, crystal structure, and some physical properties of disilvermetatitanate, Ag_2TiO_3.

So far, there are two reports on the ternary system Ag/Ti/O. $Ag_2Ti_4O_9$ was synthesized from $Tl_2Ti_4O_9$ (5) via cation exchange and is according to an X-ray powder diffractogram isostructural to the thallium titanate. "Ag_2TiO_3" was reported to have formed on shaking freshly

prepared Ag_2O with a concentrated solution of H_2TiCl_6 in hydrochloric acid. However, neither structural data nor any "finger print" were published (6).

2. EXPERIMENTAL AND RESULTS

Ag powder was precipitated from a solution of $AgNO_3$ (Merck, p.a.) in aqueous ammonia by adding $N_2H_4 \cdot H_2O$ as a reducing agent. For this purpose 15 g of $AgNO_3$ (88.3 mmol) were solved in 2000 ml bidistilled water and mixed with 250 ml of aqueous ammonia (25%, Riedel de Haen, p.a.). Then 7 ml of $N_2H_4 \cdot H_2O$ (143.9 mmol, $d = 1.029$ g ml^{-1}, Riedel de Haen, p.a.) were added dropwise. This procedure yields highly dispersed microcrystalline silver with a particle size of about 2 μm.

$K_2TiO_x(OH)_{6-2x}$ ($x \cong 1$; x was estimated by DTA/TG, see below) was obtained via sol–gel methods by hydrolysis of a potassium titanium alcoxide solution prepared from titaniumtetraisopropylate (Aldrich, 97%) and elemental potassium (Riedel-de-Haen, 98%) in isopropanole, with potassium and titanium in the molar ratio 2:1. In a typical experiment, 6 g of potassium (0.1534 mol) were solved in 400 ml of absolute isopropanol and a solution of 21.81 g of $Ti(OiPr)_4$ (0.0767 mol) in 100 ml absolute isopropanol was added while stirring rapidly. The powder obtained after hydrolysis was dried *in vacuo* at room temperature and subsequently heated to 200°C in an argon atmosphere. Simultaneous DTA/TG of this crude product showed a first step of weight loss of 8.0% accompanied by a broad endothermal effect between 310 and 480°C. This weight loss would agree to the reaction $K_2Ti(OH)_6 \rightarrow K_2TiO(OH)_4 + H_2O$ (calculated: 7.9%). As a final step the product was heated at 500°C for 24 h in dry oxygen atmosphere. According to DTA/TG, the composition of the gel is taken to be $K_2TiO_x(OH)_{6-2x}$ with x approximately equal to 1.

Ag_2TiO_3 was prepared by solid state reaction of Ag powder with $K_2TiO_x(OH)_{6-2x}$ ($x \cong 1$) in stainless steel autoclaves at a temperature of 630°C applying an elevated oxygen pressure ($p(O_2) = 0.14$ GPa). Intimate mixtures of the starting materials were reacted in gold crucibles (4 cm in height, 0.9 cm in diameter). Carbonate free bidistilled water (4 ml) was added as an accelerator. Typical starting

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mixtures consist of 0.35 g Ag powder thoroughly ground with 0.34 g of $K_2TiO_x(OH)_{6-2x}$ (3.2445 mmol Ag, 1.6224 mmol $K_2TiO_x(OH)_{6-2x}$; $x \cong 1$). The reaction product was washed with bidistilled water to remove the potassium hydroxide. The remaining bright yellow crystals of Ag_2TiO_3 are sensitive to daylight but stable to air and moisture. The compositions of the samples were checked by coupled SEM/EDX (SEM: DSM 940, Zeiss, Oberkochem; EDX: EDAX, PV 9800, Taunstein) based on the AgL and TiK X-ray emissions. The Ag/Ti ratio averaged over 16 spot measurements was found to be 2.0/1 ($\pm$ 5%). No potassium was detected (limit of detection 0.1 mass%). DTA/TG (STA 429, Netzsch, Selb) were performed simultaneously in the temperature range from 20 to 1150°C at a heating rate of 5°C/min in an argon atmosphere. By these experiments Ag_2TiO_3 was shown to decompose in one step at a temperature of 540°C into TiO_2 (rutile) and Ag, accompanied by an overall weight loss at about 4.6% (5.1% calculated). The decomposition products were identified by X-ray powder diffraction (Stoe Stadi P, Stoe & Cie, Darmstadt).

