

Mechanochemical Synthesis of Proton Conductive $M_3H(SO_4)_2$ ($M = Na, K, Rb$) Crystals

T. TEZUKA, Y. YAMASHITA, A. HAYASHI, K. TADANAGA and M. TATSUMISAGO

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, Sakai, Osaka 599-8531 (Japan)

E-mail: t-tezuka@chem.osakafu-u.ac.jp

Abstract

$M_3H(SO_4)_2$ ($M = Na, K, Rb$) crystals, which are known to undergo superprotonic phase transition in the case of $M = K$ and Rb , were prepared *via* mechanochemical process from equimolar M_2SO_4 and $MHSO_4$. The phase transitions of $M_3H(SO_4)_2$ prepared by mechanical milling using a high energy ball mill apparatus were confirmed from DTA–TG and conductivity measurements, although the phase transition temperatures were slightly lower than that of $M_3H(SO_4)_2$ prepared *via* solution process. The $Rb_3H(SO_4)_2$ prepared by mechanical milling showed reproducible ionic conductivity of $1 \cdot 10^{-3}$ S/cm at 230 °C under dry N_2 atmosphere.

INTRODUCTION

A series of solid acids with hydrogen bonds such as $MHAO_4$ and $M_3H(AO_4)_2$, where $M = K, Rb, Cs, NH_4$ and $A = S, Se$, are known to undergo superprotonic phase transition and show high proton conductivity of around 10^{-2} S/cm above the phase transition temperature [1]. Attention is paid to these materials as an electrolyte of fuel cells because of their thermal stability and anhydrous proton conduction [2]. These crystals are usually prepared by slow evaporation of water from an aqueous solution containing adjusted amount of M^+ ion and H_2SO_4 .

On the other hand, mechanical milling technique is used as a preparation method for solid state ionic conductor, such as oxide ion conductive ZnO_2 based fluorite type solid solutions [3], lithium ion conductive amorphous material in the system Li_2S-SiS_2 [4] or $Li_2S-P_2S_5$ [5] and even proton conductive amorphous materials from aluminium hydrogen phosphates [6]. Aluminium hydrogen phosphates become amorphous by the mechanical milling, and the obtained powder shows higher proton conductivity by about 1–3 orders of magnitude than that of the original crystals [6]. It is also considered that formation of amorphous superprotonic solid acid would bring about higher conductivity as seen in $CsH-SO_4-SiO_2$ composites [7].

In the present study, we applied the mechanical milling technique to prepare the solid acids of $M_3H(SO_4)_2$ ($M = Na, K, Rb$) from $MHSO_4$ and M_2SO_4 and compared their thermal properties and conductivities with those of the solid acids prepared *via* solution process.

EXPERIMENTAL

The mixtures of $MHSO_4$ and M_2SO_4 ($M = Na, K, Rb$) powders with a molar ratio of $MHSO_4/M_2SO_4 = 1.0$ were mechanically milled at room temperature in an Ar filled glove box by a planetary ball mill apparatus (Fritsch Pulverisette 7) using zirconia pots (45 ml) with ten zirconia balls (10 mm in diameter): the milling periods of time were up to 5 h and a rotation speed was 370 rpm. X-ray diffraction (XRD) measurements ($CuK\alpha$) were performed using a diffractometer (M18XHF²²-SRA, Bruker AXS). Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were carried out with a heating rate of 10 °C/min using a Rigaku Thermo Plus 8120 under dry N_2 flow. Differential scanning calorimetry (DSC) measurements were carried out with a heating rate of 10 °C/min using a Parkin Elmer Pyris 1 DSC. The electric conductivities of the samples were determined by the impedance data using an

