

Combining cold sintering and Bi₂O₃-Activated liquid-phase sintering to fabricate high-conductivity Mg-doped NASICON at reduced temperatures

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ABSTRACT

The cold sintering process (CSP) and Bi₂O₃-activated liquid-phase sintering (LPS) are combined to densify Mg-doped NASICON (Na_{3.256}Mg_{0.128}Zr_{1.872}Si₂PO₁₂) to achieve high densities and conductivities at reduced temperatures. As an example, a cold-sintered specimen with the addition of 1.1 wt % Bi₂O₃ sintering additive achieved a high conductivity of 0.91 mS/cm (with ~96% relative density) after annealing at 1000 °C; this conductivity is >70% higher than that of a cold-sintered specimen without adding the Bi₂O₃ sintering additive, and it is >700% of the conductivity of a dry-pressed counterpart with the same amount of Bi₂O₃ added, all of which are subjected to the same heating profile. The highest conductivity achieved in this study via combining CSP and Bi₂O₃-activated LPS is > 1.5 mS/cm. This study suggests an opportunity to combine the new CSP with the traditional LPS to sinter solid electrolytes to achieve high densities and conductivities at reduced temperatures. This combined CSP-LPS approach can be extended to a broad range of other materials to fabricate the “thermally fragile” solid electrolytes or solid-state battery systems, where reducing the processing temperature is often desirable.

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1. Introduction

The development of sodium-ion batteries, with sodium being a much more abundant resource than lithium, attracts significant interests due to the high demand of large-scale energy storages, such as sustainable energy applications in power grids and electric vehicles [1–4]. However, serious safety issues, such as leakage and explosion risks, exist with the uses of flammable liquid electrolytes [5,6]. To overcome these safety issues, the solid-state sodium batteries were explored. Particularly, the research of solid-state sodium batteries with inorganic oxide solid electrolytes has attracted great attentions due to their potential benefits, including low costs, high stability (moisture/air stable), high energy density, and high safety [7–9].

The sodium-ion solid electrolytes are one of the key components of solid-state sodium batteries and it should have high durability and sodium ionic conductivity. Specifically, sodium (Na) superionic

conductor (NASICON) with the general formula of Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (0 ≤ x ≤ 3) was demonstrated as a promising sodium-ion solid electrolyte with a wide electrochemical window and high ion transference numbers [10–12]. The NASICON solid electrolytes are more air and moisture stable than some other electrolytes such as sulfides and the room-temperature total ionic conductivities of undoped NASICON are on the order 0.1 mS/cm [13–16]. More recently, several reports have showed that the addition of metal oxides, including Fe₂O₃, NiO, ZnO, Y₂O₃, Al₂O₃, TiO₂ and MgO, in NASICON materials can increase their conductivities [17–19]. As an example, Mg doped NASICON can exhibit a high room-temperature ionic conductivities of >1 mS/cm and a combined experimental and modeling study attributed the conductivity enhancement to the formation of conductive secondary (or interfacial) Na₃PO₄ phase at NASICON grain boundaries (GBs) [20].

However, the poor sinterability of the NASICON based materials limits their applications for solid-state sodium batteries. High sintering temperatures (typically ≥1200 °C) with prolonged durations are typically required to densify NASICON based solid electrolytes, which can cause the sodium and phosphorus evaporation and lead to NASICON decomposition [21–23], besides adding energy consumption and significant cost. It will also result in various

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compatibility and technical issues when co-sintering is used to fabricate the solid state batteries, including over-sintering and possible degradation of the active electrode materials as well as undesirable side reactions at the interface between solid electrolytes and electrodes [7,24]. Therefore, it is highly desirable to decrease the processing temperatures of the NASICON based materials to promote their applications in solid-state batteries.

On the one hand, an innovative sintering technology, namely cold sintering process (CSP), was recently developed by Randall and co-workers at Pennsylvania State University [25,26]. It can densify a variety of ceramic materials, including chlorides, carbonates, phosphates and oxides at low temperatures (<300 °C) in short durations (generally 15–60 min) [25,26]. The densification process is mainly caused by the assistance of the aqueous solutions under pressures (100–500 MPa) with a dissolution-precipitation process; in many cases, post-CSP annealing, typically at temperatures lower than the normal sintering temperatures, is still needed to achieve nearly full densities as well as improve properties [25,26]. Most recently, we applied CSP with post-CSP annealing to fabricate Mg-doped NASICON ($\text{Na}_{3.256}\text{Mg}_{0.128}\text{Zr}_{1.872}\text{Si}_2\text{PO}_{12}$) specimens; we achieved, e.g., ~82% density and ~0.5 mS/cm conductivity with post-annealing at as low as 800 °C, but the conductivity only increased moderately when the annealed temperature was further increased up to 1100 °C [27]. In this case, post-CSP annealing was found necessary to increase the ionic conductivities of cold-sintered specimens mainly via increasing their GB conductivities [27]. Berbano et al. also demonstrated that the $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) solid electrolytes could be densified at low temperatures by applying the CSP [28]. In addition, the feasibility of applying the CSP in fabricating solid-state batteries has been investigated and discussed [29].

On the other hand, the addition of Li_3PO_4 [30], LiBO_2 [31], Li_2O [32], Na_3BO_3 [33] and $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$ glass [13,15] with low melting points were found effective to promote the densification of solid electrolytes at low temperatures via the classical liquid phase sintering (LPS). Suzuki et al. reported that the NASICON-based solid electrolytes can be sintered at a low temperature of 700 °C by adding Na_3BO_3 to achieve ~0.1 mS/cm room-temperature ionic conductivity [24]. Recently, Lee et al. showed that the Bi_2O_3 sintering additive (with a low melting point of 820 °C) can be used to reduce the sintering temperature of the LATP via LPS while simultaneously enhance its ionic conductivity [34]. Yet, the effect of adding Bi_2O_3 sintering aid in the densification and conductivity of NASICON has not been investigated.

In this work, we first applied Bi_2O_3 -activated LPS to densify a Mg-doped NASICON ($\text{Na}_{3.256}\text{Mg}_{0.128}\text{Zr}_{1.872}\text{Si}_2\text{PO}_{12}$) for the first time to our knowledge. We successfully demonstrated that adding Bi_2O_3 can substantially enhance the density and conductivity at (but only) at 1100 °C. Subsequently, we combined CSP and Bi_2O_3 -activated LPS to densify the same Mg-doped NASICON, again for the first time to combine these two enhancing sintering techniques.

