Reticular merohedral twinning within the La$_9$Sb$_5$O$_5$ structure family: structure of Pr$_9$Sb$_5$O$_5$, Sm$_9$Sb$_5$O$_5$ and Dy$_9$Sb$_5$O$_5$

Jürgen Nuss and Martin Jansen
Reticular merohedral twinning within the La₉Sb₅O₅ structure family: structure of Pr₉Sb₅O₅, Sm₉Sb₅O₅ and Dy₉Sb₅O₅

The novel antimonide oxides Pr₉Sb₅O₅, Sm₉Sb₅O₅, and Dy₉Sb₅O₅ were synthesized from the respective RESb, the rare-earth metals (RE = Pr, Sm, Dy), and RES₂O₃ (RE = Sm, Dy) or Pr₂O₃, respectively, in sealed tantalum ampoules at 1920 K. Those compounds, which are sensitive against air and moisture, form black cube-like crystals with metallic lustre. They crystallize in the La₉Sb₅O₅ type of structure, which represents a fivefold superstructure of the KCoO₂ structure: O₁₀K₅Co₅ ⊃ La₉Sb₅O₅. The investigated crystals of the Sm and Dy compounds were twinned using the reticular merohedral law, with the twin symmetry 4/mmm, and the (310) and (120) mirror planes as twinning symmetry elements. The twin index is [j] = 5.

1. Introduction

The Zintl–Klemm concept (Zintl, 1939; Klemm, 1958; Schäfer et al., 1973a,b) has proven a versatile and rather conclusive approach to the understanding of structural and bonding principles in intermetallic compounds composed of combinations of elements that differ significantly in electronegativity. Naturally, when crossing the borderlines to predominantly covalent, ionic or metallic bonding schemes the Zintl–Klemm concept loses its stringency, and finally its validity. However, examples documenting failure have also been reported for compounds within the Zintl–Klemm regime. In some cases, like Sr₂Sb, Eu₂Sb (Martinez-Ripoll et al., 1973) or Ba₂Sb (Eisenmann & Deller, 1975), where the electron counts appeared to not comply with the Zintl rules, the discrepancies have been resolved by the structure re-determination, resulting in the correct compositions Eu₄Sb₂O (Schaal et al., 1998) or Ba₄Sb₂O (Röhr & George, 1996), which represent the electron-precise antimonide oxides.

On the other hand, La₉Sb₅O₅, again an antimonide oxide, hosts two excess electrons: \((\text{La}^{3+})₉(\text{Sb}^{3–})₅(\text{O}^{2–})₅ + 2e^–\). This electron count has been confirmed independently and is in accordance with the material showing metallic conductivity (Nuss et al., 2004). Its structure may be regarded as a stuffed defect derivative of the Sc₂Sb type, which can be expressed by the formula La₉Sb₅O₅ ⊃ Sc₁₀Sb₅O₅.

In this paper we demonstrate that La₉Sb₅O₅ represents the first member of a series of isostructural compounds, and we analyse the crystallographic implications resulting from the interplay between filling existing interstices and generating new vacancies of a given matrix. These circumstances bring
2. Experimental

2.1. Synthesis

The $RE_{x}Sb_{5}O_{y}$ ($RE = Pr, Sm, Dy$) compounds have been synthesized in $\sim 1$ g batches from $RE$Sb, the rare-earth metals (ChemPur, Karlsruhe, Germany 99.9%), and $RE_{x}O_{y}$ ($RE = Sm, Dy$, ChemPur, 99.9%) or $Pr_{x}O_{y}$ (ChemPur, 99.9%), respectively. The rare-earth antimonides, $RESb$, were prepared from the elements in closed tantalum ampoules. The ampoules were heated at 1300 K for 48 h under dynamic vacuum. The phase purity of the starting materials was confirmed by X-ray analysis.

