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Synthesis of Sulfide Solid Electrolytes from Li₂S and P₂S₅ in Anisole

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We report the liquid-phase synthesis of sulfide solid electrolytes from Li₂S and P₂S₅ using anisole at 200–300 °C under microwave radiation, in which β-Li₃PS₄ and Li₇P₃S₁₁ were directly precipitated in anisole in 30 min. Anisole afforded reasonable reactivity toward Li₂S and P₂S₅ to form β-Li₃PS₄ and Li₇P₃S₁₁ powders at 200–300 °C. Moreover, a Li₆PS₅Cl precursor solution was synthesized from a Li₃PS₄-anisole suspension by adding ethanol, Li₂S, and LiCl. The proposed synthesis using anisole is advantageous as a simple, short-time process and would be applicable for the production of all-solid-state batteries.

1. Introduction

The development of next-generation Li-ion secondary batteries is desired in various fields, including mobile phones, electric vehicles, and power storage systems.^{1–4} One urgent targets for next-generation of Li-ion secondary batteries is to improve their safety. The current Li-ion secondary batteries use organic electrolytes, which involve the risk of leakage and flammability. For this reason, all-solid-state lithium batteries, in which liquid electrolytes are replaced with flame-retardant inorganic solid electrolytes, have drawn considerable attention.

Sulfide solid electrolytes are attractive because of their high ion conductivity, which in some cases is comparable to that in liquid electrolytes.^{5–7} In addition, the good ductility of sulfide solid electrolytes is advantageous for producing all-solid-state batteries because the resistance between grain boundaries can be greatly reduced by only cold pressing.⁸ Among the sulfide solid electrolytes, Li₂S-P₂S₅ systems with different structures and compositions have been reported with a conductivity ranging between 10⁻⁶ and 10⁻² S cm⁻¹.^{9–11} For example, α-, β-, and γ-Li₃PS₄ each comprise different arrangement of PS₄³⁻.¹² Li₇P₃S₁₁ is composed of Li⁺, PS₄³⁻ and P₂S₇⁴⁻, and shows a higher ionic conductivity (1.7×10⁻² S cm⁻¹) than that of β-Li₃PS₄ (3.3×10⁻⁴ S cm⁻¹).^{6,13} In addition to the simple Li₂S-P₂S₅ system, Li₂S-P₂S₅-LiX (X:Cl, Br, I) is a well-known system for producing sulfide electrolytes with a high ionic conductivity (~10⁻³ S cm⁻¹), such as Li₆PS₅X.^{14,15}

Liquid-phase synthesis is a promising approach for producing sulfide electrolytes because it has the potential for large-scale synthesis and production of composite electrodes.^{16–19} β-Li₃PS₄ and Li₇P₃S₁₁ are synthesized in two steps: formation of Li₃PS₄-solvent complexes from Li₂S and P₂S₅ precursors in a solvent;

and their decomposition via post heat treatment in an inert atmosphere.^{13,20–28} Synthesis of the complexes generally takes more than several hours, and thus a number of studies have focused on shortening the synthesis time of Li₃PS₄-solvent complexes by ultrasonic and microwave irradiations.^{24,25,29} Li₆PS₅X halide-containing argyrodite can be synthesized by adding ethanol to dissolve all ion species, followed by heat treatment to remove the ethanol.²⁹

In liquid phase synthesis, selection of solvents is a key issue. Synthesis has been reported with solvents such as acetonitrile (ACN),^{22,24,25,27,28,30,31} THF^{20,25,32,33} and ethyl propionate.^{21,29} In the present study, we focused on anisole as a solvent for the synthesis of Li₂S-P₂S₅ based solid electrolytes. There are four reasons for our selection. First, anisole is an aprotic solvent. When protons are present in the solvent, there is a risk of toxic hydrogen sulfide generation through the exchange reaction between Li⁺ in Li₂S and H⁺ in the solvent. Second, P₂S₅ is easily dissolved in anisole.³⁴ It can be expected that the reaction will proceed uniformly and quickly in the liquid phase. Third, the electron-donating ability, which can be quantified by the donor number, is suitable for the synthesis reaction. While a donor number of 0, such as toluene, does not advance the reaction for the synthesis of electrolytes, a number of 14 or above, such as acetonitrile and ethanol, decomposes the solid electrolytes.³⁵ The donor number for anisole is 9,³⁶ which is suitable for the synthesis reaction without decomposing the synthesized electrolytes.³⁵ Fourth, anisole is a solvent that dissolves rubber-based binders.³⁵ A suspension of the electrode composite, in which the binder is dissolved, can be applied. A sheet-type all-solid-state battery with good uniformity can be constructed. Thus, the proposed liquid-phase synthesis will be easy to apply in the future fabrication of electrode composites.

