

Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ Single Crystals: Growth, Structure and Optical Property

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Abstract: Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ single crystals of high quality were successfully synthesized by solid-state reaction method using NaI as flux. Both compounds crystallize in the rocksalt structure type of a cubic Fm-3m space group. The preferred orientation growth of lattice face (111) were observed in both two compounds. The optical absorption measurements show that the band gap of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compounds are 1.29 eV and 1.45 eV, respectively. Two compounds were fabricated into devices that exhibit notable photoelectric behavior, suggesting their potential for applications as photoelectric switches.

Key words: single crystal growth; Na_{1.88}Bi_{1.88}S₄; Na_{1.36}Ca_{1.28}Bi_{1.36}S₄; semiconducting materials

For decades, researchers have shown great interests in exploring group VA chalcogenides, because the compounds of group VA chalcogenides had been found to have various interesting properties and promising applications in the fields including photocatalyst (BiOCl^[1]), thermoelectric (Bi₂Te₃^[2]), superconductivity (LaO_{1-x}F_xBiS₂^[3], Bi₄O₄S₃^[4], and Bi₃O₂S₃^[5]), and topologic physics (Sr_xBi₂Se₃^[6]).

Compared with most of other chalcogenides of group VA with common layered structure, the *M*BiQ₂ (*M*=Li, Na and K; *Q*=S and Se) compounds^[7-10] have a rare NaCl-type cubic structure, which are isomorphous with AgBiSe₂^[11], in which alkali metal and bismuth atoms disorderly occupy the 4a sites, and the sulfur or selenium atoms occupy the 4b sites. Structural information of *M*BiQ₂ compounds were only solved from powder X-ray diffraction data. Kang, *et al*^[12] had prepared the NaBiS₂ plates by solvothermal method, but the product is not pure and the yield of the target compound was relatively low.

According to the theoretical calculations of NaBiS₂ reported by Gabrel'yann^[10], the compound NaBiS₂ is a semiconductor with direct energy band of 1.28 eV, which indicates that the series of *M*BiQ₂ materials are promising candidates for thermoelectric and photoelectric study and application. But so far, the physical properties of *M*BiQ₂ and their derivatives were rarely investigated.

Thus, it is worthy and necessary to seek a new and high-output method to synthesize pure and large single crystals for structural analysis and intrinsic physical properties study.

On the other hand, element doping as means of band engineering is always an effective way to adjust and control the band gap^[13]. The selection of element for doping is of much importance, since the introduced atoms may change the energy and electronic structure of the parent compounds^[14-16]. Obviously, the element chemical valences of parent compounds will be changed to other states according to the kinds of doping atoms. In previous works, many interesting properties were induced by changing the valences of group VA from common states to mix-valences. A famous superconductor Ba_xK_{1-x}BiO₃^[17] with *T_c* of about 30 K was obtained by bringing Ba²⁺ into KBiO₃^[18] compound, which made the valence of Bi lower than its common state +5. The same observations happen in the other compounds including BaBi_{1-x}Pb_xO₃^[19], AgSnSe₂^[20] and doped TiO₂^[21-22].

In this work, we intend to design different NaBiS₂-based compounds of chemical valence for Bi element by other elements. It is possible that substituting Na⁺ or Bi³⁺ ions by partial Ca²⁺ ions may lead to different valence of Bi in the rock salt structure. And the calcium-inducing

Received date: 2017-03-27; **Modified date:** 2017-05-14

Foundation item: National Key Research and Development Program (2016YFB0901600); Science and Technology Commission of Shanghai (16JC1401700); National Natural Science Foundation of China (11404358, 51402335)

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method is possible, since the radius of Ca²⁺ ion is just between the radii of Na⁺ and Bi³⁺ ions in the same chemical environment. Besides, the introduction of Ca²⁺ ions would obviously turn the disorder of cation occupation into higher degree, which may introduce novel physical properties in parent compound NaBiS₂.

It has been well known that appropriate molten salt flux using in solid-state reaction could play a key role in the process of crystal growth. Flux became liquid phase at high temperature, helping ions to diffuse faster than that in solid-state and obviously accelerate the growth of single crystal. Herein, by using NaI as flux, large-size, high-quality, stable ternary and quaternary bismuth-chalcogenide single crystals Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were successfully grown. Their crystal structure and physical properties, including optical and photoelectrical properties were systematically investigated.

