Available online at www.sciencedirect.com

ScienceDirect

Journal of Solid State Chemistry 181 (2008) 319–324

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

A new approach for the synthesis of layered niobium sulfide and restacking route of NbS_2 nanosheet

Kazuyoshi Izawa[a], Shintaro Ida[a,*], Ugur Unal[a], Tomoki Yamaguchi[a], Joo-Hee Kang[b], Jin-Ho Choy[b], Yasumichi Matsumoto[a]

[a] *Department of Nano Science and Technology, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan*

[b] *Center for Intelligent Nano-Bio Materials (CINBM), Division of Nanoscience and Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea*

Received 18 October 2007; received in revised form 23 November 2007; accepted 9 December 2007
Available online 14 December 2007

Abstract

We have developed a new process for the synthesis of a layered niobium sulfide that involves heating $K_4Nb_6O_{17} \cdot 3H_2O$ with a H_2S/N_2 gas mixture. It was confirmed that heating the starting layered oxide at 750 °C for 10 h under the gas flow yielded a highly crystalline, single-phase $K_{0.34}(H_2O)_{0.7}NbS_2$. The layered sulfide slabs had a large plate-like shape. Potassium ions in the interlayer of $K_{0.34}(H_2O)_{0.7}NbS_2$ could be exchanged with protons by stirring in 2 M H_2SO_4. It was found that the proton in the proton-exchanged form can be easily exchanged with other cations. The proton-exchanged form was exfoliated into NbS_2 nanosheets by ultrasonication in water. According to the atomic force microscopy (AFM) images, NbS_2 nanosheets had a thickness of around 4 Å, which roughly corresponded to the thickness of a single NbS_2 host layer. NbS_2 nanosheets could be restacked with the intercalation of Eu^{3+} or tetrabutylammonium ions by an electrostatic self-assembly deposition (ESD) technique.

Keywords: Layered niobium sulfide; Ion exchange; Intercalation; Exfoliation; Electrostatic self-assembly deposition

1. Introduction

2H–NbS_2 has a hexagonally packed layer composed of edge-sharing trigonal units with sulfur in the corners around a niobium atom. Each host layer exhibits weak van der Waals bonds in the interlayer [1]. Previous researches on 2H–NbS_2 involved intercalation of various organic molecules [2–4] and some inorganic species [5–10].

In general, a cation-intercalated layered niobium sulfide is prepared by the following multi-step process. First, 2H–NbS_2 is synthesized by heating a mixture of the powder of the respective elements repeatedly in quartz ampules at low pressure [1,2,4–7,9,11–13]. Next, for the intercalation of cations, the obtained powder is reheated in the presence of an alkali halide [6,7,13] or treated by an electrochemical process [4,10] or stirred in an aqueous solution of the corresponding cation [2]. Thus, preparation of the desired compound requires a complicated process and heating for a long time.

In this study, we have developed a new process for the synthesis of layered niobium sulfides. In this process, the layered niobium oxide intercalated with an alkali cation is heated under a H_2S/N_2 gas mixture. The alkali ion intercalated form of the layered niobium sulfide can be synthesized much more easily and rapidly than by the process described above. Thus, the desired layered sulfide is synthesized only through a single process. This is a promising technique for synthesizing new types of layered niobium sulfides with several combinations of various guest species.

It is very important to exfoliate a layered niobium sulfide exchanged with proton into single NbS_2 layers called nanosheets. The nanosheets produced by the exfoliation of a layered material are promising materials for the preparation of new functional materials, which can be

---

*Corresponding author. Fax: +81 96 342 3679.
E-mail address: s_ida@chem.chem.kumamoto-u.ac.jp (S. Ida).

0022-4596/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.12.002

fabricated by restacking the nanosheets with various cations. So far, we have prepared various restacked layered oxides by the electrostatic self-assembly deposition (ESD) technique, which can intercalate trivalent cations and large metal complexes [14–17]. In this report, restacked layered niobium sulfides were tried to prepare using NbS_2 nanosheets and cationic species by ESD technique.

The present study demonstrates that $K_{0.34}(H_2O)_{0.7}NbS_2$ can be directly synthesized by the sulfuration of $K_4Nb_6O_{17}\cdot 3H_2O$ through heating in a H_2S/N_2 gas mixture, where the intercalated K^+ plays an important role in maintaining the layered structure even at high temperature. We have observed mono-nanosheets with an atomic force microscopy (AFM). Moreover, NbS_2 nanosheets could be restacked into new layered sulfides with intercalated cationic species by the ESD technique.

