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Two metal chalcogenides, $Hg_2Te_2X_2$ ($X=$Br, I): 3-D framework constructed from novel left-handed helices

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Abstract

Two isostructural metal chalcogenides, $Hg_2Te_2Br_2$ (**1**) and $Hg_2Te_2I_2$ (**2**), were obtained by solid-state reactions and structurally characterized. Compounds **1** and **2** crystallize in the acentric space group $P4_32_12$ of the tetragonal system with eight formula units in a cell: $a=10.2388(9)$, $c=14.480(2)$ Å, $V=1518.0(3)$ Å^3, $R_1/wR_2=0.0670/0.1328$ for **1** and $a=10.711(3)$, $c=15.025(8)$ Å, $V=1724(1)$ Å^3, $R_1/wR_2=0.0637/0.1233$ for **2**. Both compounds are characterized by a three-dimensional (3-D) framework structure, which is composed by interconnected left-handed helices formed by both tetrahedral and trigonal Hg atoms. Optical absorption spectra of **1** and **2** reveal the presence of sharp optical gaps of 2.06 and 1.85 eV, respectively, suggesting that both materials are semiconductors. TG-DTA measurements show that both compounds are thermally stable up to 200 °C. The composition of both compounds is well confirmed by the semiquantitative microscope analyses.

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Keywords: Chalcogenide; Crystal structure; Halide; Mercury; Solid-state reaction; Tellurium

1. Introduction

The transition and main group metal chalcogenides show rich structural chemistry and useful physical and chemical properties for potential applications in nonlinear optics [1], optical storage [2], solar energy conversion [3], thermal electrics [4], ion-exchange [5], second harmonic generation [6], chemical absorption [7], ferroelectrics [8], and so forth. As an important branch of metal chalcogenides, a tremendous amount of ternary metal chalcogenides have been synthesized and some of them have been widely used in military and civil areas, famous examples including $CuInSe_2$ (CIS) and $Hg_{1-x}Cd_xTe$ (MCT), whose primary applications are found in photovoltaic devices for solar energy conversion and infrared detection [3,9].

Among the known ternary metal chalcogenides, many are A–M–Q ($A=$ alkali metal or alkaline-earth metal; $M=$ p-block metal; $Q=$ chalcogen $=$ S, Se, Te) systems, while group *IIB*–*Q*–*X* (*IIB* $=$ Zn, Cd, Hg; $X=$ F, Cl, Br, I) systems are relatively rare, to our knowledge, amounting to 12 compounds in two stoichiometric ratio types of 3:2:2 and 3:1:4:$Hg_3S_2F_2$, $Hg_3S_2Cl_2$, $Hg_3S_2Br_2$, $Hg_3S_2I_2$, $Hg_3Se_2Cl_2$, $Hg_3Se_2Br_2$, $Hg_3Se_2I_2$, $Hg_3Te_2Cl_2$, $Hg_3Te_2Br_2$, $Hg_3Te_2I_2$, Hg_3TeCl_4 and Hg_3TeBr_4 [10]. To obtain new materials which may possess the excellent photovoltaic and optical properties, our recent efforts in synthesizing novel *IIB*-based compounds have focused largely on the systems containing both chalcogenide and halide anions. Herein, we describe the syntheses of two new *IIB* metal chalcogenides: $Hg_2Te_2Br_2$ (**1**) and $Hg_2Te_2I_2$ (**2**), which possess a new 2:2:2 stoichiometric ratio type and were obtained from the solid-state reactions at intermediate temperatures ($150<T<500$ °C). Both compounds are characterized by a three-dimensional (3-D) framework

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structure, which contains novel interconnected left-handed helices.

2. Experimental

2.1. Syntheses and characterization

All reactants of A.R. grade were obtained commercially and used without further purification. The UV–vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV–vis spectrometer equipped with an integrating sphere in the wavelength range 190–1100 nm. $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function [11]: $\alpha/S=(1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance. Thermogravimetry-differential thermal analyses (TG-DTA) were performed on an NETZSCH STA 449C analyzer. Powdery samples were loaded into an alumina pan and heated from 30 to 700 °C with a ramp rate of 10 °C/min. Semiquantitive microscope analyses were performed on a field emission scanning electron microscope (FESEM, JSM6700F) or JSM-35CF equipped with an energy dispersive X-ray spectroscope (EDS).