1 Experimental

1.1 Sample preparation

1.1.1 Preparation of polycrystalline samples

Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ polycrystalline powders were synthesized by using conventional solid-state reaction method. Starting materials of Na₂S powders, Ca bulk (99%), Bi particles (99.9%), S powders (99.999%) and Bi₂S₃ powders were used without further purification. Na₂S powders was prepared by the liquid ammonia method in lab, and Bi₂S₃ powders was obtained by solid-state reaction using Bi particles and S powders as raw materials at 1073 K. Stoichiometric amounts of Na₂S and Bi₂S₃ powders (all the starting materials are stored in Argon-filled glove box) were mixed to yield 0.5 g of samples to obtain compound Na_{1.88}Bi_{1.88}S₄. Likewise, stoichiometric amounts of Na₂S, Bi₂S₃, S powders and Ca bulk were mixed to yield 0.5 g samples to obtain Na_{1.36}Ca_{1.28}Bi_{1.36}S₄. The mixtures were fire-sealed in evacuated (<0.1333 Pa) silica tubes. Subsequently, the tubes were loaded into a furnace, slowly elevated to 1073 K and kept at same temperature as Na_{1.88}Bi_{1.88}S₄ compound for 24 h. After that, the polycrystalline samples were obtained as the furnace cooled to room temperature.

1.1.2 Growth of single crystals

The single crystal samples of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were grown using NaI as flux. The obtained polycrystalline Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ powders were ground, mixed with 1 g NaI, then evacuated and fire-sealed in silica tubes. The NaI powders was heated at 473 K over night to eliminate water. The tubes were reloaded into a furnace as before, elevated to 1073 K at a rate of 10 K/min, kept at this temperature for 1 d, and then slowly cooled to 873 K for 2 d to allow crystal

growth. After cooling to room temperature, the samples were washed with de-ionized water and alcohol, and then the single crystals Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were obtained after drying in an oven at room temperature for 3 h.

1.2 Characterization

1.2.1 Powder X-ray diffraction

Powder X-ray diffraction data of these two samples were collected using a Bruker powder diffractometer at room temperature (filtered Cu K α radiation). The patterns were collected using a θ - 2θ scan mode and a step size of 0.02° at a rate of 2°/min. The powdered samples were fixed on the sample holder tightly to make a flat glass surface. The obtained powder diffraction patterns were analyzed to determine the purity of these two samples using the Jade 6.5 software package.

1.2.2 Single-crystal X-ray diffraction

Double cone-like Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ single crystals suitable for X-ray diffraction were chosen from the as-prepared samples. Data collections were performed on a Bruker D8 QUEST diffractometer equipped with mirror-monochromated Mo K α radiation. Data was collected by ω - and ψ -scan method at room temperature using APEX3 program^[23]. The structures of the two compounds were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package^[24]. Multi-scan absorption corrections (SADABS)^[25] were performed. The crystal data and refinement details are summarized in Table 1.

Table 1 The crystal data and refinement details for Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄

Formula	Na _{1.88} Bi _{1.88} S ₄	Na _{1.36} Ca _{1.28} Bi _{1.36} S ₄
Formula	563.42	495.02
weight/(g·mol ⁻¹)		
Temperature/K	273	273
Wavelength/nm	0.07107	0.07107
Space group	Fm-3m	Fm-3m
Crystal system	cubic	cubic
Unit cell/nm	0.57715(3)	0.5745(4)
V/nm^3	0.19225(3)	0.1896(4)
Z	1	1
$\rho/(\text{g}\cdot\text{cm}^{-3})$	4.866	4.336
Index ranges	$-6 \leq h \leq 6, -6 \leq k \leq 6, -6 \leq l \leq 6$	$-7 \leq h \leq 7, -7 \leq k \leq 7, -7 \leq l \leq 6$
Reflns collected	1428	773
Unique reflns	18	22
Goodness-of-fits on F^2	1.447	1.317
$R_1[I > 2\sigma(I)]$	0.0106(2)	0.0154(2)
$wR_2[I > 2\sigma(I)]$	0.0236(2)	0.0314(2)
$R_1(\text{all})$	0.0106(2)	0.0154(2)
$wR_2(\text{all})$	0.0236(2)	0.0314(2)

1.2.3 UV-Vis light spectroscopy

Optical diffuse-reflectance measurements for two title compounds were carried out using a UV-4100 spectrophotometer operating from 2000 nm to 300 nm at room temperature. The BaSO₄ powders was used as a 100% reflectance standard. These two samples were ground and spread on a compacted base of BaSO₄ powder. The generated reflectance-versus-wavelength data were used to measure the band gap of the two materials. The reflectance data was converted to absorbance data using the Kubelka-Munk equation^[26] based on the direct band of NaBiS₂.