The starting materials were mixed in a dry-box (M. Braun, Garching, Germany) under argon atmosphere (less than 0.1 p.p.m. $O_{2}$, $H_{2}O$ in the ratio required according to (1), ground thoroughly in an agate mortar and sealed in tantalum ampoules.

$$15RESb + 5RE_{x}O_{y} + 2RE \rightarrow 3RE_{x}Sb_{5}O_{y} \quad (RE = Sm, Dy)$$

3$Pr_{x}Sb + 5Pr_{x}O_{y} + 8Pr \rightarrow 7Pr_{x}Sb_{5}O_{y}$

(1)

The reactions were carried out in a high-temperature furnace with molybdenum disiclide heating elements (Supertherm RH 08/16, Nabatherm, Liliental, Germany). In order to protect the tantalum ampoules from corrosion, an argon-filled, gas-proof zirconia tube ($Y_{2}O_{3}$ partially stabilized) was used. The following temperature profile was applied: 298 $\rightarrow$ 1920 K (100 K $h^{-1}$, subsequent annealing for 2 h); 1920 $\rightarrow$ 1770 K (20 K $h^{-1}$, subsequent annealing for 48 h); 1770 $\rightarrow$ 298 K (50 K $h^{-1}$).

The solidified black reguli with metallic lustre are sensitive to air and moisture, and they must be handled in an inert atmosphere.
2.2. X-ray diffraction

For X-ray diffraction experiments, single crystals were selected in a dry-box (M. Braun, Garching, Germany) under an argon atmosphere (< 0.1 p.p.m. O₂, H₂O) and mounted in sealed glass capillaries. Collection of the diffraction intensities was performed on a Smart APEX II three-circle diffractometer with an APEX II CCD detector (Bruker AXS Inc.) at 296 K. The intensities were integrated with the SAINT program in the Bruker Suite software package (Bruker AXS, 2005). An absorption correction was applied using SADABS (Sheldrick, 2007) for Pr₉Sb₅O₅, and TWINABS (Sheldrick, 2007) for Sm₉Sb₅O₅ and Dy₉Sb₅O₅, respectively. Experimental details are given in Table 1; atomic coordinates have been deposited.

3. Structure determination

The diffraction intensities of the three crystals of RE₉Sb₅O₅ (RE = Pr, Sm, Dy) could be indexed and integrated on the basis of the tetragonal crystal system. However, the translation lattices of Sm₉Sb₅O₅ and Dy₉Sb₅O₅, as determined in the initial stage, correspond to a fivefold superstructure in comparison to the values found for Pr₉Sb₅O₅ (Table 1). No peak-splitting is observed with Mo Kα radiation; Fig. 1 shows the zeroth layer of the reciprocal space of the Pr₉Sb₅O₅ and Dy₉Sb₅O₅ crystals, constructed pixel by pixel from the original CCD frames using the Precession module of the Bruker Suite software package (Bruker AXS, 2005). This procedure allows a detailed exploration of the reciprocal space, without restrictions to integer hkl values (Nuss et al., 2007).

For Pr₉Sb₅O₅, the Laue group 4/m together with the extinction rule h0k: h + k = 2n has led to the space group P4/n, unambiguously. The heavy atoms Pr and Sb were located from the Patterson map. During the structure refinement oxygen positions were identified in the difference Fourier map. As a final result Pr₉Sb₅O₅ turns out to be isotypic with La₉Sb₅O₅ (Nuss et al., 2004).

In contrast, analysis of the systematic absences in the diffraction patterns of Sm₉Sb₅O₅ and Dy₉Sb₅O₅ showed that the observed reflections fulfill one of two conditions [see (2)]

\[ 2h + k = 5n \text{ or } h + 2k = 5n. \]  

Apparent systematic absences, which are not consistent with any known space group, are one of the characteristic warning signs for twinning (Herbst-Irmer & Sheldrick, 1998). Such a distribution of intensities (2) in the reciprocal space is indicative of a special kind of twinning in the tetragonal system, with twin reflection planes (120) or (310) (Tamazyan et al., 2000). The full pattern can be interpreted as a superposition of two differently oriented but identical diffraction patterns (Figs. 1b and c), and the initially found fivefold superlattice represents a twin lattice. The angle needed to rotate one domain around the common fourfold axis into the orientation of the other is 36.87° = 2tan⁻¹(1/3). The transformation matrices generating the two twin domains from the twin lattice are

