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四元硫属化合物 La_2CuBiS_5 的合成、结构及光学性能研究

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摘要:通过高温固相反应合成了首例镧系-过渡金属-铋-四元硫属化合物:La_2CuBiS_5。该化合物属于正交晶系,空间群:*Pnma*。其结构含有沿 *b* 方向的一维$[BiCuS_5^{6-}]_\infty$带,带与带之间被 La^{3+}离子隔开。一维$[BiCuS_5^{6-}]_\infty$带由$[CuS_4]$四面体双链与 BiS_6 八面体单链通过公顶点连接而成。漫反射光谱研究表明该化合物为半导体,能隙 1.30 eV。理论研究表明其为直接半导体,光学能隙跃迁来源于 S3*p* 到 La5*d* 轨道的电子迁移。

关键词:铋硫属化合物;晶体结构;电子结构;光学性质

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Syntheses, Crystal and Electronic Structures, and Optical Properties of Quaternary Sulfide: La_2CuBiS_5

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Abstract: The first quaternary sulfide La_2CuBiS_5 in the Ln/Bi/Q/TM (TM=transition metal, Ln=lanthanide metal, Q=S, Se, Te) system has been synthesized from the stoichiometric mixture of elements by solid-state reactions at 1 100 ℃. The compound crystallizes in the orthorhombic space group *Pnma*. The structure contains one-dimensional (1D) $[BiCuS_5^{6-}]_\infty$ ribbons running down the [010] direction that are separated by La^{3+} ion. The one-dimensional $[BiCuS_5^{6-}]_\infty$ ribbons constitutes $[CuS_4]_2$-dimer-double chain along [010] direction that is interconnected with two BiS_6-octahedron-single-chain via sharing vertex. The UV/Vis reflectance spectroscopy study shows that La_2CuBiS_5 is a semiconductor with an optical gap of 1.30 eV and DFT study indicates an direct band gap with an electronic transfer excitation of S3*p* to La5*d* orbital electrons.

Key words: bismuth chalcogenide; crystal structure; electronic structure; optical properties

Bismuth chalcogenide compounds have a great deal of structural diversity in part because of the flexibility of the coordination environment of Bi and the so-called inert lone pair effect[1]. In addition to the common octahedral coordination of Bi, examples of trigonal-pyramidal[2], square-pyramidal[3], and capped

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trigonal-prismatic[4] coordination have been observed. The bismuth chalcogenide building blocks can form various modules that are subsequently assembled into more complex crystalline arrangements. Examples of such assemblies can be seen in various homologous series[5], as well as in the large class of minerals known as sulfosalts[6]. However, lanthanide-bismuth-chalcogenides are less studied so far, several ternary compounds are known as $La_4Bi_2S_9$[7], $Ce_{1.25}Bi_{3.78}S_8$[8], $EuBiSe_3$[9], Ln_4Bi_2Te (Ln=Eu, Yb, Sm)[10], and only a few quaternary $BaLaBi_2S_5$[11], $ALn_{1\pm x}Bi_{4\pm x}S_8$ (A=K, Rb; Ln=La, Ce, Pr, Nd)[4], $Cs_2La_xBi_{10-x}S_{16}$, and $M_2La_xBi_{8-x}S_{14}$ (M=Sr, Pb)[12] are reported. The known quaternary A/Ln/Bi/S (A =alkali or alkaline-earth metal, Ln = lanthanide) chalcogenides exhibit strong ionic bonding interactions between the cationic A and the anionic Bi/S framework. Given the same ionic charge of coinage metals (i.e. Cu, Ag) with those of the alkali ions, we chose Cu as a fourth component in quaternary Ln/Bi/Q/TM (TM =transition metal, Ln = lanthanide metal, Q=S, Se, Te) system, which has not been investigated before. The introducing of the less electropositive Cu metals, significant changes in the crystal and electronic structure are expected due to the stronger Cu-Q interactions compared with the electrostatic A-Q interactions (Q=chalcogen element). In this paper, we report the synthesis, crystal and electronic structure, and optical properties of the first quaternary La_2CuBiS_5 in the quaternary Ln/Bi/Q/TM (TM=transition metal, Ln=lanthanide metal, Q=S, Se, Te) system.