Rotation and Weissenberg photographs indicate monoclinic symmetry and the reflection conditions hkl: $h + k = 2n$, h0l: $h,l = 2n$; 0kl: $k = 2n$; hk0: $h + k = 2n$ and h00: $h = 2n$; 0k0: $k = 2n$; 00l: $l = 2n$. Thus the extinction symbol is C 1c1 and the two space groups C c and C 2/c are possible. In the course of the structure refinement the centrosymmetric space group C 2/c turned out to be the correct

one. Unit cell parameters were refined from powder data (Stoe Stadi P, Stoe & Cie, Darmstadt) based on reflections up to $2\theta = 70°$ (cf. Table 1).

Data collection (ω/θ scan) was performed using an Enraf Nonius CAD 4 diffractometer. Crystallographic data and parameters for data collection are given in Table 2. The initial description of the crystal shape was refined with the program HABITUS (7) using Ψ-scans of eight unique reflections. The refined crystal shape was used in SHELX 76 (8) for a numerical absorption correction. The structure was solved by direct methods (SHELXS 86 (9)) which produced the silver and titanium positions. During the subsequent refinements (SHELXL 93 (10)) the positions of oxygen were derived from difference Fourier synthesis (cf. Table 3). Scattering factors were taken from (11).

3. DISCUSSION

Ag_2TiO_3 is the first, and so far only, unambiguously identified and structurally well-characterized silver titanate. Exploring the synthetic access to silver titanates proved to be rather tedious. Solid state reactions of the binary components which were successful in many other systems did not work even at the upper limits of our equipment with respect to oxygen pressure and temperature ($p(O_2) = 0.6$ GPa, $T = 700°C$), or by using activated binary oxides as starting materials. It seems to be crucial to use special silver and

TABLE 1
Powder Diffraction Data of Ag_2TiO_3, $2\theta_{max} = 70°$, Cu$K\alpha$

h	k	l	Int.	D_{obs}	D_{calc}	h	k	l	Int.	D_{obs}	D_{calc}
2	0	0	6.8	8.1809	8.2045	− 5	3	1	21.6	1.9452	1.9451
1	1	0	21.8	6.8794	6.8900	6	2	1	4.6	1.9075	1.9065
− 1	1	1	2.7	4.1850	4.1888	0	4	0	25.7	1.8994	1.8979
1	1	1	2.8	3.8567	3.8547	− 7	1	2	3.0	1.8509	1.8522
0	2	0	3.8	3.7937	3.7958	5	3	1	2.0	1.7778	1.7793
− 3	1	1	3.8	3.6122	3.6180	9	1	0	4.6	1.7722	1.7728
2	2	0	2.3	3.4455	3.4450	8	0	1	5.2	1.7665	1.7677
5	1	0	10.5	3.0117	3.0124	− 2	4	1	2.2	1.7589	1.7589
− 2	2	1	8.6	2.9485	2.9484	4	4	0	1.4	1.7222	1.7225
4	2	0	2.1	2.7856	2.7861	− 7	3	1	2.6	1.7075	1.7071
6	0	0	34.6	2.7360	2.7348	− 4	4	1	2.1	1.6725	1.6725
2	2	1	100.0	2.7171	2.7151	− 8	2	2	13.4	1.6045	1.6034
− 4	2	1	96.8	2.5875	2.5881	− 6	0	3	10.6	1.5607	1.5605
− 2	0	2	59.2	2.5110	2.5113	6	2	2	5.9	1.5248	1.5262
0	0	2	1.5	2.4662	2.4668	7	1	2	19.2	1.5151	1.5148
− 1	1	2	5.7	2.3902	2.3899	1	5	0	21.0	1.5102	1.5119
− 4	0	2	4.4	2.3403	2.3407	0	4	2	2.8	1.5041	1.5042
− 3	1	2	6.0	2.3294	2.3301	2	4	2	1.9	1.4479	1.4473
4	2	1	4.0	2.2939	2.2910	− 6	2	3	8.6	1.4431	1.4433
6	2	0	1.4	2.2203	2.2189	− 8	0	3	2.4	1.4377	1.4378
1	3	1	11.9	2.2037	2.2027	− 1	3	3	1.8	1.3941	1.3946
− 3	3	1	3.6	2.1572	2.1556	10	2	1	2.4	1.3689	1.3692
− 8	0	1	3.2	2.0519	2.0518	− 5	3	3	6.0	1.3596	1.3590
3	1	2	5.6	2.0176	2.0161	9	3	1	2.5	1.3562	1.3552

