First single crystal growth and structural analysis of superconducting layered bismuth oxyselenide; $\text{La}(\text{O},\text{F})\text{BiSe}_2$

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Abstract

Single crystals of La(O,F)BiSe_2 were successfully grown for the first time by a CsCl flux method. Single crystal X-ray structural analysis clearly showed that La(O,F)BiSe_2 crystalizes with space group $P4/nmm$ (lattice parameters $a = 4.1408(2) \text{ \AA}$, $c = 14.1096(6) \text{ \AA}$). The structure is composed of alternating BiSe_2 and La(O,F) layers. The bond distances and angles are similar to those of La(O,F)BiS_2 . The bond valence sum calculation indicates the refined structure is slightly cation rich, suggesting the charge neutrality should be kept by modification of valence state of the cations. Magnetic susceptibility and resistivity measurements showed the compound is a superconductor with a transition temperature of 3.6 K, which is higher than that of as-grown La(O,F)BiS_2 .

Keywords:

Single crystals growth; Single crystal X-ray structural analysis; BiSe_2 -based superconductor

1. Introduction

After the discovery of superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$ [1], much attention has been paid to synthesizing BiS_2 -based compounds. The BiS_2 -based compounds have a layered structure composed of superconducting BiS_2 layers and charge reservoir blocking layers similar to that of cuprate or Fe-based superconductors. For the $\text{Bi}_4\text{O}_4\text{S}_3$ case, it is composed of a superconducting layer Bi_2S_4 and a blocking layer $\text{Bi}_4\text{O}_4(\text{SO}_4)_{1-x}$. There are other BiS_2 -based superconductors with another type of the blocking layer $\text{La}(\text{O},\text{F})$ (similar to the Fe-based superconductor $\text{La}(\text{O},\text{F})\text{FeAs}$ [2]). $\text{La}(\text{O},\text{F})\text{BiS}_2$ synthesized under ambient pressure shows superconductivity with a transition temperature (T_c) of ~ 2.5 K [3]. The T_c is enhanced as high as 11.5 K under high pressure [4], and this is the current record for a BiS_2 -based superconductors. BiS_2 -based superconductors with various types of blocking layers have been developed so far, such as $\text{Ln}(\text{O},\text{F})\text{BiS}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Yb}$) [3, 5-9], $(\text{La},\text{M})\text{OBiS}_2$ ($\text{M} = \text{Th}, \text{Hf}, \text{Zr}, \text{Ti}$) [10], $(\text{Sr},\text{La})\text{FBiS}_2$ [11]. $\text{Ln}(\text{O},\text{F})\text{BiS}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$) have been prepared as single crystals using alkali metal chloride flux methods [12-14]. The single crystal X-ray structural analysis for $\text{La}(\text{O},\text{F})\text{BiS}_2$ and $\text{Nd}(\text{O},\text{F})\text{BiS}_2$ determined the bonding distances and angles precisely [15, 12]. Especially in the case of $\text{La}(\text{O},\text{F})\text{BiS}_2$, the structural investigation of different F contents were performed by Miura *et al.* [15]. They showed that the substitution of O by F results in the distortion of the Bi-S plane.

On the other hand, modification of superconducting layers is a very challenging issue. Only two cases have been reported in polycrystalline samples: $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSSe}$ ($T_c \sim 3.8$ K) [16] and

La(O,F)BiSe_2 ($T_c \sim 2.6$ K) [17]. It is necessary to obtain single crystals of the BiSe_2 -based material in order to clarify the superconducting mechanism and precise crystal structure so as to be able to design a new compound with a higher T_c .

In this study, we have succeeded in preparing single crystals of La(O,F)BiSe_2 by a CsCl flux method and carried out various characteristic measurements including single crystal X-ray diffraction. Here, we discuss the bonding nature and superconductivity of this compound.

