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(54) Title: OXY-THIO-NITRIDE MIXED NETWORK FORMER SOLID ELECTROLYTES

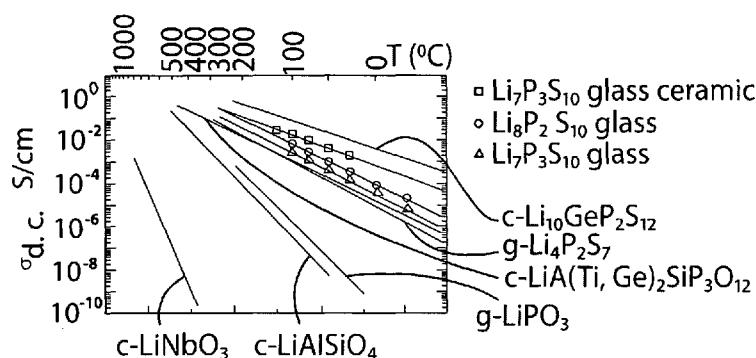


FIG. 1

(57) Abstract: An ion conductivity mixed chalcogenide (e.g. oxy-sulfide), mixed network former solid electrolyte is provided for use in solid state batteries.

Oxy-Thio-Nitride Mixed Network Former Solid Electrolytes

RELATED APPLICATION

This application claims benefit and priority of provisional application Serial No. 62/495,270 filed September 8, 2016, the entire disclosure of which is incorporated herein by reference.

CONTRACTUAL ORIGIN OF THE INVENTION

The invention was made with government support under Grant Nos. DMR1304977 and CBET438223 awarded by the National Science Foundation. The government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention involves ion conductive solid electrolytes.

BACKGROUND OF THE INVENTION

All-oxide solid electrolytes are poorly conducting, but they can be highly stable. Despite the many compositions and structures investigated, few have reached the 10^{-3} S/cm ionic conductivity threshold, Figure 1. More critically, their low ionic conductivity arises from a high conductivity activation energy that sharply decreases the conductivity at lower temperatures, Figure 1. All-oxide solid electrolytes have three other disadvantages: (1) their high conductivities are not achieved unless they are sintered at high temperatures; (2) their typically low ion concentrations create high interfacial impedances; and (3) they must be fabricated off-line which limits them to low-surface area, long-diffusion-length, planar 2D battery designs.

In contrast, all-sulfide solid electrolytes are very highly conducting (Figure 1) but chemically unstable and hence expensive to manufacture. Li^+ ion conducting all-sulfide solid electrolytes are significantly more studied than Na^+ solid electrolytes. It has been shown that Li^+ ion conductivities as high as 10^{-2} S/cm at 25°C and 10^{-3} S/cm at -30°C can be obtained.

Only a few reports exist for all-sulfide Na^+ ion conducting solid electrolytes. The higher polarizability of the larger sulfide anion compared to the smaller oxide anion is believed to be the reason for their 100,000 times higher conductivity, and binary $\text{Li}_2\text{S} + \text{P}_2\text{S}_5$ glasses can be partially crystallized to produce glass-ceramic all-sulfide solid electrolytes with even higher conductivities. One investigator showed that $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, based on mixing the network formers (Ge and P), exhibits the highest Li^+ ion conductivity of any solid electrolyte reported,

about 1.2×10^{-2} S/cm at 25°C. (Li/Na)⁺ analogues of these all-sulfide solid electrolytes are unexplored.

The typical $75\text{Li}_2\text{S} + 25\text{P}_2\text{S}_5$ all-sulfide solid electrolyte is Li⁺ rich with low intergranular impedances since they are 3D Li⁺ ion conductors. They can be pressed into solid discs at modest pressures at room temperature to yield conductivities orders of magnitude higher than the all-oxide ceramics, which dramatically decreases their cost. Further, they can be prepared by highly scalable continuous batching and mechanical milling. Li_3PS_4 material can be produced as a high-surface-area fine-grained powder that is ideal for low-temperature low-cost solid-state battery forming operations. The near room temperature processing for all-sulfide electrolytes greatly expands the range of battery forming operations for fabricating low-cost, high-volume Li or Na batteries. All-sulfide fine-grained powder precursor electrolytes can easily take advantage of high-surface-area, short-diffusion-length, high-volume, 3D designs to dramatically increase both energy and power densities. The ASSSB (all sulfide solid state battery) design will be greatly facilitated by the low-temperature processing of these solid electrolytes to create entirely new battery designs.