Here, we proposed a new approach to synthesize various sulfide solid electrolytes using anisole and microwave irradiation. By irradiating with microwaves, the suspension of anisole and sulfide electrolytes was directly obtained from Li₂S and P₂S₅ in 30 min.

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2. Experimental

2.1 Synthesis of solid electrolyte

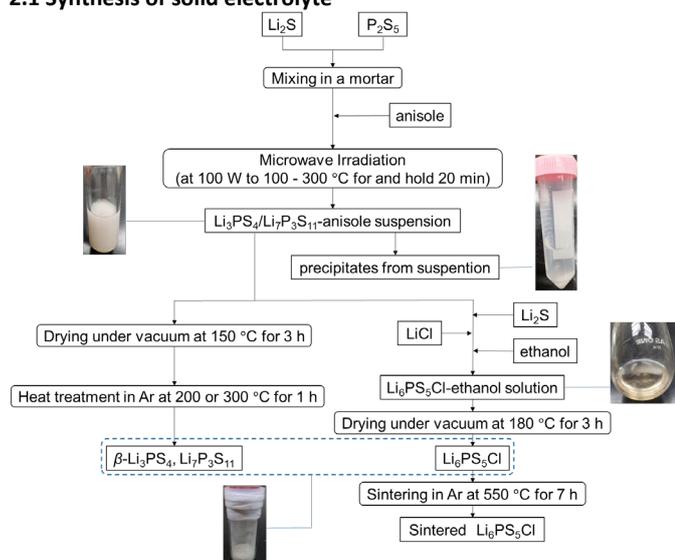


Figure 1. Synthesis process and obtained suspension, solution and powders. Precipitates from suspension, vacuumed powders and sintered $\text{Li}_6\text{PS}_5\text{Cl}$ were characterized.

Figure 1 shows overall synthesis scheme. For the synthesis of $\beta\text{-Li}_3\text{PS}_4$ and $\text{Li}_7\text{P}_3\text{S}_{11}$, the starting materials were Li_2S (Mitsuwa Chemical, 99.9%) and P_2S_5 (Aldrich, 99%), and anisole (Fujifilm Wako Pure Chemical) was used as a solvent. After heating by microwave irradiation, a white suspension was obtained. The suspension was centrifuged, and the obtained precipitates were evaluated. The solid electrolyte powders were obtained by drying under vacuum followed by heat-treatment. For $\text{Li}_6\text{PS}_5\text{Cl}$, Li_2S , LiCl (Aldrich, 99.9%) and ethanol (Fujifilm Wako Pure Chemical) were added to the suspension, producing transparent solution. This solution was dried under vacuum and powders were sintered. Detailed reagent and solvent amounts are summarized in the supplementary information (Table S1).

2.1.1. Synthesis of $\beta\text{-Li}_3\text{PS}_4$

Anisole was kept in the bottles with molecular sieve to remove water. Pristine Li_2S and pulverized Li_2S by planetary ball milling in a zirconium jar at 500 rpm for 12 hours were used. This ball-milled Li_2S were used only for $\beta\text{-Li}_3\text{PS}_4$ composition after heat treatment in order to examine the effect of the size of Li_2S particle on Li_2S residual (shown in Figure 5). These samples were treated under an Ar atmosphere to avoid moisture.