Synthesis of $\mathbf{Hg_2Te_2Br_2}$ **(1)**: This compound was prepared from the reaction of $HgBr_2$ (1 mmol, 360.4 mg) and Te (1 mmol, 127.6 mg). The starting materials were ground into fine powders in an agate mortar before they were pressed into a pellet of 1 cm in diameter. Then the pellet was loaded into a silica tube, which was flame-sealed under a 10^{-3} Torr atmosphere and subsequently placed into a furnace. The tube was heated to 300 °C in 12 h from room temperature and kept for 6 days, followed by cooling to 100 °C at a rate of 6 °C/h to promote crystal growth, then power off. Yield: 23% (based on mercury). Analyses of the products with SEM/EDS showed only the presence of Hg, Te and Br in a ratio of 2.2:2:2.2, which is close to the chemical formula of $Hg_2Te_2Br_2$ established by the X-ray diffraction analysis. The products are very stable in air and water.

Synthesis of $\mathbf{Hg_2Te_2I_2}$ **(2)**: This compound was prepared by the procedure described for **1** using HgI_2 (1 mmol, 454.4 mg) instead of $HgBr_2$. Yield: 20% (based on mercury). SEM/EDS analysis of several of these crystals led to a composition of $Hg_2Te_2I_{2.2}$, which is close to the chemical formula of $Hg_2Te_2I_2$ established from the X-ray diffraction analysis; no other elements were detected. The products are very stable in air and water.

2.2. Structure determinations

The intensity data sets were collected on Rigaku Mercury CCD (**1**) and Rigaku AFC7R (**2**) X-ray diffractometers with graphite monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) using ω and ω–2θ scan technique, respectively. CrystalClear (**1**) and CrystalStructure (**2**) softwares were used for data reduction and empirical absorption corrections [12]. The structures were solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software [13]. The difference Fourier maps based on the atomic positions yield all the atoms. The structures were refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. The Te_{2A} and Te_{2B} atoms are positional disorder. The summary of crystallographic data and structure analyses for **1** and **2** is listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. The selected bond lengths and bond angles are listed in Table 3.

Table 1
Summary of crystallographic data and structure analyses for **1** and **2**

Compounds	**1**	**2**
Formula	$Br_2Hg_2Te_2$	$Hg_2I_2Te_2$
Fw	816.20	910.18
Color	Orange	Red
Crystal size/mm^3	0.16 0.16 0.15	0.09 0.07 0.05
Crystal system	Tetragonal	Tetragonal
Space group	$P4_32_12$	$P4_32_12$
a (Å)	10.2388(9)	10.711(3)
c (Å)	14.480(2)	15.025(8)
V (Å^3)	1518.0(3)	1724(1)
Z	8	8
$2\theta_{max}$ (deg)	50	50
Reflections collected	9162	1017
Independent, observed reflections	1339, 947	945, 585
(R_{int})	(0.1105)	(0.0257)
$d_{calcd.}$ (g/cm^3)	7.143	7.014
μ (mm^{-1})	58.352	49.275
T (K)	293(2)	293(2)
F(000)	2672	2960
R_1, wR_2	0.0670, 0.1328	0.0637, 0.1233
S	0.995	1.001
Largest and mean Δ/σ	0, 0	0, 0
$\Delta\rho$(max/min) (e/Å^3)	3.284/−4.658	2.042/−2.675

Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku DMAX2500 powder diffractometer at 40 kV and 100 mA using Cu*K*α ($\lambda = 1.54056$ Å), with a scan speed of 0.375 s/step and a step size of 0.05°. The simulated powder patterns were calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center, as shown in Fig. S1.