Notably, we showed that combining CSP and LPS can achieve higher densities and ionic conductivities than either CSP or LPS alone, at reduced temperatures. Thus, the success of this study opens up a new opportunity to fabricate solid-state electrolytes for solid-state batteries at reduced temperatures by combining CSP with LPS as a new processing route to reduce sintering temperature beyond that can be achieved by any single technology (CSP or LPS), which can be subsequently extended to a broad range of other “thermally fragile” solid electrolytes.

2. Experimental

2.1. Materials synthesis

The Mg-doped NASICON powder with the composition of

$\text{Na}_{3.256}\text{Mg}_{0.128}\text{Zr}_{1.872}\text{Si}_2\text{PO}_{12}$ was synthesized by a solid-state reaction method. The stoichiometric amounts of Na_2CO_3 (Fisher Chemical, 99.5%), MgO (Alfa Aesar, 99.95%), ZrO_2 (Fisher Chemical, Laboratory Grade), SiO_2 (Alfa Aesar, 99.9%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma Aldrich, 99.99%) were used as raw materials. The mixtures were milled in isopropyl alcohol by planetary ball milling for 24 h, dried in air at 85 °C for 12 h and then calcinated in an oven at 1150 °C for 5 h. The calcined powder was ground by hands with a mortar and pestle and then mixed with 1.1 wt % Bi_2O_3 (Sigma Aldrich, 99.999%) by ball milling in isopropyl alcohol for 48 h. For comparison, Bi_2O_3 -free Mg-doped NASICON ($\text{Na}_{3.256}\text{Mg}_{0.128}\text{Zr}_{1.872}\text{Si}_2\text{PO}_{12}$) powder was also prepared by using the same procedure.

2.2. Specimen preparation

30 wt % polyvinyl alcohol (PVA) solution was prepared by dissolving 2 wt % PVA powder in deionized (DI) water and added to Mg-doped NASICON powder (with and without 1.1 wt % Bi_2O_3 sintering additive) and then mixed by hands using mortar and pestle for 2–3 min; noting that this procedure was slightly different from a prior procedure for cold sintering NASICON [27] as we added PVA as binder here. PVA will be burnt out in the subsequent annealing. The prepared powder was then transferred into a ¼ inch die and a following pre-pressing step was applied by uniaxially pressing the die at 780 MPa at room temperature for 2 min. Finally, the cold-sintered specimens were prepared at 140 °C for 1 h at 780 MPa [27]. For comparison, dry-pressed specimens were also prepared by applying the identical pressure of 780 MPa (also for 1 h) at room temperature. The cold-sintered and dry-pressed specimens were subsequently annealed at 850–1200 °C for 6 h in a furnace with a heating rate of 5 °C/min.

2.3. Characterization

The specimen densities were calculated by the weights and dimensions and the theoretical density of 3.27 g/cm³ was adopted for NASICON. X-ray diffraction (XRD) experiments were carried out by using a Rigaku diffractometer with Cu K_α radiation. The microstructures of fractured surfaces were observed by scanning electron microscopy (SEM) using a FEI Apreo microscope.

Pt blocking electrodes were sputtered on both surfaces of the pellets to prepare the specimens for ionic conductivity measurements; the specimen thicknesses were in the range of 0.9–1.3 mm. Electrochemical impedance spectroscopy (EIS) experiments were carried out to measure the sodium ion conductivity at room temperature (25 °C) using a Solartron 1255B EIS analyzer from 10⁶ to 1 Hz at 25, 50, or 75 mV. The ionic conductivities were determined by fitting EIS data using the Z-View software (Scribner, Inc.).

Thermal gravimetric analysis (TGA) measurement was performed using Perkin Elmer Pyris 1 Thermogravimetric Analyzer in the temperature range of 25–200 °C with the heating rate of 1 °C/min in flowing air.

3. Results and discussion

High relative densities of ~82.4% were achieved for cold-sintered Mg-doped NASICON specimens with and without Bi_2O_3 (with almost same densities) processed at a low temperature of 140 °C for 1 h at 780 MPa, in comparison with only ~68% densities for the dry-pressed specimens at an identical pressure of 780 MPa for 1 h. The microstructures of the dry-pressed and cold-sintered specimens are shown in Fig. 2(a) and (b). Typical sintering microstructures, including particle packing and neck growth, can be observed in the cold-sintered specimen (Fig. 2(b)), indicating the occurrence of densification during CSP. The measured relative densities vs.

