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Reversible Reconstructive Phase Transition of Ba_2SnSe_5: A New High Temperature Modification with Completely Different Structural Motifs

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A new modification of Ba_2SnSe_5 was prepared by high temperature synthesis. In contrast to its low temperature modification that adopts the orthorhombic space group $P2_12_12_1$, the new β-Ba_2SnSe_5 crystallizes in the monoclinic system, space group $P2_1/c$, with the lattice parameters a = 9.3949(6) Å, b = 8.8656(6) Å, c = 12.5745(7) Å, β = 113.299(4)°, V = 961.9(1) Å^3, Z = 4. α-Ba_2SnSe_5 is comprised of $Sn_3Se_{10}{}^{8-}$ units, $SnSe_4{}^{4-}$ tetrahedra, and isolated $Se_3{}^{2-}$ units, while β-Ba_2SnSe_5 contains only $SnSe_5{}^{4-}$ units, wherein Sn is tetrahedrally coordinated by four Se atoms. The fifth Se atom is connected to one Se atom of the $SnSe_4{}^{4-}$ tetrahedron, thereby forming a $Se_2{}^{2-}$ dumbbell. Different band gaps are a result of the different structure motifs, which are reflected in different colors of the two Ba_2SnSe_5 modifications, the α-form being dark brown and the β-form being red.

Introduction

Chalcogenides are used in semiconductor devices, including thermoelectric devices,[1–4] rechargeable batteries,[5] and data storage devices including phase-change materials.[6–8] In some chalcogenides, e.g. in $KInSnSe_4$[9] and $AGaSnSe_4$ (A = K, Rb, Cs),[10] polymorphic transitions have been observed. Other chalcogenides undergo reconstructive phase transitions, whereby primary interatomic bonds are broken,[11,12] e.g. $Ag_{10}Te_4Br_3$,[13] CdTe,[14] HgSe, and HgTe.[15,16]

In recent years, new alkaline earth tin polychalcogenides have been discovered with unique structural motifs, including 5-fold coordinated Sn atoms in Sr_2SnSe_5,[17] $Sr_4Sn_2Se_9$,[18] and Ba_2SnTe_5,[19] 6-fold coordinated Sn atoms in Ba_2SnSe_5[20] and an unusual $Te_5{}^{4-}$ unit in Ba_2SnTe_5. Of these materials, Ba_2SnTe_5 is the only one thus far with two known modifications, one accessible under thermodynamic control[19] and one prepared at lower temperatures with a Na_2Te/BaTe/Te or a K_2Te/BaTe/Te flux.[21]

With this contribution, we report on a new modification, the β form, of Ba_2SnSe_5, and the reversible reconstructive phase transition between the two forms.

Experimental Section

Syntheses and Analyses. The following elements, stored in a glovebox under argon, were used for the syntheses as obtained from the suppliers without further treatment: barium (Aldrich, 99.9%), tin (Aldrich, 99.99%), and selenium (Aldrich, 99.99%). Shiny red prismatic crystals of β-Ba_2SnSe_5 can be obtained starting from the elements in the stoichiometric 2:1:5 ratio. The reaction mixture was loaded into a silica tube within the glovebox, and then sealed under vacuum ($< 10^{-3}$ mbar). The tube was placed into a programmable resistance furnace, heated to 523 K within 6 h, kept at 523 K for 12 h, followed by heating to 1123 K within 24 h. Finally, the tube was slowly cooled to

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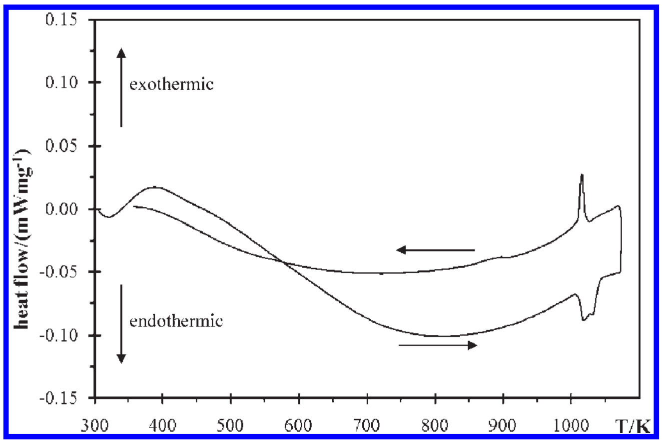

Figure 1. Thermal analysis of α-Ba_2SnSe_5.