2. Experimental

2.1. Preparation of single crystals

Single crystals of $\text{La}(\text{O},\text{F})\text{BiSe}_2$ were prepared by an alkali metal chloride flux method. Since CsCl exhibits less reactivity with the quartz tube at high temperature (unlike other alkali metal chlorides), CsCl was selected as the flux material. The powders of La (Kojundo, 99.9%), Bi_2O_3 (Wako, 99.9%), BiF_3 (Kojundo, 99.9%), Bi (Kojundo, 99.99%), Bi_2Se_3 (Kojundo, 99.9%), Se (Kojundo, 99.9%) were mixed with the ratio of $\text{La} : \text{Bi}_2\text{O}_3 : \text{BiF}_3 : \text{Bi} : \text{Bi}_2\text{Se}_3 : \text{Se} = 6 : 1 : 1 : 1 : 1 : 9$, which corresponds to nominal composition of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSe}_2$. Selenium vaporizes and increases its vapor pressure above $\sim 690^\circ\text{C}$. In order to reduce the risk of explosion of the quartz tube, the Bi_2Se_3 powder was used as a starting material for Se as well as the Bi sources. The starting powders of 0.8 g were mixed with 5 g of CsCl (Kojundo, 99.9%). The mixture was sealed in an evacuated quartz tube, and then heated to 880°C in 10 h, then gradually heated up to 900°C in 2h. The temperature was kept for 10 h, followed by cooling to 650°C at a rate of $1^\circ\text{C}/\text{h}$, then the sample was cooled down to room temperature in the furnace. The obtained materials were washed and rinsed by water, ethanol, and acetone in order to remove the flux material CsCl .

2.2. Characterization

Single crystal X-ray structural analysis was carried out using a Rigaku AFC11 Saturn CCD diffractometer with a VariMax confocal X-ray optical system for $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

Prior to the diffraction experiment, the crystals were cooled to 160 K in a cold N₂ gas flow, in order to suppress the thermal displacement factor. Cell refinement and data reduction were carried out by the program d*trek package in CrystalClear software suite [18]. The structure was solved by the direct method using SHELXS [19], and was refined with the program SHELXL [19] in the WinGX software package [20]. Back scattered electron (BSE) images and energy-dispersive X-ray (EDX) spectra were observed using a scanning electron microscope (Hitachi SU-70, EDAX Genesis XM2).

Temperature dependence of magnetic susceptibility was measured using a SQUID magnetometer (MPMS, Quantum Design) down to 1.8 K under a field of 10 Oe, and the field was applied parallel to the *c*-axis. Temperature dependence of electrical resistivity was measured down to 2.0 K, using a standard four-probe method with constant current mode by a Physical Property Measurement System (PPMS, Quantum Design). The electrodes were attached in the *ab*-plane with silver paste.

3. Results and Discussion

3.1 Crystal structure of $\text{La}(\text{O},\text{F})\text{BiSe}_2$

BSE image of a typical single crystal is shown in Fig.1(a). The image suggests the crystal has a uniform composition, and no local precipitation of metal. The composition was analyzed by EDX point analysis at several sections of the crystal. Fig.1(b) shows a typical EDX spectrum at a point marked by the red cross in Fig.1(a). The averaged compositional ratio of elements is estimated to be $\text{La} : \text{Bi} : \text{Se} : \text{O} : \text{F} = 0.98 : 0.92 : 2 : 0.50 : 0.19$, in which the ratio was normalized to $\text{Se} = 2$. The atomic ratio except for O and F elements is in good agreement with the nominal composition, suggesting that the single crystal has a composition $\text{La}(\text{O}_{1-x}\text{F}_x)\text{BiSe}_2$. It should be noted that the analysis always detected a slight excess of La in relation to Bi.

Figure 1. BSE image (a) and EDX result (b) of an obtained single crystal.

The X-ray single crystal analysis was successfully performed. Details of the single-crystal structure analysis at 160 K and crystallographic parameters are listed in Table 1 and Table 2. The compound crystallizes with space group $P4/nmm$ (lattice parameters $a = 4.1408(2)$ Å, $c = 14.1096(6)$ Å, and $Z = 1$). All atoms were located at special positions and their anisotropic displacement factors were all positive with similar values, appearing physically reasonable. The ratio of O and F was estimated to be O : F = 0.82 : 0.18, namely $\text{La}(\text{O}_{0.82}\text{F}_{0.18})\text{BiSe}_2$, from the occupancy refinement under constrain of $\text{Occ.}(\text{O}) + \text{Occ.}(\text{F}) = 1$. A F content of 0.18 is in good agreement with the F ratio to Se in the EDX result, 0.19.

