



(22) Date de dépôt/Filing Date: 2021/03/17

(41) Mise à la disp. pub./Open to Public Insp.: 2021/10/29

(45) Date de délivrance/Issue Date: 2023/10/31

(30) Priorité/Priority: 2020/04/29 (DE10 2020 111 624.1)

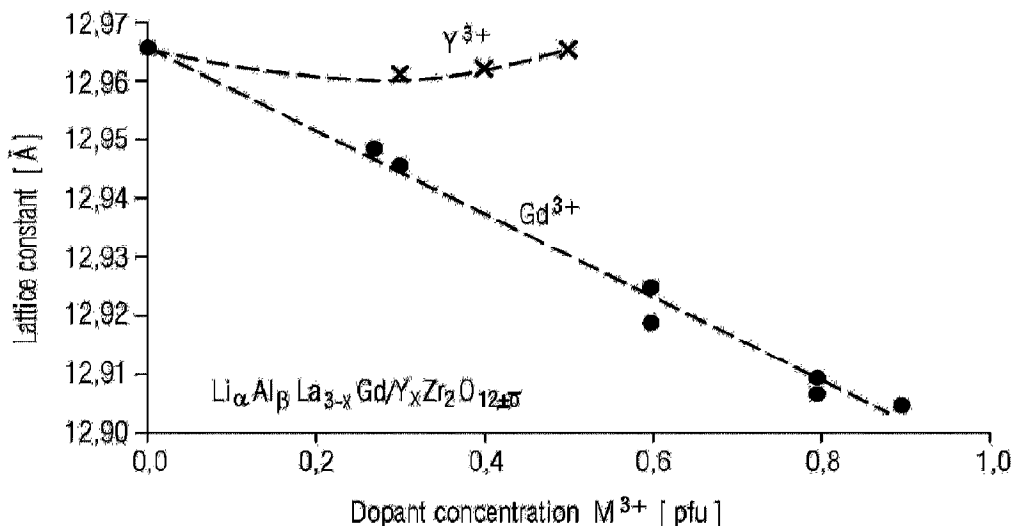
(51) Cl.Int./Int.Cl. *H01B 1/02* (2006.01),
C30B 29/22 (2006.01), *C30B 29/28* (2006.01),
H01M 10/0562 (2010.01), *H01M 4/06* (2006.01),
H01M 4/131 (2010.01), *H01M 50/431* (2021.01),
H01M 6/18 (2006.01)

(72) Inventeurs/Inventors:
LEUKEL, SEBASTIAN, DE;
SCHNEIDER, MEIKE, DE;
SCHMIDBAUER, WOLFGANG, DE;
RUDINGER, BERND, DE;
ROTTERS, ANDREAS, DE;
SCHUMACHER, JORG, DE

(73) Propriétaire/Owner:

(54) Titre : CONDUCTEUR AU LITHIUM-ION A DOPAGE EN ALUMINIUM FONDE SUR UNE STRUCTURE DE GRENAT

(54) Title: ALUMINUM-DOPED LITHIUM ION CONDUCTOR BASED ON A GARNET STRUCTURE



(57) Abrégé/Abstract:

The invention relates to an aluminum-doped lithium ion conductor based on a garnet structure, comprising lanthanum, in particular an aluminum-doped lithium lanthanum zirconate (LLZO), wherein the latter is co-doped with at least one trivalent M^{3+} ion on the

(73) Propriétaires(suite)/Owners(continued):SCHOTT AG, DE

(74) Agent: MARKS & CLERK

(57) Abrégé(suite)/Abstract(continued):

lanthanum site, wherein the trivalent M^{3+} ion has an ionic radius that is smaller than that of La^{3+} , and a higher lithium content is present in comparison to a stoichiometric garnet structure, with the provision that if M^{3+} is yttrium, a further trivalent M^{3+} ion, which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} , is co-doped on the lanthanum site. A co-doping strategy is carried out, in which a doping on the lanthanum site with ions of the same valence, but smaller diameter brings about the change in the lattice geometry to the cubic modification. This leads to a stabilization of the cubic crystal modification that is present also with superstoichiometric quantities of lithium.

