Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ Single Crystals: Growth, Structure and Optical Property

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Abstract: Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ 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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ 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$_{1.88}$S$_4$; Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$; 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 (Bi$_2$Te$_3$$^{[2]}$), superconductivity (LaO$_{1-x}$F$_x$Bi$_2$$^{[3]}$, Bi$_4$O$_6$S$_3$$^{[4]}$, and Bi$_2$O$_2$S$_2$$^{[5]}$), and topologic physics (SrBi$_2$Se$_2$$^{[6]}$).

Compared with most of other chalcogenides of group VA with common layered structure, the MBi$Q_2$ (M=Li, Na and K; Q=S and Se) compounds$^{[7-10]}$ have a rare NaCl-type cubic structure, which are isomorphous with AgBiSe$_2$$^{[11]}$, in which alkali metal and bismuth atoms disorderly occupy the 4a sites, and the sulfur or selenium atoms occupy the 4b sites. Structural information of MBi$Q_2$ compounds were only solved from powder X-ray diffraction data. Kang, et al$^{[12]}$ had prepared the NaBiS$_2$ 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 NaBiS$_2$ reported by Gabrel'yan$^{[10]}$, the compound NaBiS$_2$ is a semiconductor with direct energy band of 1.28 eV, which indicates that the series of MBi$Q_2$ materials are promising candidates for thermoelectric and photoelectric study and application. But so far, the physical properties of MBi$Q_2$ 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 bang 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$_{1.4}$K$_{0.6}$Bi$_2$O$_3$ with $T_c$ of about 30 K was obtained by bringing Ba$^{2+}$ into KBiO$_3$$^{[18]}$, compound, which made the valence of Bi lower than its common state +5. The same observations happen in the other compounds including BaBi$_{1-x}$Pb$_x$O$_3$$^{[19]}$, AgSnSe$_2$$^{[20]}$ and doped TiO$_2$$^{[21-22]}$.

In this work, we intend to design different NaBiS$_2$-based compounds of chemical valence for Bi element by other elements. It is possible that substituting Na$^+$ or Bi$^{3+}$ ions by partial Ca$^{2+}$ ions may lead to different valence of Bi in the rock salt structure. And the calcium-inducing
method is possible, since the radius of Ca$^{2+}$ ion is just between the radii of Na$^+$ and Bi$^{3+}$ ions in the same chemical environment. Besides, the introduction of Ca$^{2+}$ ions would obviously turn the disorder of cation occupation into higher degree, which may introduce novel physical properties in parent compound NaBiS$_2$.

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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ 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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ polycrystalline powders were synthesized by using conventional solid-state reaction method. Starting materials of Na$_2$S powders, Ca bulk (99%), Bi particles (99.9%), S powders (99.999%) and Bi$_2$S$_3$ powders were used without further purification. Na$_2$S powders was prepared by the liquid ammonia method in lab, and Bi$_2$S$_3$ powders was obtained from the as-prepared samples. Data collections were performed on a Bruker D8 QUEST diffractometer equipped with mirror-monochromated Mo K$_\alpha$ radiation. Data was collected by o- and ω-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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ |
|---------|--------------------------------------------------|
| Formula | Na$_{1.88}$Bi$_{1.88}$S$_4$ | Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ |
| Formula weight/(g·mol$^{-1}$) | 563.42 | 495.02 |
| 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(4) | 0.5745(4) |
| $V$/nm$^3$ | 0.19225(3) | 0.1896(4) |
| Reflns collected | 1428 | 773 |
| Unique reflns | 18 | 22 |
| Goodness--of--fits on $F^2$ | 1.447 | 1.317 |
| $R_1$[I > 2σ(I)] | 0.0106(2) | 0.0154(2) |
| w$R_1$[I > 2σ(I)] | 0.0236(2) | 0.0314(2) |
| $R_1$(all) | 0.0106(2) | 0.0154(2) |
| w$R_1$(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\(_{1.88}\)S\(_4\) and Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\) 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 diagram of the tests.

2 Results and discussion

The single crystal data of Na\(_{1.88}\)Bi\(_{1.88}\)S\(_4\) and Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\) were performed on a Bruker D8 QUEST diffractometer equipped with mirror-monochromated Mo Kα 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\(_{1.88}\)S\(_4\) and Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\) were determined from the refinement results, respectively. \(R_{\text{all}}(all)=0.0106(2), \ wR_{\text{all}}(all)=0.0236(2), \) \(s=1.447\) for Na\(_{1.88}\)Bi\(_{1.88}\)S\(_4\) compound, \(R_{\text{all}}(all)=0.0154(2), \ wR_{\text{all}}(all)=0.0314(2), \) and \(s=1.317\) for Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\) 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\(_{1.88}\)S\(_4\) and Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\) |
|-----------------|-----------------|--------|-----------------|--------|
| Atom            | Symmetry        | \(x\)  | \(y\)  | \(z\)  | \(U_{eq}^*\) | Occupancy |
| 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              | 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 (\(\times10^{-6}, \text{nm}^2\)) of Na\(_{1.88}\)Bi\(_{1.88}\)S\(_4\) and Na\(_{1.36}\)Ca\(_{1.28}\)Bi\(_{1.36}\)S\(_4\)* |
|-----------------|-----------------|--------|--------|--------|--------|--------|--------|
| Atom            | \(U_{11}\)      | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
| 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              | 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       |