3. Results and discussion

3.1. Syntheses

In recent years, hydro(solvo)thermal and high-temperature molten salt synthesis or reactive flux method

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	Compound **1**					Compound **2**				
	x	y	z	U (eq)	SOF	x	y	z	U (eq)	SOF
Hg(1)	0.2582(1)	0.5418(1)	0.13380(8)	0.0461(3)	1	0.2580(2)	0.5372(1)	0.13769(8)	0.0460(4)	1
Hg(2)	0.2516(2)	0.5078(1)	−0.12683(8)	0.0527(4)	1	0.2427(2)	0.4900(2)	−0.1200 (1)	0.0804(6)	1
Br(1)	0.2593(2)	0.7407(2)	−0.2500	0.0249(8)	1	0.2703(2)	0.7297(2)	−0.2500	0.0308(7)	1
Br(2)	0.3473(2)	0.3570(2)	0.2536(2)	0.0234(6)	1	0.3448(2)	0.3516(2)	0.2566(1)	0.0342(5)	1
Br(3)	0.2529(3)	0.7471(3)	0.2500	0.051(1)	1	0.2477(2)	0.7523(2)	0.2500	0.0352(7)	1
Te(1)	0.4217(1)	0.6134(1)	−0.0051(1)	0.0212(4)	1	0.4091(2)	0.5916(2)	−0.0047(1)	0.0287(5)	1
Te(2*A*)	−0.0098(6)	0.5055(6)	0.1529(3)	0.066(2)	0.50	−0.0050(4)	0.5060(4)	0.1524(3)	0.028(1)	0.50
Te(2*B*)	−0.0050(4)	0.5087(4)	0.0963(3)	0.027(1)	0.50	−0.0028(4)	0.5117(4)	0.0958(3)	0.033(1)	0.50

Table 3
Selected bond lengths (Å) and bond angles (deg)

Compound **1**			
Hg$_1$–Te$_1$	2.718(2)	Br$_3$–Hg$_1$–Te$_1$	105.33(5)
Hg$_1$–Br$_2$	2.725 (3)	Br$_3$–Hg$_1$–Br$_2$	98.69(8)
Hg$_1$–Br$_3$	2.693(2)	Te$_1$–Hg$_1$–Br$_2$	116.88(8)
Hg$_1$–Te$_{2A}$	2.782(6)	Br$_3$–Hg$_1$–Te$_{2A}$	91.3(1)
Hg$_2$–Te$_1$	2.703(2)	Te$_1$–Hg$_1$–Te$_{2A}$	135.8(1)
Hg$_2$–Te$_{2A}$#1	2.673(6)	Br$_2$–Hg$_1$–Te$_{2A}$	100.0(1)
Hg$_2$–Br1	2.979(2)	Te$_{2A}$#1–Hg$_2$–Br$_2$#2	117.6(1)
Hg$_2$–Br$_2$#2	2.690(3)	Te$_{2A}$#1–Hg$_2$–Te$_1$	123.8(1)
Te$_1$–Te$_1$#2	2.780(3)	Br$_2$#2–Hg$_2$–Te$_1$	115.52(8)
Compound **2**			
Hg$_1$–Te$_1$	2.745(3)		
Hg$_1$–Te$_{2A}$	2.845(5)	Te$_1$–Hg$_1$–I$_2$	116.56(8)
Hg$_1$–I$_2$	2.830(3)	Te$_1$–Hg$_1$–Te$_{2A}$	132.0(1)
Hg$_1$–I$_3$	2.858(2)	I$_2$–Hg$_1$–Te$_{2A}$	101.2(1)
Hg$_2$–Te$_1$	2.713(3)	Te$_1$–Hg$_1$–I$_3$	108.18(7)
Hg$_2$–Te$_{2A}$#1	2.686(5)	I$_2$–Hg$_1$–I$_3$	101.92(7)
Hg$_2$–I$_1$	3.240(2)	Te$_{2A}$–Hg$_1$–I$_3$	90.6(1)
Hg$_2$–I$_1$#3	3.323(3)	Te$_{2A}$#1–Hg$_2$–Te$_1$	124.3(1)
Hg$_2$–I$_2$#2	2.827(3)	Te$_{2A}$#1–Hg$_2$–I$_2$#2	120.7(1)
Te$_1$–Te$_1$#2	2.768(4)	Te$_1$–Hg$_2$–I$_2$#2	114.4(1)

Symmetry codes: #1 $-y+1/2$, $x+1/2$, $z-1/4$; #2 y, x, $-z$; #3 $y-1/2$, $-x+1/2$, $z+1/4$.