Abstract

The invention relates to an aluminum-doped lithium ion conductor based on a garnet structure, comprising lanthanum, in particular an aluminum-doped lithium lanthanum zirconate (LLZO), wherein the latter is co-doped with at least one trivalent M^{3+} ion on the lanthanum site, wherein the trivalent M^{3+} ion has an ionic radius that is smaller than that of La^{3+} , and a higher lithium content is present in comparison to a stoichiometric garnet structure, with the provision that if M^{3+} is yttrium, a further trivalent M^{3+} ion, which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} , is co-doped on the lanthanum site. A co-doping strategy is carried out, in which a doping on the lanthanum site with ions of the same valence, but smaller diameter brings about the change in the lattice geometry to the cubic modification. This leads to a stabilization of the cubic crystal modification that is present also with superstoichiometric quantities of lithium.

Aluminum-doped lithium ion conductor based on a garnet structure

The present invention relates to an aluminum-doped lithium ion conductor based on a garnet structure, a method for its production, as well as use thereof.

Background of the prior art

In battery technology in the last few years, battery systems based on lithium ions have become increasingly widespread. These are particularly characterized by their high energy density and expected long service life, so that more efficient battery configurations are possible. The high chemical reactivity and the small mass of the lithium ions as well as their high mobility play a central role here. There is thus great interest in the development of solid state lithium ion conductors,

In the case of solid state batteries or solid state rechargeable batteries, both electrodes and the electrolyte are composed of solid material. In lithium ion batteries or rechargeable batteries, lithium compounds are present in all three phases of the electrochemical cell, i.e., the batteries contain lithium ions in the negative electrode, the positive electrode, and the electrolyte. The general advantage of lithium-based solid state batteries or rechargeable batteries in this case is that a liquid electrolyte that is frequently readily combustible or toxic and has a tendency toward decomposition is replaced, and thus an improvement of safety and reliability of lithium-based batteries is possible.

Lithium ion conductors that crystallize in a garnet structure or garnet-like structure, which are also called lithium garnets, such as lithium lanthanum zirconate (LLZO), due to their high ion conductivity at room temperature, are promising materials for use as solid electrolytes in solid state lithium ion batteries or all solid state batteries (ASSB)

(Murugan R., Thangadurai V., Weppner W., Fast lithium ion conduction in garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, *Angew. Chem. Int. Ed.* 46, 2007, 7778–7781).

These materials can be synthesized via different methods: With the help of a solid state reaction from a mixture of oxides, carbonates or hydroxides, via a sol-gel synthesis, based on the hydrolysis and condensation of nitrates and alkoxides, with spray pyrolysis, or from the gas phase or from plasma (sputtering process or CVD).

Although in the case of the solid state reaction, the latter should actually involve a simple synthesis pathway, this method has essential disadvantages in practical application. The high sintering temperatures and long residence times that are required at these high temperatures lead to a vaporizing of lithium, which makes difficult a precise control of the stoichiometry. Also, this vaporization presents a problem for the service life of ovens and other equipment used in the process, since lithium can form low-melting alloys with a number of metals.

Another problem is the formation of inhomogeneities in the product, which must frequently be compensated by costly additional processes, such as repeated grinding and repeated sintering steps. The formation of foreign phases is also observed.

Solvent-based production processes, such as, e.g., sol-gel methods or spray pyrolysis have the disadvantages that frequently large quantities of solvents and, as a rule, costly initial materials, such as, e.g., alkoxides, must be used.

In contrast thereto, the production via a melting method, for example, by melting and homogenizing the initial materials as well as cooling the melt, by direct solidifying or a targeted, controlled cooling or quenching of the melt, followed by a temperature treatment (ceramicizing treatment), such as described, for example in DE 10 2014 100 684 A1, offers a number of advantages with respect to scalability and cost efficiency. Oxides, hydroxides, carbonates, and/or salts can be used as initial materials in this case—each time selected depending on cost and availability. The initial materials are then melted together and homogenized in the melt. After this, a cooling process takes

place, and optionally, additional processes for shaping, thermal post-treatment, and crushing. It is therefore particularly advantageous to carry out the production of a lithium ion conductor by way of a melting method.

