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The ternary sulfide Ag_7TaS_6 displays high Ag-ion conductivity at ambient temperature, and the framework TaS_6 and Ag ions can be respectively regarded as the host structure and guest ions. Two low-temperature phases, *i.e.* Ag_7TaS_6 II and Ag_7TaS_6 III, were found. The Rietveld analysis of Ag_7TaS_6 II has been performed based on the X-ray data measured at 240K using a wave length 0.64997Å by a high-resolution powder diffraction instrument combined with the beam line BM1B at the European Synchrotron Radiation Facilities. Smooth convergence has been obtained (R_{WP}=0.066), and the crystal structure was described based on a space group Pn with monoclinic lattice constants a=7.4462, b=7.4013, c=10.5296Å and β=90.069°. The narrow widths of reflections even at high angle have made possible the analysis of individual thermal parameters for Ag ions. In Ag_7TaS_6 II, Ag-Ag linkage rather than Ag-S coordination seem to affect the thermal parameters of Ag ions. The guest-guest interaction can be important for mobility of guest ions in the ionic conductor.

Keywords: Ag-ion conductor; crystal structure; Rietveld analysis; Ag_7TaS_6

INTRODUCTION

The ternary sulfide Ag_7TaS_6 was synthesized and its Ag ion conductivity at ambient temperature was found [1,2]. The room-temperature phase, Ag_7TaS_6 I, was identified as a cubic phase of the argyrodite-family [3,4] with space group F $\bar{4}$3m and a=10.514Å. In the structure model of Ag_7TaS_6 I, Ag ions are distributed statistically over many tetrahedral and triangular

coordination sites in the framework with the composition TaS_6 [1,5]. The framework TaS_6 and Ag ions can be respectively regarded as the host structure and guest ions.

Low-temperature powder X-ray diffraction studies revealed two low-temperature phases, *i.e.* Ag_7TaS_6 II (between approx. 280 and approx. 170K) and Ag_7TaS_6 III (below approx. 170K) [6, 7]. The crystal structure of Ag_7TaS_6 II was described based on a space group Pn with the lattice constants a=7.453, b=7.403, c=10.540Å and β=90.069° from a Rietveld analysis[7]. However, thermal parameters derived from the conventional powder X-ray diffraction data are not very reliable, because a large number of overlapped $K\alpha_1$ and $K\alpha_2$ reflections hide the background intensities especially at high diffraction angle.

In this paper, a reinvestigation of Ag_7TaS_6 II using a high-resolution diffractometer for synchrotron X-ray radiation is reported. The Rietveld analyses of Ag_7TaS_6 II have been performed using the program PREMOS [8] based on the new data.

EXPERIMENTAL

The details of the preparation processes of the powder specimen of Ag_7TaS_6 were similar to those described in the previous paper [1]. The specimen sealed into a glass capillary with a diameter of 0.3mm was set in the high-resolution powder diffractometer installed at the Swiss-Norwegian beam-line (BM1B) at the European Synchrotron Radiation Facilities (ESRF). Step scan data of the low-temperature phase Ag_7TaS_6 II were collected at 240±0.5K with a step size 0.005 degree using the wave length of 0.64997Å.

RIETVELD ANALYSIS

The new diffraction data have been obtained from a high-resolution diffractometer and synchrotron X-ray source. Although the narrow widths of reflections allow a better analysis of the structure including

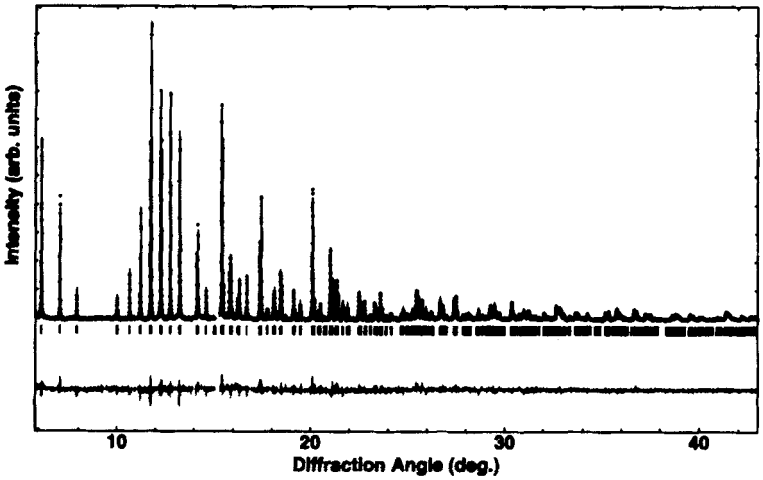

FIGURE 1 The Rietveld pattern of Ag_7TaS_6 II (240K, λ=0.64997Å) based on the data measured on the high-resolution powder diffraction instrument installed on beamline BM1B at the ESRF.