1 Experimental

1.1 Synthesis

The elements were used as acquired and stored in a nitrogen-filled glovebox (moisture and oxygen level is less than 0.1 $\mu L \cdot L^{-1}$), and all manipulations were performed inside the glovebox. The La (99.99%) was purchased from Huhhot Jinrui Rare Earth Co. Ltd.. The Cu (99.98%), S (99.999%) and Se (99.999%) were purchased from Alfa Aesar China (Tianjin) Co. Ltd. The Bi (99.99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All reactants in evacuated fused-silicon tubes were placed in resistance furnaces with controlled temperature.

The stoichiometric elements were weighed accordingly and loaded into a silicon tube, which was evacuated, sealed and then heated to 1 100 ℃ in 36 h and kept at that temperature for 10 h. After that they were cooled (30 ℃·h^{-1}) to 600 ℃ and annealed at this temperature for 393 h, then quenched in cold water. Good quality single crystals were obtained. The single crystal diffraction data of a prismatic crystal in black color yielded a refined formula La_2CuBiS_5. The elemental analyses have been examined with the aid of a fieldemission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDX, Oxford INCA) which confirmed the presence of La, Cu, Bi, and S in a molar ratio about 2∶1∶1∶5. No other element, such as Si, O from the reaction container, was found. The homogeneity of the sample was confirmed by XRD patterns (Fig.1). No corrosion was observed. This compound is stable in air.

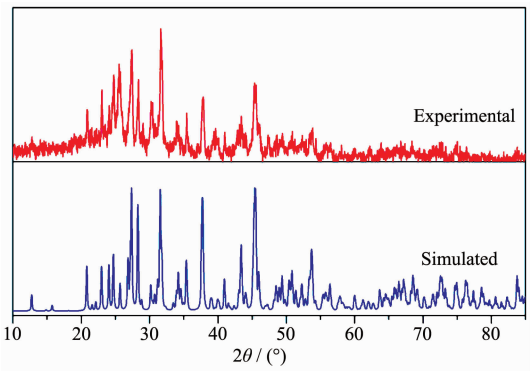


Fig.1 Experimental and simulated X-ray powder diffraction patterns of La_2CuBiS_5

1.2 Crystal structure determinations

Data collections were performed on a Rigaku Mercury CCD equipped with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K. A total of 6 129 reflections and 1 071 unique one were collected in the θ range from 2.08° to 27.48° with R_{int}=0.050 7, of which 995 reflections with $I>2\sigma(I)$ were considered as observes and used in the succeeding structural calculations. The data were corrected for Lorentz and polarization factors. Absorption corrections were

performed by the multiscan method[13]. The structure was solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 by SHELX-97[14]. All atoms were refined with anisotropic thermal parameters except Cu(1)′. Crystallographic data and structural refinement details are summarized in Table 1 and some important bond distances and angles are listed in Table 2.

1.3 X-ray powder diffraction

The XRD pattern was collected on a Rigaku DMAX 2500 diffractometer. The measured XRD pattern is in good agreement with the calculated one (Fig.1).

1.4 UV/Vis diffuse reflectance spectroscopy

The optical diffuse reflectance spectrum of powdery sample was measured at room temperature using a Perkin-Elmer Lambda 900 UV-vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as a reference. The absorption spectrum was calculated from the reflection spectrum via the Kubel-Munk function: $\alpha/S=(1-R)^2/(2R)$, in which α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance[15].