It is known that lithium lanthanum zirconate (LLZO) displays polymorphism, having a tetragonal structure at room temperature and a cubic structure at high temperature. However, only the cubic high-temperature structure provides the necessary high conductivity of more than 10^{-5} S/cm, whereas the tetragonal modification has only a clearly smaller ion conductivity of $< 10^{-6}$ S/cm. For this reason, a number of dopants, such as Nb, Ta, Ga, W, Sb, Te, Al, are used in order to stabilize the cubic phase at room temperature. The way in which this is done is achieved here, as a rule, always by the same procedure: By substituting one ion with another of higher valence, lithium vacancies are produced, and in this way, the cubic phase is stabilized (Gu W., Ezbiri M., Prasada Rao R., Avdeev M., Adams S., Effects of penta- and trivalent dopants on structure and conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, Solid State Ionics, 274, 2015, 100-105). This type of doping is in principle possible at any lattice site of the lithium lanthanum zirconate (LLZO) ($\text{Li}^+ \rightarrow \text{M}^{2/3+}$, $\text{La}^{3+} \rightarrow \text{M}^{4+}$, $\text{Zr}^{4+} \rightarrow \text{M}^{5/6+}$).

Another problem may occur, however, as a function of the type of dopant. If lithium lanthanum zirconate (LLZO) is to be used in contact with lithium metal, for example, as an anode in an all solid state battery (ASSB), polyvalent dopants cannot be used, such as niobium, for example (Ohta S., Kobayashi T., Asaoka T., High lithium ionic conductivity in the garnet-type oxide $\text{Li}_{7-x}\text{La}_3(\text{Zr}_{2-x}\text{Nb}_x)\text{O}_{12}$ ($x = 0-2$), J. Power Sources, 196, 2011, 3342-3345), tungsten (Dhivya L., Janani N., Palanivel B. and Murugan R., Li^+ transport properties of W substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ cubic lithium garnets, AIP Advances, 3, 2013, 082115), antimony (Ramakumar S., Satyanarayana L., Manorama S. V., Murugan R., Structure and Li^+ dynamics of Sb-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ fast lithium ion conductors, Phys. Chem. Chem. Phys. 15, 2013, 11327-11338, Abstract), or tellurium (Deviannapoorani C., Dhivya L., Ramakumar S., Murugan R., Lithium ion transport properties of high conductive tellurium substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ cubic lithium garnets, Journal of Power Sources, 240, 2013, 18-25), since they will be reduced and converted to isolating reaction products, or in fact can form electrically conducting reaction

products. Less reduction-stable dopants also include several of no interest for commercial use due to their high material costs, such as tantalum, for example (Wang Y., Lai W., High Ionic Conductivity Lithium Garnet Oxides of $\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$ Compositions, *Electrochem. Solid-State Lett.* 15, 2012, 68-71, Abstract) and gallium (Wu J.-F., Chen E.-Y., Yu Y., Liu L., Wu Y., Pang W. K., Peterson V. K., Guo X., Gallium-Doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Garnet-Type Electrolytes with High Lithium-Ion Conductivity, *ACS Appl. Mater. Interfaces*, 9, 2017, 1542-1552, Abstract).

Aluminum is particularly promising, since it is especially cost effective and is also stable against reduction. The stabilization of the cubic phase by aluminum is described in numerous publications (e.g.: Rangasamy E., Wolfenstine J., Sakamoto J., The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, *Solid State Ionics*, 206, 2012, 28-32).

Aluminum-doped lithium lanthanum zirconate (LLZO), however, is relatively sensitive to fluctuations in lithium content and also with respect to the temperature of the method. Since aluminum and lithium occupy the same lattice site, a lithium excess, which could actually compensate for the lithium loss during the production, and would positively influence the sintering behavior, leads to a preferred formation of the tetragonal phase and thus to a lack of stabilization of the cubic phase. Therefore, a mixture of cubic and tetragonal lithium lanthanum zirconate (LLZO) is formed (Rangasamy E. et al., 2012, loc. cit.).

This problem is intensified during production via a melting method, since here the diffusion in the melt is particularly great. In addition, a de-mixing can occur in cubic and tetragonal lithium lanthanum zirconate (LLZO) and secondary phases may appear in aluminum-doped, cubic lithium lanthanum zirconate (LLZO) during cooling or in downstream thermal processes. This represents a clear disadvantage for the use of aluminum-lithium lanthanum zirconate (LLZO) in an all solid state battery (ASSB), since the production frequently includes a sintering at high temperatures.

Doping with aluminum as a single dopant is described in numerous publications. Reference shall be made only by way of example to EP 2 159 867 A1, which relates to a solid electrolyte made of aluminum-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ as well as a method for the production thereof.