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Figure 1
Reciprocal layers hkl of (a) the single crystal of Pr₉Sb₅O₅, and (b) and (c) the twin of Dy₉Sb₅O₅. The reflections of the corresponding two twin domains are emphasized by circles in (b) and (c). The directions of the reciprocal axes of each domain are drawn.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5006). Services for accessing these data are described at the back of the journal.
Reticular merohedral twinning

The reflection intensities were corrected for absorption and the complete data set, including both domains, it was possible to perform unrestricted structure refinements for Sm$_5$Sb$_5$O$_5$ and Dy$_5$Sb$_5$O$_5$ with figures on the merits comparable to those obtained for untwinned crystals. All atoms were refined with anisotropic displacement parameters and the resulting twin volume fractions showed reasonable values of the order of magnitude 1/2, for both compounds (see Table 1). It is very important to use the reflections common to both domains [all of them are fulfilling both (2)] in the refinements, because most of the intensity is concentrated in these reflections; they can be easily found in the precession images (Fig. 1) as having the highest intensities.

4. Crystal structure and discussion

Three new isotypic compounds crystallize in the La$_5$Sb$_5$O$_5$ type of structure (Nuss et al., 2004). The structure can be described as consisting of stacked layers. The atoms RE$_2$Sb$_2$O$_4$ and SB$_1,2$ are arranged in a corrugated double layer \([\text{Sb}]\) as an \([\text{NaCl}]\) analogous slab. The orange sticks between the rare-earth metals illustrate the puckered double layer \([\text{RESb}]\) as an \([\text{NaCl}]\) analogous slab.

The reflection intensities were corrected for absorption and analyzed with the program TWINABS (Sheldrick, 2007b). The analysis (included in Table 1) confirms that the special orientation of the twin domains generates a reticular merohedral twin: from all reflections \(I_{all}\) of \(e.g.\) domain I, \(4I_{all}/5\) belong to this domain exclusively and \(I_{all}/5\) belong to both domains. There are either completely overlapping or non-overlapping reflections, however, no partially overlapping ones by coincidence, as is observed for \(e.g.\) dovetail twins. The twin lattice is also tetragonal, and the twin lattice index is \([j] = V_{tw}/V_{1,2} = 5\) (cf. Table 1; Hahn & Klapper, 2003). Fig. 1 shows the zeroth reciprocal layer of Dy$_5$Sb$_5$O$_5$ with the reflections of each domain highlighted \((b, c)\), and that of the single crystal of Pr$_5$Sb$_5$O$_5$ \((a)\) for comparison. It is obvious that all visible intensities are indexed by at least one of the two twinning domains, and the ‘empty’ reciprocal space is left unindexed.

With the atomic parameters of Pr$_5$Sb$_5$O$_5$ as starting values and the complete data set, including both domains, it was possible to perform unrestricted structure refinements for Sm$_5$Sb$_5$O$_5$ and Dy$_5$Sb$_5$O$_5$ with figures on the merits comparable to those obtained for untwinned crystals. All atoms were refined with anisotropic displacement parameters and the resulting twin volume fractions showed reasonable values of the order of magnitude 1/2, for both compounds (see Table 1). It is very important to use the reflections common to both domains [all of them are fulfilling both (2)] in the refinements, because most of the intensity is concentrated in these reflections; they can be easily found in the precession images (Fig. 1) as having the highest intensities.

Figure 2

Crystal structure of RE$_5$Sb$_5$O$_5$ \((RE = \text{Pr, Sm, Dy})\), with unit cell (black). The orange sticks between the rare-earth metals RE$_2$Sb$_2$ and antimony illustrate the puckered double layer \([\text{RESb}]\) as an \([\text{NaCl}]\) analogous slab.

#### Table 2

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<th></th>
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<th>Sm$_5$Sb$_5$O$_5$</th>
<th>Dy$_5$Sb$_5$O$_5$</th>
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<td>2.502 (1)</td>
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\[
(a_1, b_1, c_1) = (a_{lw}, b_{lw}, c_{lw}) = \begin{pmatrix} 2/5 & 1/5 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

\[
(a_2, b_2, c_2) = (a_{lw}, b_{lw}, c_{lw}) = \begin{pmatrix} 2/5 & -1/5 & 0 \\ 1/5 & 2/5 & 0 \end{pmatrix} \cdot (3)
\]

