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The open-framework structure of KSbGe_3O_9 flux-grown crystals investigated by X-ray diffraction, vibrational spectroscopy, and DFT calculations.

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Abstract

We report on the preparation and the X-ray crystal structure of colorless KSbGe_3O_9 , its vibrational properties (Raman and infrared studies) and density functional theory (DFT) calculations. KSbGe_3O_9 , grown by the high-temperature flux method from $\text{K}_2\text{Mo}_4\text{O}_{13}$ flux, is thermally stable at least up to 1200°C and is isostructural to the benitoite $\text{BaTiSi}_3\text{O}_9$ (space group $P\bar{6}c2$ (n°. 188)). The hexagonal unit cell contains two formula units and the structure was refined to $R1 = 0.0324$ from single-crystal X-ray diffraction data. KSbGe_3O_9 is characterized with only one crystallographically independent Ge atom involved in three-member units $[\text{Ge}_3\text{O}_9]^{6-}$ of regular germanate tetrahedra. The K^+ ions are located in channels and, like Sb^{V} , are octahedrally surrounded by oxygen atoms. The KSbGe_3O_9 local structure and the planarity of Ge_3O_3 rings are also studied by a room-temperature vibrational investigation using non-polarized infrared and Raman spectroscopy. Both the infrared and Raman phonon modes have been assigned from the excellent agreement observed between our experimental data and the corresponding DFT ones. In particular, two $\text{E}'(\text{TO})$ modes (both IR and Raman active) characterize the planarity of the Ge_3O_3 ring in the ab plane.

KEYWORDS:

A.oxide materials, C.crystal structure, C.phonons, D. computer simulation, D. optical spectroscopy, D.X-ray diffraction

1. INTRODUCTION

Non-centrosymmetric germanate crystals with large nonlinear optical (NLO) properties are potential materials in the area of photonics and optical devices as they present electro-optical effects and second-order harmonic generation capabilities which able them to switch an optical signal and to generate a light with a frequency twice as the fundamental laser light [1-3]. Non-centrosymmetric germanate may also present interesting piezoelectric properties which are appropriate for volume- or surface-acoustic wave devices [4, 5]. In this context, the searching and the development of transparent and colorless germanate single-crystals with a non-centrosymmetric structure and enhanced properties are important. For industrial applications in harsh environment (with $T > 600^{\circ}\text{C}$), lead-free materials that can operate under extreme stress without degradation should have a stoichiometric chemical composition and structural stability in a large thermal domain as encountered for the non-polar uniaxial $\alpha\text{-GeO}_2$ single crystal [6, 7].

Based on the relationship between the tunnel structure and the physical properties of acentric germanate frameworks [8, 9], we have been interested in the AMGe_3O_9 family with a monovalent or bivalent ($A = \text{K, Rb, Ba, Ca, Tl}$) and a pentavalent or tetravalent ($M = \text{Sn, Nd, Ti, Ta}$) chemical element. These oxides which display the benitoite-type structure are characterized by a mixed framework built with MO_6 octahedra and GeO_4 tetrahedra, the latter forming a 3-member ring $[\text{Ge}_3\text{O}_9]^{6-}$ with C_{3h} symmetry [10-15]. The GeO_4 units are known as microscopic NLO-active motifs and, when associated with a strongly electropositive alkaline element, the NLO efficiency of such oxide could be improved

[16]. Furthermore, these double germanate with an open-framework structure and well-defined channels may be suitable for ion-exchange and gas adsorption applications.

This paper reports on the spontaneous crystallization of the compound KSbGe_3O_9 using the high-temperature flux method and on its single crystal structure determination associated with a vibrational characterization. The experimental study is completed by a group theory analysis and density functional theory (DFT) calculations to investigate the KSbGe_3O_9 infrared (IR) and Raman spectra.