2. Experimental section

$K_4Nb_6O_{17}$ was synthesized by a conventional solid-state reaction. Nb_2O_5 and K_2CO_3 were mixed at a molar ratio of 2.1:3 and heated at 1100 °C for 10 h in a Pt crucible [18]. The powder was washed with distilled water (Milli-Q reagent water system) under ultrasonication for 60 min to remove the excess amount of a potassium reagent. The obtained powder was heat-treated in a mixture of H_2S/N_2 for 10 h. The flow rate of H_2S was about 3.2 ml/min, and that of N_2 was 50 ml/min. During the heating process, the powder was always exposed to the gas mixture, which flowed continuously. The heating temperature ranged from 550 to 750 °C. After sulfuration, all powders were washed with distilled water to remove any impurities. The stability of the layered potassium niobium sulfide in air was confirmed by thermogravimetric differential thermal analysis (TG/DTA) and XRD pattern. The decomposition of the layered structure of the layered sulfide occurred at 510 °C and we have observed no change in the layered structure even after heat treatment at 400 °C for 5 h. Therefore, the layered potassium niobium sulfide will be relatively stable in air. However, the samples were always preserved in vacuumed desiccators to minimize the contact with air. In order to study the ion exchange and intercalation properties, the final product was treated in 2 M H_2SO_4 for 48 h under stirring to exchange the potassium ion in the interlayer. The yield of the proton exchange process, calculated based on the molar ratio, was confirmed to be almost 100%. Aqueous 0.01 M Eu^{3+} ($(CH_3COO)_3Eu$) and 0.02 M TBA^+ (tetrabutylammonium hydroxide (TBA^+OH^-)) solutions were used to replace the protons of $(H_3O^+)_xNbS_2$ in the interlayer. The protonated powder was exfoliated under ultrasonication for 60 min in distilled water in an ice bath. Subsequent centrifugation under 3000 rpm for 30 min yielded colloidal suspensions containing exfoliated nanosheets. Various cations were intercalated into the interlayer of NbS_2 nanosheets using the ESD technique. The ESD technique was performed by simply adding an aqueous solution of the cationic species into 50 ml of a colloidal solution containing NbS_2 nanosheets with a negative charge, as described below. The aqueous 0.01 M Eu^{3+} and 0.02 M TBA^+ solutions used contained the counter ion. Mixing of the cation and NbS_2 nanosheet solutions resulted in a precipitate of the layered niobium sulfide intercalated with the cations. The precipitate was rinsed with distilled water to remove excess non-intercalated cations and other undesired ions. The crystal structures and the orientations were analyzed by XRD (using Cu*Kα* radiation, Rigaku RINT-2500VHF). Before all measurements, the sulfurated samples were washed with distilled water to remove the potassium compounds adsorbed on the surface of the sulfurated powder. Thermal analyses of the powders were performed by TG/DTA (Seiko Instruments, TG/DTA6300). A quantitative analysis of metal ions was made by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Seiko Instruments, SPS7800). The sulfurated sample was dissolved in HF and HNO_3 to determine the K/Nb ratio. Fourier-transformed infrared spectra (FT-IR Perkin-Elmer) were obtained with the KBr technique. The morphology of layered materials was determined by scanning electron microscopy (SEM, JEOL, JSM-6060LV). The oxidation state of the powder was estimated by X-ray photoelectron spectroscopy (XPS, VG Scientific Σprobe) and Nb K-edge XANES spectra. The binding energy of elements was referenced to C 1*s* at 285.0 eV for XPS measurements. The reference sample used for the XANES measurements was NbS_2 (99%, High Purity Chemicals). Zeta potential measurement was carried out by an ELS-8000KW (Otsuka Electronics). The morphology and thickness of NbS_2 nanosheets were characterized by AFM (Molecular Imaging).

3. Result and discussion

Fig. 1 shows the XRD patterns of the starting material and the materials produced by heat treatment in a H_2S/N_2 gas mixture at various temperatures between 550 and 750 °C. The crystal structure of the starting material was confirmed to be $K_4Nb_6O_{17}\cdot H_2O$ ($P22_12_1$) [19] on the basis of its XRD pattern (see Fig. 1(a)). The color of all samples changed from white to black upon heat treatment. The XRD pattern shows that the dehydrated form of $K_4Nb_6O_{17}$ remained intact until 650 °C. Upon heat treatment at 750 °C, however, the $K_4Nb_6O_{17}$ phase disappeared and only the diffraction pattern of the layered material $K_x(H_2O)_yNbS_2$ ($P\bar{6}2c$) [6,10] was observed. That is, most of the oxygen bonded to Nb in the host layer was substituted with sulfur during the heat treatment in H_2S/N_2. The water in the formula was intercalated into the interlayer during the washing process following the heat treatment.