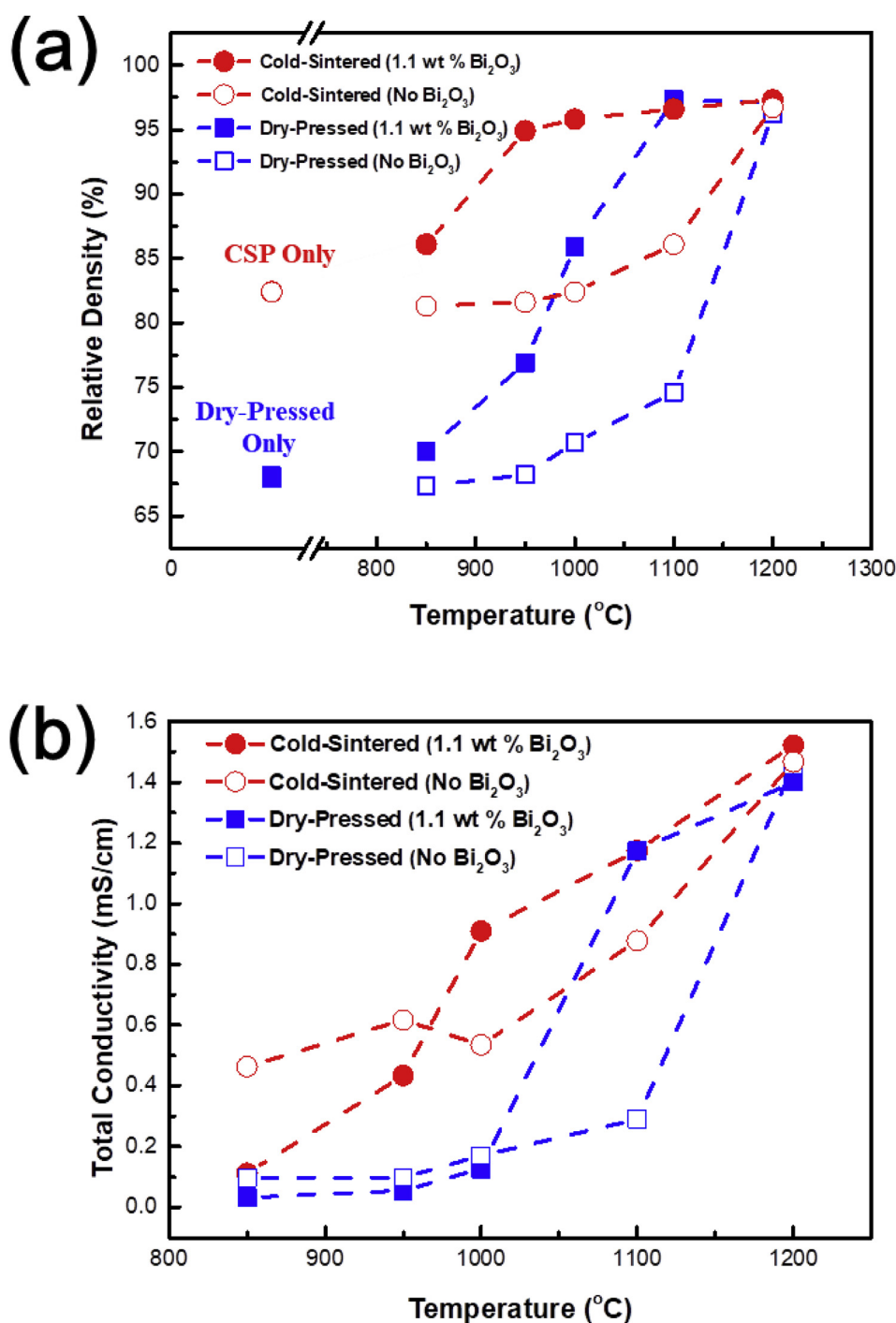


Fig. 1. The measured curves of (a) relative density and (b) total ionic conductivity (at room temperature) of the cold-sintered and dry-pressed Mg-doped NASICON ($\text{Na}_{3.256}\text{Mg}_{0.128}\text{Zr}_{1.872}\text{Si}_2\text{PO}_{12}$) specimens, with and without the addition of 1.1 wt % Bi_2O_3 sintering additives, vs. annealing temperature. All cold-sintered and dry-pressed specimens were annealed for 6 h. The estimated errors of measured densities are $\pm 1.5\%$.

annealing/sintering (processing) temperature curves are shown in Fig. 1(a). The cold-sintered specimens have higher densities than the dry-pressed specimens, both increased gradually with increasing processing temperature. Without the addition of Bi_2O_3 , high densities were only achieved at 1200 °C for both cases (Fig. 1(a) and Table 1). The addition of 1.1 wt % Bi_2O_3 increased the densification drastically for both dry-pressed and cold-sintered specimens. For the dry-pressed specimens, the density increased substantially at 950 °C (to ~77%) but high densities were only achieved at 1100 °C. The cold-sintered specimens with Bi_2O_3

addition have highest densities, which achieved ~95% density at a lower temperature of 950 °C. Fig. 2(c) and (d) show the dry-pressed and cold-sintered specimens with 1.1 wt % Bi_2O_3 after 950 °C $\times$ 6 h annealing; the denser microstructure with larger grains and fewer pores can be observed for the cold-sintered specimen. Finally, high relative densities of ~97% were obtained for all the cold-sintered and dry-pressed specimens annealed at 1200 °C for 6 h.

Fig. 3 shows the TGA curves for a cold-sintered Mg-doped NASICON with 1.1 wt % Bi_2O_3 pellet and polyvinyl alcohol (PVA) powder. A slight mass loss can be observed in the TGA curve of the

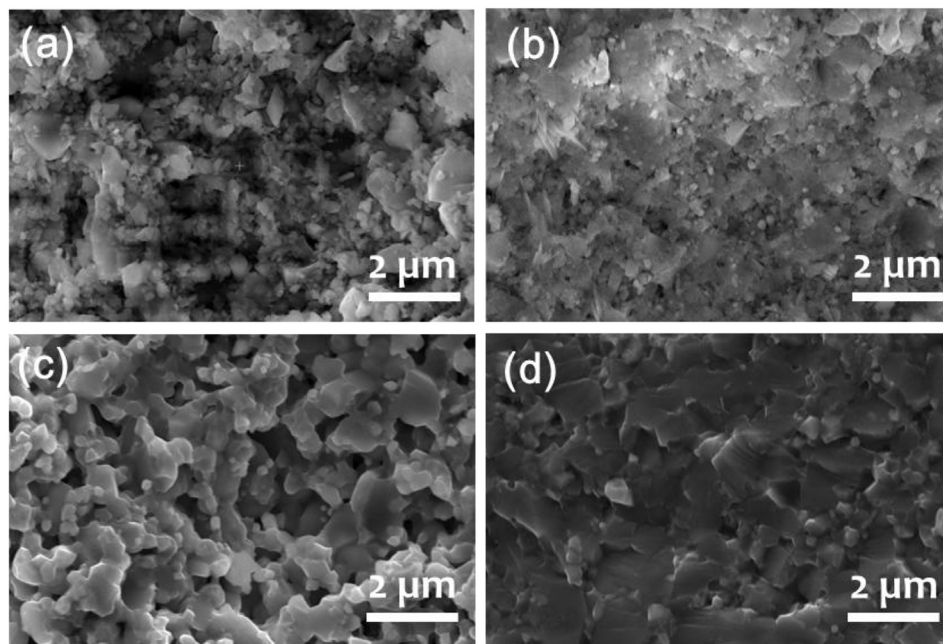


Fig. 2. SEM micrographs of the fractured surfaces of the “Mg-doped NASICON + 1.1 wt % Bi₂O₃ sintering additive” specimens (a) dry-pressed at 25 °C and (b) cold-sintered at 140 °C, respectively, at 780 MPa for 1 h, as well as (c) dry-pressed and (d) cold-sintered specimens after subsequent annealing at 950 °C for 6 h.