Table 1. Crystallographic Data of β-Ba_2SnSe_5

empirical formula	β-Ba_2SnSe_5
formula weight [g mol^{-1}]	788.17
temperature [K]	298(2)
wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$
cell dimensions	
a [Å]	9.3949(6)
b [Å]	8.8656(6)
c [Å]	12.5745(7)
β [deg]	113.299(4)
V [Å^3]	961.9(1)
no. of formula units per cell	4
calculated density [g cm^{-3}]	5.442
absorp coeff [mm^{-1}]	29.51
F(000)	1328
crystal size [μm]	200 × 100 × 40
2θ range [deg]	4.72−60.0
reflections collected	7598
independent reflections (R_{int})	2784 (0.042)
reflections\refined parameters	2784\74
goodness-of-fit on F^2	1.16
$R1$, $wR2$ (all data)	0.039, 0.086
extinction coefficient	0.00032(12)
max. diff. peak, hole [e Å^{-3}]	3.81, −2.26

1023 K, then annealed at 1023 K for 2 weeks, and then quenched in a cold water bath.

The reaction mixture was ground and analyzed by means of X-ray powder diffraction (INEL diffractometer with position-sensitive detector (Cu Kα_1 radiation)). Because no peaks of known materials were detected, a single crystal was selected for the structure determination as described below. This structure determination led to the formula Ba_2SnSe_5 (denoted as β-Ba_2SnSe_5).

Scanning electronic microscopy was performed using the electron microscope LEO 1530 with an additional EDAX device, EDAX Pegasus 1200 (EDAX: energy dispersive analysis of X-rays). No impurity elements (e.g., Si stemming from the reaction container) were detected. For β-Ba_2SnSe_5, the Ba/Sn/Se ratio was determined to be 26: 14: 60 (in atomic percent), respectively, averaged over three crystals, which compares nicely with the nominal atomic percent ratio of 25:12.5:62.5.

Differential scanning calorimetry (DSC) was carried out on a computer-controlled NETZSCH 409PC thermal analyzer. A sample (85.9 mg) of ground crystalline α-Ba_2SnSe_5, prepared as published before[20] was sealed in a quartz ampule under vacuum. The ampule was heated to 1073 at 10 K min^{-1} and then cooled at the same rate. A (reversible) phase transition commenced at about 1000 K (Figure 1). After that experiment, the X-ray powder diagram contained α-Ba_2SnSe_5 as the major phase and traces of β-Ba_2SnSe_5, indicating that the β-modification formed upon heating, and then changed back slightly incompletely upon cooling.

Table 2. Atomic Coordinates and Equivalent Displacement Parameters of β-Ba_2SnSe_5[a]

atom	x	y	z	U_{eq}/Å^2
Ba1	0.07968(4)	0.63605(4)	0.32516(3)	0.0141(1)
Ba2	0.53670(4)	0.12800(5)	0.34596(4)	0.0169(1)
Sn	0.16165(5)	0.29243(5)	0.01696(4)	0.0136(1)
Se1	0.09835(7)	0.82219(8)	0.09646(6)	0.0152(2)
Se2	0.21493(7)	0.00824(7)	0.39682(6)	0.0156(2)
Se3	0.23586(8)	0.37265(7)	0.22309(6)	0.0150(2)
Se4	0.35770(7)	0.07271(8)	0.05731(6)	0.0173(2)
Se5	0.55746(7)	0.25736(7)	0.10049(6)	0.0160(2)

[a] All atoms are on Wyckoff site 4e.

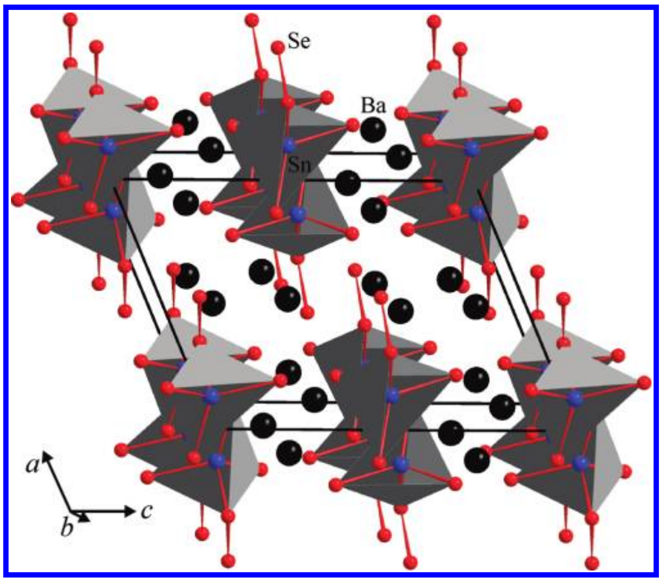

Figure 2. Crystal structure of β-Ba_2SnSe_5 in a projection along the b axis.