A lithium ion-conducting glass ceramic with garnet-like crystal structure is also described in DE 10 2014 100 684 A1. The lithium ion-conducting glass ceramic with garnet-like primary crystal phase has an amorphous percentage of at least 5 wt.%. Preferably, the garnet-like primary crystal phase has the empirical formula: $\text{Li}_{7+x-y}\text{M}_x^{\text{II}}\text{M}_{3-x}^{\text{III}}\text{M}_{2-y}^{\text{IV}}\text{M}_y^{\text{V}}\text{O}_{12}$ wherein M^{II} is a divalent cation, M^{III} is a trivalent cation, M^{IV} is a tetravalent cation, M^{V} is a pentavalent cation, wherein preferably $0 \leq x < 3$, more preferably $0 \leq x \leq 2$, $0 \leq y < 2$ and most preferably $0 \leq y \leq 1$. Lanthanum and zirconium are preferably present in addition to lithium, wherein additional dopants, such as aluminum, for example, can be included. The use of trivalent ions that have an ionic radius that is smaller than the lanthanum ion as co-dopants on the lanthanum site is not described.

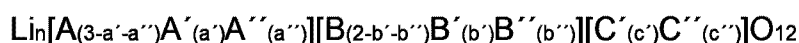
A doping of lithium lanthanum zirconate (LLZO) with trivalent ions on the lanthanum site is described in JP 2013-134852 A and JP 2013-149493 A. JP 2013-134852 A discloses a lithium ion conductor material that is a composite oxide having the chemical formula $\text{Li}_7\text{La}_{3-x}\text{A}_x\text{Zr}_2\text{O}_{12}$, wherein A is at least one metal, selected from the group Y, Nd, Sm and Gd, and x lies in the range $0 < x < 3$. JP 2013-149493 A relates to a lithium ion conductor material that is a composite oxide having the chemical formula $\text{Li}_{7-y}\text{La}_{3-x}\text{A}_x\text{Zr}_{2-y}\text{M}_y\text{O}_{12}$, wherein A is at least one metal, selected from the group Y, Nd, Sm and Gd, with $0 < x < 3$, and M is at least one metal selected from the group Nb, Ta, Sb, Bi and Pb, with $0 < y < 2$. However, a co-doping with aluminum is not described in the two documents, nor is the possibility disclosed of how the cubic phase can be stabilized with an excess of lithium.

In CN 107732298 A, a method is described for the ceramic production of stoichiometric $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ that is doped with Gd, but a co-doping with aluminum and the positive effects that are associated therewith due to the doping are not mentioned.

Also, JP 2018-195483 A relates to a solid electrolyte with garnet structure and a doping with Y, Nd, Sm or Gd in combination with an Nb or Ta doping on the zirconium site. A co-doping with aluminum is not mentioned, however.

US 2011/244337 A1 describes a lithium lanthanum zirconate (LLZO) with the formula $\text{Li}_{5+x}\text{La}_3(\text{Zr}_x\text{A}_{2-x})\text{O}_{12}$ that can be doped on the Zr site with one or more of the following elements: Sc, Ti, V, Y, Nb, Hf, Ta, Al, Si, Ga, Ge and Sn, wherein the following applies to x: $1.4 \leq x < 2$. In contrast to the present invention, the doping herein is produced by a replacement of Zr and not of La. This also means that the condition $(\text{La}^{3+} + \text{M}^{3+} + \text{M}^{2+} + \text{M}^{1+})/(\text{Zr}^{4+} + \text{M}^{6+} + \text{M}^{5+} + \text{M}^{4+} + \text{M}^{3+}) < 1.5$, wherein M^{3+} is always present and is therefore not zero, cannot be fulfilled. A stabilizing of the cubic phase in the case of a superstoichiometric Li content without the formation of foreign phases thus cannot be achieved in the US patent application. Also, a doping with a trivalent ion, with the exception of Al, Ga and Y, is not described here.

A compound with garnet-like structure that can contain La, Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb on the lanthanum site and optionally contains Al is described in DE 10 2011 079 401 A1. Specifically, a compound having a garnet-like crystal structure is disclosed herein, which has the following general chemical formula:



wherein A, A' and A'' stand for a dodecahedral position of the garnet-like crystal structure,

wherein A stands for at least one element selected from the group composed of La, Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb,

A' stands for at least one element selected from the group composed of Ca, Sr and Ba,

A'' stands for at least one element selected from the group composed of Na and K,

$0 \leq a' < 2$ and $0 \leq a'' < 1$,

wherein B, B' and B'' stand for an octahedral position of the garnet-like crystal structure,

wherein B stands for at least one element selected from the group composed of Zr, Hf and Sn,