2. EXPERIMENTAL SECTION

Crystals were obtained using the flux method described elsewhere [17]. For the present study, $\text{K}_2\text{Mo}_4\text{O}_{13}$ was chosen as flux and synthesized via a solid-state reaction at 500°C during two weeks, from alkali carbonate K_2CO_3 and molybdenum oxide MoO_3 powders. The compound was characterized through classical methods and more precision on the conditions for EDX, spectroscopy or X-ray diffraction experiments can be found in our previous paper [17].

Calculations on KSbGe_3O_9 were performed within the density functional theory (DFT) framework as implemented in the ABINIT package [18]. The all-electron potentials are replaced by norm-conserving pseudopotentials generated according to the local density approximation [19]. K ($4s^1$), Sb ($5s^2, 5p^3$), Ge ($4s^2, 4p^2$) and O ($2s^2, 2p^4$)-electrons are considered as valence states. The electronic wave functions are expanded in plane-waves up to a kinetic energy cutoff of 65 Ha and the integrals over the Brillouin zone were approximated by sums over an $8 \times 8 \times 6$ mesh of special k-points according to the Monkhorst-Pack scheme [20]. The lattice parameters and the atomic positions were fully relaxed using a Broyden-Fletcher-Goldfarb-Shanno algorithm until the maximum stresses and residual forces were less than 2×10^{-4} GPa and 6×10^{-6} Ha/Bohr, respectively. Born effective charges, dielectric tensors, and dynamical matrix (yielding the phonon frequencies and eigenvectors) were obtained within a variational approach of the density functional perturbation theory, whereas the Raman susceptibilities were calculated from a nonlinear response formalism taking advantage of the $2n+1$ theorem [21].

3. RESULTS AND DISCUSSION

3.1 Flux-growth result

Visually transparent and colorless as-grown crystals of almost millimeter size were obtained via spontaneous nucleation from the high-temperature flux method. Their chemical analysis shows the presence of only Ge, K and Sb in atomic ratios K/Sb of 1 and Ge/Sb of 3 which gives the nominal composition KSbGe_3O_9 . DSC measurement from room temperature to 1200°C with a $10^\circ/\text{min}$ heating rate did not point out any endo- or exo-thermal event. This means that the structure of KSbGe_3O_9 is thermally stable at least up to 1200°C , and that its melting temperature is over 1200°C .

Figure 1 shows the X-ray diffraction pattern θ - 2θ scan registered at room temperature for KSbGe_3O_9 . The reflections can be indexed within the hexagonal $P\bar{6}c2$ space group (188) according to the JCPDS card number 00-038-1334 [22]. A small reflection attributed to the flux $\text{K}_2\text{Mo}_4\text{O}_{13}$ is present on the X-ray diffraction pattern (indicated by an arrow).

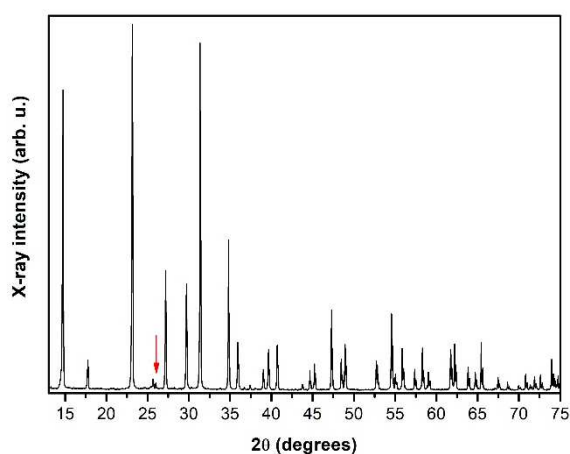


Figure 1: Powder X-ray diffraction pattern of KSbGe_3O_9 sample.

