Structural Phase Transitions in Ag₂Se (Naumannite)

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Dedicated to Professor Dieter Naumann on the Occasion of his 65th Birthday.

Bei der Redaktion eingegangen am

Abstract Ag₂Se (naumannite) was investigated by means of temperature dependent synchrotron powder diffraction and DTA. Upon heating in air the known 1st order phase transition from orthorhombic low-temperature Ag₂Se (P2₁2₁2₁, Z = 4) to cubic ion conducting high-temperature Ag₂Se (Im $\bar{3}$ m, Z = 2) was observed at approx. 140°C. Upon cooling a small hysteresis was detected (T_{PU} = 120°C). It was found that when heated in air Ag₂Se segregates elemental selenium. After cooling to ambient temperature the resulting low-temperature Ag₂Se can no longer be described in the known structural model with harmonic terms, the use of anharmonic terms is probably necessary. The phase transition and the segregation of selenium are accompanied by an increased crystallinity of the sample, as the halfwidths of the reflections become significantly smaller. Approaching the phase transition the lattice parameters of orthorhombic Ag₂Se show a distinct anisotropic behaviour: *b* and *c* show a positive and *a* a negative thermal expansion. When heated in argon the segregation of selenium is not observed.

Keywords: Chalcogenide; Ion conductor; Phase transition; Silver; X-ray powder diffraction

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1 Introduction

The mineral naumannite was first discovered in Tilkerode (Abberode), Harz Mts, Saxony-Anhalt, Germany in 1828 and is named after the German crystallographer and geologist *Karl Friedrich Naumann* (1797-1873). It is a grey-black mineral with a metallic lustre. Its composition is given as Ag_2Se . A full description of its crystal structure was published by *Wiegers* in 1971 based on X-ray powder diffraction data [1]. Ag_2Se crystallizes in an orthorhombic unit cell ($P2_12_12_1$, $a = 4.333 \text{ \AA}$, $b = 7.062 \text{ \AA}$, $c = 7.764 \text{ \AA}$, $Z = 4$) with two crystallographically distinct silver atoms. Ag1 is coordinated tetrahedrally, whereas the coordination sphere of Ag2 is almost triangular (Figure 1). For thin sublimed films another orthorhombic crystal structure was found ($P2_122$, $Z = 4$) with similar cell constants [2]. This structural model, which is based on electron diffraction data, could not be confirmed for the bulk material and seems to be only stable in thin layers.

Figure 1: Crystal structure of Ag_2Se at room temperature ($P2_12_12_1$, $Z = 4$). Silver atoms are shown as dark grey cycles, selenium atoms as larger light grey cycles.

Already since 1936 it was known that Ag_2Se undergoes a phase transition to a cubic high-temperature form at about 133°C [3]. In this high-temperature modification ($\text{Im}\bar{3}m$, $a = 4.983$

$\text{\AA}$, $Z = 2$) selenium atoms form a body-centred packing, while silver atoms are statistically distributed over several interstitial sites. The cation distribution of this ion conducting modification of Ag_2Se was subject of a detailed investigation using single crystal neutron diffraction data [4]. It was found that the silver cations are delocalized in channels along [100] consisting of octahedral and tetrahedral sites. Anharmonic terms were necessary to describe the density at the tetrahedral sites. With increasing temperature the occupancy of the octahedral sites decreases.

The phase transition itself was, however, not investigated in great detail. Only a short note is given upon this subject [5]. X-ray single crystal diffraction data using the oscillation method and diffractograms were used in this investigation. The data reveal an isotropic increase of all lattice parameters with increasing temperature. But the quality of the reported data is low and no further details of the phase transition were extracted. As powder diffraction, especially based on synchrotron data, has proven to be a powerful tool for the investigation of subtle lattice changes we have decided to re-investigate the structural phase transition in Ag_2Se using synchrotron powder diffraction data. A detailed description of the changes of the lattice parameters around the transition temperature was a special focus of this investigation. Attention should also be paid to the fact that varying transition temperatures had been reported in the literature (see Table 1 in [5]). It was unclear whether this is a real effect of the compound or just a result of inaccurate measurements.