However, the benefits (ultra-high conductivity and low temperature processing) of these electrolytes will be difficult to realize if their atmospheric chemical stability cannot be dramatically improved. Upon exposure to air, these materials produce hazardous H_2S gas.

Class of Mixed Oxy-Sulfide Solid Electrolytes:

Li⁺ ion conductivities of 10^{-2} S/cm at 25°C for $\text{Li}_2\text{S} + \text{GeS}_2$ solid electrolytes, higher than lithium salt-doped organic liquid electrolytes have been reported. Further, dramatic increases in the Li⁺ ion conductivity, chemical stability, and mechanical strength can all be achieved by selective “pre-oxidation” of these bulk sulfide glasses. Figure 2a shows that 5 mole % oxygen added to a $\text{Li}_2\text{S} + \text{GeS}_2$ glass increases the Li⁺ ion conductivity by a factor of 10, dramatically suppresses the reaction in air (Figure 2B), and increases the glass transition temperature, T_g (Figure 2C). Due to the dramatic increase in the Li⁺ ion conductivity with added oxygen, the conductivity does not drop below (and the conductivity activation energy does not rise above) that of the parent all-sulfide glass until about 50 mole% of the sulfur has been replaced by oxygen; see “Anomalous Ionic Conductivity Increase in $\text{Li}_2\text{S} + \text{GeS}_2 + \text{GeO}_2$ Glasses”, by Youngsik Kim, Jason Saienga, and Steve W. Martin, J. Phys. Chem. B, 2006, 110 (33), pp 16318–16325.

The invention involves providing a ion conducting solid electrolyte that blends the advantages of both oxide and sulfide solid electrolytes and addresses a need for an ion

conducting solid-state electrolyte that meets the combined requirements of high conductivity, chemical stability, and low cost needed for high capacity, stable, and low-cost solid state batteries.

SUMMARY OF THE INVENTION

The present invention provides an ion conductive mixed chalcogenide, mixed network former solid electrolyte to this end. One embodiment provides a solid electrolyte comprising an ion conductive mixed oxy-sulfide, mixed network former solid electrolyte that can be doped with nitrogen.

An illustrative preferred embodiment of the invention involves initially making particular mixed network former glasses represented by:

$$x(Li / Na / K / Rb / Cs)_2 S_u O_{1-u} + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z} O_z, \text{ where typically } 0 \leq u \leq 1, 0.5 \leq x \leq$$

0.90, m is the number of glass formers $G_i S_{c_i-z} O_z$ and is typically $1 \leq m \leq 10$, but preferably $2 \leq m \leq 5$, g_i is the mole fraction of each glass (network) former $G_i S_{c_i-z} O_z$, and is $0 \leq g_i \leq 1$ and $1 = \sum_{i=1}^m g_i$, where $c_i = v_i/2$ and v_i is the formal valence of G_i of each respective glass former,

and $0 \leq \text{each } z \leq c_i$. That is, there will be a value of z (a z_i value) for each respective glass former. Illustrative G_i elements include at least two different of Si, Ge, P, B, Sb, As, Sn, Ga, V, and Al among others, although two or more of Si, P, and B are preferred.

These glasses can be subjected to nitrogen-doping to yield $(Li/Na)^+$ ion conductive, mixed

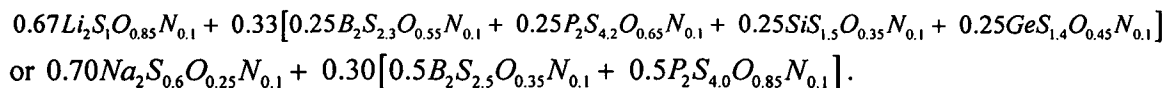
$$x(Li / Na / K / Rb / Cs)_2 S_u O_{1-u} + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z} O_z, \text{ after ammonolysis (or other nitrogen}$$

doping treatment), yields a solid electrolyte having a general composition

$$x(Li / Na)_2 S_{u-1.5fp} O_{1-u-1.5(1-f)p} N_p + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z-1.5ft} O_{z-(1-f)1.5t} N_t,$$