TABLE 2
Crystallographic Data and Parameters of Data Collection

Formula weight	$311.64 \, g \, mol^{-1}$
Space group	$C \, 2/c$
Wavelength, monochromator	0.7107 Å, Graphite
Unit cell dimensions	$a = 16.813(4)$ Å
	$b = 7.6116(13)$ Å, $\beta = 101.95(2)°$
	$c = 5.0545(9)$ Å
Volume	$632.8(2) \, Å^3$
Density (calc.)	$6.542 \, g \, cm^{-3}$
Z	8
Absorption coeff.	$14.510 \, mm^{-1}$
$F(000)$	1120
Crystal size	$0.28 \times 0.22 \times 0.13 \, mm^3$
2θ range	$2°$ to $60°$
hkl ranges	-23 to 23, 0 to 10, -7 to 7
Reflections collected, R_{int}	1801, 0.014
Data, constraints, parameters	877, 0, 57
GOOF	1.093
Extinction coeff.	0.00163(11)
Largest diff. peak/hole	2.319 and $-2.482 \, e \, Å^3$
Min./max. transmission	0.1112/0.2105
R indices (all data)	$R_1 = 3.5\%$, $wR_2 = 7.4\%$

TABLE 3
Atomic Coordinates [$\times 10^4$] and Anisotropic Thermal Parameters [$Å^2 \times 10^3$]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	925(1)	988(1)	859(1)	70(1)	21(1)	16(1)	2(1)	0(1)	17(1)
Ag(2)	2477(1)	3715(1)	2366(1)	14(1)	28(1)	20(1)	1(1)	$-2(1)$	6(1)
Ti(1)	779(1)	3777(1)	6090(2)	10(1)	9(1)	8(1)	0(1)	2(1)	0(1)
O(1)	0	2312(6)	7500	15(2)	10(2)	12(2)	0	3(2)	0
O(2)	0	5750(6)	7500	13(2)	9(2)	8(2)	0	0(2)	0
O(3)	1367(2)	1918(5)	5247(7)	14(2)	13(2)	17(2)	$-1(2)$	1(1)	3(1)
O(4)	1371(2)	4320(5)	9642(7)	11(2)	15(2)	9(1)	0(1)	$-1(1)$	3(1)

titanium source substances, e.g., potassium-oxo-hydroxo-titanate, which add an alien component to the reaction mixture. Fortunately, in the case of Ag_2TiO_3, potassium is virtually not included into the final product and can be removed as potassium hydroxide by washing the crude product with water. Ag_2TiO_3 forms bright yellow, transpar-

ent crystals which are insensitive to air and moisture, but have to be protected from daylight.

The crystal structure of Ag_2TiO_3 exhibits a novel polymeric metatitanate anion, which consists of distorted TiO_6 octahedra. The Ti–O distances within these octahedra range from 1.82 to 2.21 Å (cf. Table 4 and Fig. 1). This rather wide range may be explained by crystal chemical arguments. The shortest distance is observed to terminal oxygen atoms. The increasing coordination number of oxygen with respect to titanium results in an increase in the respective Ti–O bond distances (cf. Table 4). In addition, the *trans* effect causes an elongation of the bridging Ti–O–Ti bonds being opposite to terminal oxygen atoms. The TiO_6 octahedra are connected via adjacent edges to form zigzag chains. Two such chains are linked, again via edges, to form a novel oxotitanate chain anion ${}^1_\infty[TiO_3]^{2n-}_n$. Thus each TiO_6 octahedron

