

KSbO(Ge_{0.32}Si_{0.68})O₄, a KTP isomorph

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A structural model of potassium antimony germanate/silicate (0.32/0.68), KSbO(Ge_{0.32}Si_{0.68})O₄, has been determined at room temperature. KSbO(Ge_{0.32}Si_{0.68})O₄ belongs to the KTiOPO₄ (KTP) isomorph family and is composed of SbO₆ octahedra (site symmetry $\bar{1}$ and 2) arranged in helical chains bridged by (Ge/Si)O₄ tetrahedra. Germanium and silicon have a similar distribution in the crystallographically independent tetrahedra (site symmetry 2). The structure contains large cavities occupied by the K atom. Two partially occupied potassium positions have been identified 1.273 (8) Å apart, with an indication of a third potassium position between them. At room temperature, KSbO(Ge_{0.32}Si_{0.68})O₄ crystallizes in the paraelectric phase of space group *Pnan*. This phase is found at elevated temperatures for almost all KTiOPO₄ isomorphous compounds and KSbO(Ge_{0.32}Si_{0.68})O₄ is the second isomorph that is paraelectric at room temperature.

Comment

Since the structure determination by Tordjman *et al.* (1974) of potassium titanyl phosphate, KTiOPO₄ (KTP), it has become a well known material for use in non-linear optical processes (Zumsteg *et al.*, 1976), such as second harmonic generation (SHG; Bierlein *et al.*, 1989). The high non-linearity of KTP extends to many isomorphous compounds with the general chemical formula *AMOBO*₄ (*A* = K, Rb, Cs or Tl; *M* = Ti; *B* = P or As). Several of these isomorphs have been extensively studied (Stucky *et al.*, 1989, and references therein). Recently, another group of isomorphs have been explored, with substitutions in the *MO*₆ octahedra and the *BO*₄ tetrahedra (*A* = Na, K, Rb, Tl or Ag; *M* = Sb, Nb or Ta; *B* = Si or Ge). The isomorphs with Sb in the octahedra have been fairly well studied. KSbOSiO₄ (KSS) was prepared by Crosnier *et al.* (1990) in a solid-state reaction and the structure of KSbOGeO₄ (KSG) was published independently by Pagnoux *et al.* (1991) and Belokoneva *et al.* (1991). Other compounds include NaSbOSiO₄ (Pagnoux *et al.*, 1992), RbSbOGeO₄ (Favard *et al.*, 1992), TlSbOGeO₄ (Belokoneva & Mill, 1992*a*), RbSbOGeO₄ (Belokoneva & Mill, 1992*b*), NaSbOGeO₄, AgSbOGeO₄ and AgSbOSiO₄ (Mill *et al.*, 1993).

The KTP isomorphous materials with Sb in the oxygen octahedra all have weak non-linear optical coefficients, which are orders of magnitudes lower than those of KTP. This is mainly due to the low polarizability of Sb^V and the regularity of the SbO₆ octahedra. Butashin *et al.* (1994) reported that an exchange of Sb^V with Nb^V greatly increases the non-linear optical coefficients. The solid solution system of KSb_{1-x}Nb_xOGeO₄ extends to *x* = 0.75, but no KTP phase has been detected in the *A*₂O–Nb₂O₅BO₂ (*A* = Na, K, Rb, Tl or Ag; *B* = Si or Ge) system (Belokoneva *et al.*, 1991).

As a part of our ongoing investigation of new modifications and isomorphous materials in the KTP family, we have prepared a new member of the Sb family with mixed occupation of Ge and Si in the tetrahedral positions, *viz.* KSbO(Ge_{0.32}Si_{0.68})O₄ (KSGS).

The structure of KSGS is very similar to the KTP structure (Thomas *et al.*, 1990). It comprises SbO₆ octahedra that are corner linked at alternating *cis* and *trans* positions, forming helical chains in the [011] direction. These chains are further linked by (Ge/Si)O₄ tetrahedra. The framework built by the octahedra and tetrahedra has large cavities which are occupied by the K⁺ cations. Fig. 1 gives a view of the structure in the (010) plane.

All SbO₆ octahedra are fairly regular with maximum and minimum Sb–O bond lengths of 2.004 (5) and 1.955 (6) Å, respectively, and a mean (s.u.) of 1.97 (2) Å. The AO₄ tetrahedra (*A* = Ge, Si) are also regular with maximum and minimum bond lengths of 1.683 (6) and 1.648 (6) Å and a mean (s.u.) of 1.664 (15) Å. The mean (s.u.) Si–O bond length of the SiO₄ tetrahedra in KSS is 1.62 (2) Å (Crosnier *et al.*, 1990), while that of the GeO₄ tetrahedra in KSG is 1.742 (14) Å (Belokoneva *et al.*, 1991). It should also be noted that the shape and bond lengths of the SbO₆ octahedra are almost identical in KSS, KSG and the new KSGS. There is,