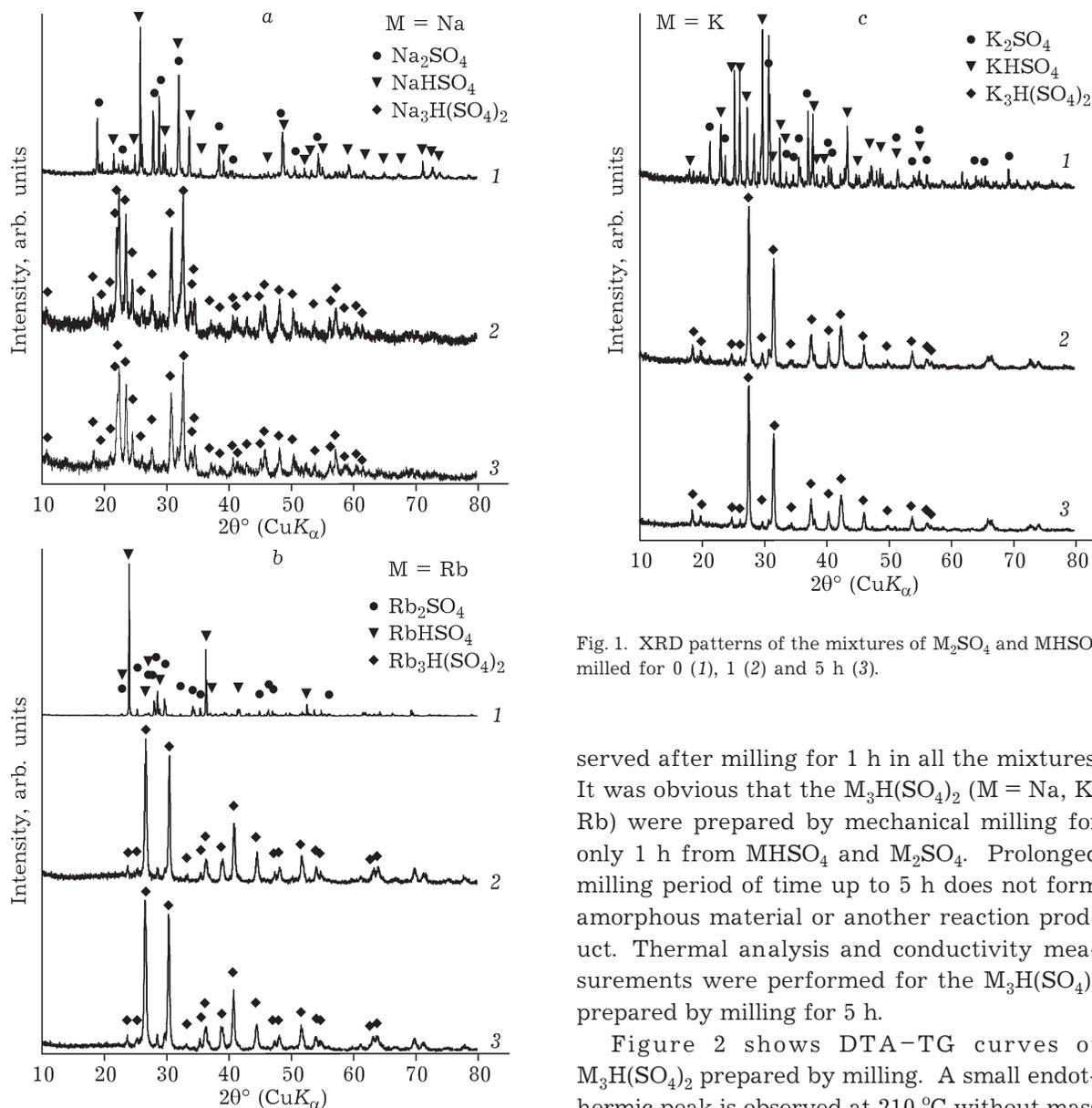


Fig. 1. XRD patterns of the mixtures of M_2SO_4 and $MHSO_4$ milled for 0 (1), 1 (2) and 5 h (3).

impedance analyzer (Solartron SI 1260) in a frequency range of 10 to $8 \cdot 10^6$ Hz. Gold as electrodes was sputtered on both sides of pelletized sample. Conductivity measurements were carried out in cooling process from 220–240 °C and following heating and cooling process after holding for 30 min at each temperature under dry N_2 atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the mixtures of M_2SO_4 and $MHSO_4$ milled for 0, 1 and 5 h. Peaks due to starting materials disappear and the peaks assigned to $M_3H(SO_4)_2$ are ob-

served after milling for 1 h in all the mixtures. It was obvious that the $M_3H(SO_4)_2$ ($M = Na, K, Rb$) were prepared by mechanical milling for only 1 h from $MHSO_4$ and M_2SO_4 . Prolonged milling period of time up to 5 h does not form amorphous material or another reaction product. Thermal analysis and conductivity measurements were performed for the $M_3H(SO_4)_2$ prepared by milling for 5 h.