In order to shed more light on the phase transformation, both α- and β-Ba_2SnSe_5 were annealed for 48 h both above and below the transition point, and then quenched in cold water. After annealing at 923 K, the resulting phase was α-Ba_2SnSe_5, and after annealing at 1023 K, the result was β-Ba_2SnSe_5, regardless whether the starting material was the α- or the β-modification. Thus, the phase transition is fully reversible.

Crystal Structure Determination. A red plate-shaped crystal was selected under an optical microscope and then mounted on a glass fiber. Single crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 298 K on a Bruker APEX CCD diffractometer. The scans of 0.3° in ω were done in two groups of 606 frames (each with an exposure time of 40 s) at $\varphi = 0°$ and at $\varphi = 90°$. The data were corrected for Lorentz and polarization effects. An absorption correction was performed based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements using SADABS.[22]

The lattice parameters pointed toward the monoclinic crystal system, and the systematic absences ($0\,k\,0$: $k = 2n$, $h\,0\,l = 2n$) were in accord with the space group $P2_1/c$. The structure model was obtained by direct methods and refined by full-matrix least-squares refinement based on F^2 using the SHELXTL5.12 package.[23] The

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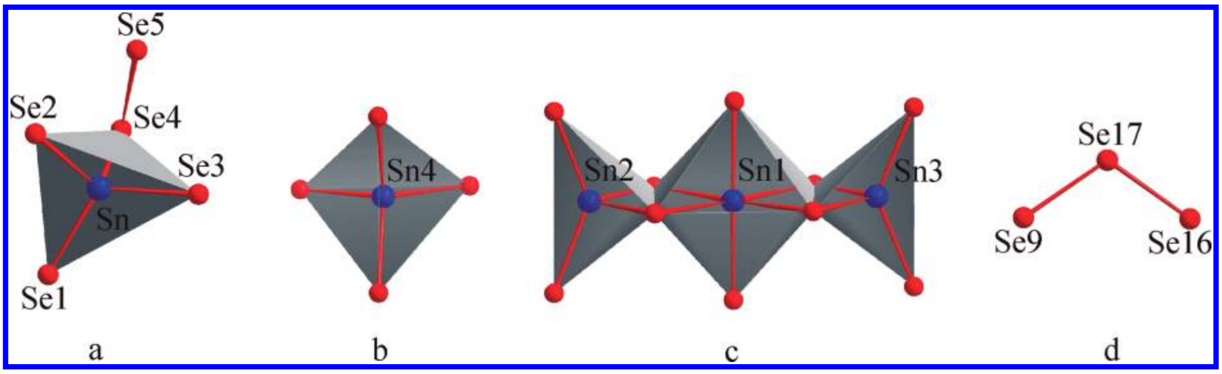

Figure 3. Different structure motifs of α- and β-Ba_2SnSe_5. From left to right, (a) $SnSe_5^{4-}$ unit of β-Ba_2SnSe_5, (b) $SnSe_4^{4-}$, (c) $Sn_3Se_{10}^{8-}$, and (d) Se_3^{2-} of α-Ba_2SnSe_5.

Table 3. Selected Interatomic Distances [Å] of β-Ba_2SnSe_5

Ba1−Se2	3.2595(8)	Ba2−Se5	3.2895(8)
Ba1−Se3	3.2777(8)	Ba2−Se5	3.3701(8)
Ba1−Se5	3.3363(7)	Ba2−Se2	3.3756(8)
Ba1−Se1	3.3665(8)	Ba2−Se4	3.3785(8)
Ba1−Se1	3.3798(8)	Ba2−Se3	3.4096(8)
Ba1−Se3	3.4833(8)	Ba2−Se3	3.4514(8)
Ba1−Se2	3.5226(8)	Ba2−Se2	3.4934(8)
Ba1−Se4	3.5690(8)	Ba2−Se5	3.5362(8)
Ba1−Se1	3.5798(8)	Ba2−Se1	3.6443(8)
Sn−Se2	2.5008(8)	Se4−Se5	2.3856(9)
Sn−Se1	2.5055(8)		
Sn−Se3	2.5061(9)		
Sn−Se4	2.5895(8)		

structure solution in this space group was successful, yielding eight symmetry independent atom sites. The five sites occupied by the lightest atom were expected to be—and thus refined as—Se positions. Then, the two sites with no contacts to the Se atoms <3 Å were identified as Ba positions. The remaining site displayed bonds to Se atoms around 2.5 Å, typical for an Sn^{IV} atom. This model was confirmed by the uniform distribution of equivalent displacement factors, U_{eq}, all being of the order of 0.015 Å^2. Finally, the positions were standardized with the TIDY program within the PLATON package.[24] The final refinement converged with a residual factor of $wR2 = 0.086$ (all data). Crystallographic details and atomic coordinates with the equivalent thermal displacement parameters are summarized in Tables 1 and 2.