In general, the amount of intercalated guest species for any given layered material is constant. It is reported, however, that niobium sulfide can intercalate a varying amount of K^+ in the interlayer, and that the layered crystal

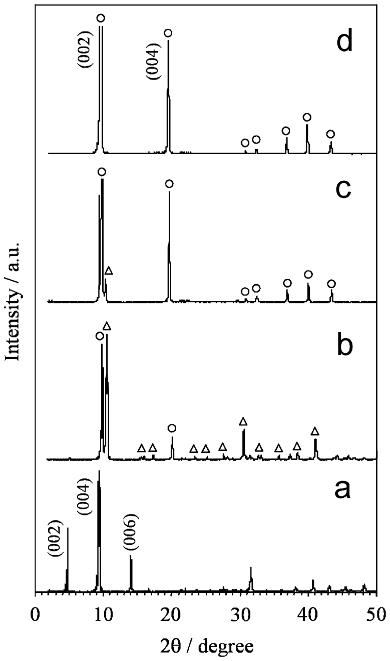

Fig. 1. XRD patterns of (a) $K_4Nb_6O_{17} \cdot 3H_2O$ as a starting material and of samples sulfurated at (b) 550 °C, (c) 650 °C, (d) 750 °C. The open circles and triangles indicate the $K_{0.34}(H_2O)_{0.7}NbS_2$ and $K_4Nb_6O_{17}$ anhydride peaks, respectively.

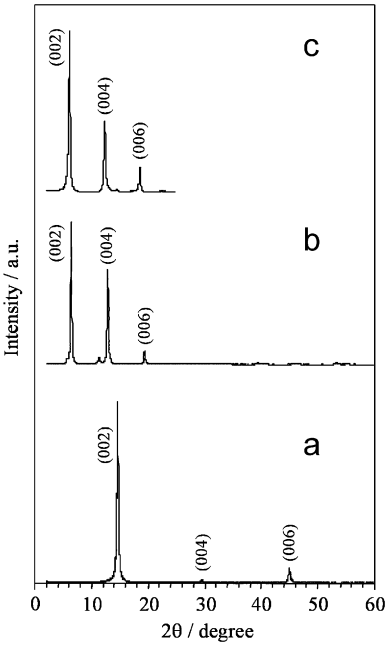

Fig. 2. XRD patterns of ion-exchanged and intercalated samples of layered niobium sulfide: (a) proton-exchanged sample, $(H_3O^+)_xNbS_2$, (b) EX-Eu^{3+}/NbS_2 and (c) EX-TBA^+/NbS_2.

structure changes depending on the amount of K^+ in the interlayer [10]. In the case of $K_x(H_2O)_yNbS_2$, diffraction peaks appear at (0 0 8) and (0 0 1 0) for $x > 0.24$. The K/Nb ratio of the niobium sulfide was analyzed through an ICP measurement. According to this detailed analysis, the atomic ratio was K/Nb $\approx$ 0.34. That is, the amount of potassium decreased from K/Nb = 0.67 (in the starting material) to 0.34 upon sulfuration. In addition, the TG/DTA analysis showed a mass decreasing in the range from room temperature to 200 °C due to the release of intercalated water. Since the total decreasing ratio was about 9.74%, the y value in $K_x(H_2O)_yNbS_2$ was estimated to be about 0.7. From above results, the chemical formula was determined to be $K_{0.34}(H_2O)_{0.7}NbS_2$.

We have also examined the preparation of a layered niobium sulfide using the proton-exchanged form of $K_4Nb_6O_{17} \cdot 3H_2O$ as a starting material, in which most of the K^+ were replaced by H_3O^+. The proton-exchanged form was sulfurated by 10 h heat treatment at 750 °C. This reaction did not produce any highly crystalline NbS_2 layered single phase. It is known that alkali ions in the interlayers of a layered structure contribute to the thermal stability of the structure, and that the proton-exchanged form decomposes easily at low temperature [20]. In the present case, as a result of the lack of K^+ in the interlayer due to the proton exchange, the layered structure decomposed easily. Thus, K^+ in the interlayer plays an important role in maintaining the layered structure in this new sulfuration process. In all samples synthesized hereafter, $K_4Nb_6O_{17} \cdot 3H_2O$ was heated with H_2S/N_2 gas at 750 °C.