where typically $0 \leq u \leq 1$, $0 \leq f \leq 1$, $0 \leq p \leq 1$, and $0 \leq t \leq 1$, $0.5 \leq x \leq 0.90$, m is the number of glass (network) formers $G_i S_{c_i-z} O_z$, and is typically $1 \leq m \leq 10$, preferably $2 \leq m \leq 5$, g_i is the mole fraction of each glass former $G_i S_{c_i-z} O_z$, and is $0 \leq g_i \leq 1$ and $1 = \sum_{i=1}^m g_i$, where $c_i = v_i/2$ and v_i is the formal valence of G_i of each glass former, and $0 \leq \text{each } z \leq c_i$ where there will be a value of z (a z_i value) for each glass former.

Particular illustrative solid electrolyte embodiments can include, but are not limited to,



In these compositions, alkaline earth metal ions, such as Mg^{+2} and/or Ca^{+2} ions, can be used in lieu of or in addition to alkali cations, $x = Li^+, Na^+, K^+, Rb^+, \text{ and } Cs^+$ as conductors.

In another embodiment, the present invention provides a method of making a solid electrolyte comprising melting a mixed chalcogenide, mixed network former glass and contacting the melted glass with a nitrogen source for a time to dope the glass with nitrogen.

The present invention provides a new class of solid electrolytes that may be simultaneously highly conducting, electrochemically stable, atmospherically stable, thermally stable, and mechanically strong, yet also easy and low cost to prepare and that may provide a significant key opportunity to break the existing paradigm of low conductivity/chemically stable, high conductivity/unstable.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows Arrhenius plots of low conductivity and high activation energy oxide solid electrolytes compared to high conductivity and low activation energy sulfide solid electrolytes.

Figure 2a shows conductivities, activation energies, and T_g values of mixed oxy-sulfide $0.5Li_2S + 0.5[xGeO_2 + (1-x)GeS_2]$ solid electrolytes.

Figure 2B shows TGA scans of two unstable pure sulfide solid electrolytes compared to the very stable mixed oxy-sulfide solid electrolyte.

Figure 2C shows conductivities, activation energies, and T_g values for mixed network former all-oxide $0.33Li_2O + [xB_2O_3 + (1-x)P_2O_5]$ solid electrolytes, showing that a dramatic, nearly 100-fold increase in the conductivity can be achieved by mixing network formers, P for B.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides ion conductive mixed oxy-sulfide-nitride, mixed network former solid electrolytes wherein the following examples are offered to further illustrate the invention, but not limit the scope thereof. Conductivity of the solid electrolytes can be provided by at least one of the alkali cations, $Li^+, Na^+, K^+, Rb^+, \text{ and } Cs^+$ as conductors,

although at least one of the alkaline earth metal ions, such as Mg^{+2} and/or Ca^{+2} ions, can be used in lieu of or in addition to alkali cations as conductors.

The following examples are offered to further illustrate, but not limit, the invention.

Mixed Oxy-Sulfide, Mixed Network Former Solid Electrolytes:

Glasses were prepared and are represented by:

$$x(Li / Na / K / Rb / Cs)_2 S_u O_{1-u} + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z} O_z \text{ glasses,}$$

where typically $0 \leq u \leq 1$, $0.5 \leq x \leq 0.90$, m is the number of glass formers $G_i S_{c_i-z} O_z$ and is typically $1 \leq m \leq 10$, but more preferably $2 \leq m \leq 5$, g_i is the mole fraction of each glass

(network) former $G_i S_{c_i-z} O_z$, and is $0 \leq g_i \leq 1$ and $1 = \sum_{i=1}^m g_i$, where $c_i = v_i/2$ and v_i is the

formal valence of G_i of each respective glass former, and $0 \leq \text{each } z \leq c_i$ where there is a value of z (a z_i value) for each respective glass former. For example, illustrative Li/Na glasses can be represented by:

$$x(Li / Na)_2 S_u O_{1-u} + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z_i} O_{z_i} .$$

In addition to glasses represented by the above formula, non-stoichiometric variations from the above formula are included within the scope of the invention. These non-stoichiometric variations in composition result when typically more or less glass former G_i is added to the glass composition or when more or less sulfur (S) and/or oxygen (O) is added to the composition and this creates ratios of the glass former G_i to S and/or O different than the typical valence of the glass formers G_i would predict. For example, when the glass former G_i is Si, and has a valence of typically +4, the normally expected ratio of glass former to S or O, would be 1 to 2. However, additional S can be added to the composition, or equivalently, less Si can be added to the composition to give S rich off stoichiometric ratios such as 1 to 1, 1 to 1.5, or any other ratio.