2 Experimental

Ag_2Se was purchased from Aldrich ($\rho = 8.22 \text{ g/ml}$ at 25°C) and used as delivered. Temperature-dependent synchrotron powder diffraction data were recorded at the powder diffractometer of beamline B2 of the Hamburg synchrotron facility (HASYLAB, Hamburg/Germany) with a position sensitive imaging plate detector system (OBI [6]). The ground sample was filled in a capillary ($\varnothing = 0.3 \text{ mm}$, Lindemann glass), which was not sealed. A STOE capillary furnace was used for heating. For temperature calibration of the furnace the lattice expansion of NaCl was measured prior to the experiment. But due to only small deviations between the set point temperature and the real temperature in the temperature range under investigation no correction was applied. The wavelength ($\lambda = 0.68541 \text{ \AA}$) was determined from a measurement of a LaB_6 standard prior to the experiment. No internal or external standard was used in the temperature dependent measurements themselves. In a first

cycle the sample was heated from 30°C to 230°C and cooled down to 30°C. Diffraction patterns were recorded at different temperatures within this range. In a second cycle the same sample was heated to 260°C. The exposure time of each diffraction pattern (approx. 20 min) was corrected for fluctuations and decay of the synchrotron beam by using monitor counts collected between the incident beam and the sample. In summary, 19 patterns were recorded in the first and 17 patterns in the second cycle.

Each diffraction pattern was subject of a Rietveld refinement (GSAS [7]). To obtain reliable and comparable results the same sets of variables were used in the final Rietveld refinements of the diffractograms if possible. For diffraction patterns containing the room temperature modification of Ag₂Se the following 25 variables were refined: 9 positional and 3 thermal (isotropic) parameters for Ag(1), Ag(2) and Se; 3 lattice parameters (a , b , c); zero shift; scale; 6 background parameters (linear interpolation function); 2 parameters for a Pseudovoigt profile [8]; refined range: $7^\circ < 2\theta < 50^\circ$. For diffraction patterns containing the high-temperature modification of Ag₂Se the following 17 variables were refined: 2 thermal (isotropic) parameters for Ag(1), Ag(2) and Se (the thermal parameters of the silver atoms were constrained to each other); one occupancy factor for Ag(1) and Ag(2); one cubic lattice parameter (a); zero shift; scale; 9 background parameters (linear interpolation function); 2 parameters for a Pseudovoigt profile [8]; refined range: $10.7^\circ < 2\theta < 50^\circ$. The number of background parameters had to be increased for patterns containing the high-temperature modification due to a broad background feature at $2\theta < 20^\circ$. The occupancy parameter for the silver sites 12(d) and 6(b) was defined in a way that the overall composition of the compound remained at Ag₂Se. In the second cycle the pattern recorded at 140°C contained both modifications so that in this case the number of refined variables increased to 35 (refined range: $7^\circ < 2\theta < 50^\circ$).

The refinement of the diffraction pattern recorded at 30°C in the first cycle confirmed that the sample is single-phase. No additional reflections were found. Upon heating weak additional reflections appear, which could not be assigned to the room or high-temperature modification of Ag₂Se. In the first cycle the intensities of these reflections increase upon heating up to 180°C. At 230°C they disappear, but they appear again at 180°C upon cooling. They are also present after cooling to 30°C. In the second heating cycle these reflections are still present in the range 30°C to 220°C, but that are no longer present at 240°C and 260°C. Five such reflections were identified, the strongest at $2\theta \approx 13^\circ$. They were assigned to elemental selenium (P3₁21, $Z = 3$). But as these reflections are very weak, elemental selenium was not

included as an additional phase in all Rietveld refinements. However, to estimate the ratio of selenium the diffraction pattern of the first cycle at 180°C upon cooling was refined with selenium as an additional phase, as in this pattern the relatively strongest reflections of elemental selenium were observed. From this refinement a weight fraction of approx. 3 % Se was obtained. The fact that the reflections of selenium disappear at temperatures above 220°C is in good agreement with its melting-point of 217°C.