Powder of Li_2S (Mitsuwa Chemical, 99.9%) and P_2S_5 (Aldrich, 99%) at a molar ratio of $\text{Li}_2\text{S}:\text{P}_2\text{S}_5=75:25$ were mixed in a mortar and pestle. The powders and anisole were placed in a 20 mL borosilicate microwave vial (Anton Paar). Microwave irradiation (2.45 GHz) was applied to the mixture using a microwave reactor (Monowave 400, Anton Paar). The microwave output power was set to 100 W, and an infrared sensor was used to control the temperature. The microwave irradiation was

applied until the temperature reached 180–300 °C in 2–7 min (stirring rate was 1200 rpm). Liquid-phase synthesis above the boiling point (anisole:153.8 °C) was performed using a closed vial. After heating to the target temperature, the temperature was maintained for 20 min by adjusting the microwave output. A portion of the suspension was centrifuged, and the precipitates were evaluated. The obtained suspension was dried at 150 °C for 3 h under vacuum to remove the solvent, and the powder was subsequently heat-treated at 200 °C for 1 h.

2.1.2. Synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$

Powders of Li_2S without ball milling and P_2S_5 at a molar ratio of $\text{Li}_2\text{S}:\text{P}_2\text{S}_5=70:30$ were mixed. The powder and anhydrous anisole were heated to 260 °C by microwave irradiation and dried under vacuum under the same conditions as for $\beta\text{-Li}_3\text{PS}_4$. The powder was heat-treated at 300 °C for 1 h.

2.1.3. Synthesis of argyrodite, $\text{Li}_6\text{PS}_5\text{Cl}$

Powders of Li_2S without ball milling and P_2S_5 at a molar ratio of $\text{Li}_2\text{S}:\text{P}_2\text{S}_5=75:25$ were mixed. The powder and anhydrous anisole were heated to 220 °C by microwave irradiation under the same conditions as for $\beta\text{-Li}_3\text{PS}_4$. Then, Li_2S , LiCl , and super anhydrous ethanol were mixed into the obtained suspension (total molar ratio $\text{Li}_2\text{S}:\text{P}_2\text{S}_5:\text{LiCl} = 5:1:2$). This addition changed the suspension to a transparent solution. The solution was dried at 180 °C for 4 h under vacuum to remove the solvent to produce the sulfide electrolyte powder. A portion of the electrolyte powder was pressed under 360 MPa and sintered at 550 °C for 7 h in a sealed glass tube.

2.2 Characterization

X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (Miniflex 600, Rigaku). Diffraction data were collected in the 2θ range between 10° and 40° at a step size of 0.02°.

Raman spectra were measured using a Raman spectrometer (XploRA PLUS, Horiba Scientific) to identify structural units of the solid electrolyte samples. The excitation and intensity of the laser beam were 532 nm and 17 mW, respectively. The ionic conductivity of the pelletized samples was evaluated by electrochemical impedance spectroscopy (EIS). The solid electrolyte powders (30 or 80 mg) were pressed under 360 MPa (at room temperature) and two stainless steel (SS) disks were used as the current collectors. EIS was performed using an impedance analyzer (SI 1260, Solartron) in the frequency range of 0.1 Hz to 1 MHz at the amplitude of 10~30 mV.

3. Results and discussion

3.1 Reaction requirements under microwave irradiation

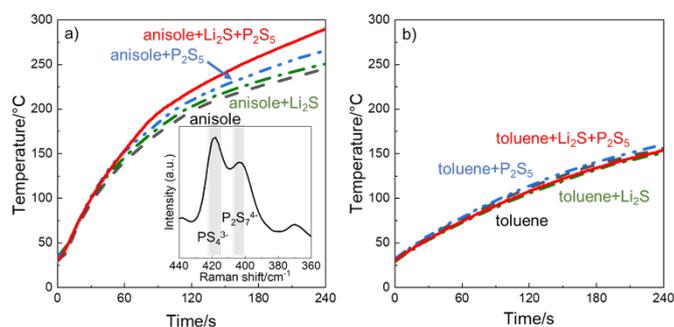
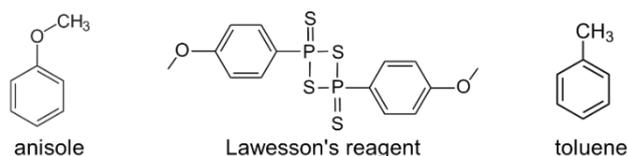


Figure 2. a) The temperature change in anisole during microwave irradiation and Raman spectrum after microwave irradiation (anisole+Li₂S+P₂S₅). b) Temperature change in toluene during microwave irradiation. The microwave output power was 100 W.