Table 1
Measured total conductivities for Mg-doped NASICON specimens with and without the addition of 1.1 wt % Bi₂O₃ sintering additives. Noting that cold sintering of Mg-doped NASICON specimens without Bi₂O₃ has been reported in our prior study [27], where the specimens were fabricated with a slightly different procedure (without PVA binder, which has a moderate impact on the final densities and ionic conductivities). In this study, four sets of Bi₂O₃-added or Bi₂O₃-free and dry-pressed or cold-sintered specimens were fabricated and measured with the same procedure, all with PVA added as binder. The new data with and without Bi₂O₃ fabricated under identical processing conditions are reported here for a fair comparison.

Specimen	Processing Condition	σ_t (mS/cm)	Relative Density (%)
1.1 wt % Bi ₂ O ₃ added	CSP + 850 °C × 6 h	0.112	86.1
no Bi ₂ O ₃		0.463	81.3
1.1 wt % Bi ₂ O ₃ added	Dry-Pressed + 850 °C × 6 h	0.032	70
no Bi ₂ O ₃		0.097	67.3
1.1 wt % Bi ₂ O ₃ added	CSP + 950 °C × 6 h	0.434	94.9
no Bi ₂ O ₃		0.617	81.6
1.1 wt % Bi ₂ O ₃ added	Dry-Pressed + 950 °C × 6 h	0.055	76.9
no Bi ₂ O ₃		0.098	68.2
1.1 wt % Bi ₂ O ₃ added	CSP + 1000 °C × 6 h	0.91	95.8
no Bi ₂ O ₃		0.535	82.4
1.1 wt % Bi ₂ O ₃ added	Dry-Pressed + 1000 °C × 6 h	0.127	85.9
no Bi ₂ O ₃		0.17	70.7
1.1 wt % Bi ₂ O ₃ added	CSP + 1100 °C × 6 h	1.175	96.6
no Bi ₂ O ₃		0.878	86.1
1.1 wt % Bi ₂ O ₃ added	Dry-Pressed + 1100 °C × 6 h	1.174	97.3
no Bi ₂ O ₃		0.29	74.6
1.1 wt % Bi ₂ O ₃ added	CSP + 1200 °C × 6 h	1.522	97.3
no Bi ₂ O ₃		1.467	96.7
1.1 wt % Bi ₂ O ₃ added	Dry-Pressed + 1200 °C × 6 h	1.4	97.1
no Bi ₂ O ₃		1.455	96.2

cold-sintered pellet at the temperature range of 25–200 °C. The TGA curve for PVA powder exhibits a significant mass loss at the same temperature range, indicating the possible decomposition of PVA powder in this temperature range. Furthermore, our recent investigation shows that no water was left in cold-sintered pellet after 1 h at 140 °C at an identical condition (but without PVA) [27]. Therefore, this slight mass loss in the TGA curve of cold-sintered pellet should be mainly caused by decomposition of the PVA binder (rather than water evaporation).

Fig. 1(b) shows the total ionic conductivities measured at 25 °C for all cold-sintered and dry-pressed specimens (with and without

Bi₂O₃) annealed at different temperatures. For cold-sintered specimens with Bi₂O₃, it is interesting to note that increasing the processing temperature from 950 to 1100 °C can keep increasing the ionic conductivities while there are no significant improvements in specimen densities. This can be an effect of reducing the GB resistivity. The ionic conductivity of the specimen with Bi₂O₃ reached ~0.43 mS/cm after annealing at 950 °C for 6 h, which is almost 700% or seven times of that of a dry-pressed specimen annealed at the identical condition (~0.06 mS/cm). The ionic conductivity was further increased to ~0.91 mS/cm, which again represent an approximately seven-fold increase in the conductivity

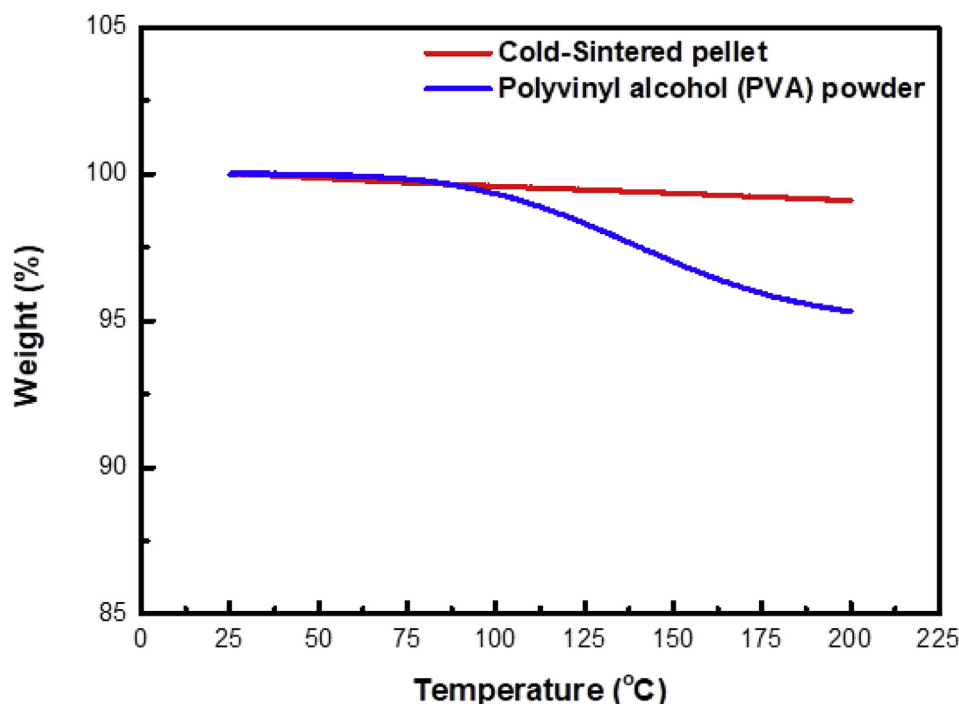


Fig. 3. TGA curves for a cold-sintered Mg-doped NASICON pellet with 1.1 wt % Bi_2O_3 sintering additive added and polyvinyl alcohol (PVA) powder.

in comparison with the dry-pressed counterpart annealed at the identical condition (~ 0.13 mS/cm). This clearly illustrated that minor Bi_2O_3 sintering additive can substantially improve the conductivity of the cold-sintered Mg-doped NASICON specimens with annealing at 950–1000 °C.

