Crystal chemistry of the halite-related cation-deficient superstructure phase $Yb_{7+\delta}Se_8$ with $\delta = 0.24$ and its relation to $YbSe^*$

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Abstract

Systematic phase studies on the system YbSe-Yb₂Se₃ revealed besides the two terminal compounds three intermediate phases Yb_{0.91}Se, Yb_{0.83}Se and Yb_{0.75}Se, all of them without significant phase width, which is characteristic for the so-called room temperature equilibrium. Lattice parameters are given for all phases. Structure determinations from X-ray powder diffraction data have been carried out for Yb_{0.91}Se = Yb_{7.24}Se₈ as well as for YbSe for comparison. The superstructure of Yb_{0.91}Se is halite related (NaCl type) with ordering of vacancies in the cationic sublattice and partial ordering of Yb²⁺ and Yb³⁺. Therefore the ideal formula of the mixed valence compound is Yb₇Se₈ = \Box_1 Yb₅²⁺Yb₂³⁺Se₈²⁻. The actual phase Yb_{0.91}Se has additional ytterbium statistically distributed over the sites of vacancies. The change in the Yb–Se distance of 2.966 Å in YbSe to 2.830 and 2.938 Å in Yb_{7.24}Se₈ definitely proves the simultaneous appearance of Yb²⁺ and Yb³⁺, both octahedrally coordinated.

1. Introduction

The preparation of ytterbium(II) selenide has been described in great detail in a recent paper on the thermodynamics of sublimation and formation of this compound by Marx and Petzel [1]. Surprisingly and in apparent contradiction with the literature [2–8], YbSe proved to be a stoichiometric compound (NaCl structure). The reduction of Yb₂Se₃ with H₂ at 1370 K for 3 h as well a the sublimation of YbSe in a temperature gradient inside a molybdenum Knudsen cell in high vacuum at about 2000 K and several deliberate attempts to prepare non-stoichiometric samples by reaction of YbSe and Se at temperatures lower than 750 K did not give the slightest indication that YbSe could display any phase width at temperatures of 750 K or less. In contrast, Guittard et al. [2] and Souleau et al. [6], who studied the system YbSe-Yb₂Se₃ extensively, found YbSe to be non-stoichiometric with a phase width up to 26 mol% Yb₂Se₃ (NaCl-related cubic solid solution), directly followed by another solid solution with a phase width between 26 and 67 mol% Yb₂Se₃ and an NaClrelated rhombohedral structure. Density measurements and their correlations with lattice parameters indicated a continuous loss of cations in the NaCl-type parent structure from YbSe to Yb_{0.75} $\Box_{0.25}$ Se. The latter terminal phase is then the high temperature β -form of Yb₃Se₄ stable above 1498 K [2, 5, 6].

While such extended solid solutions may reflect high temperature phase relationships, it seems to be somewhat unusual that a continuous change from cubic to rhombohedral symmetry should occur and that both phases show superstructure reflections on their X-ray powder diffraction patterns. Such observations indicate the existence of some kind of order more characteristic for low temperature phase relationships.

Therefore we have performed a new study of the system YbSe-Yb₂Se₃ aimed at the elucidation of the phase equilibria related to temperatures of 750 K or less. In this paper we describe in detail the super-structure of Yb_{7+ δ}Se₈ and its relation to YbSe and give some rudimentary results on the crystal data of Yb₂Se₃, α -Yb₃Se₄ and the rhombohedral phase Yb_{0.83}Se. While preliminary results have already been presented at international conferences [9, 10], the X-ray powder diffraction data (*d* values, I_{obs}/I_{calc} , F_{obs}/F_{calc}) of YbSe and Yb_{7+ δ}Se₈ are being published elsewhere [11].

^{*}This paper is dedicated to Professor Georg Brauer on the occasion of his 85th birthday.