We have also studied the ion-exchange and intercalation properties of the present proton-exchanged niobium sulfide ($(H_3O^+)_xNbS_2$). Fig. 2(a) shows the XRD pattern of the proton-exchanged form ($(H_3O^+)_xNbS_2$) prepared from $K_{0.34}(H_2O)_{0.7}NbS_2$. The d value of $(H_3O^+)_xNbS_2$ was estimated to be 6.0 Å from the diffraction peak at 14.7°. The thickness of the non-intercalated NbS_2 host layer is calculated to be 3.1 Å from its crystal structure [2]. Thus, the distance of the interlayer space was estimated to be 2.9 Å, which is close to the size of H_3O^+. Fig. 2(b) and (c) show the XRD diffraction patterns of the cation-exchanged samples, which were prepared by stirring $(H_3O^+)_xNbS_2$ in the Eu^{3+} or TBA solutions for 10 h. The presence of Eu^{3+} in the exchanged samples was confirmed by ICP measurement. On the other hand, the presence of TBA was confirmed by FT-IR measurement, because the C–H stretching bands depend on TBA which were observed at 2865 and 2958 cm^{-1}. The Eu/Nb ratio of the Eu^{3+}-exchanged sample (EX-Eu^{3+}/NbS_2) was 0.17. It is also confirmed that $K_{0.34}(H_2O)_{0.7}NbS_2$ of K^+ can be exchanged the Eu^{3+} with the almost same Eu/Nb ratio. These results indicate that cation exchange is very easy for the prepared layered niobium sulfide. It is considered that the difference between the theoretical ratio (Eu/Nb = 0.11, calculated based on the charge balance) and experimental one might be caused by the surface-adsorbed Eu^{3+} cation. The amount of Eu^{3+} might contain not only the intercalated Eu^{3+} but also adsorbed one on the NbS_2 surface. In addition, Eu^{3+} can be intercalated with NbS_2 nanosheets by an ESD, as described below. According to the XRD patterns, the interlayer distance (10.7 Å) of

EX-Eu^{3+}/NbS_2 is much larger than that of ESD-Eu^{3+}/NbS_2 (6.0 Å). This is based on higher content of intercalated water molecules for the former sample than the latter sample. According to the TG/DTA analysis of both samples, mass decreasing was observed from room temperature to 280 °C due to release intercalated water molecules. Since the total decreasing ratio was about 27.77%, the value of z in $Eu(H_2O)_zNbS_2$ (EX-Eu^{3+}/NbS_2) was estimated to be about 2.4. On the other hand, z-value for ESD-Eu^{3+}/NbS_2 was calculated to be about 1.4 from the mass decrease.

Fig. 3 shows the SEM images of $K_{0.34}(H_2O)_{0.7}NbS_2$ before and after proton exchange. $K_{0.34}(H_2O)_{0.7}NbS_2$ was plate-like with an average size of 50 µm, while $(H_3O^+)_xNbS_2$ was a foil-like thin sheet.

The oxidation states of Nb and S in $K_{0.34}(H_2O)_{0.7}NbS_2$ and the proton-exchanged form, $(H_3O^+)_xNbS_2$, were estimated by XPS analysis, as shown in Fig. 4. Both sulfurated samples had several oxidation states of Nb, whose spectrum can be resolved into three components with the oxidation states of +5, +4, $+4-\delta$. The oxidation state of Nb(+5) is determined from the binding energies of Nb $3d_{3/2}$ at 210.5 eV and Nb $3d_{5/2}$ at 207.7 eV, which are governed by the oxidation of the powder surface. The presence of Nb(+4) is confirmed from the peaks of Nb $3d_{3/2}$ at 206.8 eV and Nb $3d_{5/2}$ at 204.1 eV [21]. Finally, the peaks of Nb $3d_{3/2}$ at 206.0 eV and Nb $3d_{5/2}$ at 203.3 eV indicate the presence of the oxidation state of Nb($+4-\delta$). The presence of the oxidation state of Nb($+4-\delta$) is maintained by the intercalation of cationic species bringing about charge balance. Since on the XPS spectra of S 2p, the main peaks of S $2p_{3/2}$ are observed around 161 eV, the oxidation state of S is a "−2" in both samples [22], and the spectra were scarcely changed by proton exchange. On the other hand, no K 2p peaks were observed for the proton-exchanged sample. According to the quantitative