B' stands for at least one element selected from the group composed of Ta, Nb, Sb and Bi,

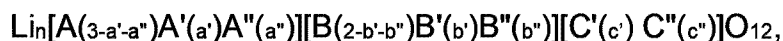
B'' stands for at least one element selected from the group composed of Te, W and Mo,
 $0 \leq b' \leq 2$ and $0 \leq b'' \leq 2$,

wherein C', and C'' stand for a tetrahedral position of the garnet-like crystal structure,
 wherein C' stands for at least one element selected from the group composed of Al and Ga,

C'' stands for at least one element selected from the group composed of Si and Ge,
 $0 \leq c' \leq 0.5$ and $0 \leq c'' \leq 0.4$, and wherein $n = 7 + a' + 2 \cdot a'' - b' - 2 \cdot b'' - 3 \cdot c' - 4 \cdot c''$ and
 $5.5 \leq n \leq 6.875$, wherein if $b' = 2$, $6.0 < n < 6.875$ or $5.5 \leq n \leq 6.875$ and $c' + c'' > 0$, and
 wherein if B' is Nb, $6.0 < n < 6.4$ or $5.5 \leq n \leq 6.875$ and $c' + c'' > 0$ and/or $a' + a'' > 0$.

Of course, here the lithium content corresponding to these garnet structural formulas must lie between 5.5 and a maximum of 6.875, and therefore corresponds to the stoichiometric lithium content, predefined by the dopings. A superstoichiometric lithium content is accordingly not included, unlike the case in the present invention. A superstoichiometric lithium content, however, acts positively on sintering behavior, for example, by lowering the sintering temperatures, and serves for the purpose of compensating for possible lithium losses arising during the production or further processing. This is not possible according to DE 10 2011 079 401 A1.

An analogous material is proposed in WO 2019/055730 A1 for use in the extraction of alkali metals from solutions. In particular, the document relates to an ion-conducting solid state electrolyte membrane, comprising an oxide material with garnet-like structure having the general formula:



wherein A, A', and A'' stand for a dodecahedron position of the crystal:

A stands for one or more trivalent rare-earth elements, such as La, Ce, Sc, Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb,

A' stands for one or more alkaline-earth metal elements such as Mg, Ca, Sr, and Ba.

A" stands for one or more alkali metal elements, except for Li, such as Na and K.

The following applies: $0 < a' < 2$ and $0 < a'' \leq 1$.

B, B', and B" stand for an octahedron position of the crystal:

B stands for one or more tetravalent elements, such as Zr, Hf, and Ti.

B' stands for one or more pentavalent elements, such as Ta, Nb, V, Sb, and Bi.

B" stands for one or more hexavalent elements, such as Te, W, and Mo.

The following applies: $0 < b' + b'' < 2$.

C and C" stand for a tetrahedron position of the crystal structure:

C stands for one or more of Al, Ga and boron.

C" stands for one or more of Si and Ge.

The following applies: $0 < c' < 0.5$ and $0 < c'' < 0.4$; and $n = 7 + a' + 2a'' - b' - 2b'' - 3c' - 4c''$ and $4.5 < n < 7.5$.

Here also, however, a possible lithium excess is explicitly excluded.

A doping of lithium lanthanum zirconate (LLZO) with rare earths, preferably Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu is disclosed also in US 2016/268630 A1. The following formula is described: $\text{Li}_{7+x}\text{La}_3\text{Zr}_{2-x}\text{A}_x\text{O}_{12}$, wherein A represents one or more rare-earth elements. The material can contain, in addition, 0.3 to 2 wt.% aluminum. The doping is produced here, however, on the zirconium site. Therefore, the ratio of $(\text{La}^{3+} + \text{M}^{3+} + \text{M}^{2+} + \text{M}^{1+})/(\text{Zr}^{4+} + \text{M}^{6+} + \text{M}^{5+} + \text{M}^{4+} + \text{M}^{3+}) < 1.5$, wherein M^{3+} is always present and is therefore non-zero, cannot be fulfilled at all, since doping does not take place on the lanthanum site. In US 2016/268630 A1, the incorporation of the described ions, which have a greater ionic radius than the Zr^{4+} , on the zirconium site leads to an increase in the lattice constant of the lithium lanthanum zirconate (LLZO). In contrast thereto, in the present invention, the incorporation of rare-earth ions on the lanthanum site leads to a decrease of the lattice constant (see Fig. 1 of the present invention, Gd doping). Therefore, there are effects present herein that are opposite to the present invention.