techniques proved to be a powerful method for access to a huge number of new binary, ternary, and quaternary chalcogenido compounds [14]. Differently, we adopt intermediate-temperature ($150<T<500\,^{\circ}\mathrm{C}$) solid-state reactions to prepare new ternary chalcogenides. Considering the melting and boiling points of HgBr$_2$ (MP = 237, BP = 322 °C) and HgI$_2$ (MP = 259, BP = 354 °C), we decided to exploit a heating temperature of 300 °C. At this temperature, HgBr$_2$ and HgI$_2$ are melted, which makes the reaction similar to molten salt or reactive flux method synthesis. Therefore, it is proposed that this method may promote the reactions.

3.2. Crystal structures

X-ray diffraction analyses reveal that compounds **1** and **2** are isomorphous and only compound **2** is discussed in detail here. The structural novelty of Hg$_2$Te$_2$I$_2$ derives from the fact that its 3-D framework consists of interconnected left-handed helices, as shown in Fig. 1(a).

An ORTEP drawing of the asymmetric unit of **2** is shown in Fig. S3. The two crystallographically different mercury atoms are in general positions and have different coordination geometries. The Hg$_1$ atom is tetrahedrally coordinated by two telluride atoms and two iodide atoms with the bond lengths of Hg$_1$–Te$_1$, Hg$_1$–Te$_{2A}$, Hg$_1$–I$_2$ and Hg$_1$–I$_3$ being 2.745(3), 2.845(5), 2.830(3) and 2.858(2) Å, respectively, and the bond angles of Te$_1$–Hg$_1$–I$_2$, Te$_1$–Hg$_1$–Te$_{2A}$, I$_2$–Hg$_1$–Te$_{2A}$, Te$_1$–Hg$_1$–I$_3$, I$_2$–Hg$_1$–I$_3$ and Te$_{2A}$–Hg$_1$–I$_3$ being 116.56(8)°, 132.0(1)°, 101.2(1)°, 108.18(7)°, 101.92(7)° and 90.6(1)°, respectively. The bond lengths of Hg–Te are in the normal range and comparable with those previously reported [15]. The Hg$_2$ atom has an approximately right trigonal geometry if we arbitrarily choose a cutoff of 3.0 Å for the Hg–I distances [10d], coordinating with two telluride atoms and one iodide atom with the bond lengths of Hg$_2$–Te$_1$, Hg$_2$–Te$_{2A}$($-y+1/2, x+1/2, z-1/4$) and Hg$_2$–I$_2$($y, x, -z$) of 2.713(3), 2.686(5) and 2.827(3) Å, respectively, and the bond angles of Te$_{2A}$($-y+1/2, x+1/2, z-1/4$)–Hg$_2$–Te$_1$, Te$_{2A}$ ($-y+1/2, x+1/2, z-1/4$)–Hg$_2$–I$_2$($y, x, -$z) and Te$_1$–Hg$_2$–I$_2$ ($y, x, -z$) being 124.3(1)°, 120.7(1)° and 114.4(1)°, respectively. It should be note that the positional disordered Te$_{2A}$ and Te$_{2B}$ atoms are located very close to the crystallographic 4_3 axis, so they are refined as disordered over two symmetry-related sites with an occupancy factor 1:1 to get rational [Te$_2$]$^{2-}$ structural model. The [Te$_{2A}$–Te$_{2B'}$]$^{2-}$ species arrange approximately along the 4_3 axis with a separation of ca. 4.6 Å.Therefore, an infinite linear [Te$_2\cdots$Te$_2$]$_n$ chain constructed from these [Te$_{2A}$–Te$_{2B'}$]$^{2-}$ species can be regarded as the axis of the above-mentioned helix. The Hg$_1$-tetrahedra and Hg$_2$-trigons connect to each other via a Te$_1$ atom, forming a blade fixed on the [Te$_2\cdots$Te$_2$]$_n$ axis (Fig. 1(a)). The neighboring blades rotate 90° and slip along the [Te$_2\cdots$Te$_2$]$_n$ chain with a slippage of 3.761(2) Å to construct a unit of four-bladed propeller or a left-handed helix (Fig. 1(a)), to our knowledge, this left-handed helix is the first example in the metal chalcogenides. The helices are interconnected via μ_2-I$_2$ and μ_2-I$_3$ atoms, yielding a layer approximately in the *ac* plane (Fig. 1(b)). In the layer, the helices are further

