

# Fluorine and Oxygen *K*-edge X-ray Absorption Near Edge Structure of Ytterbium Fluoride Sulfide

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Materials using multiple anion compounds are expected to be a new direction for realizing functional materials. In this study, compounds using fluoride and sulfide ions as anions were synthesized, and the electronic structures were analyzed by F *K*-edge and O *K*-edge X-ray absorption spectra. The analytical results of the spectra with the total electron yield mode providing the surface information and the fluorescence mode providing the bulk information show the difficulty for the removal of oxygen sources contained in the starting material during the synthesis process and uniformly distribution internally by a calcination process.

## 1. Introduction

In the field of material sciences, multiple-anion compounds have recently attracted attention, and novel structures with multiple anions have been reported<sup>1</sup>. Using multiple-anion compounds could realize much higher physical properties than ever before. Examples of multiple-anion compounds using oxide ions are increasing recently<sup>2-4</sup>. However, compounds based on fluoride-ions have not been reported so much except oxide fluorides<sup>5</sup>. Inorganic metal fluorides have the potential to exhibit abundant functionality (electrical, optical and magnetic properties, etc.) because of a variety of crystal structures<sup>6</sup>. However, their stability of fluoride compounds is low because the activity of fluorine in the air is extremely low compared to that of oxygen. Therefore, in many cases, controlling the synthesis atmosphere is required, resulting in few research examples of multiple-anion compound using fluoride ion.

In order to bring out the functionality of fluoride compounds, it is necessary to understand its electronic structure. X-ray absorption spectroscopy (XAS) is a powerful tool for analyzing the electronic structure of compounds to provide the information corresponding to the unoccupied orbital<sup>7</sup>. However, there are few reports about F *K*-edge XAS of fluoride compounds<sup>8</sup> and XAS is not a useful technique for analysis of fluoride compounds at present. On the other hand, in oxide compounds, electronic structure analysis of oxide ions using XAS are often conducted. In particular, in battery electrode materials, the anion redox behavior has been reported<sup>9</sup>, which enhances the extra capacity in addition to the redox reaction with the transition metal. Therefore, XAS measurements of the multiple-anion compounds containing fluoride ion and analyzing its electronic structure are informative for the creation of new functionality.

In this study, we focus on the tritytterbium tetrafluoride disulfide, Yb<sub>3</sub>F<sub>4</sub>S<sub>2</sub>, that contains both a highly ionic fluoride-ion and a strongly covalent sulfide ion, which may provide new functionality.

There are two reports on the synthesis of Yb<sub>3</sub>F<sub>4</sub>S<sub>2</sub>, in which the crystal structure and the magnetic property were reported. Thomas *et al.* reported the crystal structure of Yb<sub>3</sub>F<sub>4</sub>S<sub>2</sub> synthesized by the flux method<sup>10</sup>. Kosaka *et al.* succeeded in synthesizing Yb<sub>3</sub>F<sub>4</sub>S<sub>2</sub> by the chemical vapor transport and evaluated the magnetic property<sup>11</sup>. In this study, we synthesized Yb<sub>3</sub>F<sub>4</sub>S<sub>2</sub> by the solid-state reaction which is easier to synthesize. The crystal structure of the synthesized compound was characterized by X-ray diffraction (XRD), and the chemical state of the compound was analyzed by F *K*-edge and O *K*-edge XAS spectra.

## 2. Experimental

Yb metal (Sigma-Aldrich, 99.9%), S powder (Wako Pure Chemical Industries, Ltd., 98.0%) and YbF<sub>3</sub> powder (Kojundo Chemical Industries, Ltd., 99.9%) were weighted with an atomic ratio of 5:6:4 and mixed with mortar under Ar atmosphere. The pellet sample was placed in a container made of Ta and vacuum sealed in a quartz tube. The sample was calcined at 850°C for 48 hours.

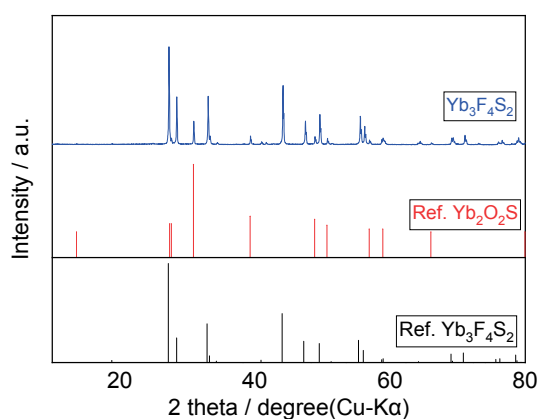
To identify the phase of the prepared samples, powder XRD measurement was performed using Ultima-IV (Rigaku) with the X-ray source of monochromatized Cu-*K* $\alpha$  radiation (40 kV, 40 mA). Data collection was performed in steps of 0.02°. The sample was ground sufficiently to make the particles uniform and then smoothed by grinding with a glass plate.