Electronic Structure Calculations. LMTO (linear muffin tin orbitals) band structure calculations[25,26] were carried out in order to understand the electronic structure of β-Ba_2SnSe_5. In the LMTO approach, the density functional theory is used with the local density approximation (LDA).[27] The integrations in k space were performed by an improved tetrahedron method on a grid of 434 unique k points of the first Brillouin zone.[28]

Results and Discussion

Crystal Structure. The new structure of β-Ba_2SnSe_5 could be described using only two motifs, namely Ba^{2+} cations surrounded by nine Se atoms and $SnSe_5$ units (Figure 2). The $SnSe_5$ unit is comprised of a central Sn atom, tetrahedrally coordinated by four Se atoms, Se1, Se2, Se3, and Se4. The fifth Se atom, Se5, bonds to Se4 and not to the Sn atom. Thus, the Se4−Se5 unit is a regular Se_2^{2-} dumbbell, and the $SnSe_5$ unit may then be written as $Sn^{IV}(Se^{2-})_3Se_2^{2-}$, in analogy to the Se_2^{2-} dumbbells within the PSe_5 units of $K_4In_2(PSe_5)_2(P_2Se_6)$ and $Rb_3Sn(PSe_5)(P_2Se_6)$.[29]

In contrast to the $SnSe_5$ units of β-Ba_2SnSe_5, linear chains of Ba^{2+} cations surround bent Se_3^{2-} units, trimeric $Sn_3Se_{10}^{8-}$ units, and isolated $SnSe_4^{4-}$ tetrahedra in the structure of α-Ba_2SnSe_5.[20] These different motifs are compared in Figure 3.

Since we were able to convert α-Ba_2SnSe_5 into β-Ba_2SnSe_5 at 1023 K as well as β-Ba_2SnSe_5 into α-Ba_2SnSe_5 at 923 K, eq 1 is fully reversible:

$$SnSe_4^{4-} + Sn_3Se_{10}^{8-} + 2Se_3^{2-} \rightleftarrows 4SnSe_5^{4-} \qquad (1)$$

As is typical for a reconstructive phase transition like this one, there is no direct group−subgroup relation between the two modifications in the space groups $P2_12_12_1$ and $P2_1/c$. The reversible transition occurs in the solid state, wherein several covalent bonds, both Sn−Se and Se−Se, must be broken and formed: for example from α to β, the 6-fold coordinated Sn atom changes into a 4-fold coordinated Sn atom, i.e. a breakage of two Sn−Se bonds occurs, and one Se−Se bond of the Se_3 unit gets broken as well. Thereby, a redox reaction occurs, because the central Se atom of the Se_3^{2-} unit of α-Ba_2SnSe_5 is in the oxidation state zero, while the Se atoms of β-Ba_2SnSe_5 are either in the −1 or the −2 state (eq 2). Equation 2 can, of course, be simplified to correspond to the synproportionation of one Se^{2-} and one Se^0 to two Se^{1-}.

$$14Se^{2-} + 4Se^{1-} + 2Se^0 \rightleftarrows 12Se^{2-} + 8Se^{1-} \qquad (2)$$

While the motifs change as described above, the interatomic distances change to different extents. The 9-fold Se-coordination of the Ba^{2+} cations with Ba−Se distances between 3.26 and 3.58 Å of β-Ba_2SnSe_5 (Table 3) compares well with the ones in α-Ba_2SnSe_5 (3.24−3.70 Å). The Se−Se bond lengths are almost identical, being 2.39 Å in the Se_2^{2-} unit and 2.38 Å in the Se_3^{2-} unit, indicative of Se−Se single bonds.[30,31] The Sn−Se distances of the 4-fold coordinated Sn atoms are between 2.50 and 2.58 Å

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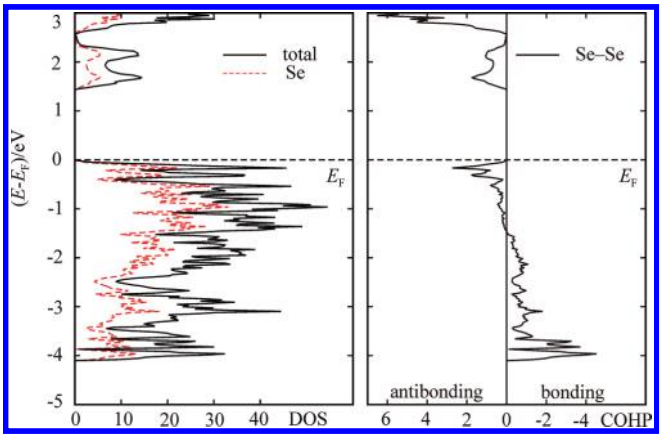