3.2. X-ray crystal structure.

The as-grown transparent platelets are not single-crystals as they look bright in any orientation under polarized light. Some attempts were made to carefully cut them into smaller single-crystals, but it rapidly became obvious, from their X-ray diffraction images, that such pieces were systematically twinned. However, two specimens were selected using a stereomicroscope equipped with a polarizing filter and the intensities diffracted by these crystals were collected. Because twinning occurs by very weak offset in the ab plane, a multi-crystal treatment of the data has been impossible (reflections are too close to be separated).

The structure was solved and further refined by the full-matrix least-squares method using the SHELXTL software package [23, 24]. The positional and anisotropic displacement parameters have been refined for all atoms using all the measured reflections in refinements on F^2 . The total filling of the atomic sites has been checked by free refinement of the occupational factors which did not deviate from unity within the standard deviation limits.

For both crystals, the recorded reflections have been indexed in a primitive hexagonal lattice ($a = b \approx 7$, $c \approx 10$ Å) and the statistical tests on intensities indicated a non-centrosymmetric space group. But, because the structure of KSbGe_3O_9 was previously reported, from X-ray powder diffraction studies, with the larger hexagonal cell $a = b = 13$ Å and $c = 10$ Å in the $P\bar{6}c2$ space group [22], we also tried to index our data in a $2 \times 2 \times 1$ supercell, which gives rise to additional reflections ($h = 2n+1$) of extremely low intensity and high $\sigma(I)$ values. No solution was found in this supercell and the refinement of a model built from twice the sub-cell structure did not converge either properly, giving arguments to reject a parameter doubling.

Furthermore, structure solutions have been found in the basic cell of parameters $a=b \approx 7$, $c \approx 10$ Å, and those obtained in the most probable space groups differ only by the z -coordinates of Ge and O atoms. Constrained by the symmetry in $P\bar{6}c2$ ($z = 0$ or 0.25) or free to vary in $P3c1$, they lead to Ge_3O_3

rings either flat or wavy. Refinement of the structural model in the lowermost symmetry $P3c1$ (which allows the greatest freedom degree) conducted for both crystal data sets shows that the deviation, in regard to the plane, remains lower than 0.007\AA within the Ge_3O_3 rings. In these conditions, the structure is given in the highest hexagonal symmetry $P\bar{6}c2$ usually reported for the AMGe_3O_9 compounds [10-15]. An essential characteristic in the structure of KSbGe_3O_9 lies in the flatness of the Ge_3O_3 rings, a situation differing from $\text{RbSbGe}_3\text{O}_9$ which a structural study has just been published [17].

The main crystal data and refinement parameters are given in Table 1 while the atomic positions and the equivalent displacement parameters are listed in Table 2. The full CIF files (CCDC numbers 1990049-50) can be obtained free of charge from the Cambridge Crystallographic Data Center [25].

Table 1. Crystal structure and refinement parameters for the two studied crystals of KSbGe_3O_9 .

Space group	$P\bar{6}c2$ (188)	
Temperature (K)	298 (2)	
Diffractometer, radiation	Bruker D8 Venture, $K\alpha$ Mo	
Wavelength (\AA)	0.7107	
Lattice (\AA)	$a = 6.9436(1), c = 9.9934(2)$	$a = 6.9527(1), c = 10.0117(2)$
Volume (\AA^3)	419.13(2)	418.27(2)
Z	2	
Density (g/cm^3)	4.14	4.15
μ (mm^{-1})	14.4	
Absorption correction	multi-scan method (SADABS)	
Crystal (mm)	$0.086 \times 0.085 \times 0.042$	$0.10 \times 0.08 \times 0.03$
θ range ($^\circ$)	3.39 - 62.22	3.38 - 72.37
Index ranges	$-16 \leq h \leq 17, -17 \leq k \leq 17$ $-24 \leq l \leq 24$	$-17 \leq h \leq 18, -18 \leq k \leq 18$ $-26 \leq l \leq 26$
Collected reflections	40471	69478
Independent reflections	2313 [$R_{\text{int}} = 0.0568$]	2886 [$R_{\text{int}} = 0.0522$]
Goodness-of-fit on F^2	1.271	1.132
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0324, wR2 = 0.0578$	$R1 = 0.0233, wR2 = 0.0550$
R indices (all data)	$R1 = 0.0377, wR2 = 0.0592$	$R1 = 0.0245, wR2 = 0.0552$
Absolute structure parameter	0.043(16)	0.083(11)
Extinction coefficient	0.044(3)	0.040(3)
$\Delta\rho$ Fourier residuals (e.\AA^{-3})	3.49 / -1.72	2.29 / -1.96