In addition to the mixed oxy-sulfide glasses represented by the formulas above, it is envisioned that there can be any other combination of the chalcogenide elements, S, Se, and Te, with O and/or any of the other chalcogens to produce mixed chalcogenide, mixed network former glasses. For example, a simple extension of the formula above for any combination of chalcogen elements would be

$x(Li/Na/K/Rb/Cs)_2 X_u Y_{1-u} + (1-x) \sum_{i=1}^m g_i G_i X_{c_i-z} Y_z$, where X and Y are two different

chalcogenide elements selected from the list O, S, Se and Te. It is a further extension of this formula to recognize that there are glasses where there are two, three, and four mixed chalcogen elements in the formula, such as

$x(Li/Na/K/Rb/Cs)_2 X_u Y_{1-t-v-u} S_t W_v + (1-x) \sum_{i=1}^m g_i G_i X_{c_i-z-q-p} Y_z S_q W_p$, where X, Y, S and W

are different chalcogen elements selected from group of chalcogen elements, O, S, Se, and Te.

It is further envisioned that there can be any combination of off-stoichiometric mixed glass former mixed chalcogen glass compositions as described above.

It is still further envisioned, that while there may be preferred compositions that contain glass formers G_i , the term glass former G_i in the compositional formulas described above and below is not meant to restrict the claimed compositions to only those compounds based on elements G_i (both stoichiometric and non-stoichiometric) that are known to be glass formers themselves such as GeS_2 and B_2S_3 among many others. The term G_i can also include other compounds (both stoichiometric and non-stoichiometric) that are not glass forming on their own. For example, G_i could be selected from many different elements such as Al, Ga, La, Zr, In and many others that are known to help improve the properties of glass. A typical, but not necessarily limiting criteria is that these other G_i elements are called glass intermediates.

In the above formula, "x" can be at least one of the alkali cations selected from Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , although at least one of alkaline earth metal ions, such as Mg^{+2} and/or Ca^{+2} ions, can be used in the formula in lieu of or in addition to the alkali cation(s).

As illustrative compositions, the above glasses would yield a particular glass composition such as $0.67Li_2S_{0.5}O_{0.5} + 0.33[0.25B_2S_{2.5}O_{0.5} + 0.25P_2S_{4.5}O_{0.5} + 0.25SiS_{1.67}O_{0.33} + 0.25GeS_{1.5}O_{0.5}]$ or such as $0.70Na_2S_{0.67}O_{0.33} + 0.30[0.5B_2S_{2.7}O_{0.3} + 0.5P_2S_{4.2}O_{0.8}]$. These values span the range of the conductivity maximum, Figure 2C.

In a typical illustrative synthesis procedure, appropriate amounts of high purity Li_2S , Li_2O , Na_2S , Na_2O , B_2S_3 , B_2O_3 , P_2S_5 , P_2O_5 , SiO_2 , SiS_2 , GeS_2 , and/or GeO_2 for a typical batch of up to 200 grams or more yielding a general composition of $x(Li/Na)_2S + (1-x)[zB_2S_{3-x}O_x + (1-z)P_2S_{5-y}O_y]$, are milled using a Spex vibratory mill inside a high quality state-of-the-art glove box (MBraun), with typically 2 ppm O_2 and H_2O . This batch is then transferred to a

hermetically sealed ZrO₂ pot and lid with ZrO₂ milling media. It is planetary milled or similarly milled for up to or exceeding about 20 hrs at room temperature or heated using a planetary mill or equivalent. The resulting fine-grained glass, semi-crystalline ceramic, partially crystalline ceramic, or a crystalline ceramic solid material will be collected inside the glove box.

Alternatively, these same batch materials can be weighed out in the correct proportions as above to yield a glass batch as described above, and then hand milled or otherwise mixed and /or agitated to create an evenly mixed mixture. This mixture is then melted in a crucible in a furnace at a temperature appropriate to melt the mixed ingredients to a homogeneous liquid. This liquid is then quenched to room temperature at a cooling rate to yield a glass, semi-crystalline ceramic, partially crystalline ceramic, or a crystalline ceramic solid.