Notably, a cold-sintered Mg-doped NASICON specimen with 1.1 wt % Bi_2O_3 achieved a high conductivity of 0.91 mS/cm (with $\sim 96\%$ relative density) after annealing at 1000 °C, which was $>700\%$ of the conductivity of a dry-pressed counterpart with the same amount of Bi_2O_3 . This conductivity was also $>70\%$ higher than that of a cold-sintered specimen without adding the Bi_2O_3 sintering additive but subjected to the same heating profile. This case clearly exemplifies that combining CSP and Bi_2O_3 -activated LPS can achieve higher conductivities (as well as densities, as shown in Fig. 1(a)) at reduced temperatures than either CSP and LPS alone.

Moreover, the ionic conductivities of the cold-sintered Mg-doped NASICON specimens were always significantly higher than that of the dry-pressed specimens annealed at the identical conditions (850–1100 °C for 6 h), with or without the addition of Bi_2O_3 . High ionic conductivities of ~ 1.2 mS/cm and high densities of $\sim 97\%$ were achieved for both cold-sintered and dry-pressed Mg-doped NASICON specimens with the addition of 1.1 wt % Bi_2O_3 after annealing at a relative high temperature of 1100 °C for 6 h, indicating that benefits of CSP only existed at relative low annealing temperatures (<1100 °C). The highest conductivity achieved in this study via combining CSP and Bi_2O_3 -activated LSP is >1.5 mS/cm with $>97\%$ of the theoretical density with 1200 °C annealing.

Fig. 4 shows the XRD patterns of the cold-sintered Mg-doped NASICON specimens with 1.1 wt % Bi_2O_3 after annealing at 850 °C, 950 °C, 1000 °C, 1100 °C, and 1200 °C, respectively. All specimens exhibit a primary monoclinic NASICON phase. The common secondary phases such as Na_3PO_4 and ZrO_2 were also observed and labeled in Fig. 4. These secondary phases were commonly found in sintered NASICON in prior studies [17,22,35]. Moreover, a minor secondary phase (ZrSiO_4) was identified in the specimens annealed at 950 °C and 1000 °C. No Peaks from Bi_2O_3 was evident in all

specimens.

As shown in Fig. 1(a), addition of 1.1 wt % Bi_2O_3 always increased both densities, as well as the ionic conductivities (Fig. 1(b)), at relative low temperatures. The results indicate that the addition of Bi_2O_3 can effectively promote the sintering process of both dry-pressed and cold-sintered Mg-doped NASICON, resulting in enhanced densification at reduced sintering temperatures. This effect can be explained by the classical LPS mechanism [34,36,37]. The Bi_2O_3 additive, which has a low melting point of 820 °C, can promote the formation of a liquid phase that wets the Mg-doped NASICON grain boundaries to enhance mass transfer via dissolution and re-precipitation.

Fig. 5(a) and (b) show the (conventional) SEM images of the fractured surfaces of the dry-pressed specimens after 1100 °C $\times$ 6 h annealing with combined secondary electron (SE) and back-scattered electron (BSE) signals. Fig. 5(c) and (d) further show the BSE images of the fractured surfaces of the same set of specimens. The areas in the BSE images with dark contrast (light elements) and bright contrast (heavy elements), respectively, correspond to the monoclinic NASICON phase and ZrO_2 secondary phase, respectively. In addition, we can observe the dense microstructure with large grains for the Bi_2O_3 -added specimen, while the Bi_2O_3 -free specimen only displays a porous microstructure with small grains (Fig. 5), which further confirms that the Bi_2O_3 additive promotes the densification. The reduced porosity and enhanced grain growth brought by Bi_2O_3 additive can also decrease the effective grain boundary resistance, leading to higher ionic conductivities (Fig. 1(b) and Table 1).

Fig. 6 displays the impedance spectra of the cold-sintered Mg-doped NASICON + 1.1 wt % Bi_2O_3 specimen after annealing at 850–1200 °C. An equivalent circuit model used for the data fitting is shown in the inset in Fig. 6. Furthermore, Fig. 7 shows the impedance spectra of the dry-pressed Mg-doped NASICON specimens with and without Bi_2O_3 after 1100 °C $\times$ 6 h annealing. The total resistances, including both the bulk and grain boundary contributions, of two specimens are shown in Fig. 7.