Table 2. Atomic coordinates and equivalent displacement parameters ($\text{\AA}^2 \times 10^5$) for KSbGe_3O_9 (*italics* for crystal 2). U_{eq} is defined as $\frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Sb	0	0	0	613(3)
	<i>0</i>	<i>0</i>	<i>0</i>	<i>686(4)</i>
Ge	0.12135(3)	0.37281(3)	0.25	706(1)
	<i>0.12133(4)</i>	<i>0.37280(4)</i>	<i>0.25</i>	<i>784(4)</i>
K	0.66667	0.33333	0	3850(5)
	<i>0.66667</i>	<i>0.33333</i>	<i>0</i>	<i>3840(5)</i>
O1	0.0663(3)	0.5931(3)	0.25	1560(3)
	<i>0.0668(3)</i>	<i>0.5935(3)</i>	<i>0.25</i>	<i>1620(4)</i>
O2	0.2411(3)	0.0136(4)	0.1071(2)	2690(3)
	<i>0.2409(4)</i>	<i>0.1140(4)</i>	<i>0.1073(2)</i>	<i>2730(4)</i>

The compound KSbGe_3O_9 is isostructural with the benitoite $\text{BaTiSi}_3\text{O}_9$ which is known as a structural type [10, 11, 15]. It is characterized by SbO_6 octahedra and GeO_4 tetrahedra which arrangement provides $[\text{Ge}_3\text{O}_9]^{6-}$ units formed with Ge_3O_3 planar rings (see in Figure 2 the structure representations drawn using Diamond software [26]). The relevant interatomic distances and angles in this three-dimensional open-framework structure are given in Table 3. The non-distorted SbO_6 octahedra share its vertices with six GeO_4 tetrahedral units, the latter display regular tetrahedral geometry and share vertices with two GeO_4 tetrahedra and two SbO_6 octahedra. The SbO_6 octahedra are separated by Ge_3O_3 rings. The voids between the polyhedra, filled with K atoms, form channels along the c -axis. The atomic arrangement in KSbGe_3O_9 can also be viewed as composed of two planes of Ge_3O_3 rings perpendicular to the c axis (at $z = 0.25$ and $z = 0.75$) followed, above and below, by an oxygen layer and then a layer containing both Sb and K atoms.