The use of further dopants in addition to aluminum is described in JP 2012-031025 A.

Here, an aluminum-doped lithium-garnet compound having the formula



is described, wherein

Ln = one or more elements selected from the group composed of La, Pr, Nd, Sm, Lu, Y, K, Mg, Ba, Ca, Sr;

M^1 = one or more elements selected from the group composed of Si, Sc, Ti, V, Ga, Ge, Y, Zr, Nb, In, Sb, Te, Hf, Ta, W, Bi;

M^2 = one or more elements selected from the group composed of Sc, Ti, V, Y, Nb, Hf, Ta, Si, Ga, Ge, different from M^1 ;

wherein $3 \leq x \leq 8$; $y > 0$; $z \geq 0$; $1.9 \leq y + z \leq 2.1$ and $11 \leq t \leq 13$. Although this corresponds to the specified garnet formula, a co-doping of an aluminum-containing material having a trivalent ion on the lanthanum site also would be possible, a co-doping with the use of smaller, preferably non-polyvalent ions is not disclosed herein. Also, the preferred doping with rare-earth ions, such as Gd, on the lanthanum site is not described here.

EP 3 518 251 A1 discloses a solid electrolyte with the formula $(Li_{7-ax+y}, A_x)La_3(Zr_{2-y}B_y)O_{12}$, wherein A is selected from Mg, Zn, Al, Ga and Sc, a = valence of A; B is selected from Al, Ga, Sc, Yb, Dy, and Y, and $0 < x < 1.0$, $0 < y < 1.0$ and $5.5 < (7 - ax + y) < 7.0$. Therefore, adjusting the ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+})$ to < 1.5 is not possible here. Also, a superstoichiometric lithium content that would be made possible thereby is generally excluded by the condition $(7 - ax + y) < 7$.

CN 106129463 proposes the use of a lithium lanthanum zirconate (LLZO) material with the formula $Li_{6+x}Al_y(La_zA_{3-z})(Zr_nG_{2-n})O_{12}$, which is mixed with 0 to 3 wt.% SiO_2 , Bi_2O_3 , B_2O_3 , CeO_2 , ZnO , CuO , MnO_2 , Co_2O_3 and SnO_2 , in order improve sinterability. Elements A, selected from at least one of Ca, Sr, Y or Ba, can be doped on the lanthanum site; elements G, selected from at least one of Ti, Nb, Ta, Sb and V, can be doped on the zirconium site. The following applies to the remaining parameters: $0 \leq x \leq 2$, $0 \leq y \leq 1$, $2 \leq z \leq 3$, $1 \leq n \leq 2$. The advantageous use of aluminum in combination with a smaller trivalent ion, except for yttrium, on the lanthanum site is not described. In the experiments relating to the present invention, it has been shown that the desired effect of the doping of a smaller ion on the lanthanum site cannot be achieved with the use of yttrium as the only dopant, since this element is incorporated partly on the zirconium site in the case of higher dopings, which leads to the formation of undesired secondary

phases (see Figure 2 of the present invention). Therefore, according to the invention, yttrium is always present in combination with an additional trivalent ion M^{3+} , which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} . This cannot be taken from the prior art. Also, according to the invention, preferably small quantities of yttrium of up to < 0.2 per formula unit of the aluminum-doped lithium ion conductor will be used, which promote the stabilization of the cubic phase and do not produce secondary phases. This also cannot be taken from CN 106129463.

The use of lanthanides and/or actinides as dopant is also the subject of US 2018/013171 A1 and US 2019/006707 A1 of the University of Michigan. The described ceramic has a structure corresponding to the formula $Li_wA_xRe_{3-y}M_2O_z$, wherein A is selected from B, Al, Ga, In, Zn, Cd, Y, Sc, Mg, Ca, Sr and Ba and combinations thereof; Re comprises one or more lanthanides and/or actinides; and M comprises the elements Zr, Hf, Nb, Ta, Mo, W, Sn, Ge, Si, Sb, Se, Te with $w = 5 - 7.5$, $x = 0 - 2$, $y = 0.01 - 0.75$, $z = 10.875 - 13.125$. Although here a trivalent ion with aluminum-doped garnet containing lanthanum and another trivalent ion at the site of Re also would be possible in a purely formal manner, this combination is not explicitly disclosed in the present document, and the positive effects are also not described. The lithium content is independently limited to a maximum of 7.5 by the doping.