TABLE I Crystal data and the atomic parameters of phase II of Ag_7TaS_6 at 240K.

Crystal data (monoclinic, space group No.7)
Space group Pn (with nearly rectangular β angle)
a=7.4462(1), b=7.4013(1), c=10.5296(1)Å, β=90.0687(1)°,
Space group Pc
a'=7.4462(1), b'=7.4013(1), c'=12.9040(1)Å, β'=125.3120(1)°,
Z=2 (according to the formula Ag_7TaS_6)

Atomic parameters based on the unit cell with β=90.0687°
Coordinates of equivalent positions: x,y,z; 1/2+x,-y,1/2+z

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
Ag1	0.293(2)	0.027(2)	-.013(2)	3.2(4)	Ta	0.5	0.251(1)	0.5	0.56(8)
Ag2	-.300(3)	0.090(2)	0.190(2)	3.1(4)	S1	0.251(6)	0.241(7)	0.637(4)	1.4(3)
Ag3	0.299(3)	0.345(3)	0.151(2)	7.3(7)	S2	-.233(3)	0.268(7)	0.610(4)	1.4
Ag4	-.211(3)	0.473(2)	0.265(2)	6.2(6)	S3	0.463(5)	-.003(4)	0.370(3)	1.4
Ag5	0.579(3)	0.120(3)	0.799(3)	8.1(8)	S4	0.487(7)	0.496(4)	0.361(4)	1.4
Ag6	0.063(3)	0.420(2)	0.453(2)	7.4(7)	S5	0.015(8)	0.222(5)	0.273(4)	1.4
Ag7	-.053(2)	0.288(2)	0.035(2)	3.4(5)	S6	0.539(5)	0.263(6)	0.014(5)	1.4

thermal parameters, large fluctuations in background may be responsible for the unfavorable reliability factor and large standard deviations of the parameters. Therefore three-point smoothing of the data have been used for the present Rietveld analysis. Smooth convergence has been obtained (R_{wp}=0.066) based on the structure model which is the same as that used previously [7]. The Rietveld analysis pattern and the final parameters are shown in Fig. 1 and Table I, respectively. From the parameters of Table I, selective interatomic distances are calculated

TABLE II Selected interatomic distances (Å) in Ag_7TaS_6 II.

Ag1-Ag2(i)	3.26(3)	Ag5-Ag1(viii)	2.99(3)
-Ag3	2.97(3)	-Ag2(ix)	3.40(3)
-Ag5(ii)	2.99(3)	-S1	3.13(5)
-Ag7	3.25(2)	-S2(x)	2.67(5)
-S2(i)	2.56(5)	-S3(ix)	3.08(4)
-S3(iii)	2.75(4)	-S5(ix)	2.59(4)
-S6	2.54(4)	-S6(viii)	2.56(6)
Ag2-Ag1(iv)	3.26(3)	Ag6-Ag4	2.87(3)
-Ag4	3.00(2)	-S1	2.73(5)
-Ag5(iii)	3.40(3)	-S2	2.98(4)
-Ag7	2.91(3)	-S5	2.42(4)
-S1(iii)	2.56(5)	-S6(xi)	2.46(5)
-S3(v)	2.63(4)	Ag7-Ag1	3.25(2)
-S5	2.67(6)	-Ag2	2.91(3)
-S6(v)	2.55(5)	-Ag3	2.97(3)
Ag3-Ag1	2.94(3)	-Ag4	3.04(3)
-Ag7	2.97(3)	-S3(iii)	2.73(4)
-S2(vi)	2.92(6)	-S4(vii)	2.45(4)
-S4	2.76(5)	-S5	2.60(5)
-S5	2.59(6)	-S6(v)	3.06(4)
-S6	2.40(5)	Ta -S1	2.36(4)
Ag4-Ag2	3.00(2)	-S2(x)	2.30(3)
-Ag6	2.87(3)	-S3	2.34(3)
-Ag7	3.03(3)	-S4	2.33(4)
-S1(vii)	2.53(5)		
-S4(v)	2.47(6)		
-S5	2.51(5)		