1.2.4 Photoelectric response tests

The as-synthesized single crystals of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were crashed, ground into powders, pressed, and then incised into regular bars. The photoelectric response tests were using two-electrodes method. The tests were performed at room temperature under solar light irradiation with 500 W Xenon lamp on the Model 4200-SCS Semiconductor Characterization System. The inset of Fig. 5 shows the schematic device dia-

gram of the tests.

2 Results and discussion

The single crystal data of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were performed on a Bruker D8 QUEST diffractometer equipped with mirror-monochromated Mo K α radiation. The experimental details are summarized in Table 1. The two title compounds crystallize in NaCl-type structure of a cubic *Fm-3m* space group. The Na/Bi/S and Na/Ca/Bi/S ratio of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ were determined from the refinement results, respectively. $R_1(\text{all})=0.0106(2)$, $wR_2(\text{all})=0.0236(2)$, and $s=1.447$ for Na_{1.88}Bi_{1.88}S₄ compound, $R_1(\text{all})=0.0154(2)$, $wR_2(\text{all})=0.0314(2)$, and $s=1.317$ for Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compound. While there still exist 'poor data / parameter ratio' alerts during the Checkcif^[27] process due to the high symmetry of the *Fm-3m* space group of both these two compounds. The atomic parameters information for these two compounds are listed in Table 2-4.

Table 2 Atomic coordinates of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄

Atom	Symmetry	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*	Occupancy
Na _{1.88} Bi _{1.88} S ₄						
Na	4a	0.5	1.0	0.5	0.0222(1)	0.47(2)
Bi	4a	0.5	1.0	0.5	0.0222(1)	0.47(2)
S	4b	1.0	0.5	0.5	0.0210(2)	1.00
Na _{1.36} Ca _{1.28} Bi _{1.36} S ₄						
Na	4b	0.5	0.5	0.5	0.0600(1)	0.34(2)
Ca	4b	0.5	0.5	0.5	0.0500(9)	0.32(3)
Bi	4b	0.5	0.5	0.5	0.0170(3)	0.34(2)
S	4a	1.0	0.5	0.5	0.0210(3)	1.00

* U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 3 Anisotropic displacement parameters ($\times 10^{-6}$, nm²) of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na _{1.88} Bi _{1.88} S ₄						
Na	0.0222(3)	0.0222(3)	0.0222(3)	0	0	0
Bi	0.0222(3)	0.0222(3)	0.0222(3)	0	0	0
S	0.0213(5)	0.0213(5)	0.0213(5)	0	0	0
Na _{1.36} Ca _{1.28} Bi _{1.36} S ₄						
Na	0.0588(2)	0.0588(2)	0.0588(2)	0	0	0
Ca	0.0511(8)	0.0511(8)	0.0511(8)	0	0	0
Bi	0.0171(6)	0.0171(6)	0.0171(6)	0	0	0
S	0.0206(9)	0.0206(9)	0.0206(9)	0	0	0

*The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$

Table 4 Representative bond lengths (nm) and bond angles (°) of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄

Atom-atom	Bond length	Atom-atom-atom	Bond angle/(°)
Na _{1.88} Bi _{1.88} S ₄			
Na(1)-S(1)	0.28857(5)	S(1)-Na(1)-S(1)	90
Bi(1)-S(1)	0.28857(5)	S(1)-Bi(1)-S(1)	90
Na _{1.36} Ca _{1.28} Bi _{1.36} S ₄			
Na(1)-S(1)	0.2872(2)	S(1)-Na(1)-S(1)	90
Ca(1)-S(1)	0.2872(2)	S(1)-Ca(1)-S(1)	90
Bi(1)-S(1)	0.2872(2)	S(1)-Bi(1)-S(1)	90