A schematic illustration of the crystal structure is shown in Fig. 2(a). The crystal has an alternate stacking of BiSe_2 pyramids and $\text{La}_2(\text{O/F})_2$ layers; the basic structure of this crystal is isostructural with $\text{La}(\text{O,F})\text{BiS}_2$ [3]. The ORTEP representation is shown in Fig. 2(b). It is necessary to mention about residual peaks/holes around Bi and La sites. There are relatively large residual maximum densities ($< \sim 5 \text{ e}^-/\text{\AA}^3$) around Bi and La sites even though the $R1$ value falls as small as ~ 3 %. Fig. 3 shows the precession photographs reconstructed from the observed single crystal diffraction data. It is clearly shown that no modulated structure was observed. This finding suggests that the large residual densities are attributed to local disorder of Bi/La-sites in its crystal structure similar to X-ray absorption spectroscopy results in BiS_2 -based materials [21]. Since the EDX result always shows a La-rich content compared with that of the Bi, one possibility is that a little amount of La migrates to the Bi site as shown in Fig. 2(b) (Bi' and La' sites). In this model, the total occupancy

Table 1. Crystallographic data for the La(O,F)BiSe₂

Structural formula	La _{2.02} (O _{0.82} F _{0.18}) ₂ Bi _{1.98} Se ₄
Formula weight	1043.29
Crystal dimensions (mm)	0.100 x 0.090 x 0.030
Crystal shape	Platelet
Crystal system	Tetragonal
Space group	<i>P4/nmm</i> (No.192)
<i>a</i> (Å)	4.1408(2)
<i>c</i> (Å)	14.1096(6)
<i>V</i> (Å ³)	241.93(3)
<i>Z</i>	1
<i>d</i> _{calc} (g/cm ³)	7.174
Temperature (K)	160
λ (Å)	0.71073 (MoK α)
μ (mm ⁻¹)	59.900
Absorption correction	multi-scan
$\theta_{\max}$ (°)	46.242
Index ranges	-7< <i>h</i> <8, -8< <i>k</i> <8, -28< <i>l</i> <28
Total reflections	9173
Unique reflections	700
Observed [<i>I</i> ≥ 2σ(<i>I</i>)]	694
<i>R</i> _{int} for all reflections	0.0244
No. of variables	23
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0243/0.0634
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0244/0.0636
<i>GOF</i> on <i>F</i> _o ²	1.158
Max./Min. residual density (e ⁻ /Å ³)	4.923 / -2.039

Table 2. Atomic coordinates, atomic displacement parameters ($\text{\AA}^2$), and bond valence sum (BVS) for the $\text{La}(\text{O}_{0.82}\text{F}_{0.18})\text{BiSe}_2$

Site	Wyck.	S.O.F	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{eq}	BVS
La	$2c$	1	1/4	1/4	0.09052(3)	0.01474(10)	0.01474(10)	0.01281(14)	0.01410(9)	+2.94
Bi	$2c$	0.98	1/4	1/4	0.62301(2)	0.01420(8)	0.01420(8)	0.01177(16)	0.01339(8)	+3.10
Bi'	$2c$	0.01	1/4	1/4	0.5855(18)				0.003(5)	+0.02
La'	$2c$	0.01	1/4	1/4	0.664(2)				0.004(6)	+0.08
Se1	$2c$	1	1/4	1/4	0.81260(5)	0.01343(15)	0.01343(15)	0.0102(2)	0.01235(11)	-2.17
Se2	$2c$	1	1/4	1/4	0.38739(6)	0.01299(16)	0.01299(16)	0.0190(3)	0.01499(13)	-2.06
O	$2a$	0.82	3/4	1/4	0	0.0131(11)	0.0131(11)	0.0120(14)	0.0128(8)	-1.62
F	$2a$	0.18	3/4	1/4	0	0.0131(11)	0.0131(11)	0.0120(14)	0.0128(8)	-0.26

Note: U_{12} , U_{13} , and U_{23} are 0, and U_{eq} is defined as one third of the trace of the orthogonalized U tensor.

Figure 3. Precession images synthesized from the CCD single crystal diffraction data for La(O,F)BiSe₂. All lines are a guide for the eye.

and valence of Bi and La were constrained to keep 1.0 and +3, respectively. The final refined composition was $\text{La}_{1.010}(\text{O}_{0.82}\text{F}_{0.18})\text{Bi}_{0.992}\text{Se}_2$. This refinement converged to $R1 = 2.44\%$, which has a considerably lower value than that of the model excluding the displacement ($R1 = 2.82\%$). However, we cannot exclude the possibility of self-disorder of the Bi atoms. There are no considerable differences in $R1$ values between the case of Bi/Bi and Bi/La disorder, although the lowest $R1$ value was obtained in the model described above.