For the differential thermal analysis a Perkin Elmer DTA7 was used with Al₂O₃ as reference sample. 78 mg of Ag₂Se were heated in air with a heating rate of 5°C/min. The sample was cooled by switching off the instrument. Three subsequent heating and cooling cycles were recorded. For comparison a second DTA and TG experiment was performed in an argon stream using a Netzsch STA 409C instrument. 22.7 mg of Ag₂Se were heated to 230°C with a heating rate of 5°C/min. The sample was cooled to room temperature with 5°C/min and a second heating and cooling cycle was run under the same conditions.

3 Results and Discussion

Synchrotron Powder Diffraction

The synchrotron powder diffraction data were refined using the structural data of low and high-temperature Ag_2Se given in the literature [1, 4, 9] as starting parameters. The results of the Rietveld refinement of the synchrotron pattern taken at 30°C (1st heating cycle) confirm the structural data given in the literature [1, 9] (Table 1). The resulting crystal structure is shown in Figure 1 (see above), the quality of the measurement and the refinement can be estimated from Figure 2. The quality of the refinement is reasonable, but not perfect.

Table 1: Comparison of the structural data obtained for the low-temperature modification of Ag_2Se from synchrotron powder diffraction data (30°C , powder diffractometer of beamline B2, HASYLAB, Hamburg/Germany, $\lambda = 0.68541 \text{ \AA}$) with literature data [1, 9].

		Literature [1, 9]	This work
Space group, Z		$\text{P}2_12_12_1$, 4	$\text{P}2_12_12_1$, 4
a		4.333 $\text{\AA}$	4.3373(2) $\text{\AA}$
b		7.062 $\text{\AA}$	7.0702(3) $\text{\AA}$
c		7.764 $\text{\AA}$	7.7730(4) $\text{\AA}$
Ag (1)	x	0.857	0.8556(7)
	y	0.119	0.1121(4)
	z	0.456	0.4504(4)
Ag (2)	x	0.478	0.4745(6)
	y	0.779	0.7770(5)
	z	0.361	0.3592(4)
Se	x	0.108	0.1029(8)
	y	0.985	0.9996(6)
	z	0.149	0.1532(5)
Ag (1) – Se		2.62 $\text{\AA}$; 2.71 $\text{\AA}$; 2.79 $\text{\AA}$; 2.86 $\text{\AA}$	2.658(4) $\text{\AA}$; 2.668(5) $\text{\AA}$; 2.861(5) $\text{\AA}$; 2.937 (5) $\text{\AA}$
Ag (2) – Se		2.72 $\text{\AA}$; 2.74 $\text{\AA}$; 2.81 $\text{\AA}$; 3.28 $\text{\AA}$	2.686 (5) $\text{\AA}$; 2.764 (5) $\text{\AA}$; 2.797 (4) $\text{\AA}$; 3.182 (5) $\text{\AA}$

counts

Figure 2: Results of the Rietveld refinement of Ag₂Se at 30°C (powder diffractometer of beamline B2, HASYLAB, Hamburg/Germany, $\lambda = 0.68541$ Å) showing the observed (+) and calculated patterns (solid line) as well as the difference between them below. Vertical bars mark the positions of the reflections of Ag₂Se (P2₁2₁2₁, Z = 4).

A detailed description of the crystal structure of low-temperature Ag₂Se shall not be given here, as this has already been given in the literature [1]. Ag(1) is coordinated by four selenium atoms in a distorted tetrahedral arrangement, whereas Ag(2) is coordinated in a trigonal planar fashion by three selenium atoms. Ag(2) sits slightly (0.170 Å) above the plane formed by these three selenium atoms, the distance to a fourth selenium atom is distinctly longer (see Table 1).