Scheme 1. Structural formulas of anisole, Lawesson's reagent and toluene.

To examine which chemical species absorb microwaves, we investigated the change in temperature of the starting materials under microwave irradiation. Figure 2a shows the temperature change during microwave irradiation. The temperature of all the samples, including anisole without Li₂S and P₂S₅, increased under microwave irradiation, indicating that anisole absorb microwave. While the temperature increase in anisole with Li₂S was comparable to that of anisole alone, the temperature increase in anisole with P₂S₅ was enhanced. Furthermore, the sample with both Li₂S and P₂S₅ in anisole showed the highest temperature. The temperature increase due to microwave irradiation was also confirmed in ACN and THF (Figure S1 a, b), which have been reported as useful solvents in the liquid-phase synthesis of Li₂S-P₂S₅ electrolytes. In contrast, no temperature difference was observed in toluene (Figure 2b). The number of donors in toluene is 0, and the synthesis reaction cannot proceed in toluene.³⁵ Even though microwave absorption is also affected by the dielectric constant of each solvent, the product of the chemical reaction between Li₂S and P₂S₅ would further absorb microwaves.

The inset of Figure 2a shows the Raman spectra of the precipitate after microwave irradiation of Li₂S and P₂S₅ in the anisole suspension and subsequent centrifugation at 8000 rpm for 10 min. Two Raman bands were centered on 419 and 403 cm⁻¹, attributed to PS₄³⁻ and P₂S₇⁴⁻ units,³⁷ and the precipitates were β-Li₃PS₄ or Li₇P₃S₁₁, as described in the next section. These ion species can enhance the temperature by Joule heating

under microwave irradiation, as suggested earlier. Furthermore, we examined the reactivity between Li₂S and Lawesson's reagents, which has similar components to P₂S₄-anisole (Scheme 1) and is soluble in anisole. In a similar experiment heated at 300 °C, the only product was Li₂S (Figure S2).

To investigate how microwave irradiation affects the products, the same synthesis was performed using a SiC ampule instead of a glass ampule. Because the SiC vial absorbs almost all the microwaves to generate Joule heat, the microwave cannot reach inside the sample. Thus, the reactions proceeded only by the thermal effect. Li₂S and P₂S₅ prepared at a molar ratio of 75:25 and anisole as a solvent were added to a 6 mL SiC vial, and microwave irradiation was performed at an output of 100 W for 4 min. No significant difference was observed in the Raman spectra of the products synthesized with glass and SiC (Figure S3). Given that the P-S unit was confirmed, as shown in Figure 2a, it can be seen that Li₂S and P₂S₅ reacted even when a SiC vial was used. Therefore, the reaction of Li₂S and P₂S₅ would dominantly proceed by the thermal effect, and microwave irradiation was effective for quick heating.

3.2 Synthesis of solid electrolytes: suspension and solution

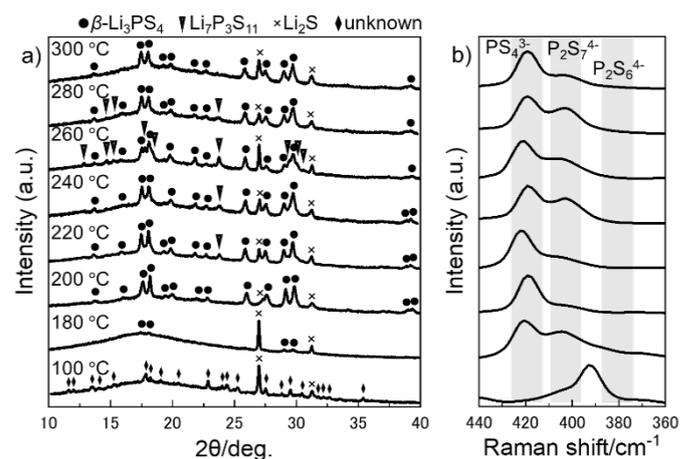


Figure 3. a) XRD pattern and b) Raman spectra of the precipitation (Li₂S:P₂S₅ = 75:25) after microwave irradiation.