High Ion Conductivity Mixed Oxy-Sulfide-Nitride, Mixed Network Former Solid Electrolytes:

The above compositions can be doped with N using ammonolysis by reacting the melt of the glass with gaseous ammonia such as NH₃, sputtering a target made of the base composition in a gas atmosphere containing nitrogen (N), and/or melted with other nitride compounds of those described above. In an illustrative process, a mixed oxy-sulfide mixed glass former glass is held in the liquid state above the melting point of the phase and NH₃ is passed over the melt. N is incorporated into the melt by displacing O and S and liberating H₂O and H₂S which will be passed through a chemical (Li/Na)OH and H₂O₂ scrubber before exiting into a chemical fume hood. The reaction is $3\text{O}^{2-}(\text{glass}) + 2\text{NH}_3 \rightarrow 2\text{N}^{3-}(\text{glass}) + 3\text{H}_2\text{O}\uparrow$ and $3\text{S}^{2-}(\text{glass}) + 2\text{NH}_3 \rightarrow 2\text{N}^{3-}(\text{glass}) + 3\text{H}_2\text{S}\uparrow$.

In a typical illustrative synthesis, a fine powder of the lithium or sodium oxy-sulfide mixed network former glass, $x(\text{Li} / \text{Na})_2 \text{S}_u \text{O}_{1-u} + (1-x) \sum_{i=1}^m g_i \text{G}_i \text{S}_{c_i-z_i} \text{O}_{z_i}$ is placed into a high surface area graphite boat, and then placed into a muffle tube inside a tube furnace which has both ends sealed except for a gas inlet and a gas outlet. The muffle tube is purged at room temperature with pure N₂ until a very low partial pressure of O₂ is achieved (< 100 ppm) inside the muffle tube. Then the furnace temperature is ramped up slowly to above the glass melt temperature, typically in the range of $400 \leq T \leq 800^\circ\text{C}$. The N₂ flow gas is then switched to NH₃ gas flow (low ppm H₂O) and the glass melt is nitrided for 3 hours. The N₂ and NH₃

flow rates are typically in the range of 10 to 1,000 mL/hour. The NH₃ is then switched off and the N₂ is then turned back on to purge the muffle tube of the remaining NH₃ and the furnace is cooled back to room temperature. The NH₃ exiting the muffle tube is safely purged from the system through a NaOH + H₂O₂ gettering solution. After a series of runs, the gettering solution is safely neutralized by adding HNO₃. The resulting glass of about 200–500 grams of nitrated materials is collected from the graphite boat and milled to a fine powder for future use and characterization. Due to charge balance considerations, the N goes into the glass melt as a N³⁻ anion and it replaces both O²⁻ and S²⁻ anions. Hence, for every 1 N³⁻ anion introduced into the glass melt a combination of 1.5(fO²⁻ + (1-f)S²⁻) anions are removed from the melt in the form of H₂O and H₂S. These reactions are given above.

Therefore, for the base mixed oxy-sulfide, mixed glass former composition describe

above, $x(Li/Na)_2 S_u O_{1-u} + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z} O_z$ ammonolysis (or other N doping treatment)

yields a solid electrolyte pursuant to the invention having a general composition:

$$x(Li/Na)_2 S_{u-1.5fp} O_{1-u-1.5(1-f)p} N_p + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z-1.5ft} O_{z-(1-f)1.5ft} N_t,$$

where typically $0 \leq u \leq 1$, $0 \leq f \leq 1$, $0 \leq p \leq 1$, and $0 \leq t \leq 1$, $0.5 \leq x \leq 0.90$, m is the number of glass (network) formers and is typically $1 \leq m \leq 10$, but more typically $2 \leq m \leq 5$, g_i is the mole fraction of the glass (network) former $G_i S_{c_i-z} O_z$, and is $0 \leq g_i \leq 1$, where $c_i = v_i/2$ and v_i is the formal valence of each respective G_i , and $0 \leq \text{each } z \leq c_i$ as described above.

