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$Bi_{6-x}Ca_xTi_5S_{16}$ (x = 3.08): The First Example of a Commensurate Structure in the Class of Misfit-Layer Compounds

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A novel mixed-valence, quasi-two-dimensional bismuth calcium titanium(III/IV) sulfide, $Bi_{6-x}Ca_xTi_5S_{16}$ (x = 3.08) is reported as a commensurate structure for the first time in the class of misfit-layer compounds. Since the first synthesis of "$PbTiS_3$",[1] a large collection of structurally categorized misfit-layer compounds have been studied with general formulations close to AMQ_3 and AM_2Q_5 (A = Sn, Pb, Bi, a rare-earth element; M = Ti, V, Cr, Nb, Ta).[1–6] Their framework consist of an intergrowth of two types of layered lattices, i.e., mixed layers of NaCl/CdI_2 for M = Ti, V, and Cr[1–3] or NaCl/MQ_2 (trigonal prismatic MQ_6) for M = Nb and Ta.[3–6] Owing to a mismatch between the two sublattices, the structural frameworks reported so far are incommensurate, subsequently structural analysis has been carried out by powder X-ray diffraction, electron diffraction, and, in some cases, single-crystal X-ray diffraction with structural solutions in two sublattices.[5] Recently, these type of compounds have been extensively investigated for their interesting superconducting properties, e.g., $(LaSe)_{1.14}(NbSe_2)_2$ (T_c = 5.3 K).[6] There are no theoretical band structures available due to a lack of integrated information concerning accurate atomic interactions in ordered lattices. The provided single-crystal structural solution will allow detailed band-structure calculations to be performed for a better understanding of bond interactions and electronic properties in this important class of misfit-layer compounds.

Table I. Crystallographic Data[a] for $Bi_{6-x}Ca_xTi_5S_{16}$ (x = 3.08)

chem formula	$Bi_{2.92}Ca_{3.08}Ti_5S_{16}$	fw	1484.44
a, Å	5.852(1)	space group	$C2/c$ (No. 15)
b, Å	17.05(2)	T, °C	23
c, Å	22.696(7)	λ, Å	0.71069
β, deg	95.25(2)	ρ_{calcd}, g cm^{-3}	4.372
V, Å^3	2255(3)	linear abs coeff, cm^{-1}	263.36
Z	4		
R^b	0.053		
$R_w{}^c$	0.060		

[a] The cell constants are refined in the monoclinic crystal system with 25 high-angle reflections (38.61° ≤ 2θ ≤ 42.96°). [b] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [c] $R_w = [\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$.

The new phase $Bi_{6-x}Ca_xTi_5S_{16}$ was synthesized as metallic silver, thin plates from a mixture of elements 2Bi:4K:3Ti:10S (0.96:1.93:1.44:4.81 mmol), with the addition of an eutectic flux of $CaCl_2$/KCl (14.58:5.12 mmol) in a mass ratio of 4:1. The potassium metal was added to dissociate $CaCl_2$ in situ to obtain reactive elemental calcium.[7] The crystal structure was determined by a single-crystal X-ray diffraction method (Table I),[8] and the composition was confirmed by quantitative elemental analysis.[9] A bulk polycrystalline sample was then prepared[10] according to the refined structural composition. We note that an extensive chemistry exists in this class of mixed-metal chalcogenides for the formation of possible high-T_c superconductors.

The title compound possesses an interesting quasi-two-dimen-

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(7) The heating program is as follows: slow heating to 750 °C at 0.4 °C/min, isotherm for 1 day at 750 °C, heating to 990 °C at 0.67 °C/min, isotherm at 990 °C for 3 days, then followed by slow cooling to room temperature at −3 °C/h. Single crystals (up to 3 mm) of the title compound (~90% yield) were isolated by washing the reaction products with deionized water, using a suction filtration method.