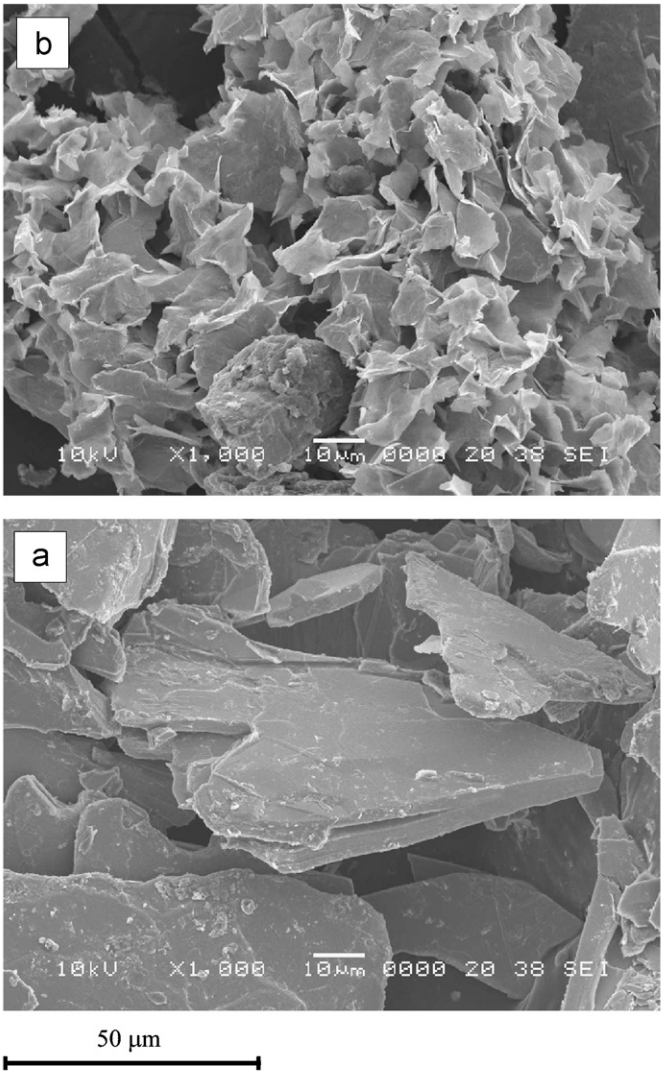

Fig. 3. SEM images of (a) the $K_{0.34}(H_2O)_{0.7}NbS_2$ sample obtained by sulfuration at 750 °C and (b) its proton-exchanged sample, $(H_3O^+)_xNbS_2$.

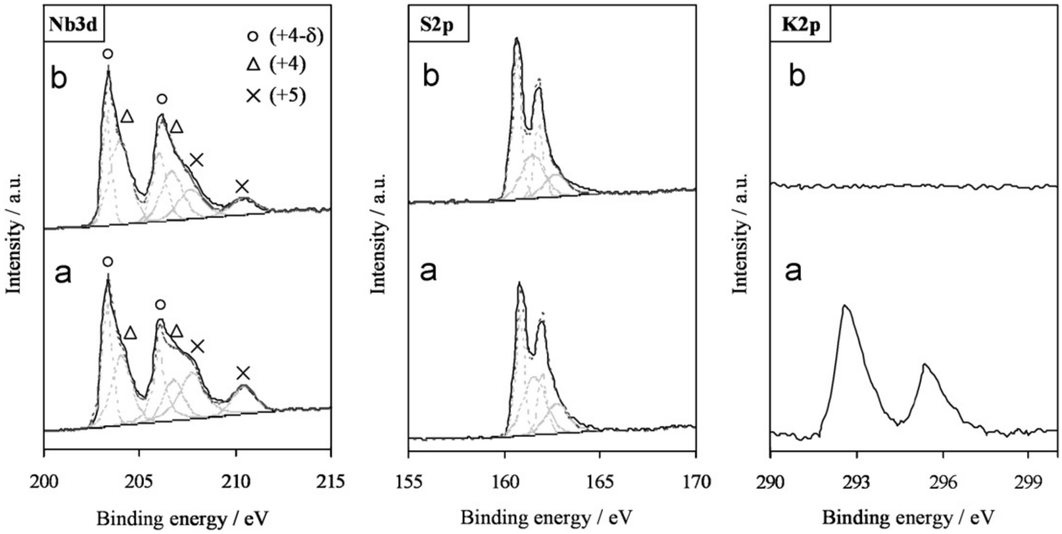

Fig. 4. XPS spectra for Nb 3d, S 2p and K 2p of (a) the $K_{0.34}(H_2O)_{0.7}NbS_2$ sample obtained by sulfuration at 750 °C and (b) its proton-exchanged sample, $(H_3O^+)_xNbS_2$. The oxidation states of Nb, $+4-\delta$, +4 and +5, are denoted by open circles, open triangles and crosses, respectively.