F *K*-edge and O *K*-edge XAS measurements were performed at BL-2 in Ritsumeikan University SR Center. The powder sample was put on a carbon tape and measured in a vacuum atmosphere. The measurement was carried out both with the total electron yield mode (TEY) and the energy selective partial fluorescence yield mode (PFY).

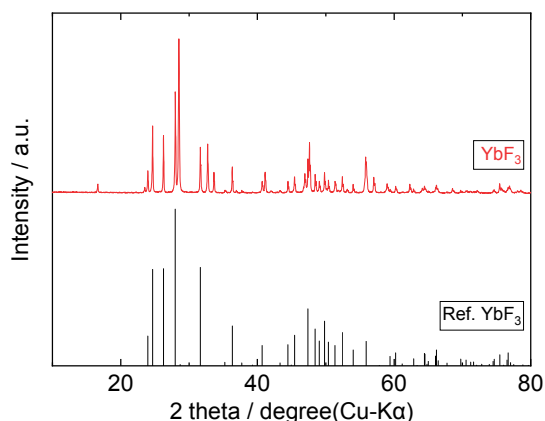
## 3. Results and Discussion

Figure 1 shows the XRD pattern of the prepared sample. The main peak is indexed as tetragonal *I4/mmm* space group based on the reported diffraction

pattern of  $\text{Yb}_3\text{F}_4\text{S}_2$ <sup>10</sup>. Based on the peak angles, the lattice constants were calculated;  $a = b = 3.827$  (1) Å,  $c = 18.79$  (1) Å. They are similar to the reported values<sup>10</sup>, indicating that the main phase is  $\text{Yb}_3\text{F}_4\text{S}_2$ . On the other hand, the peaks at 30.1 and 39.5 ° which cannot be indexed were also confirmed, and their peak positions are similar to those of  $\text{Yb}_2\text{O}_2\text{S}$  (ICDD: 01-071-1161). Therefore, the synthesized sample contains  $\text{Yb}_3\text{F}_4\text{S}_2$  as the main phase and  $\text{Yb}_2\text{O}_2\text{S}$  as an impurity. One of the reasons for the appearance of this impurity is that the oxygen source which was initially contained in the starting materials could not be removed during the synthesis process and remained in the resulting sample. The XRD pattern of the starting material of  $\text{YbF}_3$  is shown in Fig. 2. In  $\text{YbF}_3$ , diffraction peaks derived from oxides which should not be



**Fig. 1** XRD pattern of the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$ .

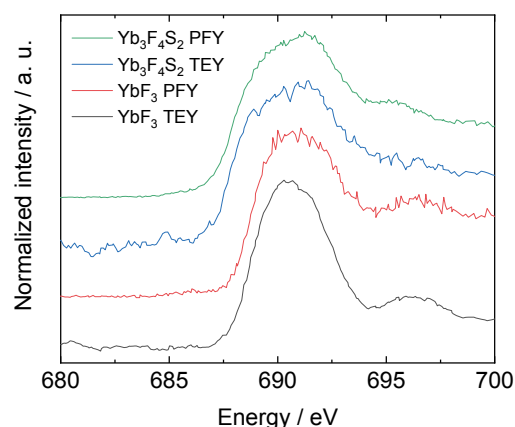


**Fig. 2** XRD pattern of the purchased  $\text{YbF}_3$ , compared with the reference (ICSD: 01-071-1161).

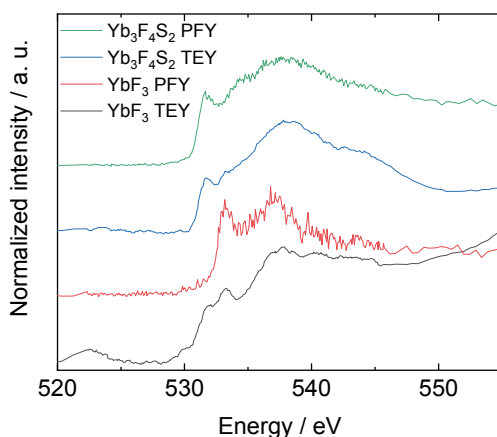
contained originally were identified as impurities. Figure 3 shows F *K*-edge XAS spectra of the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$  and the purchased  $\text{YbF}_3$  taken with the TEY and PFY modes. In  $\text{YbF}_3$ , one main peak was observed around 690.5 eV, while in  $\text{Yb}_3\text{F}_4\text{S}_2$ , doublet peaks at around 689.1 and 691.3 eV were observed. Since  $\text{LaF}_3$  gives a peak at the same position as  $\text{YbF}_3$ , it is presumed that the electronic structure of fluorine in the

rare earth trifluorides is equivalent. In contrast, in  $\text{Yb}_3\text{F}_4\text{S}_2$ , another absorption band appeared by the introduction of S. Both the TEY and PFY yield modes gave similar spectra, indicating that the electronic structure of fluorine in the bulk is same as that on the surface.