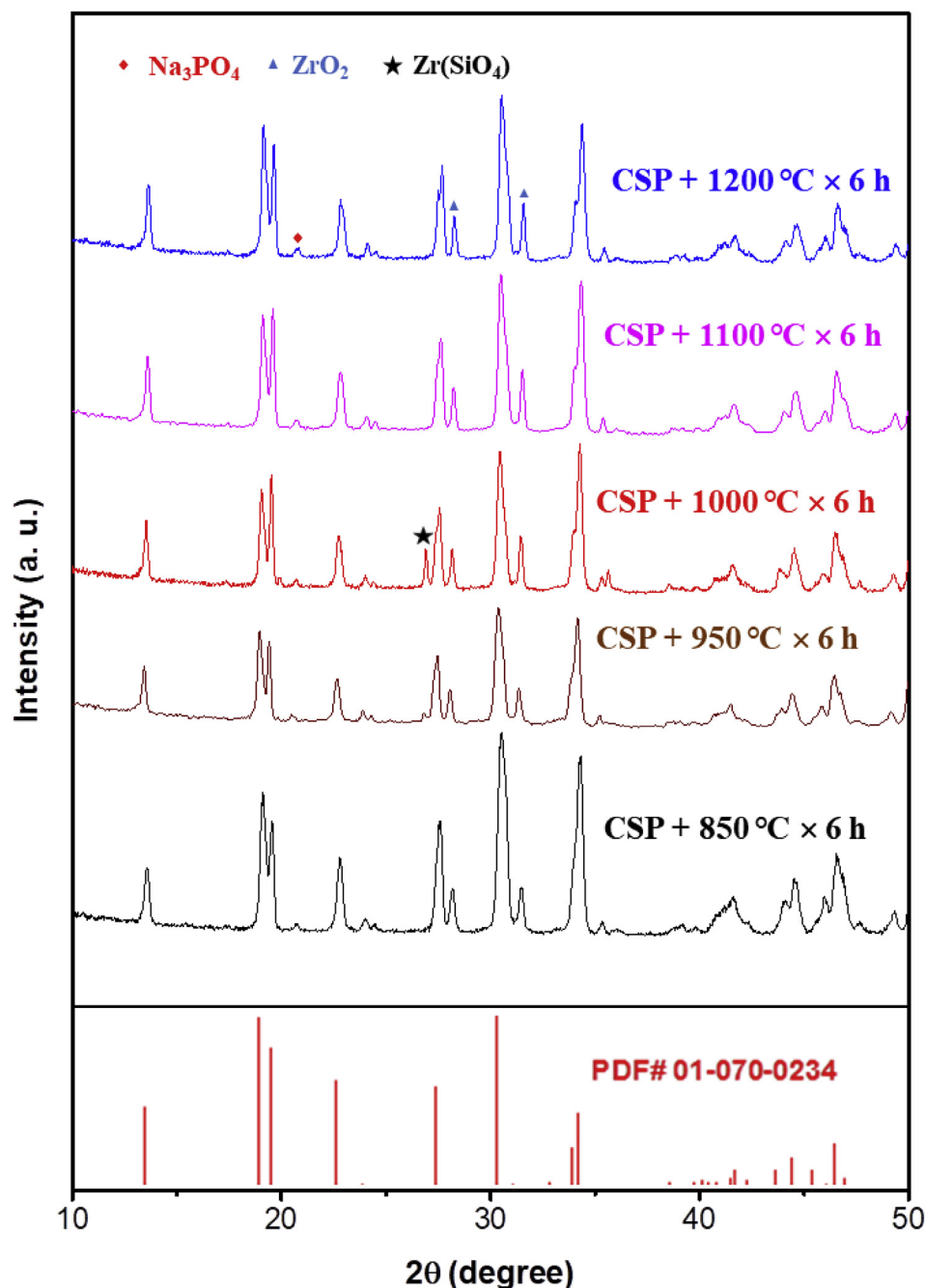


Fig. 4. XRD patterns of the cold-sintered Mg-doped NASICON specimens (with 1.1 wt % Bi₂O₃ sintering additive added) annealed at five different temperatures, along with the reference Na₃Zr₂Si₂PO₁₂ pattern (PDF No. 01-070-0234).

It is worth to compare the current study with selected prior studies in term of experimental temperatures, conductivities, and densities of the synthesized solid electrolytes. For example, the current study achieved 95.8% of the theoretical density and 0.91 mS/cm at a sintering temperature of 1000 °C. In comparison, Jolley et al. [17] achieved 96.1% relative density and 0.335 mS/cm, and Zhang et al. [8] achieved 0.67 mS/cm, both at a higher sintering temperature of 1200 °C. A very recent study by Wang et al. [15] did achieve 97.9% relative density and 1.0 mS/cm at a slightly high sintering temperature of 1045 °C, but with Na₂O–Nb₂O₅–P₂O₅ glass additive and the special spark plasma sintering. Another recent study by Suzuki et al. [24] achieved 0.1 mS/cm at a lower sintering temperature of 700 °C with the addition of Na₃BO₃.

It is interesting to note that the cold-sintered Mg-doped NASICON + 1.1 wt % Bi₂O₃ specimen with ~86.1% density reached ~0.11 mS/cm conductivity after 850 °C × 6 h annealing, which is lower than the ionic conductivity of the cold-sintered (Bi₂O₃-free) Mg-doped NASICON specimen with a lower relative density of ~81.3% density (~0.46 mS/cm), both of which were annealed at the identical condition. Moreover, a high relative density of ~94.9% was achieved for the cold-sintered Mg-doped NASICON + 1.1 wt % Bi₂O₃ specimen after 950 °C × 6 h annealing, whose ionic conductivity was ~0.43 mS/cm; this was slightly lower than the ~0.62 mS/cm ionic conductivity of the (Bi₂O₃-free) cold-sintered Mg-doped NASICON specimen with ~81.6% relative density annealed at the identical condition.

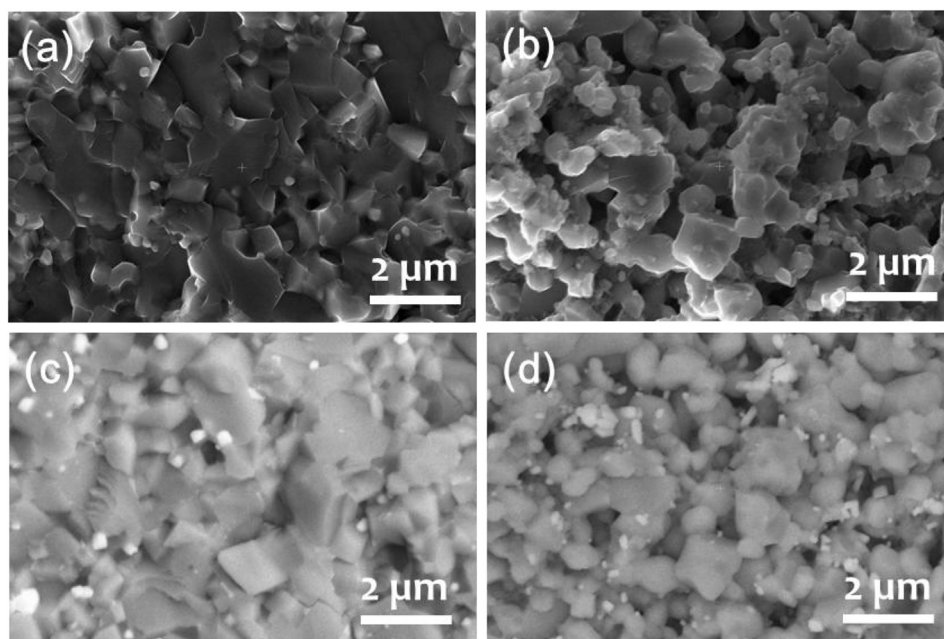


Fig. 5. SEM micrographs of the fractured surfaces of dry-pressed Mg-doped NASICON (a, c) with and (b, d) without the addition of 1.1 wt % Bi_2O_3 sintering additives, both after subsequent annealing at 1100°C for 6 h. Panels (c) and (d) are backscattered electron (BSE) images.