These matrices were used to create multi-component \(hkl\) files from the raw datasets of the Sm$_5$Sb$_5$O$_5$ and Dy$_5$Sb$_5$O$_5$ crystals during the integration procedure with the Bruker Suite software package (Bruker AXS, 2005), which can be used with the HKL5 option in SHELXL (Sheldrick, 1997b). The twinning matrix transforming the two differently oriented unit cells into each other is

\[
(a_2, b_2, c_2) = (a_1, b_1, c_1) = \begin{pmatrix} 3/5 & -4/5 & 0 \\ 4/5 & 3/5 & 0 \end{pmatrix} \cdot (4)
\]
this intergrowth structure (Grin et al., 1982) have the compositions \(\text{RE}_5\text{Sb}_5\) and \(\text{RE}_5\text{O}_5\). The \(\text{Sb}^5\) \(\text{RE}_4\) \(\text{Sb}_4\) cubes \([\text{Pr}—\text{Sb}] = 3.270, (\text{Sm}—\text{Sb}) = 3.206, (\text{Dy}—\text{Sb}) = 3.145\); see Table 2\], which is also a feature common to the structures of \(12\text{La}_2\text{Sb} \) (Wang et al., 1980), \(\text{Sc}_2\text{Sb} \) (Nuss & Jansen, 2000b) or \(\text{Eu}_2\text{Sb}_2\) (Schaal et al., 1998). The buckling of the NaCl-like slabs is an elegant way to fit the dimensions of their meshes to the sandwiched sheets in-between. This has been discussed in detail elsewhere for \(\text{Sc}_2\text{Sb} \) and analogous compounds (Nuss & Jansen, 2002; Nuss et al., 2006); in the latter family of compounds the interlayer exclusively consists of Sc atoms. In the case of the \(\text{RE}_5\text{Sb}_5\) \(\text{O}_5\) compounds these layers are composed of rare-earth metal and \(\text{O} \) atoms with the composition \(\text{RE}_4\) \(\text{O}_5\). In contrast to e.g. \(\text{Sc}_2\text{Sb} \), only 4/5 of the possible metal positions are occupied by rare-earth elements. Therefore, the structure of the \(\text{RE}_5\text{Sb}_5\) \(\text{O}_5\) compounds can be regarded as a stuffed defect variant of \(\text{Sc}_2\text{Sb} \): after removing 1/5 of the Sc atoms from the 4 \(\times\) \(\times\) net in \(\text{Sc}_2\text{Sb} \) (Fig. 3, left) a 3 \(\times\) 3 \(\times\) 4 \(\times\) net results with the same arrangement of metal and antimony atoms as in \(\text{Sc}_2\text{Sb} \). The partial structure \(\text{RE}_5\text{Sb}_5\) also corresponds to the inverted \(\text{Hf}_5\text{Sb}_5\) \(\text{O}_5\) type of structure (Assoud et al., 2004a,b). From the originally square \(\text{Sc} \) pyramids, with their tips alternating up and down along the [001] direction (Fig. 3, blue polyhedra), 4/5 transform into tetrahedra (turquoise and grey polyhedra, respectively) and 1/5 remain unchanged (green and yellow polyhedra, respectively; distances \(\text{RE}—\text{O} \) are given in Table 2). Thus, a superstructure with \(a' = a(5)^{1/2}\) results. All tetrahedral and square-pyramidal holes are filled with \(\text{O} \) atoms.

To our knowledge no ‘stuffed’ intermetallic compound of the \(\text{Sc}_2\text{Sb} \) structure is known. Instead the oxide \(\text{KCoO}_2 \) (Jansen & Hoppe, 1975) features such an example as a ‘filled antitype’. The relation between all these structures is: \(\text{KCoO}_2 = \text{Sc}_2\text{Sb} = \text{La}_9\text{Sb}_5\text{O}_5 = \text{Hf}_5\text{Sb}_9 \) \(\equiv\). The group-subgroup relation (Wondratschek & Müller, 2004; Müller, 2004) between the aristotype \(\text{KCoO}_2 \) (\(\text{Sc}_2\text{Sb} \)) and \(\text{La}_9\text{Sb}_5\) \(\text{O}_5\) includes two consecutive steps of symmetry reduction, one of type \(\text{translationalgleich (t2)} \) and an isomorphous one of index 5 (\(i5\)). Fig. 4 shows the group-subgroup relation (Bärnighausen–Stamm–baum), including all site transformations for the compounds listed above. A comparison between the atomic coordinates of \(\text{Pr}_9\text{Sb}_5\) \(\text{O}_5\), as an example, and the idealized values indicate that the major structural changes, in comparison to the \(\text{KCoO}_2 \) or \(\text{Sc}_2\text{Sb} \) structure, are related to \(xy\) shifts of the \(\text{Pr}1\) and \(\text{O}2\) atoms, mainly. The \(\text{PrSb} \) rock salt layer is nearly unaffected.