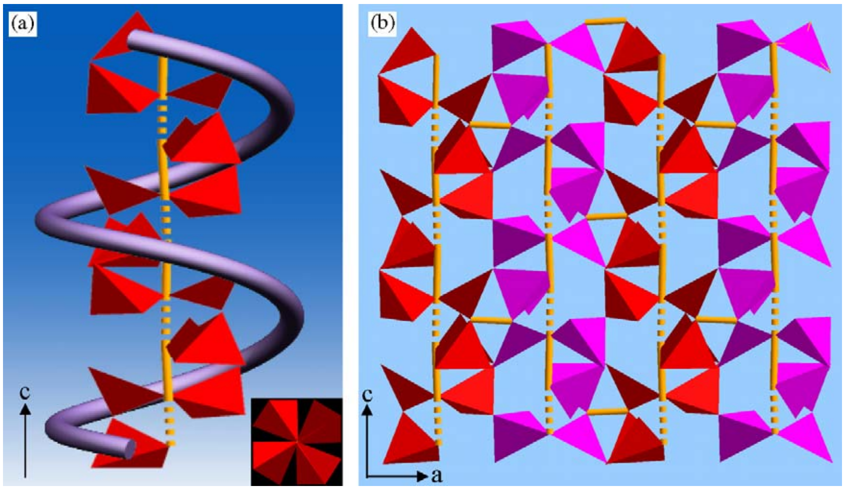

Fig. 1. (a) Polyhedral perspective of **2** shows one left-handed helix with the inset showing diagram of the helix viewed down along the *c*-axis. (b) A layer constructed from such helices. Red and purple colors are only for eye-guide. The yellow solid lines represent the Te–Te bonds and the alternately occurred solid and dashed lines indicates the $[Te_2\cdots Te_2]_n$ chain.

solidified via the Te_1–Te_1 covalent bonds with a bond length of 2.768(3) Å, which is comparable with those reported [16]. Both $[Te_1–Te_1]^{2-}$ and $[Te_{2A}–Te_{2B'}]^{2-}$ act as μ_4-bridge (Scheme S1i) to bridge four mercury atoms, as the cases found in $Cs_3Cu_8Te_{10}$ [17], $[NBu_4]_4[Hg_4Te_{12}]$ [18] and $K_2Cu_2(Te_2)(Te_3)$ [15]. The layers link to each other via μ_2-I_2, μ_2-I_3 and μ_4-$[Te_2]^{2-}$ anions to complete a 3-D framework, which looks like an aggregation of four-blade propellers when viewed down along the *c*-axis (Fig. 2).

The transparent and acentric nature of **1** and **2** suggests that they may be useful as nonlinear optical materials in IR region. Future work on this area is in progress in our group.

3.3. Thermogravimetry-differential thermal analysis (TG-DTA)

TG-DTA shows that both compounds are thermally stable up to 200 °C and underwent a three- and four-step decomposition process for **1** and **2**, respectively (Fig. S4). For **1**, the TG-DTA displays an initial mass loss of 57.67% with a beginning temperature of about 200 °C. A second weight loss of 25.49% with an endothermic peak centered at 409 °C is found in the range of 268–415 °C. The third weight loss of 17.36% is occurred in the range of 415–700 °C. Differently, compound **2** underwent a four-step decomposition process. The first step is occurred in the temperature range of 40–287 °C with the mass loss of 43.25%. The second weight loss of 20.10% is found between 287 and 340 °C. The third step is occurred in the temperature range of 340–410 °C with the mass loss of 14.83%. The last decomposition process is found in the temperature span of 410–700 °C with the mass loss of 21.61%.