1.5 Electronic structure calculations

Electronic structure calculation was performed

Table 1　Crystallographic data and refinement details for La_2CuBiS_5

Formula	La_2CuBiS_5	V / nm^3	0.815 0(5)
Formula weight	710.65	F(000)	1 224
Crystal system	orthorhombic	D_c / (g·cm^{-3})	5.792
Crystal color	black	μ / mm^{-1}	35.554
Z	4	$2\theta_{max}$ / (°)	54.96
Space group	*Pnma* (No. 62)	GOOF on F^2	1.123
a / nm	1.1929(4)	R_1, wR_2 ($I>2\sigma(I)$)[a]	0.028 2, 0.061 2
b / nm	0.400 15(14)	R_1, wR_2 (all data)[a]	0.032 0, 0.062 9
c / nm	1.707 3(6)	Largest difference peak and hole / (e·nm^{-3})	1 754 and −1 988

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$, $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table 2　Selected bond lengths (nm) and angles (°) for La_2CuBiS_5

Bi(1)-S(5)#1	0.269 63(19)	La(1)-S(2)#7	0.296 2(2)	La(2)-S(2)#5	0.300 60(19)
Bi(1)-S(5)#2	0.269 63(19)	La(1)-S(1)#7	0.297 9(2)	La(2)-S(2)#4	0.300 60(19)
Bi(1)-S(1)	0.276 3(2)	La(1)-S(1)#6	0.297 9(2)	La(2)-S(4)#11	0.301 9(3)
Bi(1)-S(2)#3	0.277 1(2)	La(1)-S(5)	0.321 6(3)	La(2)-S(5)	0.315 6(3)
Bi(1)-S(4)#2	0.293 11(19)	La(1)-S(5)#8	0.332 7(3)	Cu(1)-S(3)#14	0.228 5(3)
Bi(1)-S(4)#1	0.293 11(19)	La(2)-S(3)#5	0.296 54(18)	Cu(1)-S(1)#4	0.234 18(17)
La(1)-S(3)#4	0.295 02(18)	La(2)-S(3)#4	0.296 54(18)	Cu(1)-S(1)#5	0.234 18(17)
La(1)-S(3)#5	0.295 02(18)	La(2)-S(4)#1	0.297 4(2)	Cu(1)-S(1)#11	0.257 0(3)
La(1)-S(2)#6	0.296 2(2)	La(2)-S(4)#2	0.297 4(2)		
S(5)#1-Bi(1)-S(5)#2	95.81(9)	S(1)-Bi(1)-S(4)#2	95.84(6)	S(3)#14-Cu(1)-S(1)#5	118.95(7)
S(5)#1-Bi(1)-S(1)	88.72(7)	S(2)#3-Bi(1)-S(4)#2	84.16(6)	S(1)#4-Cu(1)-S(1)#5	117.38(13)
S(5)#2-Bi(1)-S(1)	88.72(7)	S(5)#1-Bi(1)-S(4)#1	88.89(6)	S(3)#14-Cu(1)-S(1)#11	88.23(10)
S(5)#1-Bi(1)-S(2)#3	91.28(7)	S(5)#2-Bi(1)-S(4)#1	173.54(6)	S(1)#4-Cu(1)-S(1)#11	101.77(9)
S(5)#2-Bi(1)-S(2)#3	91.28(7)	S(1)-Bi(1)-S(4)#1	95.84(6)	S(1)#5-Cu(1)-S(1)#11	101.77(9)
S(1)-Bi(1)-S(2)#3	180.00(7)	S(2)#3-Bi(1)-S(4)#1	84.16(6)	S(3)#14-Cu(1′)-S(1)#4	118.9(4)
S(5)#1-Bi(1)-S(4)#2	173.54(6)	S(4)#2-Bi(1)-S(4)#1	86.09(7)	S(3)#14-Cu(1′)-S(1)#5	118.9(4)
S(5)#2-Bi(1)-S(4)#2	88.89(6)	S(3)#14-Cu(1)-S(1)#4	118.95(7)	S(1)#4-Cu(1′)-S(1)#5	113.4(6)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1/2$, $-y+1$, $z+1/2$; #2: $-x+1/2$, $-y$, $z+1/2$; #3: $x+1/2$, y, $-z+3/2$; #4: $-x+1/2$, $-y+1$, $z-1/2$; #5: $-x+1/2$, $-y$, $z-1/2$; #6: $-x$, $-y$, $-z+1$; #7: $-x$, $-y+1$, $-z+1$; #8: $x-1/2$, y, $-z+1/2$; #9: x, $y+1$, z; #10: x, $y-1$, z; #11: $x+1/2$, y, $-z+1/2$; #12: $x-1/2$, y, $-z+3/2$; #13: x, y, $z+1$; #14: x, y, $z-1$.