Figure 1 depicts the crystal structure of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compounds, both of which crystallize in the rock salt structure of a cubic Fm-3m space group, with the Na, Ca and Bi atoms occupying 4b sites and S atoms occupying 4a sites, respectively. The Bi valence is +3.25 for Na_{1.88}Bi_{1.88}S₄ compound and +3 for Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compound. The structure and configuration of Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compound has not been changed by Calcium-doping determined by single crystal diffraction method. From Table 4, the bond distance of Na(Bi)-S is 0.28857(5) nm in Na_{1.88}Bi_{1.88}S₄, and the bond distance of Na(Ca/Bi)-S is 0.2872(2) nm in Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compound, comparable to that in the structure of Na₂S (0.2831 nm)^[28], CaS (0.2842 nm)^[29], and Bi₂S₃ (average: 0.2901 nm)^[30]. The strengthened bond of metal-sulfur in calcium-induced compound Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ are leading to the shortened bond distance compared to Na_{1.88}Bi_{1.88}S₄.

Figure 2(a) depicts the powder X-ray diffraction patterns of fine powders of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ samples. As shown in Figure 2(a), all the peaks matched well with NaBiS₂ phase (PDF 75-0065) with the rock salt structure and no extra peaks were observed, indicating high degree of phase purity. The yield of these two compounds are over 90% by this method. The diffraction peaks of these two powders are consistent with the simulated single crystal X-ray diffraction results from their crystal information files. Figure 2(b) shows the magnified pattern of the (111) lattice plane, with the peak at about 26.8° of Na_{1.36}Ca_{1.28}Bi_{1.36}S₄, which is shifting to right compared with Na_{1.88}Bi_{1.88}S₄. In the structure of Na_{1.88}Bi_{1.88}S₄ phase, sulfur atoms occupy the chlorine sites, Na and Bi atoms disorderly occupy the sodium sites with nearly the same occupancy, while replacing partial Na and Bi atoms with some amounts of Ca atoms leads to the decrease of the lattice parameter *a* from 0.28857(5) nm to 0.2872(2) nm. The lattice parameter difference is due to their different effective ion size and elements proportion of the Na, Ca and Bi atoms.

Figure 3(a) and 3(c) are the scanning electron microscopic (SEM) images of the Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ single crystals. Both of the two title compounds present

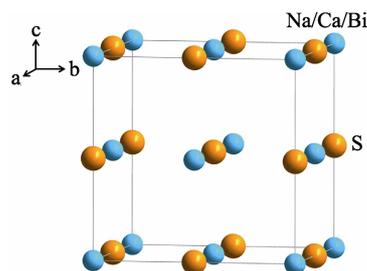


Fig. 1 Schematic crystal structure of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄. Yellow sphere represents S atom, light blue sphere represents Na(Ca/Bi) atoms

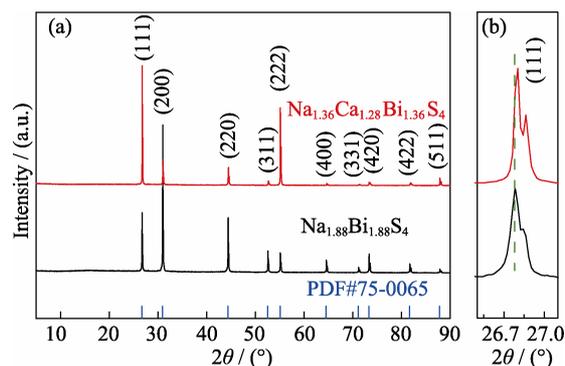


Fig. 2 (a) Powder X-ray diffraction patterns of Na_{1.88}Bi_{1.88}S₄ (black line) and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ (red line), with blue bars indicating the Bragg positions for NaBiS₂ phase; (b) Magnified pattern of the (111) lattice plane of Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄, respectively