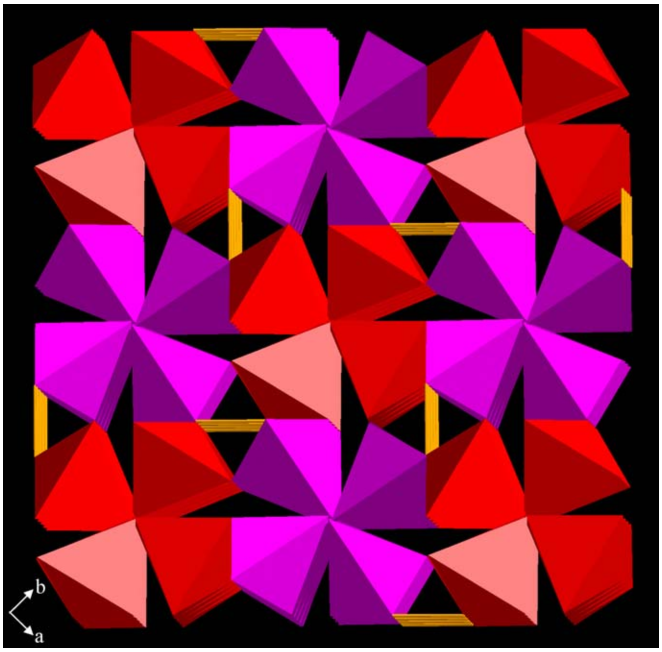

Fig. 2. A polyhedral representation of the 3-D framework of **2**.

3.4. UV–vis spectroscopy

Optical absorption spectra of **1** and **2** reveal the presence of a sharp optical gap of 2.06 and 1.85 eV (Fig. 3), respectively, which suggest that both materials are semiconductors and are consistent with the orange and red color of the crystals, as the cases found in Ref. (for example [19]). It is worth noting that, for the isostructural compounds **1** and **2**, the optical band-gap changes slightly for changes in the types of halogen. This suggests that the optical absorption of **1** and **2** is likely originated from the

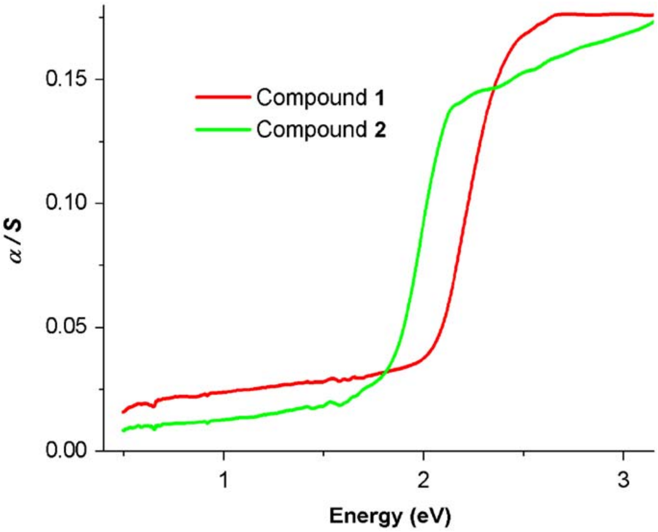

Fig. 3. The solid-state diffuse reflectance spectra for **1** and **2**.

charge-transfer excitations mainly from the *p*-like valence band of the telluride ligand to the 6*s*-like conduction band of the mercury center, similar to those occurring in red HgS [20]. The band gap of **2** is smaller than that of **1**, which is probably due to the more covalent and less ionic metal–halogen bonding with halogen changing from bromine in **1** to iodine in **2**.

4. Conclusion

Two $IIB_2Q_2X_2$ compounds have been synthesized via solid-state reactions. The title compounds possess an acentric nature, which make them to be found potential applications as nonlinear optical materials in IR region. The crystal structures are characterized by a 3-D framework structure, comprising of interconnected left-handed helices. Optical absorption spectra show that both compounds are candidates for potential photoelectric materials. Future investigations on the relationship between the crystal structure and the NLO or photoelectric properties in this field are in progress in our laboratory.

5. Supporting information

Crystallographic data in CIF format have been deposited with FIZ Karlsruhe with the following CSD numbers: 416 264 and 416 263 for **1** and **2**, respectively. These data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: 49 7247 808 666; E-mail: crysdata@fiz.karlsruhe.de).

Acknowledgments

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.07.006.

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