Figure 4. Densities of states (DOS, left) and Se−Se crystal orbital Hamilton population curve (COHP, right) of β-Ba$_2$SnSe$_5$. The Fermi level, E_F, was arbitrarily placed at 0 eV.

in the α-form and between 2.50 and 2.59 Å in the β-form. In the latter, the Sn−Se4 bond stands out with 2.59 Å, while the bonds to the Se atoms in the −2 oxidation state are all 2.50 or 2.51 Å. Finally, the four longer Sn−Se distances of the 6-fold coordinated Sn atom (from 2.74 to 2.99 Å) have no counterpart in the β-form.

Electronic Structures and Physical Properties. α-Ba$_2$SnSe$_5$ exhibits a calculated band gap of 1.2 eV, while its dark brown color is indicate of an optical gap of approximately 1.7−1.8 eV.[20] The red color of β-Ba$_2$SnSe$_5$ is typical for a larger band gap of 2.0 eV; correspondingly, its computed densities of states reveal a gap of 1.4 eV (Figure 4, left). Noting that this difference between observed and calculated gap is not atypical for LMTO calculations,[32−34] the calculations qualitatively confirmed that the β-modification has the larger gap. This is a consequence of its narrower valence band of 4.1 eV, compared to 4.4 eV in α-Ba$_2$SnSe$_5$, which in turn is caused by its smaller structure motifs.

As is the case in α-Ba$_2$SnSe$_5$, the states associated with the Se−Se bond are predominant both above and below the Fermi level, E_F. Below E_F, the filled states have π^* Se−Se character, and the empty states directly above exhibit σ^* Se−Se character, all thereof being based on the Se p-orbitals. The bonding π_{p-p} interactions commence at −4.1 eV in the Se$_2^{2-}$ units of β-Ba$_2$SnSe$_5$ (Figure 4, right) and at −4.4 eV in the Se$_3^{2-}$ units of α-Ba$_2$SnSe$_5$.

As the phase transition is reversible, the total energies have to be comparable. We calculated the total energy of β-Ba$_2$SnSe$_5$ to be 0.4 eV (per formula unit) higher than that of α-Ba$_2$SnSe$_5$, confirming that the α to β phase transition is endothermic.

Conclusion

A new modification of the polyselenide Ba$_2$SnSe$_5$ was uncovered and subsequently characterized. It is the high temperature variant, hence β-Ba$_2$SnSe$_5$, and may be prepared from the elements or via solid state transformation of α-Ba$_2$SnSe$_5$ at temperatures above 1000 K. That reaction is fully reversible, i.e. we successfully synthesized α-Ba$_2$SnSe$_5$ starting from β-Ba$_2$SnSe$_5$ at 923 K.

Like α-Ba$_2$SnSe$_5$, β-Ba$_2$SnSe$_5$ forms its own structure type. In contrast to α-Ba$_2$SnSe$_5$ with its three different covalent molecular motifs (bent Se$_3^{2-}$, Sn$_3$Se$_{10}^{8-}$ units, isolated SnSe$_4^{4-}$), all Sn and Se atoms of β-Ba$_2$SnSe$_5$ are part of its isolated SnSe$_5^{4-}$ unit, composed of an Sn^{IV} atom bonded to three Se^{2-} and one Se$_2^{2-}$ dumbbell. For comparison, the two modifications may be written as α-(Ba^{2+})$_8$(SnSe$_4$)$^{4-}$-(Sn$_3$Se$_{10}$)$^{8-}$(Se$_3^{2-}$)$_2$ and β-(Ba^{2+})$_2$(SnSe$_5$)$^{4-}$. Therefore, the α to β transformation is a reconstructive phase transition, as a major reconstruction including Sn−Se and Se−Se bond breaking takes place. It also involves a redox reaction, namely a synproportionation of Se^0 and Se^{2-} to two Se^{1-}.

Both Ba$_2$SnSe$_5$ are optical semiconductors, the α-form being dark brown and the β-form shiny red. These colors are indicative of band gaps of 1.8 and 2.0 eV, respectively. The computed band gaps exhibit the same trend, i.e. a larger band gap in the case of greater molecular β-modification, caused by its narrower valence band.

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Supporting Information Available: One crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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