On the other hand, O *K*-edge XAS derived from oxide impurity shows complicated behavior. Figure 4 shows XAS at O *K*-edge of the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$  and the purchased  $\text{YbF}_3$  taken by the TEY



**Fig. 3** F *K*-edge XAS spectra of the purchased  $\text{YbF}_3$  and the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$ , measured with the TEY and PFY modes.

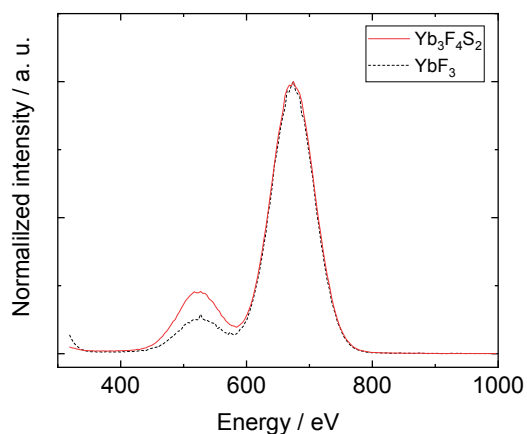


**Fig. 4** O *K*-edge XAS spectra of the purchased  $\text{YbF}_3$  and the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$  measured with the TEY and PFY modes.

and PFY modes. In the starting material  $\text{YbF}_3$ , the PFY spectrum is noisy, while the TEY spectrum shows relatively low noise. Because the sensitivity of TEY mode is different from that of PFY mode, it is difficult to discuss qualitatively the depth dependency. However, this difference is not observed in  $\text{Yb}_3\text{F}_4\text{S}_2$ . These results might indicate that the oxygen species of  $\text{YbF}_3$  are dominantly presented on the surface. The PFY spectrum shows peaks at around 533.2 and 536.7 eV, while the TEY gives a single peak at 531.9 eV. Therefore, in addition to the impurity confirmed by the

PFY mode, another impurity is present near the surface in  $\text{YbF}_3$ . However, in  $\text{Yb}_3\text{F}_4\text{S}_2$ , the PFY and TEY spectral shapes are similar to each other, where the sharp peak at 531.8 eV and a broad peak at 537.6 eV were observed. This means that the chemical state of the surface is almost same as that of the bulk, even though the oxygen-derived impurity exists in  $\text{Yb}_3\text{F}_4\text{S}_2$ . That is, a large number of oxygen sources presented near the surface in the starting material intruded into the bulk in the synthesis process, and the resulting powder has a uniform distribution of oxide impurity. It is crucial to use starting materials without oxygen source because of the difficulty of removing the oxygen source after incorporation into the bulk.

Figure 5 shows the spectra of fluorescence X-rays obtained during F *K*-edge XAS measurement. When the spectra are normalized with the peak derived from the F-*K* peak, the peak derived from O-*K* was detected for both the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$  and the purchased  $\text{YbF}_3$ , but the peak of  $\text{Yb}_3\text{F}_4\text{S}_2$  shows higher intensity. Although the fluorescence X-rays of O-*K* can be included in any materials, the peak obtained in this experiment is mainly due to the impurities of the fluoride sample, as the oxide-derived impurities are confirmed by XRD. Even though both XRD and fluorescence X-ray spectra can detect impurities derived from oxides, it is not possible to determine if they are present internally or on the surface. XAS analysis combined the total electron yield, and the fluorescence mode can distinguish the chemical state by discriminating the inside from the surface and is useful for the analysis of the impurities included in material synthesis.



**Fig. 5** X-ray fluorescence spectra of the purchased  $\text{YbF}_3$  and the prepared  $\text{Yb}_3\text{F}_4\text{S}_2$ .

#### 4. Conclusions

The multiple anion compound  $\text{Yb}_3\text{F}_4\text{S}_2$  was synthesized by the solid-state reaction under vacuum. From the results of X-ray diffraction,  $\text{Yb}_2\text{O}_2\text{S}$  is contained as an impurity, in addition to the main  $\text{Yb}_3\text{F}_4\text{S}_2$  phase. In the F *K*-edge XAS spectra, one

characteristic peak of rare earth trifluoride is confirmed in  $\text{YbF}_3$ , while the doublet peak is confirmed in  $\text{Yb}_3\text{F}_4\text{S}_2$ , indicating the formation of new levels. O *K*-edge XAS reveals that many different oxygen sources exist in the starting material especially in the surface of the purchased  $\text{YbF}_3$ . The impurities are uniformly present inside after the calcination process. In the synthesis of fluorine sulfide, it is necessary to reduce the oxygen source of elemental metal and fluoride compounds as the starting materials.

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