using the self-consistent full-potential linearized plane wave method (LAPW)[16] within density functional theory (DFT)[17] and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA)[18] for the exchange correlation energy with the aid of the WIEN2k program. The electronic configurations for La, Bi, Cu and S are as follows: La, [Xe]$5p^1 6s^2$; Bi, [Xe]$5d^{10}6s^2 6p^3$; Cu, [Ar] $3d^{10}4s^1$; S, [Ne]$3s^2 3p^4$. The values of the atomic radii were taken to be 2.50 au for La, 2.50 au for Bi, 2.27 au for Cu, and 2.01 au for S. Convergence of the self-consistent iterations was performed for 48 k points inside the irreducible Brillouin zone to within 0.000 1 Ry with a cutoff −6.0 Ry between the valence and the core states.

2 Results and discussion

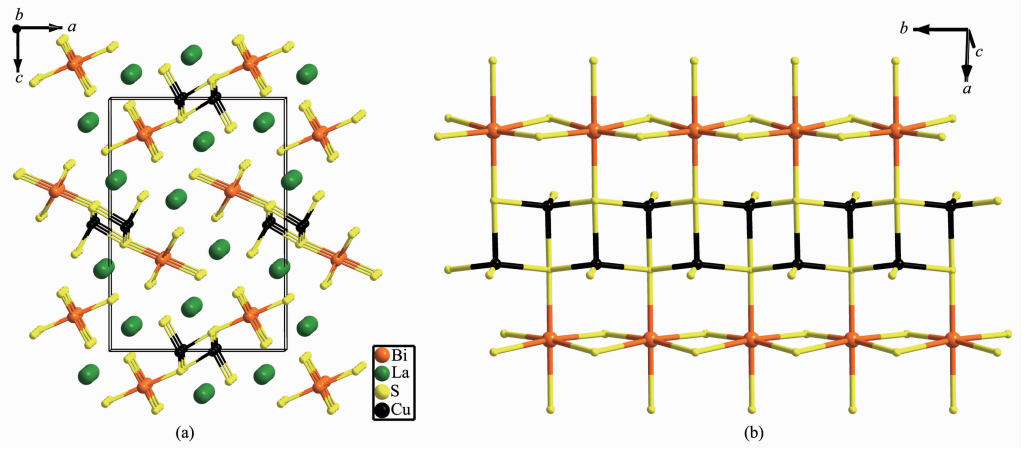
2.1 Crystal structure

La_2CuBiS_5 crystallize in the centrosymmetric orthorhombic space group *Pnma*. The structure can be described as being composed of one-dimensional (1D) $[BiCuS_5^{6-}]_\infty$ ribbons running down the [010] direction that are separated by La^{3+} ion, as shown in Fig.2a. The one-dimensional $[BiCuS_5^{6-}]_\infty$ ribbons constitute $[CuS_4]_2$ -dimer-double chain along [010] direction that is interconnected with two BiS_6-octahedron-single-chain via sharing vertex (Fig.2b). Within the $[BiS_6]$ octahedral chain, each unit shares opposite edges with two neighbors along the chain direction, while each $[CuS_4]$ tetrahedra shares corners along the b axis and shares edges with adjacent identical chains.

There is one crystallographically independent Bi atom which is 6-fold coordinated by S atoms in a distorted octahedra with four short Bi-S bonds of 0.269 63(19), 0.269 63(19), 0.276 3(2), 0.277 1(2) nm and two long Bi-S bonds of 0.293 11(19) nm (Fig.3), which is comparable to the coordinate environment of Bi(2) in the $BaLaBi_2S_5$[11], where the Bi(2) comprise three short bonds of 0.259 2(6), 0.263 3(6), and 0.273 9(7) nm and three long ones of 0.297 0(7), 0.309 3(6), and 0.311 6(7) nm.