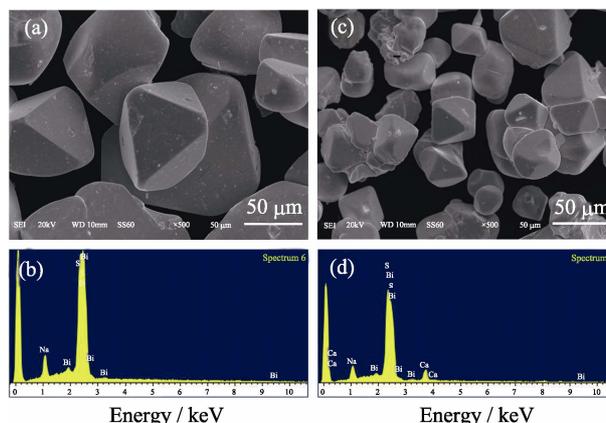


Fig. 3 SEM images of the Na_{1.88}Bi_{1.88}S₄ (a) and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ (c) and EDX spectra of the Na_{1.88}Bi_{1.88}S₄ (b) and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ (d)

smooth double cone-like appearance of high crystallinity, indicating the preferred orientation growth of lattice face (111) using NaI as flux. The average size of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ crystals is 65 μm , and the average size of $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ crystals is 40 μm . The two title compounds were prepared under the same procedure, while the $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ crystals are generally larger in size than the $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ crystals, indicating that the $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ crystal grows much easier than $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ crystal. This difference may be derived from the ion diffusion velocity and crystal symmetry of element-doping compounds^[31]. Figure 3(b) and 3(d) show the energy dispersive spectroscopy (EDS) spectra of the two compounds, The obvious characteristic energy peaks of elements can be detected, which located in the correspondent energy positions for each element. The Na/Bi/S ratio is 26.74/23.68/49.58, and the Na/Ca/Bi/S ratio is 17.26/14.82/17.48/50.44, determined from the EDS results, which are nearly the same as the single crystal diffraction refinement conclusions.

The two compounds were directly exposed in air for more than two months, and the phases remained unchanged, which were checked by powder X-ray diffraction and EDS, indicating the high stability of these two compounds. Unlike some alkali-containing compounds, for example, Na_xTaS_2 ^[32], and Li_xMoS_2 ^[33], the high stability of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ and $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ compounds under normal air conditions enables potential applications.

In order to investigate the optical properties of the two compounds, UV-Visible (UV-Vis) diffuse-reflectance spectra were measured. NaBiS_2 is a direct band gap semiconductor, the band gap can be inferred from the

$(\alpha h\nu)^2 \sim h\nu$ curves, as shown in Figure 4. The forbidden band gaps of the two compounds can be estimated from the energy value corresponding to the intersection point of the two tangent lines. From Figure 4, the energy gaps of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ and $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ compounds were found to be about 1.29 eV and 1.45 eV, respectively. Gabrel'yan reported that the calculated band gaps of NaBiS_2 to be 1.28 eV which is very close to our experimental results of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$. Thus, it can be seen that substituting partial Bi and Na atoms with Ca atoms leads to the enlargement of the band gap to 1.45 eV.

The band gap of these two compounds are potential for solar light utilization, for example, solar cell^[34] and photoelectric switch^[35], as the suitable band gap is about 1.6 eV^[36]. Photoelectric response tests for two compounds were performed on a 4200 semiconductor characterization system. The schematic graph of test device is shown in the inset of Figure 5(a). From Figure 5(a), the light

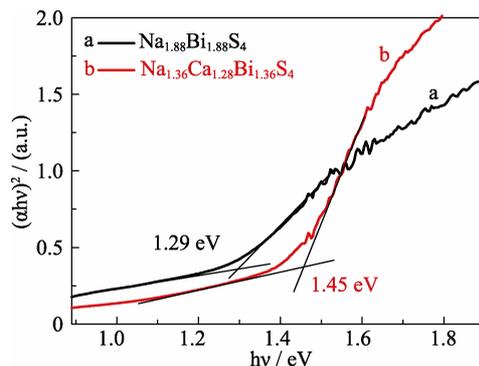


Fig. 4 Solid-state UV-Vis diffuse reflectance spectra of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ and $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$