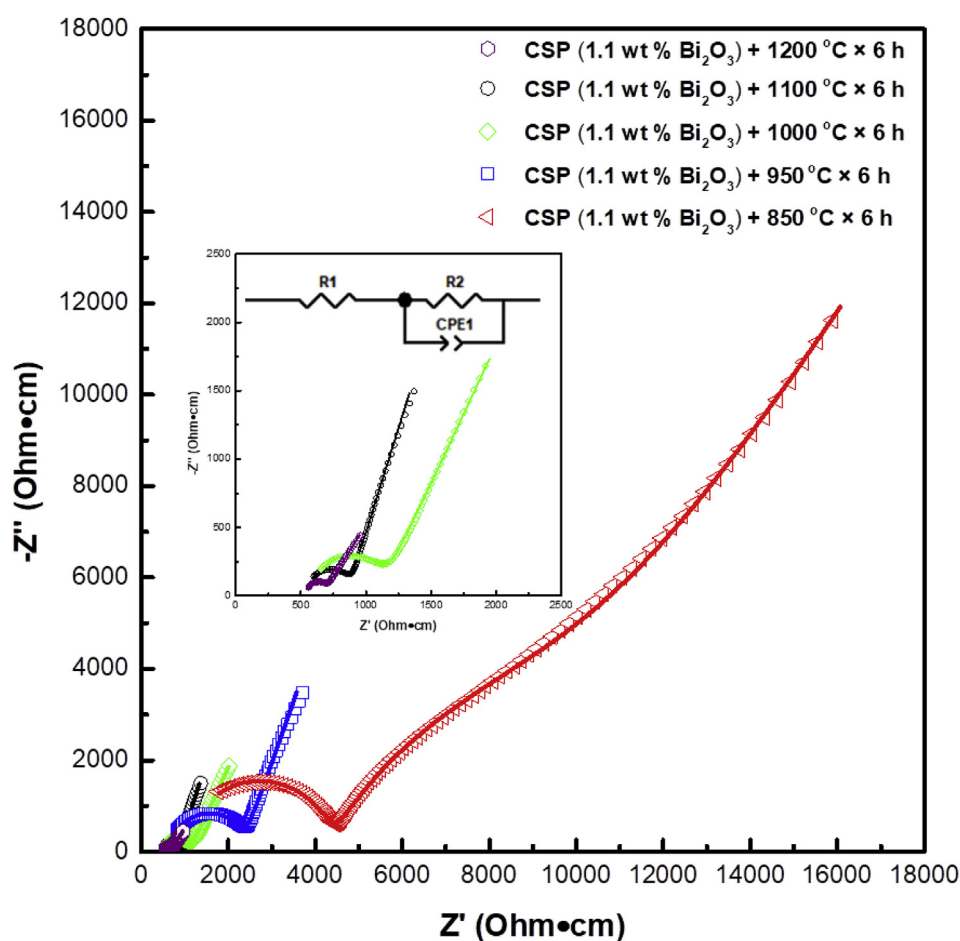


Fig. 6. EIS plots (measured at 25°C) of cold-sintered Mg-doped NASICON + 1.1 wt % Bi_2O_3 specimens annealed at five different temperatures, along with the fitted curves (represented by the solid lines). The inset is an expanded view, where the equivalent circuit for the fitting is also displayed.