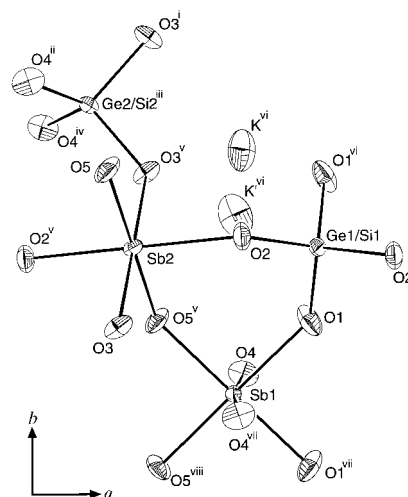


Figure 1
ORTEP (Burnett & Johnson, 1996) view of the KSbO(Ge_{0.32}Si_{0.68})O₄ structure in the (010) plane. Displacement ellipsoids are drawn at the 80% probability level. [Symmetry codes: (i) $1 - x, y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $1 - x, y - \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $1 - x, 2 - y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $-x + \frac{3}{2}, y, 1 - z$; (vii) $x, -y + \frac{3}{2}, -z + \frac{1}{2}$; (viii) $1 - x, y + \frac{1}{2}, z - \frac{1}{2}$].

however, one large difference between KSGS and the KSS and KSG structures, in that KSGS has split cation positions. The K and K' positions are separated by 1.273 (8) Å, each with an occupancy of about 0.50. Split cation positions have been reported earlier for the ASbOGeO₄ materials in the high-temperature paraelectric phase but with shorter distances between the split positions, e.g. 0.561 (5) Å for TlSbOGeO₄ at 293 K (Belokoneva & Mill, 1992a) and 0.703 (13) Å for RbSbOGeO₄ at 503 K (Belokoneva *et al.*, 1997).

The coordination sphere of O atoms around K and K' are irregular. K is coordinated by six O atoms, resulting in four short bonds [2.707 (8) < K–O < 2.866 (8) Å] and two longer interactions up to 3.112 (7) Å. K' has seven coordinating O atoms, four shorter bonds [2.659 (8) < K'–O < 2.734 (8) Å] and three longer interactions up to 3.146 (7) Å. Table 1 gives all bond lengths for K and K'. The four short K–O bonds at each split position (< 2.90 Å) are approximately in the (001) plane. A similar trend of irregular coordination around the potassium sites exists in KTP (Thomas *et al.*, 1990), but with eight coordinating O atoms for K1, interactions up to 3.057 (3) Å and nine coordinating O atoms for K2 within 3.117 (3) Å. Table 2 gives the unit-cell parameters for KSS, KSG and KSGS.

The high-temperature modifications (space group *Pnan*) of KSS and KSG were studied by Favard *et al.* (1994) at temperatures of $T_c = +30$ K. The distance between the split cation positions was 0.909 (13) Å in KSS and 0.843 (13) Å in KSG. It was noted that the deviation from centrosymmetry in the low-temperature phase (space group *Pna2*₁) was mainly due to the location of A⁺ ions and not from the framework. The changes in the framework during the phase transition are small compared with KTP, mainly due to the regularity of the SbO₆ compared with the TiO₆ octahedra, in which the Ti^{IV} atoms are off-centre. The phase transition is displacive for the framework and of order–disorder type for the cations (Favard *et al.*, 1994). The centrosymmetry of ASbO(Ge/Si)O₄ compounds arises from the partial but equal occupation of two non-equivalent cation sites, resulting in the paraelectric phase. At low temperature, the four partly occupied A⁺ sites reduce to two fully occupied sites, resulting in an ordered structure with *Pna2*₁ symmetry.

All of those previously studied Sb-containing materials are isomorphic with KTP, with a ferroelectric to paraelectric phase transition well above room temperature (from space group *Pna2*₁ to *Pnan*). An exception is TlSbOGeO₄ with a T_c of 272 K (Stefanovich *et al.*, 1993). The T_c of both KSS and KSG was determined as 600 K by Stefanovich *et al.* (1993). KSGS is the second material in the KTP family to have a T_c below room temperature. Preliminary investigations of KSGS at low temperatures (173 and 113 K) show that the space group is still *Pnan*, i.e. the value of T_c must be very low.

Experimental

The crystals were obtained in a platinum crucible by spontaneous crystallization in a PbO₂ flux containing equimolar amounts of K₂CO₃, Sb₂O₅, GeO₂ and SiO₂ carefully mixed together. The weight

Table 1
Selected bond lengths (Å).