This general solid electrolyte composition would yield illustrative solid electrolytes such as:

$$0.67Li_2S_1O_{0.85}N_{0.1} + 0.33[0.25B_2S_{2.3}O_{0.55}N_{0.1} + 0.25P_2S_{4.2}O_{0.65}N_{0.1} + 0.25SiS_{1.5}O_{0.35}N_{0.1} + 0.25GeS_{1.4}O_{0.45}N_{0.1}]$$

$$\text{or } 0.70Na_2S_{0.6}O_{0.25}N_{0.1} + 0.30[0.5B_2S_{2.5}O_{0.35}N_{0.1} + 0.5P_2S_{4.0}O_{0.85}N_{0.1}]$$

In these compositions, alkaline earth metal ions, such as Mg⁺² and/or Ca⁺² ions, can be used in lieu of or in addition to Li⁺/Na⁺ as conductors.

The following Examples are offered to further illustrate but not limit embodiments of the present invention:

Na Ion-Conductive Oxy-Sulfide, Mixed Network Former Glasses:

A) Mixed oxy-sulfide, mixed network former glasses represented by .67Na₂S + .33[(0.5)P₂S_(5-z)O_z + (0.5)B₂S_{3-z}O_z] wherein z was 0.5, 1.25, 1.65, and 2.5 and any values

between 0 and 3 for B and between 0 and 5 for P were prepared by the milling technique or the melting technique described above. The glasses were found to be conductive to Na^+ ions at 30°C and 60°C in conductivity testing using a common complex impedance type of conductivity test. These glasses can be subjected to nitriding as described above to dope them with nitrogen as described above.

B) Mixed oxy-sulfide, mixed network former glasses represented by 0.70% Na_2S + 0.25% SiS_2 + 0.04% P_2S_5 + 0.01% P_2O_5 where % are mole %'s. The glasses were prepared by the milling technique or the melting technique described above. The glasses were found to be conductive to Na^+ ions at 30°C and 60°C using the complex impedance conductivity test. These glasses can be subjected to nitriding as described above to dope them with nitrogen as described above.

C) Mixed oxy-sulfide, mixed network former glasses represented alternately by 0.70% Na_2S + 0.25% SiS_2 + 0.03% P_2S_5 + 0.02% P_2O_5 where % are mole %'s were prepared by the milling technique or the melting technique described. The glasses were found to be conductive to Na^+ ions at 25°C and 60°C using the complex impedance conductivity test. These glasses can be subjected to nitriding as described above to dope them with nitrogen as described above.

A class of solid electrolytes is provided that can be simultaneously ion conducting, electrochemically stable, atmospherically stable, thermally stable, and mechanically strong, yet also easy and low cost to prepare and that may provide a significant key opportunity to break the existing paradigm of low conductivity/chemically stable, high conductivity/unstable.

Although the present invention has been described with respect to particular illustrative embodiments, those skilled in the art will appreciate that modifications and changes can be made thereto without departing from the spirit and scope of the invention as set forth in the appended claims.

I CLAIM

CLAIMS

1. An ion conductive mixed chalcogenide, mixed network former solid electrolyte.
2. The electrolyte of claim 1 which is a mixed oxy-sulfide, mixed network former solid electrolyte.
3. The electrolyte of claim 1 wherein one mixed network former includes one or more of P, B, and/or Si and another mixed network former includes a different one or more of P, B, and/or Si.
4. The electrolyte of claim 1 wherein the mixed chalcogenide includes at least two of O, S, Se, and Te.
5. The electrolyte of claim 1 wherein the electrolyte includes a chalcogenide which includes Na and/or Li.
6. The electrolyte of claim 1 that includes nitrogen as a dopant.
7. The electrolyte of claim 1 that is conductive to alkali cations and/or alkaline earth cations.
8. The electrolyte of claim 1 which is glass, glass-ceramic, or ceramic.
9. The electrolyte of claim 1 comprising

$$x(Li/Na)_2 S_{u-1.5fp} O_{1-u1.5(1-f)p} N_p + (1-x) \sum_{i=1}^m g_i G_i S_{c_i-z-1.5ft} O_{z-(1-f)1.5ft} N_t$$
 where $0 \leq u \leq 1$, $0 \leq f \leq 1$, $0 \leq p \leq 1$, and $0 \leq t \leq 1$, $0.5 \leq x \leq 0.90$, m is the number of glass formers $G_i S_{c_i-z} O_z$ and is $1 \leq m \leq 10$, g_i is the mole fraction of each respective glass former, and is $0 \leq g_i \leq 1$, where $c_i = v_i/2$ and v_i is the formal valence of G_i of each respective glass former, and $0 \leq$ each $z \leq c_i$.
10. The electrolyte of claim 9 wherein $2 \leq m \leq 5$.
11. The electrolyte of claim 9 wherein each G_i is selected from B, P, and/or Si.