Figure 3a shows the XRD patterns of the precipitates obtained by microwave irradiation at different temperatures. The precipitates were collected by centrifugation; thus, no further heat treatment was performed after microwave irradiation. The XRD pattern of the sample heated at 100 °C exhibited peaks assigned to Li₂S as well as additional unknown XRD peaks. The XRD pattern of the sample heated at 180 °C showed Li₂S and β-Li₃PS₄ peaks. The temperature range between 200 and 300 °C showed β-Li₃PS₄ as the main phase, while Li₇P₃S₁₁ was detected as a minor phase between 240 and 280 °C. The increase in the ratio of starting materials, Li₂S and P₂S₅, to anisole at heating at 220 °C increased the amount of Li₇P₃S₁₁ and Li₂S impurities (Figure S4).

Figure 3b shows the Raman spectra of the obtained precipitates after centrifugation, corresponding to the

conditions shown in Figure 3a. The Raman spectrum of the sample heated at 100 °C exhibited a Raman band centered at 393 cm^{-1} . This band is not attributed to PS_4^{3-} (420 cm^{-1}) or $\text{P}_2\text{S}_7^{4-}$ (405 cm^{-1}) units.³⁷ The Raman spectra of all samples heated above 100 °C exhibited a Raman band at approximately 420 cm^{-1} , attributed to PS_4^{3-} units, and an additional band at approximately 405 cm^{-1} , attributed to $\text{P}_2\text{S}_7^{4-}$ units in the heating temperature range of 240–280 °C.

Unknown peaks in the XRD pattern and the Raman shift to 393 cm^{-1} of the sample heated at 100 °C can be attributed to the complex of Li_3PS_4 and anisole. The formation of $\beta\text{-Li}_3\text{PS}_4$ in the samples heated at temperatures above 100 °C was confirmed by X-ray diffraction and Raman spectroscopy. The intensity of the Raman band attributed to $\text{P}_2\text{S}_7^{4-}$ units increased at the heating temperature range of 240–280 °C, which explain the additional formation of $\text{Li}_7\text{P}_3\text{S}_{11}$, as observed by X-ray diffraction.

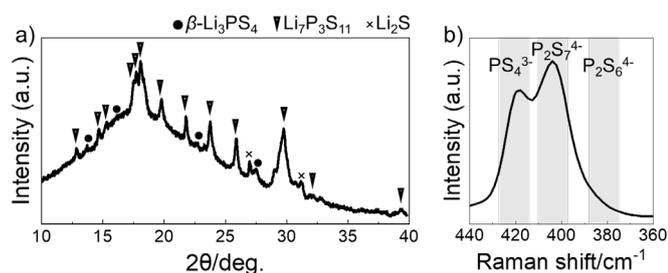


Figure 4. a) XRD pattern and b) Raman spectra of the solid electrolyte ($\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 70:30$). The suspension was heated at 260 °C by microwave irradiation.

The $\text{Li}_7\text{P}_3\text{S}_{11}$ suspension was synthesized in the same way as for the $\beta\text{-Li}_3\text{PS}_4$ suspension (Figure 3) using a heating temperature of 260 °C and a stoichiometric molar ratio of $\text{Li}_2\text{S}:\text{P}_2\text{S}_5 = 70:30$. Figure 4 shows the XRD pattern and Raman spectrum of the $\text{Li}_7\text{P}_3\text{S}_{11}$ suspension. The XRD pattern (Figure 4a) exhibited the formation of the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal phase; only minor additional XRD peaks corresponding to Li_2S were observed. The Raman spectrum (Figure 4b) exhibited two main bands at 420 and 405 cm^{-1} , assigned to PS_4^{3-} and $\text{P}_2\text{S}_7^{4-}$ units.

