Evaluation of the physical properties and the real space observation in 2H-TaS$_2$ synthesized with flux method

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Abstract. Single crystal of 2H-TaS$_2$ was synthesized with flux method using the flux in which alkali metal ions were included. Analysis of the composition and the structure by EDX measurements and X-Ray diffraction showed that the hydrates of potassium ion were intercalated in 2H-TaS$_2$ synthesized with NaCl/KCl flux. The local intercalation was confirmed by the observation of the superstructures with the period of 2$a_0$ × 2$a_0$ or $\sqrt{3}a_0$ × $\sqrt{3}a_0$ by scanning tunnelling microscopy measurements.

1. Introduction

Physical properties of layered compounds can be changed by intercalation of metal ions or organic molecules. For example, $T_c$ is increased by intercalation in iron-based superconductors. Although intercalation is a useful technique to tune physical properties, intercalation technique is restricted to a few methods, such as electrochemical or vapor transport technique. Intercalants are also restricted. Thus, it is necessary to find more methods of intercalation.

2H-TaS$_2$ is one of typical transition metal dichalcogenides (TMDCs). 2H-TaS$_2$ shows superconductivity at 0.8 K and CDW state at 75 K. [1] In the CDW state, $3a_0$ × $3a_0$ superstructure emerges. By the intercalation of metal ions, increase in $T_c$ and the appearance of superstructures which is different from the CDW in pristine material are reported. [2][3]

In this study, we synthesized 2H-TaS$_2$ with the flux method using the flux in which alkali metal atoms were included, and tried to intercalate alkali metal ions in 2H-TaS$_2$. We found that potassium was intercalated during the single crystal growth with the flux method using NaCl/KCl flux.

2. Results

The single crystals of 2H-TaS$_2$ were synthesized with flux method. In this study, the used flux were 1:1 mixture of NaCl powder (Kojyundo Chemicals Co. Ltd., 99.99%) and KCl powder (Kojyundo Chemicals Co. Ltd., 99.99%). In the following, we call this mixture as NaCl/KCl. The mixture of Ta (Kojyundo Chemicals Co. Ltd., 99.9%) and S (Kojyundo Chemicals Co. Ltd., 99.99%) with the nominal composition of TaS$_2$ (1g) and NaCl/KCl flux (5g) was sealed in a vacuumed quartz tube. The
tube was heated to 900°C for 10 hours, kept at 900°C for 12 hours, cooled to 650°C at a rate of 1°C by 1 hour, kept at 630°C for 48 hours, and then cooled in furnace to the room temperature. After this thermal process, the flux was removed from the sample by washing with distilled water. We also synthesized single crystals with chemical vapor transport (CVT) method for comparison.

The compositions of the obtained sample were measured by EDX. Table 1 shows the results of EDX measurements at the several points in the flux grown single crystal. The amount of Ta and S in the single crystal almost accorded with the composition of TaS$_2$. In addition to the constituent elements of TaS$_2$, the alkali metal ions in the flux were included. The amount of the alkali metal ions was 10% at rate of Ta at most. The amount of potassium ion is much larger than that of sodium ion and most of the included alkali metal ion is potassium ion.

|     | Ta [At %] | S [At %] | Na [At %] | K [At %] | Cl [At %] |
|-----|-----------|----------|-----------|----------|-----------|
| No.1| 33.62     | 64.15    | 0.28      | 1.95     | 0         |
| No.2| 33.89     | 63.37    | 0.58      | 2.16     | 0         |
| No.3| 33.21     | 63.82    | 0.52      | 2.45     | 0         |
| No.4| 33.11     | 63.36    | 0.79      | 2.74     | 0         |
| No.5| 29.83     | 67.64    | 0.37      | 2.16     | 0         |
| average | 32.73 | 64.47   | 0.51      | 2.29     | 0         |

Table 1 The composition (At %) of the obtained single crystal 2H-TaS$_2$ synthesized by the flux method using NaCl/KCl flux

Next, the structure was examined by XRD. XRD patterns of the single crystals were corrected by a Rigaku X-Ray diffractometer with Cu-Kα radiation using $\theta$ – 2$\theta$ method. Figure 1 shows XRD patterns of the obtained single crystal with the flux method and the single crystal synthesized with CVT method. The XRD patterns of the sample with the flux method was different from that of the sample with CVT method. The main feature has not been changed between two samples. However, the peaks split in (002) and (006). The split peaks are marked by arrows in Fig. 1(b). This change of XRD patterns is similar to that in the case of the intercalation of Cs hydrate in 2H-NbS$_2$ : Cs$_x$(H$_2$O)$_y$[NbS$_2$].[4]

![Figure 1 XRD pattern of the single crystal of 2H-TaS$_2$ synthesized with CVT method (blue line) and synthesized with flux method (red line) (a) From 5 degrees to 70 degrees (b) From 10 degrees to 20 degrees](image-url)
From this result, the hydrate of potassium ion was found to intercalate in the single crystals of $2H$-TaS$_2$ grown with the flux method with NaCl/KCl flux, though the amount of the alkali metal ions was 10% at rate of Ta at most.