\(^*The \text{anisotropic displacement factor exponent takes the form} -2\pi^2[\hbar^2a^2U_{11} + ... + 2\hbar k a^b U_{12}]\)
Table 4  Representative bond lengths (nm) and bond angles (°) of Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$

| Atom–atom bond | Bond length (nm) | Atom–atom–atom bond | Bond angle (°) |
|----------------|-----------------|----------------------|----------------|
| 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)–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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ 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$_{1.88}$S$_4$ compound and +3 for Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ compound. The structure and configuration of Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ 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$_{1.88}$S$_4$, and the bond distance of Na(Ca/Bi)–S is 0.2872(2) nm in Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ compound, comparable to that in the structure of Na$_2$S (0.2831 nm)\(^{28}\), CaS (0.2842 nm)\(^{29}\), and Bi$_2$S$_3$ (average: 0.2901 nm)\(^{30}\). The strengthened bond of metal–sulfur in calcium-induced compound Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ are leading to the shortened bond distance compared to Na$_{1.88}$Bi$_{1.88}$S$_4$.

Figure 2(a) depicts the powder X-ray diffraction patterns of fine powders of Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ samples. As shown in Figure 2(a), all the peaks matched well with NaBiS$_2$ 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$_{1.36}$S$_4$ phase, which is shifting to right compared with Na$_{1.88}$Bi$_{1.88}$S$_4$. In the structure of Na$_{1.88}$Bi$_{1.88}$S$_4$ 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$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ single crystals. Both of the two title compounds present...
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 Na$_{1.88}$Bi$_{1.88}$S$_4$ crystals is 65 μm, and the average size of Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ crystals is 40 μm. The two title compounds were prepared under the same procedure, while the Na$_{1.88}$Bi$_{1.88}$S$_4$ crystals are generally larger in size than the Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ crystals, indicating that the Na$_{1.88}$Bi$_{1.88}$S$_4$ crystal grows much easier than Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$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$_x$TaS$_2$$^{[32]}$, and Li$_x$MoS$_2$$^{[33]}$, the high stability of Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$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 spectrum were measured. NaBiS$_2$ is a direct band gap semiconductor, the band gap can be inferred from the $(\alpha h\nu)^2$-$h\nu$ 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 Na$_{1.88}$Bi$_{1.88}$S$_4$ and Na$_{1.36}$Ca$_{1.28}$Bi$_{1.36}$S$_4$ compounds were found to be about 1.29 eV and 1.45 eV, respectively. Gadrel’yan reported that the calculated band gaps of NaBiS$_2$ to be 1.28 eV which is very close to our experimental results of Na$_{1.88}$Bi$_{1.88}$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
current density of $Na_{1.88}Bi_{1.88}S_4$ 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 $Na_{1.36}Bi_{1.36}S_4$ compound is a favorable and promising photoelectric response material. The photoelectric performance patterns of $Na_{1.36}Ca_{1.28}Bi_{1.36}S_4$ 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 $Na_{1.88}Ca_{1.28}Bi_{1.36}S_4$ is about 3.6 times larger than that in $Na_{1.88}Bi_{1.88}S_4$ compound. The enhanced photoelectric performance for $Na_{1.36}Ca_{1.28}Bi_{1.36}S_4$ compound is resulted from calcium-introducing.

3 Conclusions

In summary, $Na_{1.88}Bi_{1.88}S_4$ and $Na_{1.36}Ca_{1.28}Bi_{1.36}S_4$ 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.

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**Na₁₈₈Bi₁₈₈S₄** 和 **Na₁₃₆Ca₁₂₈Bi₁₃₆S₄** 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 **Na₁₈₈Bi₁₈₈S₄** 和 **Na₁₃₆Ca₁₂₈Bi₁₃₆S₄** 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 **Na₁₈₈Bi₁₈₈S₄** 和 **Na₁₃₆Ca₁₂₈Bi₁₃₆S₄** 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种潜在的、性能优良的光电开关材料。

关 键 词: 单晶生长; **Na₁₈₈Bi₁₈₈S₄**; **Na₁₃₆Ca₁₂₈Bi₁₃₆S₄**; 半导体材料

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