Figure 2 shows DTA–TG curves of $M_3H(SO_4)_2$ prepared by milling. A small endothermic peak is observed at 210 °C without mass loss for $Na_3H(SO_4)_2$. $Na_3H(SO_4)_2$ prepared *via* solution process is reported to undergo phase transition from monoclinic to hexagonal phase, and the transition temperature is reported to be 240 [8] or 260 °C [9] by NMR study. Thus, the endothermic peak at 210 °C is probably due to the phase transition of $Na_3H(SO_4)_2$, although the thermal change is small (0.8 kJ/mol, which was estimated from DSC measurement) and appears at lower temperature than the reported values. An endothermic peak accompanied by mass loss starting at 260 °C indicates the decomposition of $Na_3H(SO_4)_2$.

In the case of $K_3H(SO_4)_2$, two endothermic peaks are observed at 184 and 195 °C, which were lower than the decomposition tempera-

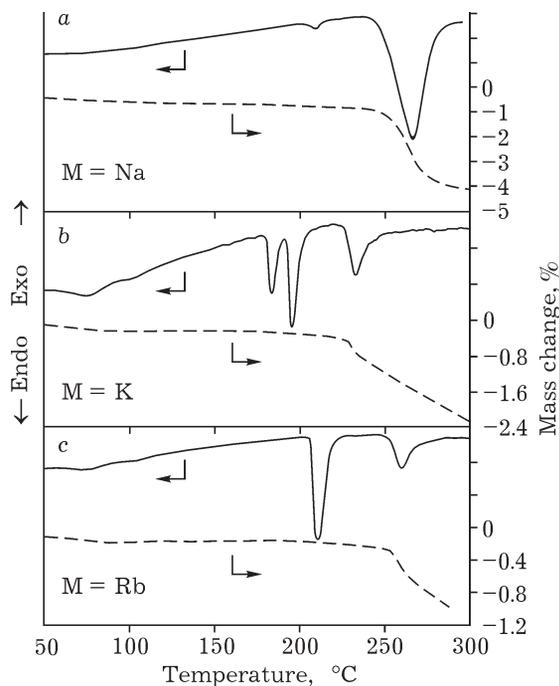


Fig. 2. DTA-TG curves of $M_3H(SO_4)_2$ prepared by milling on heating process.

ture of 233 °C. It is reported that two irreversible phase transitions of $K_3H(SO_4)_2$ prepared *via* solution process are found at 190 and 227 °C: the former peak corresponds to the transition from phase III to II and the latter phase II to I [10]. Therefore, the two endothermic peaks are caused by the sequential phase transition, though the second one is somewhat lower than the reported value. The transition enthalpies of $K_3H(SO_4)_2$ prepared by milling, which were estimated from DSC, were 5.0 kJ/mol for the former peak and 9.9 kJ/mol for the latter, respectively. The transition enthalpy for the former peak is smaller than that of $K_3H(SO_4)_2$ prepared *via* solution process (17.0 kJ/mol for the former and 7.4 kJ/mol for the latter [10]).

In the case of $Rb_3H(SO_4)_2$, an endothermic peak was observed at 210 °C, which corresponds to the irreversible phase transition at 213 °C for $Rb_3H(SO_4)_2$ prepared *via* solution process [11]. Decomposition of $Rb_3H(SO_4)_2$ prepared by milling started at 260 °C.

The phase transition temperatures are slightly lowered for some of $M_3H(SO_4)_2$ prepared by milling against that of $M_3H(SO_4)_2$ prepared *via* solution process. This tendency is similar to that observed in heterogeneous doping of SiO_2 to $CsHSO_4$ [7]. Lowering of phase transition tem-

perature in the $CsHSO_4-SiO_2$ composites is explained by the formation of defects at interface between $CsHSO_4$ and SiO_2 [7]. Thus, lower phase transition temperature in the solid acids prepared by milling indicates that they have more defects than the solid acids prepared *via* solution process owing to the difference of their preparation process.