2. Experimental details

2.1. Preparation of ytterbium selenides

Ytterbium (99.99%, Auer Remy) and selenium (99.999%, Ventron) in the molar ratio 2:3 were brought to reaction in an evacuated silica ampoule at 1370 K for 8 days. X-Ray powder diffraction patterns of the reaction product only displayed the reflections of orthorhombic Yb₂Se₃. This compound was subsequently reduced in a molybdenum boat with highly purified hydrogen at 1370 K for 3 h to yield YbSe. Further purification of the monoselenide was achieved by sublimation inside a molybdenum tube in high vacuum at 2000 K. All samples of intermediate compositions, hereafter denoted Yb, Se with 1.00 > x > 0.67, were prepared by reaction of YbSe and selenium vapour under near-equilibrium conditions in evacuated silica ampoules. The applied temperature-time programmes proved to be rather important to achieve an equilibrium or near-equilibrium situation and to obtain well-crystallized samples. As an example, the following program has been used for the preparation of monophasic superstructure phase Yb_{0.91}Se: 600 K (23 h), 710 K (24 h), 870 K (23 h), 1140 (67 h), 1290 K (23 h), 1370 K (32 h), 1260 K (17 h), 1130 K (5 h), 1000 K (18 h), 750 K (5 h), and final cooling to room temperature within 10 days. All samples were stored and handled in a dry, inert atmosphere (N_2 or Ar) in order to avoid hydrolysis and/or oxidation especially in the case of Se-rich compositions.

2.2. X-ray powder diffraction

All samples obtained after the various steps of the preparative procedures were characterized by X-ray powder diffraction: Guinier technique, Enraf-Nonius camera, Cu K α_1 radiation with $\lambda = 1.54056$ Å, silicon NBS-SRM-640A as internal standard with a = 5.43088 Å. The computer program EGUIN [12] has been used for length correction of the Guinier patterns, while refinements of the lattice parameters have been carried out by means of the program LSUCRE [13].

In the cases of YbSe and Yb_{0.91}Se, X-ray powder diffractometry has also been employed to obtain integrated intensities for structure determinations. The diffraction data were collected on a Seifert XRD-3000 powder diffractometer using the Seifert XDAL programme system: MZ-VI Θ - Θ goniometer with 250 mm measurement radius, Cu K $\bar{\alpha}$ radiation with $\lambda = 1.541$ 80 Å, slit combination 2 mm-soller-1 mm || 1 mm-0.3 mm, secondary curved graphite monochromator, SZ-20-SE scintillation counter, automatization with IBM-PS/2-55SX computer, programs PMEAS for the measurement, and SPECTRA-1&2 for integrated intensities.

Preliminary structure determinations, which have been carried out by trial-and-error methods using the program LAZY-PULVERIX [14], were already quite successful, because only a small number of variables had to be refined. At this stage, however, it became obvious that anomalous dispersion corrections were essential. Otherwise, non-linear scaling procedures had to be applied after the usual LPG corrections, but there were no physical explanations, since absorption or geometric corrections could not account for such deviations. For the final structure determinations and refinements the program POWLS-80 [15] has been used, employing least-squares procedures and atomic scattering factors corrected for anomalous dispersion corresponding to Cromer and Libermann [16, 17].

2.3. High energy electron diffraction (HEED)

All HEED experiments were performed on a Philips EM400T (100 kV, $\lambda = 0.034$ Å) or a Jeol 2000FX-II (200 kV, $\lambda = 0.025$ Å) scanning transmission electron microscope. Both were equipped with double-tilt holders $(\pm 60^{\circ}/\pm 45^{\circ} \text{ and } \pm 40^{\circ}/\pm 30^{\circ})$, which are essential for complete rotation analyses, to collect all reflections within a 45° section of the reciprocal lattice. Small crystals were supported on holey carbon films mounted on 400 mesh Cu grids (Plano, Wetzlar, Germany). Single-crystal fragments not larger than 3000 Å have been studied by selected area diffraction with an aperture of 5 μ m diameter. Before and after a complete rotation analysis, X-ray microanalyses confirmed that the chemical composition of the sample had not altered during irradiation by loss of selenium or contamination by oxygen. A Link AN1085S energy-dispersive X-ray spectrometer with an ultrathin window detector has been employed for these analyses.