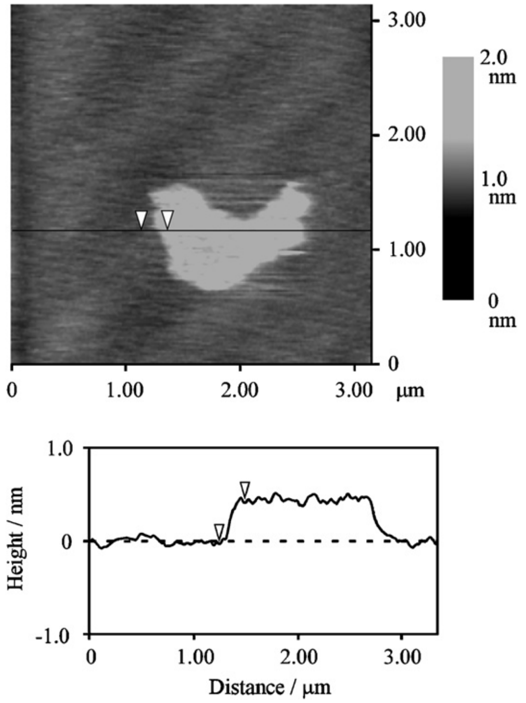

Fig. 5. AFM image of NbS_2 nanosheet exfoliated from the proton-exchanged sample, $(H_3O^+)_xNbS_2$.

analysis by XPS, the Nb/S atomic ratio scarcely changed during the proton exchange reaction. That is, the proton exchange reaction was successfully carried out without compositional change in the host NbS_2.

In order to estimate the oxidation state of Nb in the bulk, we examined Nb–K edge XANES measurement. The both absorption edge of $K_{0.34}(H_2O)_{0.7}NbS_2$ and $(H_3O^+)_xNbS_2$ exhibits a lower shift compared with the NbS_2 reference sample. The result indicates that intercalated cations (K^+, H_3O^+) caused the reduction of Nb (the oxidation state of Nb is $+4-\delta$). This result agrees with the XPS results mentioned above.

NbS_2 host layers were exfoliated by ultrasonication of the aqueous suspension of $(H_3O^+)_xNbS_2$. Fig. 5 shows the AFM image of the NbS_2 nanosheet observed on a mica substrate. The sheet thickness was about 4 Å, which is slightly larger than the calculated value for an NbS_2 host mono-layer (3.1 Å) [2]. Since pure water is used as solvent during exfoliation, water molecules may be adsorbed between or on NbS_2 nanosheet and the mica substrate, which would cause the observed deviation from the calculated value. Consequently, NbS_2 host layers are successfully exfoliated into single layers (nanosheets). It is already reported that NbS_2 was exfoliated to single layers treated by ultrasonication in water. However, according to TEM measurement, the thickness of exfoliated platelets was estimated to be 12 Å which is much thicker than the thickness of NbS_2 single host layer (3.1 Å). Probably, the NbS_2 platelets consist of a few nanosheets obtain in Ref. [11]. Anyhow, we clearly confirmed that NbS_2 mono-nanosheet was prepared by the present process.

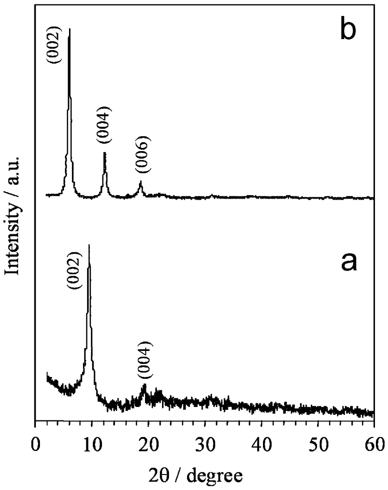

Fig. 6. XRD patterns of restacked samples of (a) ESD-Eu^{3+}/NbS_2 and (b) ESD-TBA^+/NbS_2.