K–K'	1.273 (8)	K'–O1	2.659 (8)
K–O1	2.707 (8)	K'–O2 ⁱ	2.679 (7)
K–O5 ⁱ	2.728 (7)	K'–O3 ⁱⁱ	2.700 (7)
K–O3 ⁱⁱⁱ	2.854 (7)	K'–O5 ⁱ	2.734 (8)
K–O4	2.866 (8)	K'–O4 ^{iv}	3.036 (8)
K–O2 ⁱ	3.024 (7)	K'–O1 ^{iv}	3.133 (8)
K–O3 ⁱⁱⁱ	3.112 (7)	K'–O5 ⁱⁱ	3.146 (7)

Symmetry codes: (i) $\frac{1}{2} - x, 1 + y, 1 - z$; (ii) $\frac{1}{2} + x, 1 - y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, y, 1 - z$.

Table 2
Unit-cell parameters for KSS, KSG and KSGS.

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
KSS	13.005 (1)	6.4748 (6)	10.614 (1)	893.7 (3)
KSG	13.224 (2)	6.597 (1)	10.759 (2)	938.6 (3)
KSGS	13.0970 (9)	6.5310 (5)	10.6873 (6)	914.15 (11)

ratio between PbO₂ and the crystallization material was 1:1. The mixture was heated slowly for 4 d to 1273 K in order to obtain a homogeneous melt and the temperature then decreased to 1023 K at a rate of 1.4 K h⁻¹. The brown flux was later dissolved in 5 M HCl. Most of the flux dissolved within 24 h. The small fine crystals in the resulting yellow powder had the typical KTP morphology (Bolt & Bennema, 1990). It may also be noted that mixing K₂CO₃, Sb₂O₅, GeO₂ and SiO₂ without any PbO₂ as a flux resulted in a powder (no melting occurred at 1273 K) containing small fine crystals of K₃Sb₅O₁₄, whose structure has been published by Hong (1974).

Crystal data

KsBO(Ge_{0.32}Si_{0.68})O₄
 $M_r = 283.06$
 Orthorhombic, *Pnan*
 $a = 13.0970$ (9) Å
 $b = 6.5310$ (5) Å
 $c = 10.6873$ (6) Å
 $V = 914.15$ (11) Å³
 $Z = 8$
 $D_x = 4.118$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 21 reflections
 $\theta = 35.1$ – 39.6°
 $\mu = 9.13$ mm⁻¹
 $T = 293$ K
 Prism, colourless
 0.06 × 0.05 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω – 2θ scans
 Absorption correction: analytical (Alcock, 1974)
 $T_{\min} = 0.784$, $T_{\max} = 0.804$
 6155 measured reflections
 2818 independent reflections
 1585 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.074$
 $\theta_{\text{max}} = 39.8^\circ$
 $h = 0 \rightarrow 23$
 $k = 0 \rightarrow 11$
 $l = -19 \rightarrow 19$
 3 standard reflections
 frequency: 240 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.168$
 $S = 1.00$
 2818 reflections
 89 parameters
 $w = 1/[\sigma^2(F^2) + 0.01(F^2)^2]$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 3.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -3.92$ e Å⁻³
 Extinction correction: Gaussian (Zachariasen, 1967)
 Extinction coefficient: 1.9 (9) × 10³

Wilson (1949) statistics clearly indicate a centrosymmetric structure. However, an attempt to refine the structure in space group *Pna2*₁ using the coordinates of KTP (Thomas *et al.*, 1990) as the starting set led to severe correlation problems. No indication of any twinning was found in the measured KSGS crystal. Independent

measurement of three different KSGS crystals from the same batch have each resulted in the same space group (*Pnan*). Careful examination of the reflection profiles of our CAD-4 diffractometer data shows nothing out of the ordinary and no extra peaks appear using an area detector.

The highest residual electron-density peak (based on the observed reflections) is located between the K and K' positions, while the lowest peak is 1.571 (6) Å from the K position. $\Delta\rho$ maps of the area around and between K and K' show a single larger peak positioned 0.655 (6) Å from K and 0.643 (6) Å from K'. The peak could be refined as a possible K' site to an occupancy factor of 0.07 using restraints. Because of the restraints we have chosen to neglect K' and report the structure with two split K positions as our final structural model.

An isotropic extinction parameter (Zachariassen, 1967) was refined using Larson's implementation (Larson, 1970). About 14% of the reflections were affected, with a maximum correction of $y = 0.90$ for the 022 reflection (the observed structure factor is $F_{\text{obs}} = yF_{\text{kin}}$, where F_{kin} is the kinematic value of the structure factor).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *LATCON* in *Xtal3.7* (Hall *et al.*, 2000); data reduction: *DIFDAT*, *SORTRF*, *ADDREF* and *ABSORB* in *Xtal3.7*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRILSQ* in *Xtal3.7*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *BONDLA*, *ATABLE* and *CIFIO* in *Xtal3.7*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1312). Services for accessing these data are described at the back of the journal.

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