3. Results and discussion

We found in our systematic phase study besides the two terminal compounds YbSe and $Yb_{0.667}Se \equiv Yb_2Se_3$ three intermediate phases Yb_{0.91}Se, Yb_{0.83}Se and $Yb_{0.75}Se \equiv Yb_3Se_4$, all without detectable phase width. This agrees with the literature in the case of Yb₂Se₃ and the low temperature form α -Yb₃Se₄ but not for the other three phases. The lattice parameters of all phases are listed in Table 1, while reduced formula volumes V' = V/Z for one Yb, Se unit are plotted in Fig. 1. For comparison the formula volume of the monoclinic (C2/m) high pressure phase Yb₅Se₇ studied by Range et al. [18] has been included. All phases with halite-related structures containing ytterbium entirely in octahedral coordination show a more or less linear decrease in V' with an increasing number of vacancies in the cationic sublattice from YbSe through Yb_{0.91}Se and $Yb_{0.83}$ Se to $Yb_{0.667}$ Se = Yb_2 Se₃. In contrast, α - Yb_3 Se₄ and Yb₅Se₇ are more densely packed owing to a partial

TABLE 1. Lattice parameters of Yb_xSe phases at 298 K

Yb _{0.67} Se≡Yb ₂ Se ₃	Orthorhombic, Sc ₂ S ₃ type [19, 20], <i>Fddd</i> , Z = 48, $a = 11.275(1)$ Å, $b = 8.005(2)$ Å, c = 23.986(7) Å, $V' = V/Z = 45.106(11)$ Å ³ , $a \approx 2a_p$, $b \approx 2^{1/2}a_p$, $c \approx 3 \times 2^{1/2}a_p$, $\rho_{calc} = 7.14$ g cm ⁻³ , $\rho_{cap} = 7.05$ g cm ⁻³ [6]
$Yb_{0.75}Se \approx \alpha \cdot Yb_3Se_4$	Orthorhombic, Yb ₃ S ₄ type [21, 22], <i>Pnma</i> , Z = 16, a = 13.3060(7) Å, b = 3.9909(2) Å, c = 13.5457(6) Å, $V' = V/Z = 44.957(3)$ Å ³ , $\rho_{calc} = 7.71$ g cm ⁻³ , $\rho_{exp} = 7.50$ g cm ⁻³ [6]
Yb _{0.83} Se	Rhombohedral NaCl-related superstructure, $R\bar{3}m$, $Z=6$, $a=4.0882(3)$ Å, $c=20.414(2)$ Å, $V'=V/Z=49.245(7)$ Å ³ , $a=0.5\times 2^{1/2}a_{\rm p}$, $c=2\times 3^{1/2}a_{\rm p}$, $\rho_{\rm cak}=7.50$ g cm ⁻³ , $\rho_{\rm exp}=7.30$ g cm ⁻³ [6]
$Yb_{0.91}Se \equiv Yb_{7+\delta}Se_8$	Cubic NaCl-related superstructure, $Fm\bar{3}m$, Z=32, $a=11.750(5)$ Å, $V'=V/Z=50.690(6) Å3, a=2a_p, \rho_{calc}=7.74 gcm-3, \rho_{exp}=7.63 g cm-3 [6]$
Yb _{1.00} Se ≡ YbSe	Cubic NaCl-type parent structure, $Fm\bar{3}m$, $Z = 4$, $a_p = 5.9321(3)$ Å, $V' = V/$ $Z = 52.187(5)$ Å ³ , $\rho_{cak} = 8.02$ g cm ⁻³ , $\rho_{exp} = 7.80$ g cm ⁻³ [6]