12. The electrolyte of claim 1 comprising:

$x(Li/Na/K/Rb/Cs)_2S_uO_{1-u} + (1-x)\sum_{i=1}^m g_i G_i S_{c_i-z} O_z$, where $0 \leq u \leq 1$, $0.5 \leq x \leq 0.90$, m is the number of glass formers $G_i S_{c_i-z} O_z$ and is $1 \leq m \leq 10$, preferably $2 \leq m \leq 5$, g_i is the mole fraction of each respective glass former, and is $0 \leq g_i \leq 1$ and $1 = \sum_{i=1}^m g_i$, where $c_i = v_i/2$ and v_i is the formal valence of G_i of each respective glass former, and $0 \leq \text{each } z \leq c_i$.

13. The electrolyte of claim 12 represented by:

$x(Li/Na)_2S_uO_{1-u} + (1-x)\sum_{i=1}^m g_i G_i S_{c_i-z_i} O_{z_i}$.

14. A solid state battery comprising the solid electrolyte of claim 1.

15. A method of making a solid electrolyte comprising:

melting a mixed chalcogenide, mixed network former glass and contacting the melted glass with a nitrogen source for a time to dope the glass with nitrogen.

16. The method of claim 15 wherein the melted glass is contacted with ammonia gas.

17. The method of claim 15 wherein the solid material comprises a glass or a ceramic.

18. The method of claim 15 including pulverizing the solid material to particulates.

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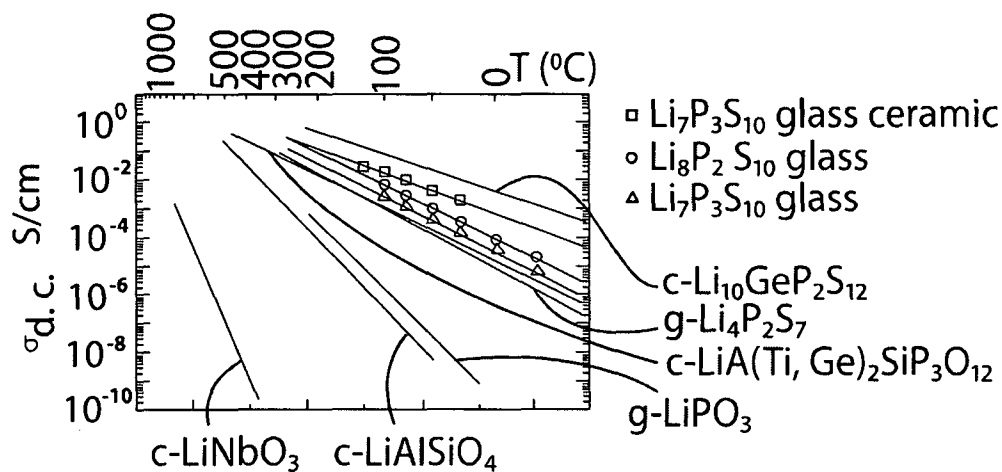