Figure 3 shows the temperature dependence of conductivities of $M_3H(SO_4)_2$ prepared by milling. Conductivities of $M_3H(SO_4)_2$ prepared *via* solution process are also shown for comparison [10–12].

The conductivity at 230 °C of $Na_3H(SO_4)_2$ prepared by milling was $7 \cdot 10^{-5}$ S/cm, which was comparable with that of high-temperature phase of $Na_3H(SO_4)_2$ prepared *via* solution process [12]. During cooling, conductivities of $Na_3H(SO_4)_2$ prepared by milling were continuously decreasing and became less than 10^{-7} S/cm, which is the same order of magnitude for low-temperature phase of $Na_3H(SO_4)_2$ prepared *via* solution process at temperatures around 140 °C. No marked change in conductivity is observed at around 210 °C, where a small endothermic peak was observed on the DTA curve shown in Fig. 2, a.

The conductivity of $K_3H(SO_4)_2$ prepared by milling on the 1st cooling is comparable with that of the 1st heating of $K_3H(SO_4)_2$ prepared *via* solution process in the whole measured temperature range. The slope in conductivity changes at 200 and 180 °C on the 1st cooling of $K_3H(SO_4)_2$ prepared by milling. The changes of slope at 200 and 180 °C are similar to the changes at 210 °C on the 1st heating and at 175 °C on the 1st cooling of $K_3H(SO_4)_2$ prepared *via* solution process, respectively. Phase transitions of $K_3H(SO_4)_2$ prepared *via* solution process are reported to be irreversible, *i.e.*, phase transition from I to II' occurs at 223 °C and II' to III' at 185 °C [10]. In the case of $K_3H(SO_4)_2$ prepared by milling, however, it is expected that two kinds of crystals which undergo phase transition reversibly and irreversibly are present. This is supported by XRD pattern of $K_3H(SO_4)_2$ prepared by milling after conductivity measurement; the peaks assigned to phase III and III' were observed at room temperature. The phase transition behaviour of the $K_3H(SO_4)_2$ solid acid prepared by milling is dif-

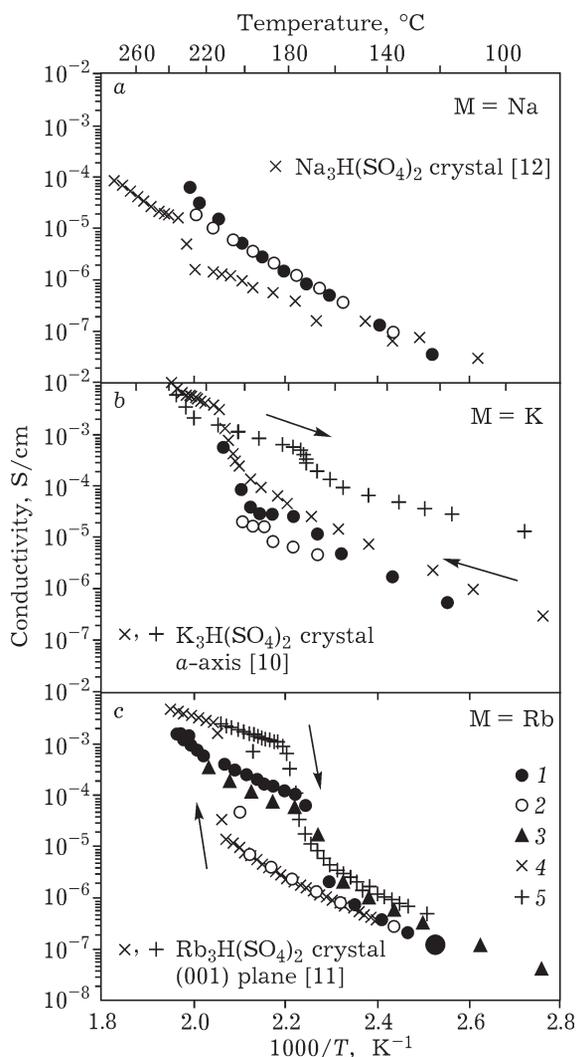


Fig. 3. Temperature dependence of conductivities of $M_3H(SO_4)_2$ prepared by milling and *via* solution process for comparison: 1–3 – denote the 1st cooling, 2nd heating and 2nd cooling of the samples prepared by milling, respectively; 4, 5 – the 1st heating and cooling of $M_3H(SO_4)_2$ prepared *via* solution process [10–12].

ferent from that of the $K_3H(SO_4)_2$ prepared *via* solution process at this point.