Fig. 1. Formula volumes V' = V/Z of different phases in the system YbSe-Yb₂Se₃.

change in the octahedral coordination of ytterbium to monocapped trigonal prisms, though both compounds, like the other intermediate phases, still contain cations of the valencies 2+ and 3+, as can be seen from the different cation-anion distances (2.81 Å for Yb³⁺ and 2.97 Å for Yb²⁺). The space group of the α -form of Yb₃Se₄ has been derived from the electron diffraction of single crystals by several rotation analyses. We choose the standard setting *Pnma* in agreement with ref. 22, while a different setting of the same space group is also reported in the literature [6]. Yb_{0.83}Se shows rhombohedral symmetry with a one-dimensional superstructure. In this paper, however, the structure of this phase is not elaborated any further. At the composition $Yb_{0.91}Se$ we found a cubic superstructure phase. The diffraction geometry and its relation to the NaCl parent structure of YbSe have been established by HEED rotation analyses (see Fig. 2).

There exists a rather simple model for the f.c.c. cation-deficient superstructure with $a_s = 2a_p$ (Fm3m or F43m). Assuming ordering of vacancies in the cationic sublattice, we obtain $Yb_7 \square_1 Se_8$ with Z = 4 (see Fig. 3). Ordering of Yb²⁺ and Yb³⁺ is certainly not a requirement for this superstructure, because its analogue has been observed in the system $Tm^{3+}(e^{-})Se^{2-}-Tm_{2}^{3+}Se_{3}^{2-}$ [23, 24], although at somewhat different compositions. In the case of $Yb_7Se_8 \equiv \Box_1 Yb_5^{2+} Yb_2^{3+}Se_8^{2-}$, complete ordering of Yb^{2+} and Yb^{3+} could not be achieved in the above space groups. Nevertheless, partial ordering achieved by placing Yb^{3+} in $\frac{1}{2}$,0,0 and $Yb^{2+} \gg Yb^{3+}$ statistically in $\frac{1}{4}$, $\frac{1}{4}$, 0 would certainly release some geometric stress. This model has been confirmed by structural refinements of selenium released from $\frac{1}{4},0,0$ to x,0,0. Although one would expect at a first glance that x should become smaller than 0.25, corresponding to a shift of Se towards the vacancy, the opposite was the case, with $x \approx 0.26$.



Fig. 2. High energy electron diffraction patterns from single crystals of Yb₇Se₈, [100] zone left and [110] zone right, both displaying a $2 \cdot 2 \cdot 2$ superstructure of the halite parent structure ($Fm\bar{3}m$).



Fig. 3. Crystal structures of YbSe (four unit cells, left) and Yb₇Se₈ (one superstructure cell, right) in [001] projection and all atoms with z=0: large circles, Se²⁻; small open circles, Yb²⁺; small filled circles, Yb³⁺; \Box , cationic vacancies.

In other words, the contraction of the selenium octahedron centred at $\frac{1}{2}$, 0, 0 confirms that the central Yb²⁺ of the NaCl parent structure has been replaced by the smaller Yb³⁺ cation. Once this somewhat idealized model has been established, the actual refinements have been carried out. First of all, the discrepancy between the ideal composition of Yb_{0.875}Se and the experimental value of Yb_{0.91}Se had to be resolved. The vacancy was found not to be completely empty but filled with 24% ytterbium (presumably Yb²⁺). At this stage least-squares refinements of all variable parameters were carried out in $Fm\bar{3}m$ and $F\bar{4}3m$. The latter space group has been reported by Thomas et al. [25] for Yb_{0 875}S. In the case of Yb_{0.91}Se, however, this space group proved to be unfavourable with $R \approx 18\%$, while $R \approx 7\%$ could be achieved for $Fm\bar{3}m$. A reliability factor of this magnitude is obviously characteristic for our experimental and evaluation procedures, because we obtained R = 8.1%for stoichiometric NaCl-type YbSe, which we investigated and evaluated in exactly the same way for the purpose of comparison (see also ref. 11). The results of both structure determinations are listed in Table 2.