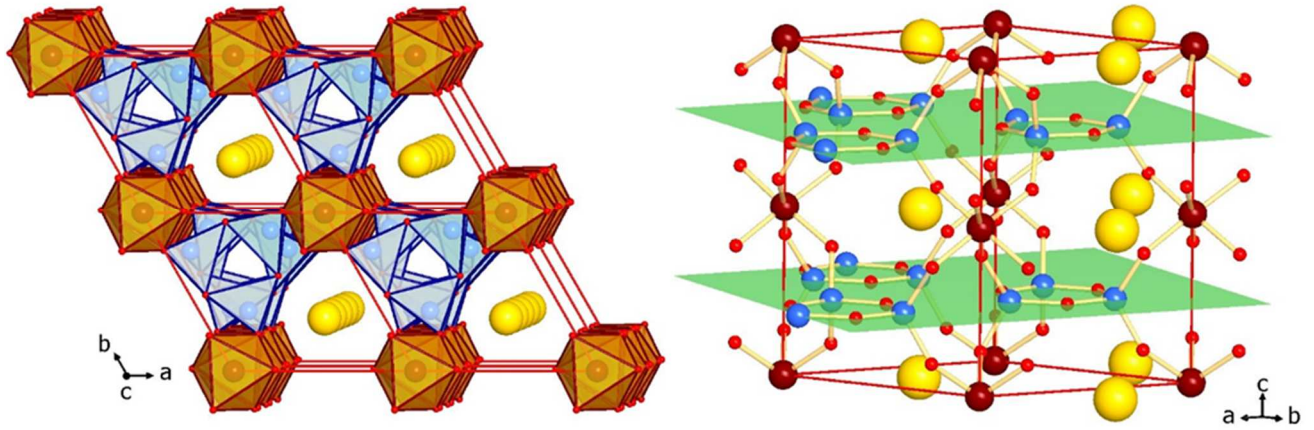


Figure 2. Structural representations of KSbGe_3O_9 emphasizing: *left*-the GeO_4 (blue) and SbO_6 (brown) regular polyhedral packing forming channels containing the K^+ ions (yellow). *right*-the Ge_3O_3 planar rings in the ab plane.

Table 3. Selected bond lengths (\AA) and angles ($^\circ$) for KSbGe_3O_9

Sb-O2	$1.9495(2) \times 6$	O1-Ge	1.741(2)
K-O2	$2.875(2) \times 6$	O1-Ge	1.754(2)
		Ge-O2	$1.7311(2) \times 2$
		Ge-O1	1.741(2)
O2-Sb-O2	$83.91(1) \times 3$	Ge-O1-Ge	129.56(1)
O2-Sb-O2	$175.04(2) \times 3$	O2-Ge-O2	111.10(2)
O2-Sb-O2	$92.61(1) \times 6$	O2-Ge-O1	$114.28(9) \times 2$
O2-Sb-O2	$91.08(2) \times 3$	O2-Ge-O1	$102.74(8) \times 2$
		O1-Ge-O1	110.44(1)

3.3. Vibrational properties

The zone-center optical phonons of KSbGe_3O_9 can be classified according to the irreducible representations of the D_{3h} -point group as $7A'_1 \oplus 9A'_2 \oplus 6A''_2 \oplus 5A''_1 \oplus 15E' \oplus 12E''$. The E' -representation is both infrared and Raman active while the E'' -representation is only Raman active. The A''_2 (resp. A'_1) representation is infrared (resp. Raman) active. The A'_2 and A''_1 modes are silent. Due to the lack of an inversion center in the crystal structure, the macroscopic electric field splits the

polar modes (infrared modes) into transverse optical (TO) and longitudinal optical (LO) modes close to the center of the Brillouin zone.

The room-temperature infrared and Raman spectra of the non-centrosymmetric KSbGe_3O_9 material are presented in Figure 3.

In the $450 - 1100 \text{ cm}^{-1}$ frequency range, the hexagonal KSbGe_3O_9 material presents 5 main experimental IR bands in Figure 3a centered at 498, 570, 798, 841, and 920 cm^{-1} and 4 shoulders at 851, 878, 943 and 1018 cm^{-1} in agreement with the literature reports [27]. These 5 main experimental bands are supported by our DFT calculation as evidenced in Figure 3a. The experimental shoulders could be combination bands or defects as their counterparts are not predicted by our calculations.

A same observation can be made regarding the high-resolution Raman data, Figure 3b. Furthermore, the frequency positions of the main experimental Raman bands are also in very good agreement with the literature [27].

This very good agreement between the experimental vibrational spectra and the theoretical ones support our structure refinement for the non-centrosymmetric KSbGe_3O_9 material and points out the high quality of the as-grown crystals.