FIG. 1

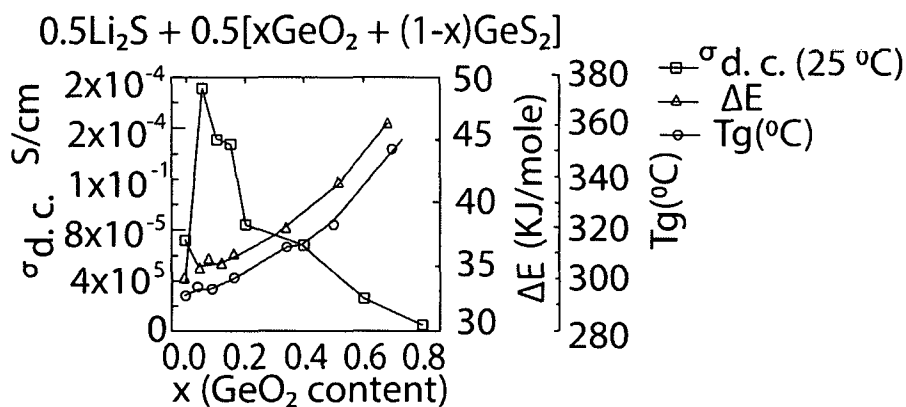


FIG. 2a

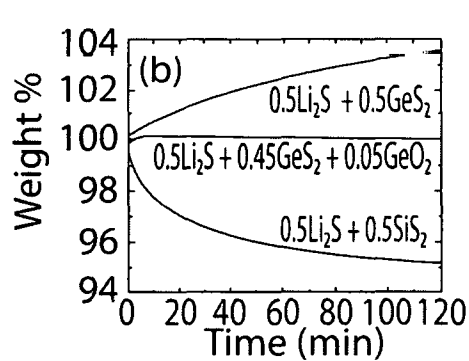


FIG. 2B

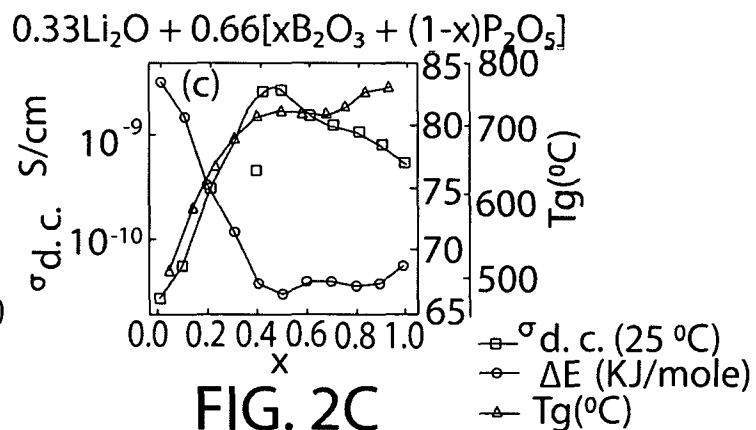


FIG. 2C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/000054**A. CLASSIFICATION OF SUBJECT MATTER****H01M 10/0562(2010.01)i, H01B 5/00(2006.01)i, H01B 1/10(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01M 10/0562; H01M 6/18; H01B 5/00; H01B 1/10Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: mixed chalcogenide, mixed network former, solid electrolyte, oxy-sulfide, dopant**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4599284 A (JAMES R. AKRIDGE) 08 July 1986 See columns 3-5; claim 1; and example 1.	1-18
Y	DIRK LARINK et al., "Structure and ionic conductivity in the mixed-network former chalcogenide glass system [Na ₂ S] _{2/3} [(B ₂ S ₃) _x (P ₂ S ₅) _{1-x}] _{1/3} ", The Journal of Physical Chemistry C, 2012, Vol. 116, No. 43, pages 22698-22710 See abstract; and pages 22699, 22709.	1-18
Y	CHRISTIAN BISCHOFF et al., "IR, raman, and NMR Studies of the short-range structures of 0.5Na ₂ S + 0.5[xGeS ₂ + (1-x)PS ₅ /2] mixed glass-former glasses", The Journal of Physical Chemistry B, 2014, Vol. 118, No. 7, pages 1943-1953 See abstract; and pages 1943, 1952.	1,2,4-10,12-18
Y	DIRK LARINK et al., "Mixed network former effects in tellurite glass systems: Structure/property correlations in the system (Na ₂ O) _{1/3} [(2TeO ₂) _x (B ₂ O ₃) _{1-x}] _{2/3} ", Journal of Non-Crystalline Solids, 2015, Vol. 426, pages 150-158 See abstract; and pages 150-152, 157.	1,2,4-10,12-18

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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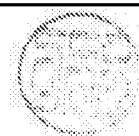
Date of the actual completion of the international search
28 December 2017 (28.12.2017)Date of mailing of the international search report
28 December 2017 (28.12.2017)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/000054

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YOUNGSIK KIM et al., "Preparation and characterization of germanium oxy-sulfide GeS ₂ -GeO ₂ glasses", Journal of Non-Crystalline Solids, 2005, Vol. 351, No. 24, pages 1973-1979 See abstract; and pages 1973-1977.	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/000054

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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