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Preparation and Crystal Data of the New Compounds Ag_7MS_6 (M=Ta and Nb)

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Synopsis. The compounds Ag_7TaS_6 and Ag_7NbS_6 were prepared by a sealed silica tube method at 500 °C for 4 d. They crystallize in the face-centered cubic system with the unit-cell dimensions of a=10.5139±0.0003 Å and a=10.5001 ±0.0006 Å, respectively. From the density measurements, it has been clarified that the unit cell contains four formula units.

In recent years there has been great interest in ternary silver sulfides with the general formula $Ag^{+}_{(12-n)}M^{n+}S_6$ (M=Al, Ga, Si, Ge, Sn, P, As, and Sb) which are usually called 'Argyrodite' compounds. Many works have been done on their crystal structures and physical properties.[1—13] A common feature of these compounds is the presence of tetrahedrally closed-packed S sublattice forming the interpenetraiting, centered, distorted icosahedra, and the highly ionic motion of Ag atoms in a 'liquid-like manner' within the rigid framework of S lattice. Hitherto, however, preparative studies reported of this type have been limited only to the compounds associated with M=group 3 (IIIB), group 4 (IVB), and group 5 (VB) cations. A similar $Ag^{+}_{(12-n)}M^{n+}S_6$ compound could be expected for other metal systems. In this connection group 5 (VA) transition metals were selected as candidates for M cations and the possibility of preparing analogous compounds was examined. In the course of the investigation of the Ag–Ta–S system, the new compound Ag_7TaS_6 whose crystal structure is face-centered cubic has been recently discovered besides $AgTaS_3$.[14] Furthermore, the analogous new compound Ag_7NbS_6 has been obtained successfully. This note is concerned with the X-ray powder diffraction studies of the compounds, Ag_7TaS_6 and Ag_7NbS_6.

Results and Discussion

For the preparation of Ag_7MS_6 (M=Ta and Nb), tantalum (3N6), niobium (3N6), sulfur (6N), and Ag_2S (3N) powders were used as starting materials. Initially TaS_2 and NbS_2 were produced from these elements at 600 °C. The title compounds were prepared by using TaS_2, NbS_2, Ag_2S, and S in the stoichiometric proportions. The materials were mixed in an agate mortar in the glove box under pure N_2 atmosphere, pressed into pellets (radius: 7 mm), and sealed in evacuated silica tubes. The heat treatments were performed at 500 °C for 4 d. At the end of runs the tubes were quenched into water. The final volume of pellet became about 2 times larger than the initial one owing to the expansion through the reaction process.

Black-colored products obtained were identified by means of X-ray powder diffraction methods. A Rigaku diffractometer (Geigerflex, RAD-B system) with graphite-monochromated Cu $K\alpha$ radiation was used. The lattice constants were calculated by least-squares method. All peaks in X-ray diffraction patterns of Ag_7TaS_6 and Ag_7NbS_6 could be indexed by means of the cubic lattice with the unit cell dimension of

Table 1. Low-Angle Powder Data of X-Ray Diffraction of Ag_7TaS_6 and Ag_7NbS_6

Ag_7TaS_6			Cu $K\alpha$ radiation			Ag_7NbS_6		
d_o/Å	d_c/Å	I/I_0	h	k	l	d_o/Å	d_c/Å	I/I_0
6.074	6.070	50	1	1	1	6.070	6.062	58
5.257	5.257	57	2	0	0	5.254	5.250	26
3.717	3.717	4	2	2	0	3.711	3.712	2
3.169	3.170	96	3	1	1	3.166	3.166	55
3.034	3.035	100	2	2	2	3.029	3.031	100
2.628	2.628	30	4	0	0	2.625	2.625	25
2.412	2.412	51	3	3	1	2.409	2.409	31
2.351	2.351	21	4	2	0	2.348	2.348	8
2.146	2.146	51	4	2	2	2.143	2.143	32
2.023	2.023	22	5	1	1	2.020	2.021	36
1.8588	1.8586	59	4	4	0	1.8560	1.8562	56
1.7771	1.7772	24	5	3	1	1.7742	1.7748	10
1.7524	1.7523	18	6	0	0	1.7508	1.7500	10
1.6623	1.6624	12	6	2	0	1.6603	1.6602	5
1.6034	1.6034	6	5	3	3	1.6011	1.6012	2
1.5848	1.5850	10	6	2	2	1.5828	1.5829	3
1.4723	1.4723	17	5	5	1	1.4704	1.4703	10
1.4580	1.4580	7	6	4	0	1.4561	1.4560	2
1.4052	1.4050	8	6	4	2	1.4030	1.4031	4
1.3688	1.3688	11	7	3	1	1.3672	1.3670	6

a=10.5137±0.0003 Å and a=10.5001±0.0006 Å, respectively. Both X-ray patterns were very similar except for the slight difference in diffraction intensities. The systematic extinction (*hkl*: $h+k=2n+1$, $k+l=2n+1$, $l+h=2n+1$) is indicative of the face centered cubic and leads to the possible space groups $F23$, $Fm3$, $Fm3m$, $F\bar{4}3m$, and $F432$. In order to determine the number of formula units per cell, density measurements were carried out by immersion method, using CCl_4. The values $d_m=6.55$ g cm^{-3} and $d_m=5.90$ g cm^{-3} were obtained for Ag_7TaS_6 and Ag_7NbS_6, respectively. These results suggest clearly that the unit cell contains four formula units ($Z=4$). In the analogy of other cubic Argyrodites compounds the space group $F\bar{4}3m$ could be considered to be most probable. The *d*-spacings, *hkl* indecies and relative intensities of both compounds are listed in Table 1. Based on the close similarity of data it can be concluded that Ag_7TaS_6 and Ag_7NbS_6 are isotypic to each other. In order to examine the transporting phenomena of these compounds, conductivity measurements were carried out on disk-shaped, cold pressed polycrystalline samples (thickness: 1.0—1.6 mm). Direct current methods were employed with Solartron 1286 electrical interface. The cell arrangement was $Ag/RbAg_4I_5/Ag_7MS_6/RbAg_4I_5/Ag$ (M=Ta or Nb), in which $RbAg_4I_5$ served as an electron blocking layer. The experiment was made by sending a constant current (less than 30 μA) and measuring the voltage drop across the specimen. The silver ionic conductivity $\log\sigma_{Ag^+}$ of Ag_7TaS_6 is −4.9 at 27 °C and rises linearly to −3.5 at 144 °C with an activation energy of 0.33 eV. This compound becomes more conductive above 144 °C based on some of the phase transition and the curvature changes rapidly. The value of $\log\sigma_{Ag^+}$ reaches −1.8 at 200 °C with an activation energy of 1.13 eV. Similarly the silver ionic conductivity of Ag_7NbS_6 is −4.6 at 27 °C and increases linearly to −3.6 at about 119 °C with an activation energy of 0.25 eV. After that the value of $\log\sigma_{Ag^+}$ rises rapidly to +0.1 at 135 °C. However, the results of preliminary experiments on the ionic transport number indicated clearly that both compounds are the mixed conductors like Ag_2S.[15] Detailed studies on their crystal structure and physical properties are now in progress.

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