At 140°C – unfortunately the temperature range between 125°C and 180°C has only been measured in the second cycle due to a failure of the heating device in the first cycle – reflections of the high-temperature modification of Ag₂Se show up for the first time. A Rietveld refinement of these patterns confirmed the structural data given in the literature [4]. As these results are based on single crystal neutron diffraction data, which is probably the best method to describe structural details in such systems, we have not tried to interpret our data in too much detail. In

Figure 3 some diffraction patterns of our temperature dependent investigations are shown. It is obvious that the patterns at 230°C (1st cycle, heating) and 260°C (2nd cycle, heating) are distinctively different to those at lower temperatures indicative of a phase transition from an orthorhombic to a cubic modification. In Figure 3 it is also obvious that the intensities in the patterns taken at 230°C and 260°C are slightly different. These differences are only found for the pattern taken at 230°C (1st heating cycle) compared to all other patterns of high-temperature Ag₂Se. In the Rietveld refinement this led to an increased occupancy of the tetrahedral site 12 (d) at 230°C (1st heating cycle), whereas the occupancy of the octahedral site 6 (d) is slightly lowered. This is in agreement with the results of the single crystal neutron work given in the literature [4]. But it is surprising that no such result was found in the second heating cycle. As single crystal neutron diffraction is much better suited for such investigations we suggest that these measurements should be repeated for at least two heating cycles.

Upon heating we obtained a transition temperature of 140°C in our investigation, which is somewhat higher than the value given in the literature (133°C [3]). Upon cooling a hysteresis is found and the transition temperature is shifted to 120°C (see Figure 4). In [5] the transition temperatures of different investigations are summarized, which differ by more than 70°C. This might be due to inaccurate measurements, but also the influence of the surrounding atmosphere (see next chapter: Thermoanalytical Investigations) cannot be neglected.

A very intriguing aspect of our investigation is the fact that the patterns of low-temperature Ag₂Se before and after heating look very different (see Figure 3). It was already mentioned that the pattern at 30°C taken before heating can be refined nicely with the structural data given for low-temperature Ag₂Se in the literature [1, 9] (see Table 1 and Figure 2). The reflections of the patterns obtained after heating can still be indexed in an orthorhombic unit cell with lattice parameters very similar to those obtained before heating, the extinction rules are still consistent with space group P2₁2₁2₁. Thus, only the intensities have changed significantly. Attempts to refine the patterns obtained after heating with the structural model of low-temperature Ag₂Se failed, as unreasonable high R factors and high electron densities in the difference fourier maps resulted. Ab initio structural solutions using different approaches were also not successful. An improved fit could only be obtained within the structural model of low-temperature Ag₂Se using anisotropic temperature factors, which refined to meaningless values. Therefore we conclude that a structural description of low-temperature Ag₂Se obtained after heating in air is not possible within a harmonic model. We believe that an anharmonic model is needed, which was also used for the refinement of high-temperature

Ag₂Se. A refinement of low-temperature Ag₂Se using anharmonic terms is part of our current investigations on Ag₂Se. We would like to recall that Ag₂Se segregates selenium upon heating (s. above). Thus, it is not too surprising that low-temperature Ag₂Se before and after heating shows different structural properties.

Figure 3: Selection of diffraction patterns of Ag₂Se taken at different temperatures and heating/cooling cycles (powder diffractometer of beamline B2, HASYLAB, Hamburg/Germany, $\lambda = 0.68541 \text{ \AA}$).

In Figure 4 the unit cell volume of Ag₂Se in dependence of the temperature is shown. The error bars of the volumes obtained from Rietveld refinements are in the range of the point sizes and have therefore been omitted. For a better comparison the unit cell volume of cubic high-temperature Ag₂Se ($\text{Im}\bar{3}\text{m}$, $Z = 2$) has been multiplied by two compared to low-temperature Ag₂Se ($\text{P2}_1\text{2}_1\text{2}_1$, $Z = 4$). It is obvious that the phase transition is accompanied by a volume jump (approx. 3 %) indicative of a 1st order transition. Furthermore a hysteresis is found, as the transition temperature is shifted by approx. 20°C upon cooling. It should be mentioned that the unit cell volumes for each temperature in the heating and cooling cycles

are in good agreement: $V(30^\circ\text{C}, 1^{\text{st}} \text{ cycle}) = 238,36(3) \text{ \AA}^3$; $V(30^\circ\text{C}, 2^{\text{nd}} \text{ cycle}) = 238,13(2) \text{ \AA}^3$. This is remarkable, as Ag_2Se irreversibly segregates selenium upon heating in air. As the expected decrease of the unit cell volume is only very small, it is possible that the segregated selenium is replaced by oxygen upon heating Ag_2Se in air, but at this point we have no experimental proof for this assumption.