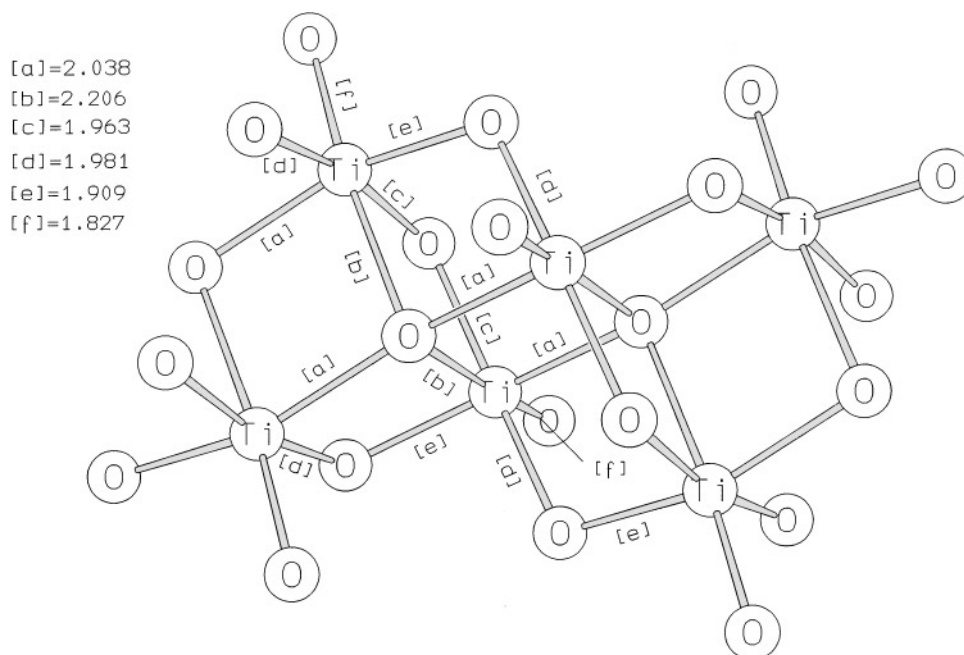|	
[a]=	2.038
[b]=	2.206
[c]=	1.963
[d]=	1.981
[e]=	1.909
[f]=	1.827

FIG. 1. Section of the ${}^1_\infty[TiO_3]^{2n-}_n$ anion, distances are given in Å.

TABLE 4
Selected Bond Distances [Å] and Angles [deg] in Ag_2TiO_3

Atoms	Distance	Atoms	Angle
Ag(1)–O(1)	2.286(2)	O(1)–Ag(1)–O(3)#1	127.94(12)
Ag(1)–O(3)#1	2.300(4)	O(1)–Ag(1)–O(3)#2	119.82(13)
Ag(1)–O(3)#2	2.374(4)	O(3)#1–Ag(1)–O(3)#2	111.42(14)
Ag(1)–Ag(1)#3	2.9409(7)	O(3)#7–Ag(2)–O(4)	174.44(14)
Ag(1)–Ag(2)#6	3.1646(9)	O(3)–Ti(1)–O(4)	100.7(2)
Ag(1)–Ti(1)	3.1831(10)	O(3)–Ti(1)–O(1)	94.5(2)
Ag(1)–Ag(2)	3.2976(10)	O(4)–Ti(1)–O(1)	92.21(12)
Ag(2)–O(3)#7	2.120(4)	O(3)–Ti(1)–O(4)#13	98.2(2)
Ag(2)–O(4)	2.123(3)	O(4)–Ti(1)–O(4)#13	89.17(13)
Ag(2)–Ag(2)#7	3.0371(10)	O(1)–Ti(1)–O(4)#13	166.7(2)
Ag(2)–Ag(2)#11	3.1960(7)	O(3)–Ti(1)–O(2)#14	102.0(2)
Ag(2)–Ag(2)#10	3.2296(10)	O(4)–Ti(1)–O(2)#14	155.9(2)
Ag(2)–Ti(1)#11	3.3835(11)	O(1)–Ti(1)–O(2)#14	93.97(8)
Ti(1)–O(3)	1.827(4)	O(4)#13–Ti(1)–O(2)#14	79.71(14)
Ti(1)–O(4)	1.909(3)	O(3)–Ti(1)–O(2)	171.6(2)
Ti(1)–O(1)	1.963(3)	O(4)–Ti(1)–O(2)	77.16(11)
Ti(1)–O(4)#13	1.981(4)	O(1)–Ti(1)–O(2)	77.53(14)
Ti(1)–O(2)#14	2.0381(12)	O(4)#13–Ti(1)–O(2)	89.94(14)
Ti(1)–O(2)	2.206(3)	O(2)#14–Ti(1)–O(2)	81.51(8)
Ti(1)–Ti(1)#13	3.1387(10)		