According to the zeta potential measurement of the suspension, the NbS_2 nanosheets were negatively charged (−25.7 mV at pH 7). Thus, we tried to restack NbS_2 nanosheets with cationic species by using the ESD technique. Fig. 6 shows the XRD patterns of ESD-Eu^{3+}/NbS_2 and ESD-TBA^+/NbS_2. The ESD-Eu^{3+}/NbS_2 sample showed diffraction peaks at 9.7° and 19.5°, which are the first and second basal reflections of the restacked layered sulfide, respectively. The *d* value of the first reflection is calculated to be 9.1 Å, and thus the interlayer distance is found to be 6.0 Å because the thickness of the NbS_2 mono-layer is 3.1 Å. The interlayer distance corresponds to the size of hydrated Eu^{3+} intercalated in a layered titanate by the ESD technique [14]. The Eu/Nb ratio was 0.15 according to ICP analysis, indicating that the chemical formula of the restacked layered sulfide is $Eu_{0.15}(H_2O)_{1.4}NbS_2$. In addition, the layered sulfide intercalated with TBA molecules showing three diffraction peaks at 6.1°, 12.3° and 18.7° can be easily prepared by the restacking route. The interlayer distance was calculated to be 11.3 Å from the above diffraction peaks. This value reflected that both water and TBA molecules were intercalated. Thus, we have succeeded in preparing layered niobium sulfides intercalated with various cationic species by the ESD technique.

Fig. 7(a)–(d) show a flow chart, which summarizes a series of processes producing NbS_2 nanosheets from the starting niobium layered oxide material as described above. The procedure we proposed will lead to prepare a new layered niobium sulfide as quickly as possible.

4. Conclusion

We have developed a new process for the synthesis of a layered niobium sulfide intercalated with various cations. The process involves the heat treatment of $K_4Nb_6O_{17} \cdot 3H_2O$ with a H_2S/N_2 gas mixture. Using this

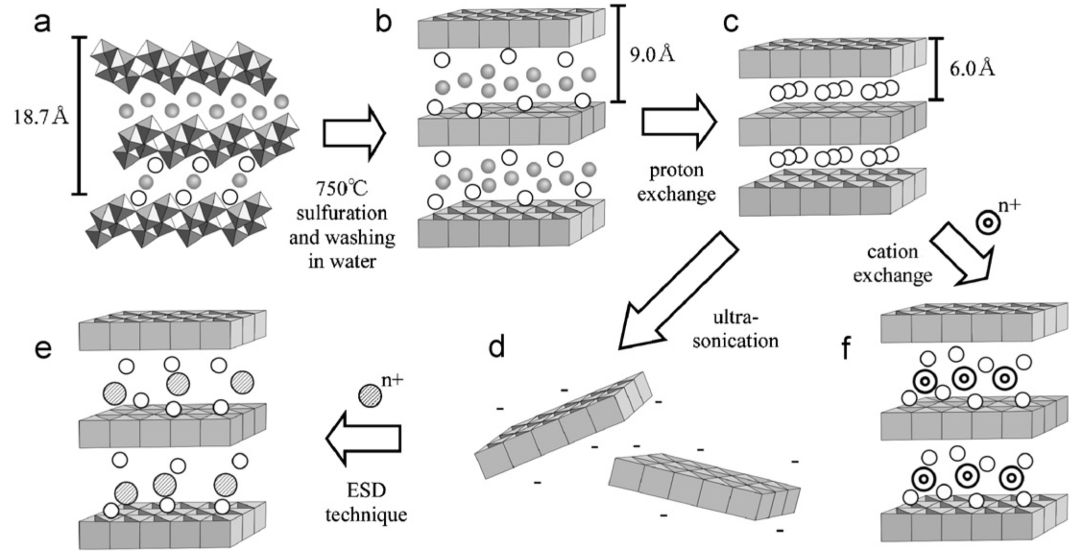

Fig. 7. A flow chart of the new process for the synthesis of new layered niobium sulfides, nanosheets and restacked layered sulfide: (a) $K_4Nb_6O_{17} \cdot 3H_2O$, (b) $K_{0.34}(H_2O)_{0.7}NbS_2$, (c) $(H_3O^+)_xNbS_2$, (d) NbS_2 nanosheets, (e) and (f) new layered niobium sulfides intercalated with various cations. Open and closed circles denote H_3O^+ or water molecules and K^+, respectively. Diagonal and double circles represent various cations.