Figure 5 shows the XRD patterns of the solid electrolytes synthesized from anisole in the present study. After microwave irradiation, the solid electrolytes were dried under vacuum at 150 or 180 °C and subsequently heat-treated at a specific temperature, as described in Figure 1. The synthesized conditions are summarized in Table S1. $\beta\text{-Li}_3\text{PS}_4$ was synthesized from Li_2S with and without ball milling treatment. While ball-milled Li_2S produced single-phase $\beta\text{-Li}_3\text{PS}_4$, Li_2S without ball milling treatment brought about $\beta\text{-Li}_3\text{PS}_4$ with Li_2S impurity. Because ball milling treatment would decrease the particle size of Li_2S , the reaction, smaller particles with larger surface area enhance the reaction between Li_2S and P_2S_5 in anisole. $\text{Li}_7\text{P}_3\text{S}_{11}$ was precipitated as a major phase with a smaller amount of Li_2S . $\text{Li}_6\text{PS}_5\text{Cl}$ was obtained as a single phase and sintering at 550 °C enhanced the crystallinity. Various sulfide solid electrolytes can

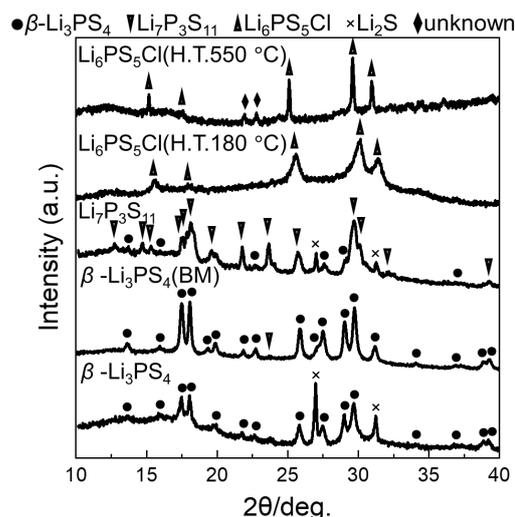


Figure 5. XRD patterns of the solid electrolytes after heat treatment in Ar or vacuum. BM: Ball-milled Li_2S .

be synthesized by a simple process using anisole for liquid-phase synthesis.

Figure 6 shows the Nyquist plots and Table 1 shows the ionic conductivity at room temperature of the prepared solid electrolytes ($\beta\text{-Li}_3\text{PS}_4$, $\text{Li}_7\text{P}_3\text{S}_{11}$, $\text{Li}_6\text{PS}_5\text{Cl}$). The ionic conductivities heated at 180–300 °C were in the range of 0.05–0.13 mS cm^{-1} . Even though further heat-treatment was necessary, $\text{Li}_6\text{PS}_5\text{Cl}$ pellet heated at 550 °C reached a higher conductivity of 2.1 mS cm^{-1} .¹⁸ Furthermore, we proved lithium-ion conducting nature of the synthesized $\text{Li}_7\text{P}_3\text{S}_{11}$ electrolyte by discharge-charge properties of the all-solid-state battery with the cathode composite composed of this synthesized $\text{Li}_7\text{P}_3\text{S}_{11}$ (Figure S5)

Compared with previous reports,^{20,24,33} the conductivities shown in table 1 tend to be slightly lower. The conductivity may be improved by completely removing any residual water, anisole, and hydrogen in the final product considering that $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte heated at 550 °C showed one-order higher conductivity than others. A recent work suggests that Li_2S residual which cannot be detected by XRD decreases the ionic conductivity of synthesized electrolytes.³⁸ Thus, further improvement of the conductivity may be achieved by complete the synthesis reaction.