symmetry operators (i)1/2+x,-y,-1/2+z;(ii)x,y,-1+z;(iii)-1/2+x,-y,-1/2+z;(iv)-1/2+x,-y,1/2+z;(v)-1+x,y,z;(vi)1/2+x,1-y,-1/2+z;(vii)-1/2+x,1-y,-1/2+z;(viii) x,y,1+z;(ix)1/2+x,-y,1/2+z; (x)1+x,y,z; (xi)-1/2+x,1-y,1/2+z.

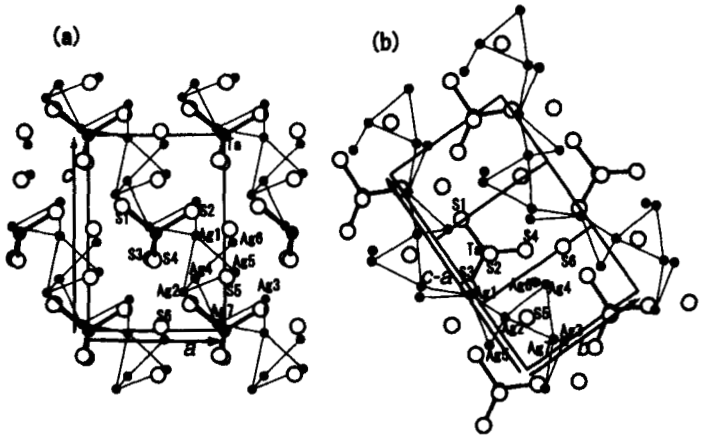

FIGURE 2 Projections of the crystal structure of Ag_7TaS_6 II along (a) [0 1 0] and (b) [-2 0 -1]. Only atoms with coordinates $0.6<x+z<1.6$ are illustrated in (b). Ag-Ag distances less than 3.4Å are shown by thin sticks.

and listed in Table II. Projections of the crystal structure of Ag_7TaS_6 II are *illustrated in Fig. 2.*

DISCUSSION

Standard deviations of positional parameters newly obtained are about 1/2 to 1/3 of the former ones [7]. The narrow widths of reflections even at high angle have made possible the analysis of individual thermal parameters for Ag ions. As Ag_7TaS_6 becomes an Ag-ionic conductor at ambient temperature, thermal parameters of Ag ions in the low-temperature phase are of interest. In Ag_7TaS_6 II, isotropic thermal parameters, B, of Ag1, Ag2 and Ag7 are respectively 3.2(4), 3.1(4) and 3.4(5)Å^2 with estimated standard deviations in brackets, while B of the other four kinds of Ag ions are about 6 to 8 Å^2 as shown in Table I. In the structure of Ag_7TaS_6 II, Ag2, Ag3 and Ag6 are in the distorted S-S tetrahedrons and the residual four kinds are in the triangles shared by two tetrahedrons as listed in Table II. From another angle, Ag1, Ag2 and Ag7 are coordinated by four Ag ions (Ag-Ag< 3.4Å) and the other four kinds of Ag ions are linked by three to one Ag ions. Ag3, Ag4, Ag5 and Ag6 are

surrounded respectively by two (Ag-Ag< 3.0Å), three (Ag-Ag< 3.1Å), two (Ag-Ag< 3.4Å) and one (Ag-Ag~2.9Å) Ag ions and their thermal parameter B(Ag3)=7.3(7) Å^2, B(Ag4)=6.2(6) Å^2, B(Ag5)=8.1(8) Å^2 and B(Ag6)=7.4(7) Å^2 are obtained from the present Rietveld analysis. As illustrated in Fig. 2, Ag ions seem to form Ag-Ag network. Ag1, Ag2 and Ag7, linked to four Ag ions, are in rather restricted environment in the Ag-Ag network. On the other hand, Ag3, Ag4, Ag5 and Ag6, linked by three to one Ag ions, are in looser environment in the Ag-Ag network and they show larger thermal parameters. Ag-Ag linkage rather than Ag-S coordination seem to affect the thermal parameters of Ag ions. Therefore, the guest-guest interaction can be important for mobility of guest ions in the ionic conductor.

Acknowledgements

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