Figure 4: Unit cell volume of Ag_2Se as obtained from Rietveld refinements. For comparison reasons the unit cell volume of high-temperature Ag_2Se ($\text{Im}\bar{3}\text{m}$, $Z = 2$) was doubled (for details see text).

From Figure 3 it is also obvious that the phase transition and the segregation of selenium is accompanied by a change of the reflection profiles: they become sharper indicative of an improved crystallinity. The halfwidths ($FWHM$ in deg. 2θ) being obtained for reflection (121) at $2\theta \approx 15.2^\circ$ of low-temperature Ag_2Se and reflection (200) at $2\theta \approx 15.8^\circ$ of high-temperature Ag_2Se are given in Table 2. Upon heating the halfwidth decreases up to a constant value of approx. 0.04 deg. 2θ , which is in the range of the resolution of the instrument. No explanation can be given for this observation at this point.

Table 2: Halfwidths ($FWHM$) of reflection $(121)_{\text{ortho}}$ and $(200)_{\text{cubic}}$ of Ag_2Se at different temperatures (powder diffractometer of beamline B2, HASYLAB, Hamburg/Germany, $\lambda = 0.68541 \text{ \AA}$).

Temperature	30°C (heating, 1 st cycle)	120°C (heating, 1 st cycle)	230°C (heating, 1 st cycle)	30°C (cooling, 1 st cycle)	30°C (heating, 2 nd cycle)	260°C (heating, 2 nd cycle)
Reflection	$(121)_{\text{ortho}}$	$(121)_{\text{ortho}}$	$(200)_{\text{cubic}}$	$(121)_{\text{ortho}}$	$(121)_{\text{ortho}}$	$(200)_{\text{cubic}}$
$FWHM$ / deg. 2θ	0.063	0.057	0.036	0.038	0.039	0.038

In Figure 5 the lattice parameters of low-temperature Ag_2Se are shown as obtained from Rietveld refinements. They are given relative to the values obtained at 30°C of the first measurement (s. Table 1). It was already mentioned that the lattice parameters at each temperature are in reasonable agreement independent of the heating cycle or the fact, whether they are a part of a heating or a cooling measurement. This is surprising, as an irreversible segregation of selenium was observed, which should lead to a distinct volume decrease (s. above). In contradiction to literature data [5: Fig. 2] no isotropic increase of all lattice parameters was found. Instead a very distinct anisotropic thermal expansion behaviour was observed. Lattice parameter c_{ortho} shows a strong and b_{ortho} a small increase with increasing temperature, whereas a_{ortho} decreases with increasing temperature. Ag_2Se undergoes severe structural changes during its transition from an orthorhombic low-temperature to a cubic ion conducting high-temperature modification. From the present data it is difficult to postulate a path for the structural rearrangements during the phase transition. Usually lattice changes before the phase transition already “prepare” the structural rearrangements. From the lattice parameters of both modifications ($a_{\text{ortho}} \approx 4.34 \text{ \AA}$, $b_{\text{ortho}} \approx 7.07 \text{ \AA}$, $c_{\text{ortho}} \approx 7.77 \text{ \AA}$; $a_{\text{cub}} \approx 4.99 \text{ \AA}$) one could assume a path for the structural rearrangement according to: $a_{\text{ortho}} \approx a_{\text{cub}}$, $b_{\text{ortho}} \approx c_{\text{ortho}} \approx \sqrt{2} \cdot a_{\text{cub}}$. But as a_{ortho} shows a negative thermal expansion and c_{ortho} a very strong positive thermal expansion, such a path is very unlikely and more complicated structural rearrangements must be assumed, which cannot be deduced from the present data.

Figure 5: Lattice parameters of low-temperature Ag_2Se ($\text{P2}_1\text{2}_1\text{2}_1$, $Z = 4$) as obtained from Rietveld refinements given relative to the lattice parameters obtained for the pattern taken at 30°C of the first heating cycle (for more details see text).