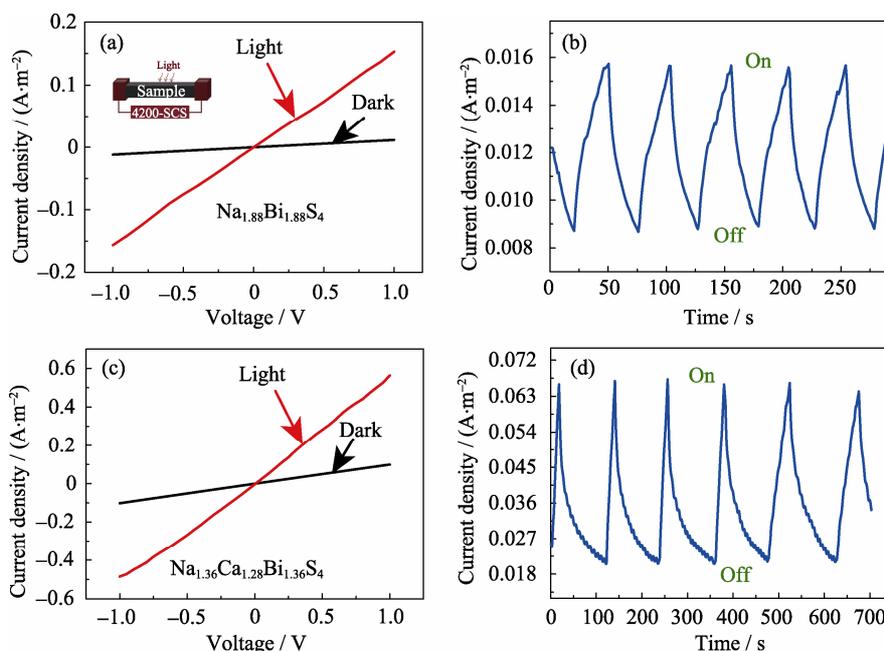


Fig. 5 Photoelectric responses and on-off curves at a bias voltage of 5 V of $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ compound (a, b) and $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ compound (c, d)

current density of Na_{1.88}Bi_{1.88}S₄ sample can reach 0.153 A/m² at the voltage of 1 V which is 13 times larger than dark current density, indicating the strong response of the light. Figure 5(b) shows the on-off curve at the bias voltage of 5 V, the current density is increased, when the light is on. Both Figure 5(a) and 5(b) demonstrate that Na_{1.88}Bi_{1.88}S₄ compound is a favorable and promising photoelectric response material. The photoelectric performance patterns of Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ sample are depicted in Figure 5(c) and 5(d), and obvious response phenomenon can be also observed, with the light current density being 5.5 A/m² which is 5.7 times larger compared to the dark current density. The obvious photoelectric response is observed from the on-off curve in Figure 5(d). Besides, the light current density of Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ is about 3.6 times larger than that in Na_{1.88}Bi_{1.88}S₄ compound. The enhanced photoelectric performance for Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ compound is resulted from calcium-introducing.

3 Conclusions

In summary, Na_{1.88}Bi_{1.88}S₄ and Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ single crystals of high purity crystallizing in the rock salt structure were successfully synthesized by solid state reaction using NaI as flux. The structures of these two compounds were solved by single crystal diffraction. The valence state of Bi element can be adjusted from 3.25 to 3 by Ca-doping along with the enlargement of band gap from 1.29 eV to 1.45 eV, accordingly. Besides, both of them perform obvious photoelectric response which can serve as favorable photoelectric response materials.

References:

- [1] CHEN JIAN-CHAI, YU CHANG-LIN, LI JIA-DE, *et al.* Preparation by grinding-calcination and photocatalytic performance of La₂O₃/BiOCl composite photocatalysts. *J. Inorg. Mater.*, 2015, **30(9)**: 943–949.
- [2] WANG W, JIA F L, HUANG Q H, *et al.* Electrochemical assembled p-type Bi₂Te₃ thermoelectric materials with nanowire array structure. *J. Inorg. Mater.*, 2004, **19(3)**: 517–522.
- [3] LEE J, STONE M B, HUQ A, *et al.* Crystal structure, lattice vibrations, and superconductivity of LaO_{1-x}F_xBiS₂. *Physical Review B*, 2013, **87(20)**: 205134.
- [4] SHRUTI, SRIVASTAVA P, PATNAIK S. Evidence for fully gapped strong coupling s-wave superconductivity in Bi₄O₄S₃. *Journal of Physics: Condensed Matter*, 2013, **25(31)**: 312202.
- [5] SHAO JIFENG, LIU ZHONGHENG, YAO XIONG, *et al.* Bulk superconductivity in single-phase Bi₅O₂S₃. *Physica Status Solidi (RRL) – Rapid Research Letters*, 2014, **8(10)**: 845–848.
- [6] SHRUTI, MAURYA V K, NEHA P, *et al.* Superconductivity by Sr intercalation in the layered topological insulator. *Physical Review B*, 2015, **92(2)**: 020506.
- [7] BOON J W. The crystal structure of NaBiS₂ and KBiS₂. *Recueil des Travaux Chimiques des Pays-Bas*, 1944, **63(2)**: 32–34.
- [8] LAVRENT'EV A A, MIGAL' YU F, NIKIFOROV I YA. Two types of shape resonances in the compounds AIBiS₂ (AI=Li, Na). *Journal of Structural Chemistry*, 1992, **33(2)**: 207–213.
- [9] PARK YOUNBONG, MCCARTHY TIMOTHY J, SUTORLK ANTHONY C, *et al.* Synthesis of Ternary Chalcogenides in Molten Polychalcogenide Salts: α-KCuQ₄, KAuS₅, NaBiS₂, KFeQ₂ (Q = S, Se). *Inorg. Synth.*, John Wiley & Sons, Inc., 2007: 88–95.
- [10] GABREL'YAN B V, LAVRENTIEV A A, NIKIFOROV I YA, *et al.* Electronic energy structure of MBiS₂ (M = Li, Na, K) calculated with allowance for the difference between the M-S and Bi-S bond lengths. *Journal of Structural Chemistry*, 2008, **49(5)**: 788–794.
- [11] PAN LIN, B RARDAN DAVID, DRAGO NITA. High thermoelectric properties of n-Type AgBiSe₂. *Journal of the American Chemical Society*, 2013, **135(13)**: 4914–4917.
- [12] KANG SUMIN, HONG YONGHOON, JEON YOUNGJIN. A facile synthesis and characterization of sodium bismuth sulfide (NaBiS₂) under hydrothermal condition. *Bulletin of the Korean Chemical Society*, 2014, **45(38)**: 279–287.
- [13] CHEN XIAOBO, CLEMENS BURDA. The electronic origin of the visible-light absorption properties of C-, N- and S-doped TiO₂ nanomaterials. *Journal of the American Chemical Society*, 2008, **130(15)**: 5018–5019.
- [14] ABDUKADER ABDUKAYUM, AILJIANG TUERDI, RENAGUL ABDURAHMAN, *et al.* Synthesis and luminescence properties of Dy,Cr co-doped ZnGa₂O₄ persistent luminescence nanoparticles. *J. Inorg. Mater.*, 2016, **31(12)**: 1363–1369.
- [15] ZHANG ZHI-XIONG, OUYANG SHAO-YE, ZHANG Yue-Pin *et al.* Enhanced luminescent properties of Pr³⁺ doped Ba₂LaF₇ glass ceramics for white light-emitting diodes. *J. Inorg. Mater.*, 2016, **31(10)**: 1046–1050.
- [16] KAMIHARA YOICHI, WATANABE TAKUMI, HIRANO MASAHIRO, *et al.* Iron-based layered superconductor La[O_{1-x}F_x]FeAs (*x* = 0.05–0.12) with *T_c* = 26 K. *Journal of the American Chemical Society*, 2008, **130(11)**: 3296–3297.
- [17] NAZIA U S, ISLAM A K M A. Model spectral function and superconductivity in Ba_xK_{1-x}BiO₃ (*x*=0.5–0.7). *Solid State Communications*, 2003, **125(1)**: 37–40.
- [18] NGUYEN T N, GIAQUINTA D M, DAVIS W M, *et al.* Electrosynthesis of KBiO₃: a potassium ion conductor with the KSbO₃ tunnel structure. *Chemistry of Materials*, 1993, **5**: 1273–1276.
- [19] SHIRAI M, SUZUKI N, MOTIZUKI K. Superconductivity in BaPb_{1-x}Bi_xO₃ and Ba_xK_{1-x}BiO₃. *Journal of Physics: Condensed Matter*, 1989, **1(17)**: 2939.
- [20] CHEN CHENG-LUNG, WANG HENG, CHEN YANG-YUAN, *et al.* Thermoelectric properties of p-type polycrystalline SnSe doped with Ag. *Journal of Materials Chemistry A*, 2014, **2(29)**: 11171–11176.
- [21] LI L, XIAO J Y, CUI M D, *et al.* Boron and sulfur co-doped TiO₂ nanofilm as high efficiency CdS quantum-dot-sensitized solar cells. *J. Inorg. Mater.*, 2016, **31(6)**: 627–633.
- [22] SUN TONG, CHEN YANG, MA XIAO-QING, *et al.* Facile synthesis of visible light activated carbon-incorporated Mn doped TiO₂ microspheres via flame thermal method. *J. Inorg. Mater.*, 2015, **30(9)**: 1002–1008.
- [23] FRANCART TOM, VAN WIERINGEN ASTRID, WOUTERS JAN. APEX 3: a multi-purpose test platform for auditory psychophysical experiments. *Journal of Neuroscience Methods*, 2008, **172(2)**: 283–293.
- [24] SHELDRIK GEORGE. Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, 2015, **71(1)**: 3–8.
- [25] SHELDRIK G M, SADABS. Program for Empirical Absorption