The superstructure results from an ordering of vacancies \(\square\) on the metal sites of the \(\text{RE}_5\text{Sb}_5\) \(\text{O}_5\) substructure. This ordering of vacancies may occur in two different ways (orientations), which are equivalent, in principle. These two orientations correspond to the two twinning domains as observed in \(\text{Sm}_9\text{Sb}_5\) \(\text{O}_5\) and \(\text{Dy}_9\text{Sb}_5\) \(\text{O}_5\) (domain I and II in Fig. 3). The twin symmetry elements are \((310) \) and \((120) \) mirror planes, which correspond to the \((100) \) and \((110) \) mirror planes of the twin lattice (twin symmetry \(4\text{mm}^*\)). The \(\text{RE}_5\text{Sb}_5\) \(\text{O}_5\) substructure is unaffected by this ordering because the twin symmetry elements are part of the \(\text{RE}_5\text{Sb}_5\) \(\text{O}_5\) layers (plane group \(\text{p}4\text{mm}^*\), \(a = 4.4001\) \(\text{Å}\) for e.g. \(\text{Dy}_9\text{Sb}_5\) \(\text{O}_5\) in contrast to the \(\text{RE}_5\text{Sb}_5\) layer.

**Figure 3**
The outer part shows the structural changes between \(\text{Sc}_2\text{Sb} \) and \(\text{Dy}_9\text{Sb}_5\) \(\text{O}_5\) (projection along [001]). The middle part represents the twinning phenomena using the example of \(\text{Dy}_9\text{Sb}_5\) \(\text{O}_5\). The unit cells, and the directions of the unit-cell axes of \(\text{Sc}_2\text{Sb} \) and the two differently oriented twinning domains of \(\text{Dy}_9\text{Sb}_5\) \(\text{O}_5\), are drawn in together with the mirror plane \([m = (310)]\), which transforms both domains into each other. [\(\text{DySb} \) layers are displayed in the ball-and-stick mode, and the [\(\text{DyO} \)] part is presented as polyhedra (see text).
(plane group $p4$, $a = 9.8389$ Å for e.g. Dy$_2$Sb$_2$O$_5$; Hahn, 2002). Consequently, the [RE$Sb$] layers show the same orientation in both twinning domains, and only the [RE$_2$O$_3$] substructure is moved by the twinning operation. These details are illustrated in Fig. 3: the [DySb] or the corresponding [ScSb] layer extends undistorted across the aristotypic ‘Sc$_2$Sb’ (the lattice constants in Fig. 3: the [DySb] or the corresponding [ScSb] layer extends moved by the twinning operation. These details are illustrated polyhedra of the O atoms located on $m$ are square pyramids (red polyhedra). It is confirmed once again: twinning usually arises for good structural reasons (Herbst-Irmer & Sheldrick, 1998).

From a purely geometric point of view, the structural response to stuffing the Sc$_2$Sb type of structure with oxygen even more reasonable alternative.

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References

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Figure 4
Group–subgroup relation between Sc$_2$Sb (KCoO$_2$, respectively) and La$_9$Sb$_3$O$_5$, including the coordinates for Pr$_3$Sb$_5$O$_9$ and Hf$_3$Sb$_5$O$_9$ and their relations to those of the aristotypes. The boxes contain: element, Wyckoff symbol, site symmetry, and atomic coordinates $x$, $y$, $z$. Lattice parameters are specified in addition *(the second transformation is included to obtain the same setting already given for La$_9$Sb$_3$O$_5$; Nuss et al., 2004).*