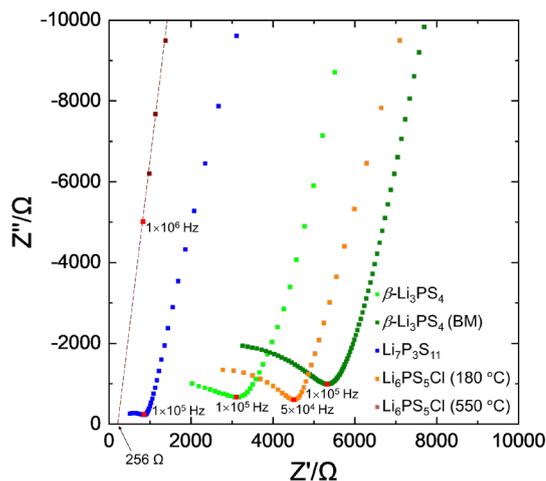


Figure 6. Room-temperature Nyquist plot of the prepared solid electrolyte after heat treatment in Ar or vacuum.

Table 1. Ionic conductivity of synthesized solid electrolyte at room temperature

Product	Microwave/°C	Heat treatment/°C	$\sigma/\text{mS cm}^{-1}$
$\beta\text{-Li}_3\text{PS}_4$	220	200	0.087
$\beta\text{-Li}_3\text{PS}_4(\text{BM})$	220	200	0.051
$\text{Li}_7\text{P}_3\text{S}_{11}$	260	300	0.13
$\text{Li}_6\text{PS}_5\text{Cl}$	220	180	0.070
$\text{Li}_6\text{PS}_5\text{Cl}$	220	550	2.1

As P_2S_5 dissolves in anisole at high temperatures (Figure S6), it is considered that dissolved P_2S_5 is involved in the reaction. In contrast, $\beta\text{-Li}_3\text{PS}_4$ was not obtained from Li_2S and Lawesson's reagent (which can be synthesized from P_2S_5 and anisole) instead of P_2S_5 , indicating that the reaction intermediate should not be Lawesson's reagent. Because unreacted Li_2S remained after the reaction to produce $\beta\text{-Li}_3\text{PS}_4$ or $\text{Li}_7\text{P}_3\text{S}_{11}$ under microwave irradiation (Figures 3 and 4), the reaction proceeded from the interface between the dissolved P_2S_5 species (but not Lawesson's reagent) and Li_2S particles. This is supported by enhanced reaction by using ball-milled Li_2S (Figure 5).

In the present study, we synthesized sulfide-based solid electrolytes by taking advantage of anisole with moderate nucleophilic aggression, having a donor number of 9. Although a reaction did not occur in toluene, having a donor number of 0, as a solvent,³⁵ it is clear that the solvent is involved in the reaction of Li_2S and P_2S_5 . The synthesis reaction proceeds in ACN (donor number is 14) to form $\beta\text{-Li}_3\text{PS}_4$ at 200 °C, but further heat treatment above 220 °C resulted in the decomposition of $\beta\text{-Li}_3\text{PS}_4$ electrolytes (Figure S7). Therefore, anisole has the advantage of high-temperature and short-time synthesis, where the reaction kinetics increase without an unfavorable decomposition reaction of $\beta\text{-Li}_3\text{PS}_4$.

4. Conclusions

We succeeded in synthesizing sulfide solid electrolytes, Li_3PS_4 , $\text{Li}_7\text{P}_3\text{S}_{11}$, and $\text{Li}_6\text{PS}_5\text{Cl}$ by rapidly heating under microwave irradiation using anisole as a solvent. The advantage of this process is the direct precipitation of solid electrolytes in a solvent, in contrast to other techniques that require a post-heating process to decompose complexes composed of Li_3PS_4 and solvents under an inert atmosphere. Moderate reactivity in anisole allows the synthesis of solid electrolytes at 200–300 °C in a short time. This proposed approach can simplify and shorten the synthesis process, and is promising for producing the components of all-solid-state batteries. These features are advantageous not only for industrial scaling-up but also for producing composite materials with electrode particles and binders. Research on the production of sheet-type batteries using this approach is currently ongoing.

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