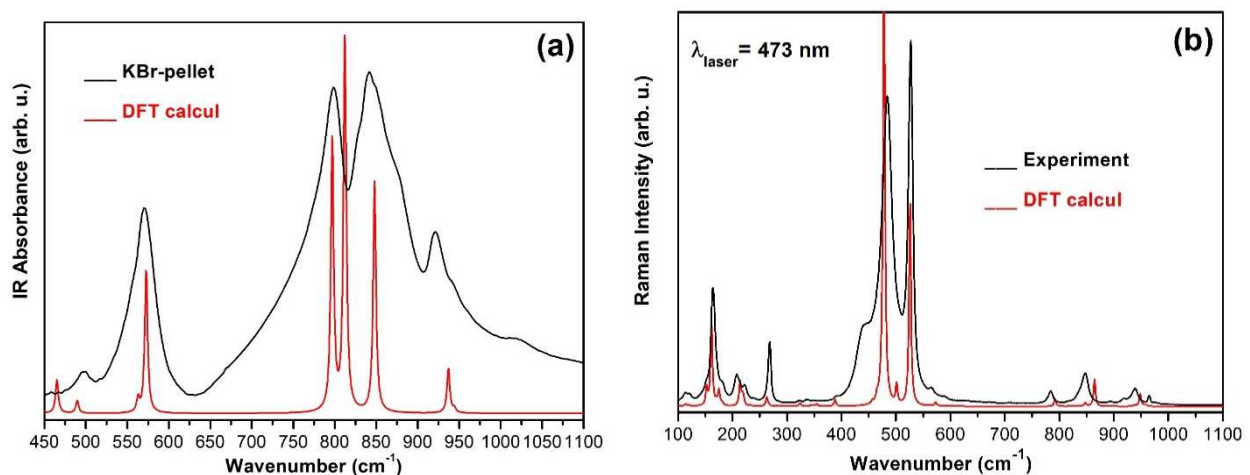


Figure 3: Room-temperature experimental and 0 K-calculated (a) infrared and (b) Raman spectra of the KSbGe_3O_9 polycrystalline sample.

The silent representations calculated at 0 K for the KSbGe_3O_9 crystal (D_{3h} point group, cell constants $a = 6.9436(1) \text{ \AA}$, $c = 9.9934(2) \text{ \AA}$) are given in Table 4. Both the experimental and DFT frequency positions along with their symmetry are presented in Table 5. All the calculated zone-center optical frequencies have been assigned to observed bands in the Raman and IR spectra.

Table 4. A'_2 and A''_1 silent mode position for KSbGe_3O_9 in the D_{3h} point group.

Symmetry	Calculated wavenumbers (cm^{-1})
A'_2	74
A'_2	145
A''_1	156
A'_2	213
A''_1	240
A'_2	251
A''_1	350
A'_2	408
A'_2	473
A''_1	495
A'_2	527
A'_2	858
A'_2	915
A''_1	965

Table 5. Position of the experimental and calculated optical modes (infrared and Raman) with their Mulliken symmetry for KSbGe_3O_9 in the D_{3h} point group.

Calculated wavenumbers (cm^{-1})	Symmetry	Observed wavenumbers (cm^{-1})	
		Raman Expt.	Infrared Expt.
65	E'' (TO)		
68	A''_2 (TO)		
92	E'' (TO)		
111	E' (TO)	108	
114	E' (TO)	113	
115	E'' (TO)	118	
133	A''_2 (TO)		
153	E'' (TO)	158	
161	A'_1 (TO)	164	
170	E' (TO)	168	
175	E'' (TO)	174	
181	E'' (TO)	183	
213	E' (TO)	207	
220	E' (LO)	222	
233	E' (TO)	233	
259	A''_2 (TO)		
263	A'_1 (TO)	268	
267	E' (TO)	278	
285	E'' (TO)	300	
324	E' (TO)	323	
326	A''_2 (TO)		
345	E'' (TO)		
388	A'_1 (TO)	392	
427	E' (TO)	439	
457	E'' (TO)		
465	E' (TO)	464	498
478	A'_1 (TO)	485	
490	A''_2 (TO)		520
501	E'' (TO)	495	
526	A'_1 (TO)	527	