Temperature dependences of conductivity on the 1st cooling for the $Rb_3H(SO_4)_2$ prepared by milling and the one prepared *via* solution process are similar, although the conductivity of high-temperature phase is slightly lower. It is reported that the phase transition of $Rb_3H(SO_4)_2$ prepared *via* solution process was irreversible; the hysteresis in conductivity is observed in Fig. 3, c [11]. In the case of $Rb_3H(SO_4)_2$ prepared by milling, however, the temperature dependence of the 2nd heating is similar to that of the 1st heating of $Rb_3H(SO_4)_2$

prepared *via* solution process and reproducible conductivity of $1 \cdot 10^{-3}$ S/cm was obtained at 230 °C. This means that the phase transition of $Rb_3H(SO_4)_2$ prepared by milling would be reversible. In fact, the XRD patterns of $Rb_3H(SO_4)_2$ prepared by milling were almost the same before and after conductivity measurements. Slight lowering of the conductivity of $Rb_3H(SO_4)_2$ prepared by milling may be caused by low crystallinity compared with $Rb_3H(SO_4)_2$ prepared *via* solution process.

CONCLUSIONS

$M_3H(SO_4)_2$ ($M = Na, K, Rb$) crystals were prepared by mechanical milling for short milling periods of time from $MHSO_4$ and M_2SO_4 . $M_3H(SO_4)_2$ prepared by mechanical milling tended to show slightly lower phase transition temperature than that of $M_3H(SO_4)_2$ prepared *via* solution process. The temperature dependence of conductivity of $M_3H(SO_4)_2$ was affected by the difference in preparation technique between mechanical milling and solution process. No steep change in conductivity accompanied by phase transition was observed in the case of $M = Na$. Reproducible proton conductivity was obtained by reversible phase transition in the case of $M = Rb$.

The differences in thermal behaviour and ionic conductivity between $M_3H(SO_4)_2$ prepared by milling and *via* solution process may be caused by a presence of defects and difference in crystallinity.

REFERENCES

- 1 A. I. Baranov, *Crystallogr. Rep.*, 48, 6 (2003) 1012.
- 2 S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merie, *Nature*, 410 (2001) 910.
- 3 D. Michel, F. Faudot, E. Gaffet and L. Mazerilles, *J. Am. Ceram. Soc.*, 76, 11 (1993) 2884.
- 4 H. Morimoto, H. Yamashita, M. Tatsumisago and T. Minami, *Ibid.*, 82, 5 (1999) 1352.
- 5 A. Hayashi, S. Hama, H. Morimoto *et al.*, *Chem. Lett.*, 30 (2001) 872.
- 6 A. Matsuda, T. Tezuka, Y. Nono *et al.*, *Solid State Ionics*, 176 (2005) 2899.
- 7 V. G. Ponomareva, N. F. Uvarov, G. V. Lavrova and E. F. Hairetdinov, *Ibid.*, 90 (1996) 161.
- 8 M. Bose, K. Roy and A. Ghoshray, *Proc. Nucl. Phys. Solid State Phys. Sym.*, 24C (1981) 393.

- 9 Y. N. Moskvich, A. M. Polyakov and A. A. Sukhovskiy, *Ferroelectrics*, 81 (1988) 197.
- 10 C. R. I. Chisholm and S. M. Haile, *Solid State Ionics*, 145 (2001) 179.
- 11 A. Pawiowski and M. Poiomska, *Ibid.*, 176 (2005) 2045.
- 12 R. H. Chen, C. S. Shen and T. Fukami, *J. Phys. Chem. Solids*, 63 (2002) 203.