Some selected bond distances and angles are given in Fig. 2(b) and Table 3. Bi atoms are six coordinated and bonded with Se atoms in three kinds such as Bi-Se1, intra-plane Bi-Se2, and inter-plane Bi-Se2 bondings. The interatomic distance of intra-plane Bi-Se2 is $2.9317(1)\text{ \AA}$. On the other hand, the inter-plane Bi-Se2 is much longer ($3.3242(9)\text{ \AA}$) and the Bi-Se1 is shorter ($2.6752(8)\text{ \AA}$) than that of the intra-plane Bi-Se2. This tendency of bond lengths is similar to that of $\text{La}(\text{O},\text{F})\text{BiS}_2$ [3]. The intra-plane Se-Bi-Se angle in the present crystal is $174.262(15)^\circ$. In $\text{La}(\text{O},\text{F})\text{BiS}_2$, it has been reported that the amount of F affects not only the carrier concentration but also creates a distortion of the Bi-S plane [14]. The Bi-Se plane is more distorted than the Bi-S plane in $\text{La}(\text{O}_{1-x}\text{F}_x)\text{BiS}_2$ with $x \sim 0.23$. Bond valence sum (BVS) was estimated from the observed bond distances and the r_0 and B values of nominal valence La^{3+} , Bi^{3+} , Se^{2-} , O^{2-} , F^- provided by Brown [22]. The BVS values are also listed in Table.2. According to the refined composition $\text{La}_{1.010}(\text{O}_{0.82}\text{F}_{0.18})\text{Bi}_{0.992}\text{Se}_2$, the nominal valence summation should be +0.19, based on nominal valences. On the other hand, the BVS of Bi and La was estimated to be +6.11, indicating +0.11 different from charge neutrality. Both results indicate the refined structure is slightly cation rich, suggesting the charge neutrality should be kept by modification of valence state of Bi like as the result of X-ray photoemission spectroscopy for BiS_2 -based compound [23].

Table 3. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) of the $\text{La}(\text{O}_{0.82}\text{F}_{0.18})\text{BiSe}_2$ single crystal

Distance			
La-O/F $\times 4$	2.4327(2)	Bi-Se1	2.6752(8)
La-Se1 $\times 4$	3.2314(4)	Bi-Se2 [inter plane]	3.3245(9)
		Bi-Se2 [in plane] $\times 4$	2.9317(1)
Angle			
La-O/F-La	105.998(8)	Se1-Bi-Se2	92.869(14)
La-Se1-La	79.690(11)	Se2-Bi-Se2 [inter-plane]	87.131(13)
		Se2-Bi-Se2 [intra-plane]	174.262(15)

3.2 Superconductivity

Fig. 4 shows the temperature dependence of the magnetic susceptibility for a single crystal of $\text{La}(\text{O},\text{F})\text{BiSe}_2$. The diamagnetic signal corresponding to superconductivity appears below 3.6 K. The shielding and Meissner volume fraction at 1.8 K was estimated to be $\sim 31.8\%$ and $\sim 14.6\%$, respectively. The inset shows the temperature dependence of the resistivity along the ab -plane in the single crystal. It showed a sharp resistivity drop at 3.6 K, and zero resistivity was observed at 3.2 K, in accordance with the superconducting transition temperature T_c found in the magnetic susceptibility measurement.

Note that the T_c is 1 K higher than that of previously reported polycrystalline result [17]. Currently, the reason of the T_c difference is unclear but assuming that it is attributed to the F content and higher crystallinity. X-ray single crystal analysis showed the corrugation in the Bi-Se layer is slightly larger than the Bi-S layer of the BiS_2 -based superconductor. A flat Bi-S plane would result in better hybridization of the p_x/p_y orbitals of Bi and S [15]. If the Bi-Se plane could be flattened by applying chemical or physical

pressure, such as optimization of the F-content or uniaxial compression, an overlapping of the Bi- and Se- p orbitals would be enhanced and may realize higher T_c in this system.

Figure 4. Temperature dependence of magnetic susceptibility of the single crystal of $\text{La}(\text{O},\text{F})\text{BiSe}_2$ in zero-field cooling (ZFC) and field cooling (FC) mode. The inset shows temperature dependence of resistivity with an enlargement of the superconducting transition.

4. Conclusion

Single crystals of $\text{La}(\text{O,F})\text{BiSe}_2$ were successfully grown by the CsCl flux method. The X-ray structural analysis revealed $\text{La}(\text{O,F})\text{BiSe}_2$ crystalized with space group $P4/nmm$ (lattice parameters $a = 4.1408(2) \text{ \AA}$, $c = 14.1096(6) \text{ \AA}$). The magnetic susceptibility and resistivity measurements show a clear superconducting transition at 3.6 K. The structural analysis suggests the possibility of raising the T_c if the corrugated Bi-Se layer can be flattened by applying chemical or physical pressure as well as BiS_2 -based superconductors.

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