563	E' (TO)	562	550
572	E' (TO)	566	570
792	E'' (TO)	787	
797	E' (TO)	795	798
812	A'' ₂ (TO)		798
848	E' (TO)	838	841
863	A' ₁ (TO)	849	
864	E'' (TO)	849	
901	E' (LO)		878
937	E' (TO)	913	920
944	E' (TO)	919	943
948	A' ₁ (TO)	940	

3.4. Vibrational frequency assignments.

The structural origin of the vibrational components was interpreted using the results of the density functional theory calculations. Only the most intense IR and Raman vibrational bands were investigated. The theoretical vibrations in the range 450 - 1000 cm⁻¹ are mainly due to the oxygen motions and, for some of them, to the vibrations of the Ge atoms in a small content. Within the Ge₃O₉ cyclic unit, there are two types of oxygen atoms (see Table 2): the bridging O (O1) bonded to two Ge atoms (Ge-O1-Ge forming the Ge₃O₃ planar ring) and the non-bridging O (O2) bonded to one Ge atom (Ge-O-K/Sb).

The first intense Raman line is found at 478 cm⁻¹ by DFT calculation against 485 cm⁻¹ experimentally, Figure 3b and Table 5. This mode is assigned as A'₁ and it is only Raman active. This vibration is mainly caused by the symmetric stretching of O2-K “pairs”, which leads to the bending of the O2-Sb-O2 angle. In this mode, the K atoms are fixed and the Ge atoms too, Figure 4.

The 563 cm⁻¹ calculated frequency which is both IR and Raman active (E'(TO), Table 5) is due to Ge-O1-Ge intra-cycle bending motions in the Ge₃O₃ ring and to the O2-K-O2 wagging motion of the KO₆ octahedra, Figure 4. Both O and Ge atoms participate in this vibration mode while K and Sb atoms are

fixed. This band characterizing the annular units appear in the IR/Raman spectra at a frequency of 500-570 cm^{-1} in three-membered rings germanates and is called the “ring band” [27, 28, 29].

Concerning the 797 cm^{-1} $E'(TO)$ vibration frequency, it concerns the symmetric stretching in the ab plane of the Ge-O1 bonds and the twisting motion of O2-K-O2 bridges, Figure 4. Both K and Sb atoms are fixed.

The O1-Ge-O1 wagging of the Ge_3O_3 central cycle along the c axis and the O2-K-O2 wagging of the KO_6 octahedra occur in the $A''_2(TO)$ band at 812 cm^{-1} which is only IR active, Table 5 and Figure 4. For this mode, the dominant motions are due to both the Ge atoms forming the Ge_3O_3 rings and the O2 atoms. The displacement of the Sb atoms is small while that of K is null.

The 848 cm^{-1} $E'(TO)$ theoretical vibration, Table 5, is due to intra-cycle symmetric stretching motions of the O1 atoms concomitant to the shear in the ab plane of the ring Ge_3O_3 and to the O2-K-O2 twisting, Figure 4. The Sb and K atoms do not move.

The 937 cm^{-1} calculated frequency which is both IR and Raman active ($E'(TO)$, Table 5) is attributed to the Ge-O1 symmetric stretching in the Ge_3O_3 ring and to the vibration associated with the rotation of whole KO_6 octahedra (libration mode), Figure 4. The Sb and K atoms do not move.