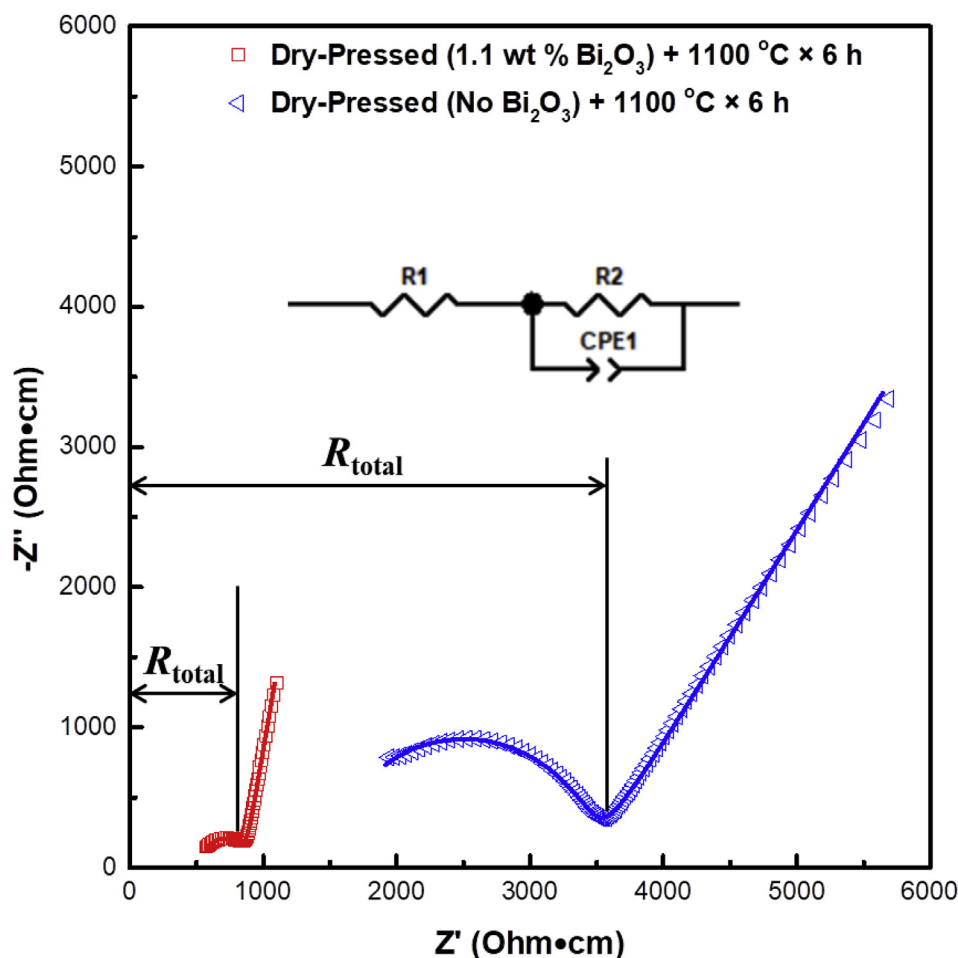


Fig. 7. EIS plots (measured at 25 °C) of dry-pressed Mg-doped NASICON specimens with and without the addition of 1.1 wt % Bi_2O_3 sintering additive, respectively, after subsequently annealing at 1100 °C for 6 h. The corresponding fitted curves are represented by the solid lines.

Thus, these two cases collectively suggest that the Bi_2O_3 additive lowers the ionic conductivity of Mg-doped NASICON at the lower annealing temperatures at 850–950 °C (despite of the enhanced densification by Bi_2O_3), which may be related to the formation of Bi_2O_3 -enriched liquid (or secondary crystalline) phase at the NASICON grain boundaries. It is important to note that the addition of Bi_2O_3 generally increased the ionic conductivity of Mg-doped NASICON, if compared with the same pre-process (dry-pressing vs. cold sintering) and heating profile, which can be attributed to the increased density at the same processing temperature. It was reported that the total resistance of NASICON solid electrolyte is often dominated by the grain boundary resistance [33,38], which is consistent with our recent report [27]. Therefore, it is likely that the grain boundary resistance is also higher than the bulk resistance for the present specimens. Again, here the low ionic conductivity (for specimens sintered as the low temperature range of 850–950 °C) may be caused by the resistive Bi_2O_3 -based liquid phase.

However, the Bi_2O_3 liquid phase can evaporate at higher annealing temperatures of 1000–1200 °C, which makes the NASICON grain boundaries less resistive. Moreover, the higher annealing temperature will also promote the grain growth, leading to coarser microstructures and decreasing the total grain boundary resistance. This is consistent with our observation of substantial increases in ionic conductivities in Bi_2O_3 -added (dry-pressed or cold-sintered) specimens in the high annealing temperature range of 1000–1200 °C (Fig. 1(b)).

The above-discussed observations illustrate the complicated,

yet interesting, interplays of the sintering additive, densification, grain boundary resistance, grain growth, and phase transformation (e.g., evaporation of the volatile sintering additive). Understanding and controlling such interplays can help us to further control the sintering and properties of solid electrolytes in general.

4. Conclusions

First, the cold-sintered Mg-doped NASICON specimens, regardless of whether 1.1 wt % Bi_2O_3 sintering was added or not, can achieve ~82.4% of the theoretical density at 140 °C. The post-CSP annealing was found effective to further enhance both the densification and ionic conductivity of the cold-sintered specimens. For example, a high ionic conductivity of ~0.88 mS/cm and relative density of ~86% were achieved for the cold-sintered Mg-doped NASICON after 1100 °C × 6 h annealing. In contrast, the dry-pressed counterpart annealed at the identical condition exhibited a much lower ionic conductivity of ~0.29 mS/cm and relative density of ~74.6%.

Second, the further addition of 1.1 wt % Bi_2O_3 sintering additive can significantly enhance the densification and further reduce the sintering/annealing temperature. The addition of 1.1 wt % Bi_2O_3 was found to increase the ionic conductivity of the cold-sintered NASICON specimen from ~0.54 mS/cm to ~0.91 mS/cm, while simultaneously increased the relative density from ~82.4% to ~95.8%, after annealing at (a lower temperature of) 1000 °C for 6 h. Furthermore, the ionic conductivity was increased from ~0.88 mS/cm to ~1.18 mS/cm at the annealing temperature 1100 °C for 6 h.

Third, the Bi_2O_3 additive can also increase the ionic conductivity of the dry-pressed specimens, e.g., from $\sim 0.29 \text{ mS/cm}$ to $\sim 1.17 \text{ mS/cm}$, along with an increase of the relative density from $\sim 74.6\%$ to $\sim 97.3\%$, after $1100^\circ\text{C} \times 6 \text{ h}$ annealing. We should note that Bi_2O_3 sintering additive increase the ionic conductivity via increasing the sintering and density of the specimen, while the presence of the Bi_2O_3 at grain boundaries appears to reduce the conductivity with the same relative density at low annealing temperatures.

As the most notable new innovative processing, we showed that combining CSP and Bi_2O_3 -activated LPS can achieve higher densities and ionic conductivities than either CSP or LPS alone, at reduced temperatures. As an example, after the identical thermal processing at 1000°C ; the measured Na-ion conductivity of the CSP + LPS specimen is $>70\%$ higher than that of the CPS only specimen (without Bi_2O_3), and $>600\%$ higher than that of the LPS only specimen (with the same amount of Bi_2O_3 being added). In addition, the high ($>95\%$) densities achieved by combining CSP and Bi_2O_3 -activated LPS (at as low as $\sim 950^\circ\text{C}$) are also highly desirable for fabricating solid-state batteries, but are unattainable by conventional sintering unless going to $\sim 1200^\circ\text{C}$.

Thus, this study suggests a new processing route to sinter dense solid electrolytes with high ionic conductivities at the reduced temperatures by combining the new and innovative CSP with the classical LPS technologies. This can be extended to other ceramic materials beyond NASICON, as well as help to develop lower-temperature co-sintering technologies to fabricate electrolytes and electrodes together for solid-state sodium batteries. This new combined CSP and LPS technology can be particularly useful for fabricating thermally fragile lithium or sodium solid electrolytes with volatile components or thermally-unstable phases, such as phosphates and sulfates, at reduced temperatures, which is highly desirable for solid state battery technologies.

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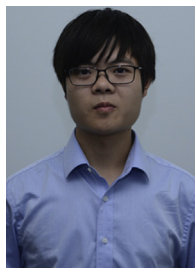
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