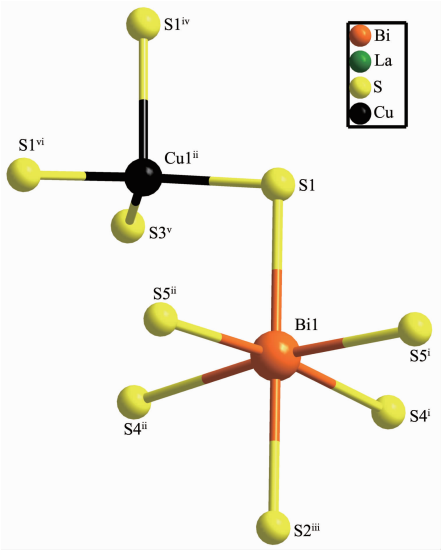
There exist two unique La atoms, both La1 and La2 exhibit eight La-S bonds between 0.295 02(18) and 0.332 7(3) nm, best described as a normal bicapped trigonal prismatic sphere, a coordination polyhedron often found in La chalcogenides. Moreover, all these La-S distances are very close to those found in the related lanthanide chalcogenides, for example, La-S bond between 0.291 1(5) and 0.321 2(6) nm in $BaLaBi_2S_5$[11], and 0.278 0(2) and 0.354 4(2) nm in $La_7Sb_9S_{24}$[19].

It includes one crystallographically unique Cu atoms, Cu(1) on the split position with Cu(1)′. The occupancy of Cu(1) and Cu(1)′ are 0.89 and 0.11. Cu(1) atom is stabilized in a distorted tetrahedral environment of S atoms (Fig.3). The four Cu (1)-S distances are 0.228 5(3), 0.234 18(17), 0.234 18(17) and 0.2570(3) nm, and S-Cu(1)-S angles are in the range of 88.23(10)° ~118.95(7)°. Similar coordination environments for Cu atoms have been found in other lanthanide copper chalcogenides, such as, Ln_2YbCuQ_5 (Ln=La, Ce, Pr,



La-S bonds are omitted for clarity

Fig.2 (a) View approximately along b axis of La_2CuBiS_5; (b) One-dimensional $[BiCuS_5^{6-}]_\infty$ ribbons along b axis in La_2CuBiS_5



Symmetry transformations used to generate equivalent atoms: [i] $-x+1/2, -y+1, z+1/2$; [ii] $-x+1/2, -y, z+1/2$; [iii] $x+1/2, -y+1/2, -z+3/2$; [iv] $-x, y-1/2, -z+1$; [v] $-x+1/2, -y, z-1/2$; [vi] $x, y-1, z$

Fig.3　Asymmetry unit and local coordination environments of Cu and Bi atom in La_2CuBiS_5

Nd, Sm; Q=S, Se)[20], and Ln_2CuInQ_5 (Ln=La, Ce, Pr, Nd, Sm; Q=S, Se)[21].

It is not surprising that La_2CuBiS_5 is isotypic with the recently reported Ln_2YbCuQ_5 (Ln=La, Ce, Pr, Nd, Sm; Q=S, Se)[20], and Ln_2CuInQ_5 (Ln=La, Ce, Pr, Nd, Sm; Q=S, Se)[21], considering the similar sizes of Bi, In and Yb. In Ln_2YbCuQ_5, two disordered Cu sites are nearly equivalent and the tetrahedra are less distorted[20]. However, in the structure of Ln_2CuInQ_5, the occupancy of Cu(1) and Cu(1)′ are 0.82 and 0.18[21], which is very close to the occupancy of Cu in La_2CuBiS_5.

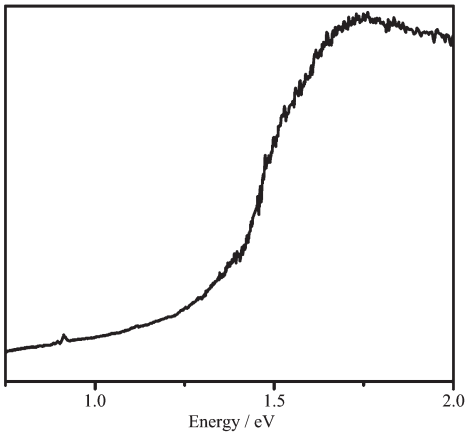


Fig.4　UV-Vis diffuse reflectance of La_2CuBiS_5

2.2　Optical properties

The optical band gap has been measured by the diffuse-reflectance spectra at room temperature. The band gap was estimated to be 1.30 eV for La_2CuBiS_5 as shown in Fig.4.