Symmetry transformations used to generate equivalent atoms

#1	$x, y, z + 1$	#2	$x, -y, z + 1/2$
#3	$x, -y, z - 1/2$	#4	$-x, -y + 1, -z$
#5	$-x, -y, -z$	#6	$-x + 1/2, y - 1/2, -z + 1/2$
#7	$-x + 1/2, -y + 1/2, -z$	#8	$-x, y, -z - 1/2$
#9	$-x, y, -z + 1/2$	#10	$-x + 1/2, -y + 1/2, -z + 1$
#11	$x, -y + 1, z + 1/2$	#12	$-x + 1/2, y + 1/2, -z + 1/2$
#13	$x, -y + 1, z - 1/2$	#14	$-x, -y + 1, -z - 1$
#15	$x, y, z - 1$		

shares four edges with neighboring ones. Alternatively, the $\frac{1}{\infty}[TiO_3]_n^{2n-}$ partial structure can be described as a section of the NaCl structure. The anionic chains run along [001] and form a close packed arrangement of rods (cf. Fig. 2).

The voids between the chains are occupied by silver cations (cf. Fig. 2). The two crystallographic independent silver cations show two different coordinations. Ag(1) exhibits a threefold coordination by oxygen. The bond distances between Ag(1) and oxygen range from 2.286(2) to 2.374(4) Å while bond angles O–Ag(1)–O vary from 111.42(14)° to 127.94(12)°. Ag(1) is located 0.12(1) Å above the plane formed by its oxygen neighbors. Ag(2) shows a typical, almost linear twofold coordination and is attached to O(3) and O(4) at distances of 2.120(4) and 2.123(3) Å with an O–Ag–O angle of 174.44(14)° (cf. Table 4).

The silver–silver distances within the cationic partial structure in Ag_2TiO_3 are significantly shorter than the van der Waals distance of 3.4 Å (3) and range from 2.9409(7) to 3.2976(10) Å. The silver cations Ag(2) are arranged to a two-dimensional net of slightly distorted rhomboidic shape perpendicular to [100], with silver–silver distances at about 3.0371(10), 3.1960(7), and 3.2296(10) Å. Ag(1) assembles to zigzag chains propagating in [001] with Ag–Ag distances of 2.9409(7) Å (cf. Fig. 2 and Table 4). These chains are connected to a net constituted by Ag(2) on one side and another chain on the other side (cf. Fig. 2).

Only a few metatitanates of alkaline metals like HT- and LT-Li_2TiO_3 (12,13), $NaKTiO_3$ (14), and Rb_2TiO_3 (15) have been characterized structurally, so far. These compounds differ considerably with respect to the Ti–O coordination.
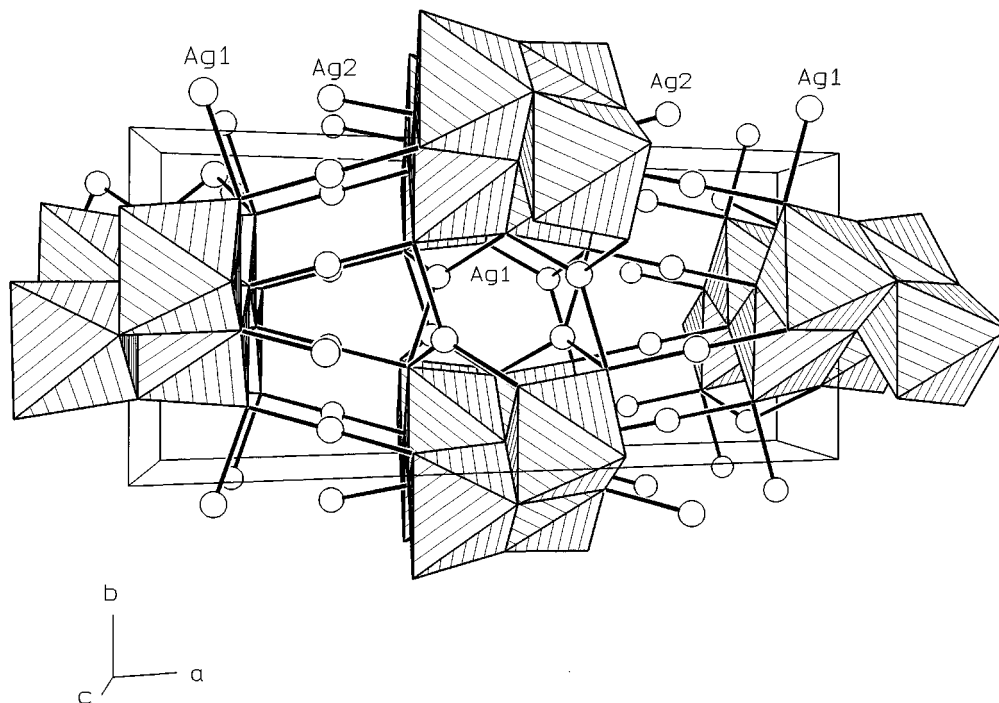