(8) Diffraction data were collected using a Rigaku AFC5S four-circle diffractometer equipped with a graphite monochromator. The *TEXSAN* (*Single Crystal Structure Analysis Software*, Verion 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989) software package was used for data reduction, intensity analysis, and space-group determination. A total of 5337 reflections ($2\theta_{max}$ = 55°) were collected (at room temperature) from four octants ($\pm h,+k,\pm l$), of which 723 unique reflections with $I > 3\sigma(I)$ were used for the structural determination. An analytical absorption correction was applied using the AGNOST program (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965,** *19,* 1014). The structure and thermal parameters were refined by full-matrix least-squares methods. Total atoms in an asymmetric unit are fourteen, including three bismuth/calcium, three titanium, and eight sulfur atoms. In each Bi site, the calcium cations are found to be statistically mixed, and the refined composition was x = 3.08.

(9) Quantitative chemical analysis by energy dispersive spectroscopy using a Hitachi S570 was performed on the data crystal and showed four elements, Bi, Ca, Ti, and S with the ratio 10.65:11.75:19.79:57.78 which are comparable with that from the calculated structural composition, 10.81:11.41:18.52:59.26.

(10) The reaction mixtures contained stoichiometric amounts of CaS (Alfa, 99.99%), Bi (Aldrich, 99.99+%), Ti (Aldrich, 99.9%), and S (Aldrich, 99.99+%) in 1.00:1.00:1.67:4.34 mmol ratio, respectively. The reactants were sealed in a fused quartz container and, to avoid explosion due to sulfur vapor, slowly heated to 750 °C and then isothermed for 2 days followed by furnace cooling.

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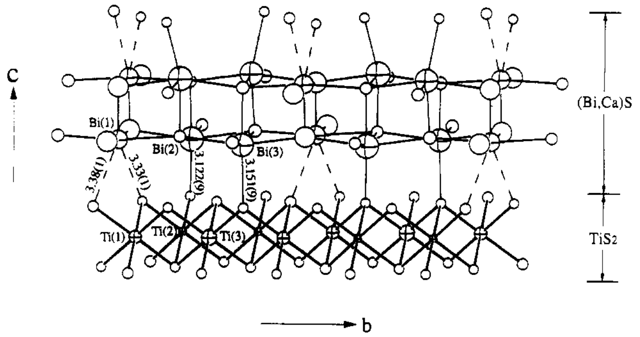

Figure 1. ORTEP drawing of the partial structure of $Bi_{6-x}Ca_xTi_5S_{16}$ (x = 3.08) showing the (Bi,Ca)S and TiS_2 sublattices. The anisotropic atoms are presented at 90% probability. The Ti and Bi atoms are labeled while the S atoms are shown by open circles. The interlayer (Bi,Ca)–S bond lengths are given in ångstroms.

sional structure that is characterized by two sublattices, i.e., double-layer (Bi,Ca)S slab and TiS_2 slab, as shown in Figure 1, stacking alternately along the *c* axis. These two structural units adopt the NaCl and CdI_2 structure types, respectively. The interaction between these two types of structural units is through inter-layer (Bi,Ca)–S bonds[11] which are relatively stronger than what would be expected for the van der Waals interactions. It is noted that, because of the mismatch of two structural units, coordinations of the mixed bismuth and calcium site are varied from six to seven. Until now, the interlayer interaction has been quite ambiguous due to a lack of single-crystal data. This has also been the reason for not being able to calculate exact structure compositions for all the previously studied misfit-layer compounds. Because of the unique arrangement of the commensurate structure, the exact composition of the title compound can be determined. The unit cell consists of (Bi,Ca)S vs TiS_2 structure units in the ratio 6:5. The structural formula can then be written as $[(Bi,Ca)S]_6(TiS_2)_5$ or $[(Bi,Ca)S]_{1.20}TiS_2$.