Next, we measured the temperature dependence of the electrical resistance in the single crystals grown with CVT and flux method. The temperature dependence of the electrical resistance was measured down to 2.3 K with four terminals method. Figure 2 shows the temperature dependence of the electrical resistance normalized at 270 K. In $2H$-TaS$_2$ synthesized with CVT method, the CDW emerges at the temperature where the slope of the electrical resistivity changes abruptly ($T_{\text{CDW}}$) as reported previously [1]. $T_{\text{CDW}}$ is marked by an arrow in the figure. The single crystal synthesized with the flux method also showed the CDW transition at the close temperature to that in the pristine sample. Thus, no effect of intercalation was observed.

In previous reports on Ag intercalated $2H$-TaS$_2$, anomalies in electrical resistivity due to the appearance of superstructure has been reported [3]. However, no such anomalies were observed in our samples prepared with the flux method. Furthermore, the increase in superconducting transition temperature was not observed down to 2.3 K. These results can be understood as the amount of the intercalants is so small that the effect of the intercalation on the transport properties is negligible.

![Figure 2](image-url) Temperature dependence of electrical resistance normalized at 270 K of the samples synthesized with CVT method (blue line) and flux method. (red line) (a) From 2.3 K to 300 K (b) From 2.3 K to 6 K

Next, we performed microscopic investigation of the intercalation with scanning tunneling microscopy (STM). STM measurements were performed with a laboratory-built STM at 4.2 K in He gas on $2H$-TaS$_2$ synthesized with the flux method. The clean surface was prepared by cleaving the single crystal at 4.2 K in situ. A bias voltage was applied to the sample.

In the sample synthesized with the flux method, three kinds of superstructures were observed. Figure 3 (a - f) shows the typical STM images and their FFT images. $3a_0 \times 3a_0$ superstructure, shown in Fig. 3 (a), was observed in the most area. This superstructure is same as that in the CDW state on non-intercalated $2H$-TaS$_2$. In addition, $2a_0 \times 2a_0$ superstructure or the superposition of $2a_0 \times 2a_0$ and $\sqrt{3}a_0 \times \sqrt{3}a_0$ superstructures were observed in some places on the surface as shown in Fig. 3 (b, c). In the FFT image, $3a_0 \times 3a_0$ superstructure and $2a_0 \times 2a_0$ superstructure had the wave vector along the same direction as Bragg peaks of the topmost sulfur lattice. On the other hand, $\sqrt{3}a_0 \times \sqrt{3}a_0$ superstructure had the wave vector along the direction shifted by 30 degrees from the Bragg peaks. Such $2a_0 \times 2a_0$ structure or $\sqrt{3}a_0 \times \sqrt{3}a_0$ superstructure have been observed in Ag intercalated $2H$-TaS$_2$, and thought to be due to the ordering of intercalants. [3] Because such superstructures were observed
in our flux grown sample, this indicates that the intercalants exist in the sample and are ordered at least locally.

3. Discussion
In this study, the following results were obtained. First, the alkali metal ions are included as intercalants in the single crystals grown with the flux method using NaCl/KCl flux. In addition, potassium was found to be preferred to sodium. XRD measurements revealed that intercalant potassium ions are hydrate. The origin of water for hydrate may come from the humidity included in the flux and/or water used to remove residual flux from the samples. Second, because the amount of the intercalants was about 10% at rate of Ta at most as measured by EDX, intercalants were not distributed over the sample. In the previous reports, the CDW transition is vanish in Na-intercalated 2H-TaS2 [2]. Lack of the vanishing CDW transition in our sample also indicates the local distribution of the intercalants in the sample. Third, we found the intercalants were ordered locally from STM measurements.

These results revealed that, in the samples grown with the flux method using NaCl/KCl flux, alkali metal ions are intercalated locally and the intercalants are well ordered in the intercalated regions. In this study, the amount of the intercalants was about 10% at rate of Ta at most. This amount may be increased by tuning the crystal growth temperature or using other salts as the flux.
4. Summary
Single crystal of $2H$-TaS$_2$ was synthesized with the flux method using NaCl/KCl flux, motivated by finding new intercalation technique. Analysis of the composition and the structure by EDX measurements and X-Ray diffraction showed that the hydrate of potassium ion was intercalated in $2H$-TaS$_2$. The amount of the intercalants was 10 % at rate of Ta at most according to the analysis of the composition. The local intercalation was confirmed by the observation of the superstructures with the period of $2a_0 \times 2a_0$ or $\sqrt{3}a_0 \times \sqrt{3}a_0$ by scanning tunneling microscopy measurements.

References
[1] Wilson J A, DiSalvo F J, and Mahajan S 1975 Adv. Phys. 24 117
[2] Fang L, Wang Y, Zou PY, Tang L, Xu Z, Chen H, Dong C, Shan L, and Wen HH 2005 Phys. Rev. B 72 014534
[3] Scholz G A, and Frindt R F 1983 Phys. Stat. Sol. 79 483
[4] Paulus W, Katzke H, and Schöllhorn R 1992 J. Solid State Chem. 96 162