The reported cation-anion distances of both structures deserve some discussion. Applying similar procedures to those of Shannon [26], we obtained for the coordination number CN = 6 the following effective ionic radii: $r=0.868\pm0.005$ Å for Yb³⁺ [27], $r=1.026\pm0.025$ Å for Yb²⁺ and $r=1.940\pm0.025$ Å for Se²⁻. These radii are consistent with the interatomic distances ob-

TABLE 2. Results of structure determinations from X-ray powder diffraction data of Yb_{7+ δ}Se₈ with δ = 0.24 and YbSe for comparison

$Yb_{7.24}Se_8 \equiv Yb_{7+\delta}Se_8$ with $\delta = 0.24$ (=	≡Yb _{0.91} SeYb _{0.91} Se)
NaCl-type related superstructure	Fm $3m$, Z = 4 (= 32) a = 11.7496(5) Å $\approx 2a_{p}$, V' = V/Z = 50.690(6) Å ³
Yb1 in 0,0,0 (4a) (24% occ.)	$B_{\rm o}({\rm Yb1}) = 0.70 {\rm ~\AA^2}$
Yb2 in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, (4b)$	$B_{\rm o}({\rm Yb2}) = 0.50 {\rm ~\AA^2}$
Yb3 in $0, \frac{1}{2}, \frac{1}{2}$ (24d)	$B_{\rm o}({\rm Yb3}) = 0.75 {\rm ~\AA^2}$
Se1 in $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ (8c)	$B_{\rm o}({\rm Se1}) = 0.99 ~{\rm \AA}^2$
Se2 in 0.2591(3),0,0 (24e)	$B_{\rm o}({\rm Se2}) = 1.15 {\rm ~\AA^2}$
Yb2-Se2 = 2.830(3) Å	dominant Yb3+
Yb3-Se2=2.939(3) Å Yb3-Se1=2.937(3) Å $\}$	Yb ²⁺ :Yb ³⁺ ≈ 11:1
$R_{\rm conv} = 6.97\%$	

YbSe

NaCl-type parent structure, $Fm\bar{3}m$, Z=4, a=5.9321(3) Å, V'=V/Z=52.187(5) Å³ Yb in 0, 0, 0 (4a), $B_0(Yb)=0.51$ Se in $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (4b), $B_0(Se)=0.59$ Yb-Se=2.966(3) Å Se-Se=4.19 Å (not in contact) $R_{conv}=8.12\%$. served in binary ytterbium selenides, which are $d = 2.81 \pm 0.02$ Å for Yb³⁺-Se²⁻ and $d = 2.97 \pm 0.03$ Å for Yb²⁺-Se²⁻. The cationic sites in Yb_{7.24}Se₈ are then occupied as follows: Yb1 by Yb²⁺, Yb2 dominantly by Yb³⁺ and Yb3 by Yb²⁺:Yb³⁺ \approx 11:1 in accordance with the structural determination of the interatomic distances and the actual chemical composition.

In summary, the superstructure of the mixed valence compound Yb_7Se_8 is caused by ordering of cationic vacancies and preference in site occupation by Yb^{2+} and Yb^{3+} . This structure can be retained almost without any significant changes in lattice parameters by incorporation of additional Yb^{2+} . The crystal chemistry of the superstructure phase $Yb_{7+\delta}Se_8$ can be described by the following terminal formulae:

$$[\Box_{4}][Yb_{20}^{2+}Yb_{4}^{3+}][Yb_{4}^{3+}]Se_{32} \qquad (\delta=0.0)$$

$$[\Box_{2}Yb_{2}^{2+}][Yb_{24}^{2+}][Yb_{4}^{3+}]Se_{32} \qquad (\delta=0.5)$$

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