The layered structure described above reminds us of the thallium copper–oxide high-T_c superconductors[12] in that the rock salt type thallium–oxide layers serve as a charge reservoir slab to the superconducting copper–oxide framework. In the title compound, the analogous charge reservoir slab can be identified as the rock salt (Bi,Ca)S slab where the trivalent bismuth and divalent calcium cations are statistically distributed. This suggests a possible solid solution series with the compound composition $Bi_{6-x}Ca_xTi_5S_{16}$, $0 \le x \le 6$.[13] The feasibility of preparing a solid solution series is further supported by the close comparison of the Shannon crystal radii[14] of six-coordinated Bi^{3+} (1.17 Å) vs Ca^{2+} (1.14 Å). Thus, the mixing of the Bi^{III}/Ca^{II} cations facilitates a chemical modification mechanism to fine tune the electronic structure at the Fermi level and in turn the metallic properties.

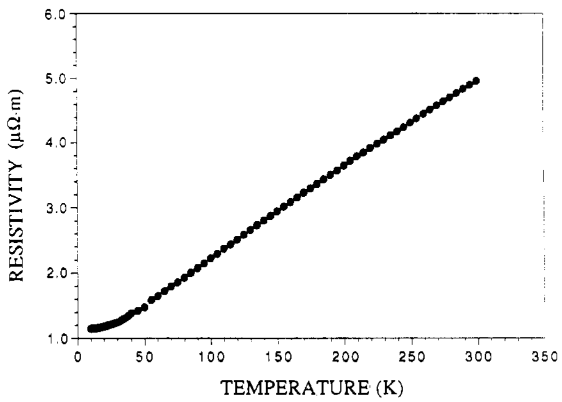

Figure 2. Resistivity (μΩ·m) vs temperature (T, K) plot of a pressed pellet sample of $Bi_{6-x}Ca_xTi_5S_{16}$.

It is commonly seen that the misfit-layer chalcogenide compounds are metallic. The electrical resistivity of the title compound was measured[15] on a pressed pellet sample. As shown in Figure 2, it is a metallic conductor with a very low resistivity of 4.96 μΩ·m at 300K. Although no detailed band structure has been calculated, presumably it is similar to that of the TiS_2 phase in the sense that the valence band is composed of primarily titanium d-orbitals. At the Fermi level, the band is likely narrow because it is composed of a single d-orbital attributed to the structural distortion from a perfect octahedron and subsequent orbital energy-level splitting. In $Bi_{6-x}Ca_xTi_5S_{16}$ (x = 3.08), the valence band is partially occupied since the formal oxidation state of the titanium cation is mixed III/IV, consistent with the observed metallic behavior.

The electron transfer from the (Bi,Ca)S charge reservoir layer to the TiS_2 slabs will have some influence not only on the chemical and physical properties but also the layer dimension. We speculate that the A-site cation mixing may be responsible for the lattice matching and consequently the long-range ordering. It is interesting to see how a different sized cation will affect the lattice matching. To study the size/charge effect, additional experiments are underway.

It is intriguing to look into the possibility of developing new series of quasi-two-dimensional compounds, especially ones associated with different layered transition metal chalcogenide frameworks, such as NbQ_2 and TaQ_2 where Q = S and Se. Indeed, the early transition metal chalcogenide compounds are interesting because of their different coordination geometries and they provide a close comparison with layered metallic and superconducting oxides.

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Supplementary Material Available: Tables of detailed crystallographic data, atomic positional and thermal parameters, and selected bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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(11) The (Bi,Ca)–S distances (5× for each cation center) in the double-layer slab are in the range 2.42–3.06 Å. The alternate stacking (Bi,Ca)–S with the TiS_2 slabs gives rise to a significant interaction and in turn comparable bond distances. The shortest interslab (Bi,Ca)–S distances are 3.33(1) Å for Bi(1)–S(4), 3.38(1) Å for Bi(1)–S(8), 3.122(9) Å for Bi(2)–S(5) and 3.151(9) Å for Bi(3)–S(7).

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(15) Dc four-probe resistivity measurements were made on a pellet with the dimensions 0.2 × 3.1 × 12.1 mm. The current source used was 10 mA from 10 to 300 K. The room-temperature I–V curve is linear.