process, we can prepare a single-phase, highly crystalline layered niobium sulfide material intercalated with K^+ cations simply by heating. Thus, it is a much simpler and a shorter process compared with conventional techniques. In this new sulfuration process, K^+ in the interlayer of the starting layered oxide plays an important role in maintaining the layered structure. The powder obtained was identified to be $K_{0.34}(H_2O)_{0.7}NbS_2$ by XRD, ICP and TG/DTA measurements. According to the SEM images and XRD patterns, the proton-exchanged form, $(H_3O^+)_xNbS_2$, which was obtained by stirring in 2 M H_2SO_4, retained the lamellar structure. Protons in the $(H_3O^+)_xNbS_2$ sample were easily exchanged with several cations. NbS_2 nanosheets were prepared by ultrasonicating in an aqueous suspension of $(H_3O^+)_xNbS_2$. The AFM image clearly indicated that the layered niobium sulfide was exfoliated into NbS_2 mono-nanosheet. We also succeeded in preparing a restacked layered niobium sulfide composed of Eu^{3+}/NbS_2 and TBA^+/NbS_2 by the ESD technique.

Acknowledgments

This work was supported by a grant-in aid for Scientific Research (no. 440, Panoscopic Assembling and high Ordered Functions for Rare Earth Materials, and no. 16080215) from the Ministry of Education, Culture, Sports, Science and Technology, and the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.12.002.

References

[1] F. Jellinek, G. Brauer, H. Müller, Nature 185 (1960) 376–377.
[2] Y. Kanzaki, M. Konuma, O. Matsumoto, J. Phys. Chem. Solids 41 (1980) 525–529.
[3] Y. Nakamuta, T. Watanabe, R. Aoki, Synth. Met. 6 (1983) 105–109.
[4] F. Wypych, M.A.B. Gomes, I. Denicoló, L.B. Adad, J. Electrochem. Soc. 143 (1996) 2522–2527.
[5] W.P.F.A.M. Omloo, F. Jellinek, J. Less-common Met. 20 (1970) 121–129.
[6] H.A. Graf, A. Lerf, R. Schöllhorn, J. Less-common Met. 55 (1977) 213–220.
[7] A. Lerf, R. Schöllhorn, Inorg. Chem. 16 (1977) 2950–2956.
[8] B.H. Chen, B. Eichhorn, J.L. Peng, R.L. Greene, J. Solid State Chem. 103 (1993) 307–313.
[9] H. Katzke, Z. Kristallogr. 217 (2002) 127–130.
[10] H. Katzke, Z. Kristallogr. 217 (2002) 149–154.
[11] C. Liu, O. Singh, P. Joensen, A.E. Curzon, R.F. Frindt, Thin Solid films 113 (1984) 165–172.
[12] R. Schöllhorn, H. Meyer, Mater. Res. Bull. 9 (1974) 1237–1246.
[13] R. Schöllhorn, A. Lerf, J. Less-common Met. 42 (1975) 89–100.
[14] Y. Matsumoto, U. Unal, Y. Kimura, S. Ohashi, K. Izawa, J. Phys. Chem. B 109 (2005) 12748–12754.
[15] K. Izawa, T. Yamada, U. Unal, S. Ida, O. Altuntasoglu, M. Koinuma, Y. Matsumoto, J. Phys. Chem. B 110 (2006) 4645–4650.
[16] S. Ida, K. Araki, U. Unal, K. Izawa, O. Altuntasoglu, C. Ogata, Y. Matsumoto, Chem. Commun. (2006) 3619–3621.
[17] U. Unal, S. Ida, K. Shimogawa, O. Altuntasoglu, K. Izawa, C. Ogata, T. Inoue, Y. Matsumoto, J. Electroanal. Chem. 595 (2006) 95–102.
[18] T. Nakato, D. Sakamoto, K. Kuroda, C. Kato, Bull. Chem. Soc. Jpn. 65 (1992) 322–328.
[19] K. Nassau, J.W. Shiever, J.L. Bernstein, J. Electrochem. Soc. 116 (1969) 348–353.
[20] U. Unal, D. Matsuo, Y. Matsumoto, M. Koinuma, J. Mater. Res. 17 (2002) 2644–2651.
[21] X. Wu, Y. Tao, X. Ke, J. Zhu, J. Hong, Mater. Res. Bull. 39 (2004) 901–908.
[22] R. St. C. Smart, W.M. Skinner, A.R. Gerson, Surf. Interface Anal. 28 (1999) 101–105.