Thermoanalytical Investigations

Thermoanalytical investigations were performed to confirm the results of the structural investigations with synchrotron radiation. In Figure 6 the DTA analysis of Ag_2Se in air is shown. The conditions of the measurement are comparable to those of the XRPD investigations with synchrotron radiation. In the DTA analysis three subsequent heating cycles were recorded. Unfortunately, with the instrument used for the experiment neither a TG analysis nor a recording of a cooling curve was possible. Thus for cooling the instrument was just switched off. The DTA analysis shows for all three heating cycles a comparable behaviour. At about 140°C the phase transition from low-temperature to high-temperature Ag_2Se is observed. The transition temperature is in good agreement with the results of the XRPD investigations. At approx. 220°C another endothermic signal can be seen, which can

be assigned to the melting point of selenium. This confirms the results of the XRPD investigations, where a segregation of selenium was observed.

Figure 6: DTA curve of Ag_2Se taken in air (Perkin Elmer DTA7, sample weight: 78 mg, heating rate: $5^\circ\text{C}/\text{min}$). Three subsequent heating cycles are shown.

To check whether a different behaviour is observed for Ag_2Se when heated in argon, we performed another DTA analysis with a different instrument. Here a parallel TG analysis was possible. In the whole temperature range under investigation no weight loss was observed. The DTA analysis of this experiment is shown in Figure 7. Two heating and cooling cycles were recorded, comparable results were found for both cycles. Upon heating an endothermic signal was measured at about 135°C indicating the phase transition of Ag_2Se . Another very weak signal is visible at approx. 220°C . This could be indicative for the melting of selenium. But this signal is much smaller than in the measurement in air and it is not found upon cooling. Upon cooling only a strong exothermic signal for the phase transition of Ag_2Se is observed at approx. 110°C with a hysteresis of approx. 25°C . The transition temperatures seem to be somewhat lower than for the experiment in air. But to confirm this new experiments with an improved temperature calibration need to be performed.

Figure 7: DTA curve of Ag_2Se taken in argon (Netzsch STA 409C, sample weight: 22.7 mg, heating rate: 5°C/min). Two subsequent heating and cooling cycles are shown.

4 Summary and Outlook

We found that Ag_2Se , although known for a long time and investigated in several publications, still offers some new and surprising results, when a combination of modern methods (synchrotron radiation, DTA/TG analysis) is used. Ag_2Se shows a completely different behaviour when heated in air or in argon. Heating in air leads to an irreversible segregation of selenium, which is not observed in argon. Obviously, the segregation of selenium has some influence on the structural properties of Ag_2Se . The crystallinity seems to be improved, as the halfwidths of the reflections decrease significantly upon heating. Furthermore the diffraction patterns of low-temperature Ag_2Se obtained after segregation of selenium can no longer be refined with the structural model known from the literature [1, 9], although unit cell and space group have not changed. We assume that a refinement using anharmonic terms is necessary. This is part of our current work on Ag_2Se . It should also be mentioned that our results on Ag_2Se are only preliminary in some respect. To corroborate the

segregation of selenium when heating Ag_2Se in air and to understand its nature, a more detailed study is necessary. Combined TG/DTA/MS investigations, which were not possible with our set-up, could be a first step. On the other hand the segregation of selenium was not observed, when Ag_2Se was heated in argon. Up to now, this was only concluded from DTA/TG measurements. We will perform complementary temperature dependent XRPD investigations using synchrotron radiation in the near future. It will be interesting to see, whether a sample of Ag_2Se heated in argon shows similar effects to those observed for Ag_2Se heated in air. Finally, electron microscopy combined with elemental analysis (EDX) would be another helpful tool to investigate the unusual behaviour of Ag_2Se in more detail. In preliminary EDX experiments we found that the surface of Ag_2Se heated in air is enriched in selenium, whereas in the bulk of freshly cut Ag_2Se the expected ratio $\text{Ag}:\text{Se} = 2:1$ was detected.

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