2.3　Electronic Structure

In order to understand the distribution of the orbitals near the Fermi level, the density of states of La_2CuBiS_5 were calculated and shown in Fig.5, in which the contribution of La4*f* orbitals are not shown. The valence band (VB) is dominated by S3*p* and Cu3*d* block, whereas the conduction band (CB) are primarily La5*d* orbitals. The electronic absorption responsible for the optical gap is likely an electronic transfer excitation from S3*p* orbitals to La5*d* orbitals. The band structure of La_2CuBiS_5 indicates that the VB maximum and CB minimum are located at the same k

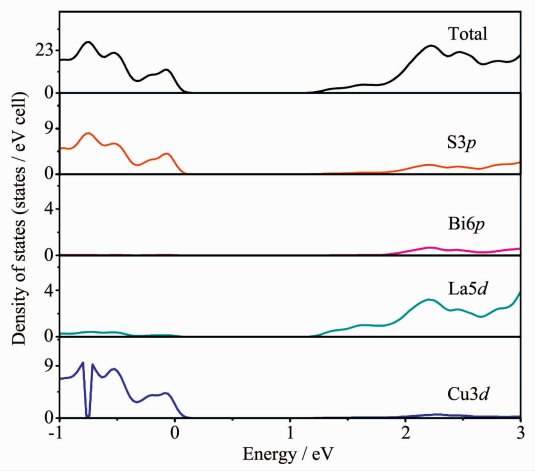


Fig.5　Total and partial densities of states of La_2CuBiS_5

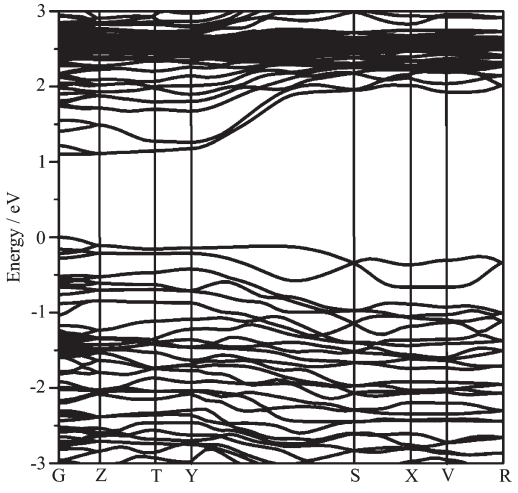


Fig.6　Band structure of La_2CuBiS_5

point (Fig.6) and its computational direct band gap is around 1.10 eV. This value is slightly lower than the experimental optical band of 1.30 eV, which may related to that the DFT method usually underestimates the band gap.

3 Conclusion

The first quaternary sulfide La_2CuBiS_5 in the Ln/Bi/Q/TM (TM=transition metal, Ln=lanthanide metal, Q =S, Se, Te) system has been synthesized and characterized. The structure comprises one-dimensional (1D) $[BiCuS_5^{6-}]_\infty$ ribbons running down the [010] direction that are separated by La^{3+} ion. The one-dimensional $[BiCuS_5^{6-}]_\infty$ ribbons is composed of $[CuS_4]_2$-dimer-double chain along [010] direction that is interconnected with two BiS_6-octahedron-single-chain via sharing vertex. The optical band gap of La_2CuBiS_5 is measured to be 1.30 eV indicating a semiconductor character and DFT study indicates an direct band gap with an electronic transfer excitation of S3*p* to La5*d* orbital electrons. Our further efforts will devote to the introduction of group 13 or 14 elements (T), such as Al, Ga, In, Si, and Ge, into the Ln/Bi/Q (Ln=lanthanides; Q=S, Se, Te) systems, the combination of TQ_4^{n-} tetrahedron and Bi^{3+} with an stereochemically active lone pair electrons may generate new compounds with noncentrosymmetric (NCS) structures that may show interesting second-harmonic generation (SHG) property.

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