FIG. 2. Unit cell of Ag_2TiO_3 and its nearest coordination, TiO_6 shown as octahedra, view along [001].
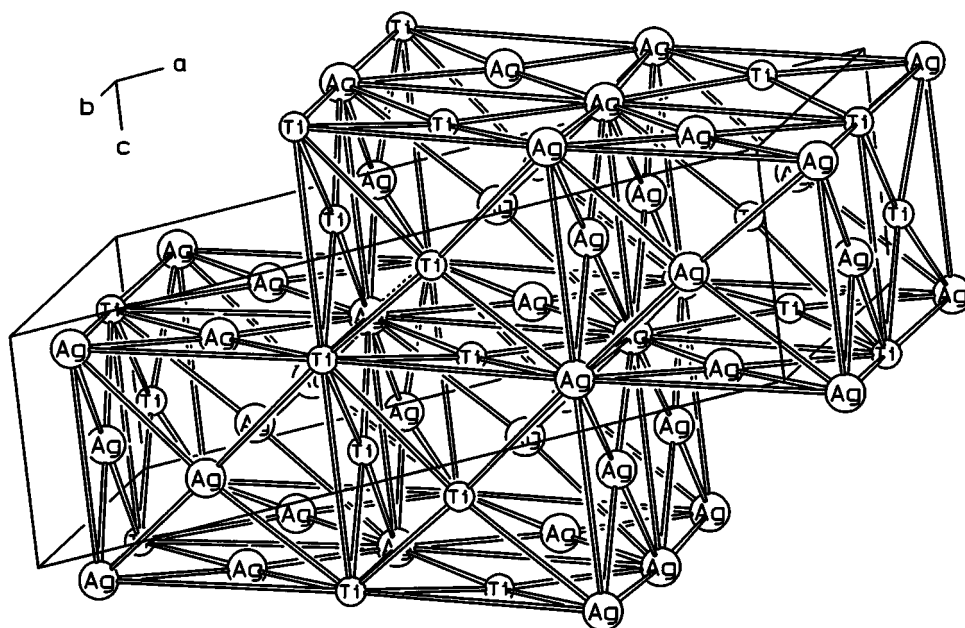
FIG. 3. Cationic partial structure and its relation to the unit cell of Ag_2TiO_3.

K_2TiO_3 is isostructural to K_2PbO_3 (16) according to X-ray powder diffraction and contains Ti^{4+} in a square pyramidal coordination. The crystal structure of LT-Li_2TiO_3 represents an ordered derivative of the NaCl structure, while HT-Li_2TiO_3 shows a random cation distribution. In NaK TiO_3, like in K_2TiO_3, chains of edge sharing square pyramids of TiO_5 are present. The crystal structure of Rb_2TiO_3 contains a one-dimensional chain of corner-sharing TiO_4 tetrahedra. Obviously, these structural tendencies are due to the increasing cation radius of the alkaline metals leading to an increasing coordination number for the alkaline cations and a decreasing coordination number for titanium.

Based on ion size considerations, one would expect the structure of Ag_2TiO_3 to be related to that of $NaKTiO_3$. However, despite the similarities in charge and cationic radii of Na^+, Ag^+, and K^+, respectively, there is no structural relationship between these two compounds. Obviously, there are other factors which influence the crystal structure of Ag_2TiO_3, e.g., the pronounced softness of silver cations (in terms of the HSAB principle) and the preference of d^{10} configurated cations for low coordination numbers. Additionally, the attractive d^{10}–d^{10} interactions come into play, which cause the silver cations in ternary silver oxides to aggregate to fragments of the ccp structure (1, 2). The fragment of the ccp structure constituted by the silver cations is completed by titanium atoms to result in a distorted ccp packing of all the cations (cf. Fig. 3). The relation between the unit cell dimensions a, b, and c of Ag_2TiO_3 and the tetragonal face-centered arrangement of the Ag cations can

be seen from Fig. 3: $a' = (a - c)/3 = 5.48$ Å, $b' = b/2 = 3.81$ Å, and $c' = c = 5.05$ Å. Thus an average cation–cation distance of 3.2 Å can be derived.

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