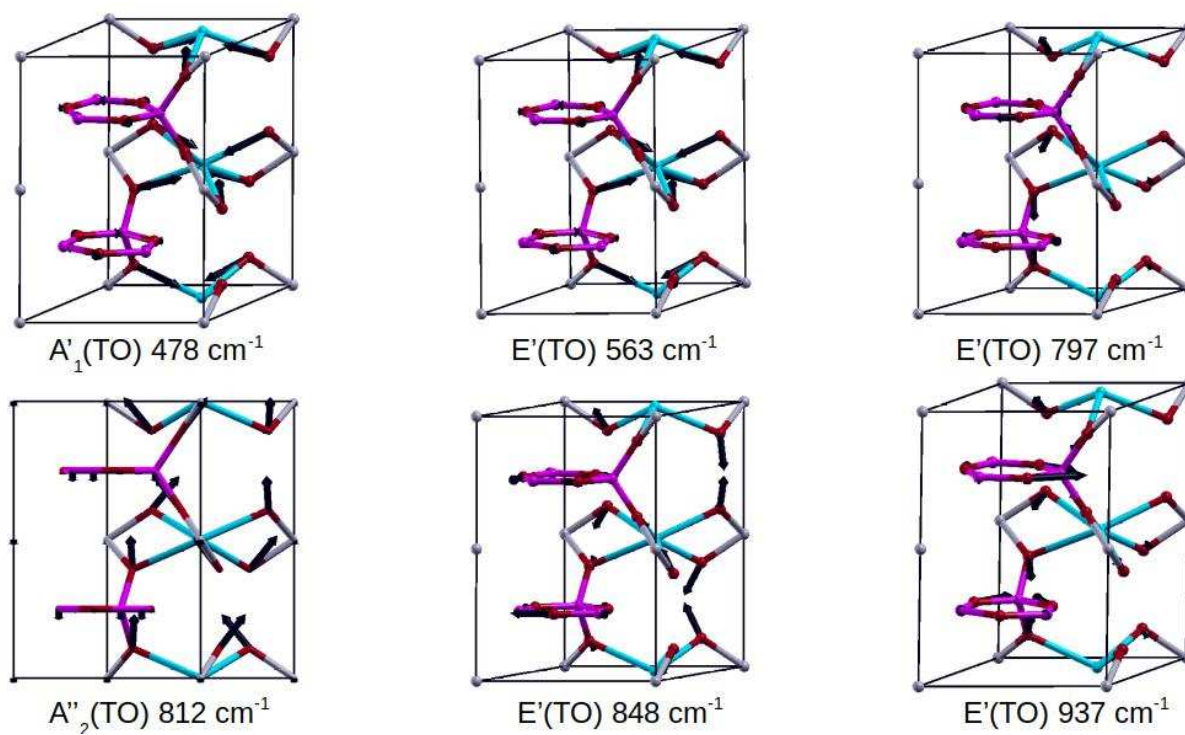


Figure 4. Structural origin of some vibrations in the non-centrosymmetric KSbGe_3O_9 compound

4. CONCLUSION

The structural and vibrational properties of the hexagonal KSbGe_3O_9 crystal have been studied for the first time by using experimental data combined with first-principles based calculations. The main conclusions are the following:

- (1) This non-centrosymmetric phase ($P\bar{6}c2$) is visually colorless and transparent, and it is structurally stable from room-temperature up to, at least, 1200°C .
- (2) The unit cell parameters refined from X-ray single-crystal data are different from those given in JCPDS card number 00-038-1334.
- (3) KSbGe_3O_9 , with planar Ge_3O_3 rings, belongs to the benitoite-type structure.
- (4) The observed IR and Raman band positions are in good agreement with the calculated ones.
- (5) The structural origin of the most intense vibrations is mainly due to the oxygen motions.
- (6) Two $E'(TO)$ vibrations (IR and Raman active) characterize the planarity of the Ge_3O_3 ring in the ab plane.

This anisotropic oxide with a stoichiometric chemical composition and a large thermal structure stability may have potential piezo-electrical and non-linear optical properties exploitable in a range of very high temperatures up to, at least, 1200°C . Lead-free materials that can operate under extreme stress without degradation are sought for industrial needs. Furthermore, this germanate with its open-framework structure and well-defined channels may be suitable for ion-exchange and gas adsorption applications.

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