- Correction of Area Detector Data. University of Göttingen, Germany, 1996.
- [26] CHRISTY ALFRED A, KVALHEIM OLAV M, VELAPOLDI RANCE A. Quantitative analysis in diffuse reflectance spectrometry: a modified Kubelka-Munk equation. *Vib. Spectrosc*, 1995, **9(1)**: 19–27.
- [27] SPEK A. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.*, 2003, **36(1)**: 7–13.
- [28] WEST C D. The crystal structures of some alkali hydrosulfides and monosulfides. *Zeitschrift für Kristallographie-Crystalline Materials*, 1934, **88**: 97.
- [29] PRIMAK W, KAUFMAN H, WARD R. X-ray diffraction studies of systems involved in the preparation of alkaline earth sulfide and selenide phosphors. *Journal of the American Chemical Society*, 1948, **70**: 2043–2046.
- [30] KUPČ K V, VESEL-NOV KOV LUDMILA. Zur Kristallstruktur des Bismuthinites, Bi_2S_3 . *Tschermaks Mineralogische und Petrographische Mitteilungen*, 1970, **14(1)**: 55–59.
- [31] KUDO AKIHIKO, NIISHIRO RYO, IWASE AKIHIDE, *et al.* Effects of doping of metal cations on morphology, activity, and visible light response of photocatalysts. *Chem. Phys.*, 2007, **339(1/2/3)**: 104–110.
- [32] FANG L, WANG Y, ZOU P Y, *et al.* Fabrication and superconductivity of Na_xTaS_2 crystals. *Physical Review B*, 2005, **72(1)**: 014534.
- [33] CHRISAFIS K, ZAMANI M, KAMBAS K, *et al.* Structural studies of MoS_2 intercalated by lithium. *Materials Science and Engineering: B*, 1989, **3(1)**: 145–151.
- [34] YANG Y, GAO J, CUI J R, *et al.* Research progress of perovskite solar cells. *J. Inorg. Mater.*, 2015, **30(11)**: 1131–1138.
- [35] MATSUO YUTAKA, ICHIKI TAKAHIKO, NAKAMURA EIICHI. Molecular photoelectric switch using a mixed SAM of organic [60]Fullerene and [70]Fullerene doped with a single iron atom. *Journal of the American Chemical Society*, 2011, **133(25)**: 9932–9937.
- [36] WANG W Q, ZHENG H F, LU G H, *et al.* Recent progress on applications of nano metal oxides in perovskite solar cells. *J. Inorg. Mater.*, 2016, **31(9)**: 897–907.

Na_{1.88}Bi_{1.88}S₄ 和 Na_{1.36}Ca_{1.28}Bi_{1.36}S₄ 单晶制备 与结构及其光学性能表征

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摘要: 采用碘化钠为助熔剂, 通过固相反应法制备了两种晶体质量较好的 $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ 和 $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ 单晶。测试结果表明, 它们属于氯化钠结构, 面心立方, 空间群为 Fm-3m 。形貌表征和物性测试结果表明, 在碘化钠的作用下, 化合物 $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$ 和 $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$ 呈现双锥状形貌, 沿(111)晶面择优取向生长, 带隙分别为 1.29 和 1.45 eV。通过光电器件性能测试, 发现两种化合物均表现出良好的光电响应特性, 说明它们可以作为一类潜在的、性能优良的光电开关材料。

关键词: 单晶生长; $\text{Na}_{1.88}\text{Bi}_{1.88}\text{S}_4$; $\text{Na}_{1.36}\text{Ca}_{1.28}\text{Bi}_{1.36}\text{S}_4$; 半导体材料

中图分类号: O782 文献标识码: A