CN 109888374 A describes a solid electrolyte material doped with Te, Ta, Ti, Nb, Ge, Ga, Gd or Bi on the zirconium site with the formula $A-Li_{7-bx}La_3Zr_{2-x}M_xO_{12}$, wherein A is selected from at least one of Al_2O_3 , $Al(NO_3)_3$, aluminum carbonate, ZnO and MgO; $0.1 \leq x \leq 1.5$ applies, $b = 0$ for tetravalent ions M and $b = 1$ for pentavalent ions M. It results from this that the lithium quantity is limited to the stoichiometric lithium quantity. In contrast to the present invention, the doping takes place exclusively on the zirconium site, for which reason $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+}) < 1.5$ is not fulfilled. The positive effects of doping with a smaller ion on the lanthanum site thus cannot be realized.

A solid electrolyte material doped with Sr, Gd on the lanthanum site and Zn, Al on the zirconium site is proposed in CN 107768715 A. The chemical formula reads:

$\text{Li}_{7+x+2m+n}\text{La}_{3-x-y}\text{Sr}_x\text{Gd}_y\text{Zr}_{2-m-n}\text{Zn}_m\text{Al}_n\text{O}_{12}$, wherein $0.2 \leq x \leq 0.4$, $0.1 \leq y \leq 0.2$, $0.1 \leq m \leq 0.2$, $0.2 \leq n \leq 0.3$. In the prior art, the use of zinc is generally viewed as completely unsuitable for generating the necessary lithium vacancies in order to ensure a high ion conductivity (see Rangasamy E., Wolfenstine J., Sakamoto J., The role of Al and Li concentration on the formation of cubic garnet solid electrolyte of nominal composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, Solid State Ionics, 206, 2012, 28-32). A doping of aluminum on the zirconium site is not provided in the present invention and is not desired, since this would counteract the generation of the desired lithium vacancies ($\text{Zr}^{4+} \rightarrow \text{Al}^{3+} + \text{Li}^+$).

Finally, EP 3 459 920 A1 describes a garnet-based ion conductor, in which both aluminum as well as further lanthanoids in addition to lanthanum can be doped. The general formula reads: $(\text{Li}_{x-3y-z}, \text{E}_y, \text{H}_z) \text{L}_\alpha \text{M}_\beta \text{O}_\gamma$, wherein E represents at least one of Al, Ga, Fe and Si; L is at least an alkaline-earth metal or lanthanoid; M is at least one element, selected from a transition element having 6-fold coordination with oxygen or a typical element in groups 12 to 15 of the Periodic Table; $3 \leq x - 3y - z \leq 7$; $0 \leq y < 0.22$; $0 \leq z \leq 2.8$; $2.5 \leq \alpha \leq 3.5$; $1.5 \leq \beta \leq 2.5$; and $11 \leq \gamma \leq 13$. Of course, here a superstoichiometric lithium content is explicitly prevented by exchanging a portion of the lithium for H^+ by treatment with water. A disadvantage of this treatment, however, is that the efficiency in the battery can clearly be adversely affected by the reduction in the quantity of Li^+ ions and a possible proton conduction that may arise. Although here a trivalent ion M^{3+} with aluminum-doped garnet containing lanthanum and another trivalent ion M^{3+} at the L site also would be possible in a purely formal manner, this combination is not explicitly disclosed in the present document, and the positive effects of the doping with smaller trivalent cations M^{3+} at the site of L are also not described.

The present invention is thus based on the object of avoiding the disadvantages illustrated in the prior art and of providing an aluminum-doped lithium ion conductor based on a garnet structure, in particular a lithium lanthanum zirconate (LLZO), which has an excess of lithium present above a stoichiometric amount, but nevertheless provides a sufficient stability in the cubic modification, in particular a stability against thermal processes. The advantageous properties of the aluminum doping, such as, for example, a cost-effective use of aluminum and a stability against reduction in contact

with lithium metal, shall be maintained. In addition, the aluminum-doped lithium ion conductor based on a garnet structure shall be producible by way of a melting method.

Description of the invention

The object depicted in the preceding is achieved according to the invention by the following features and embodiments.

In a surprising way, it was established that the above object is achieved by an aluminum-doped lithium ion conductor based on a garnet structure, comprising lanthanum, in particular an aluminum-doped lithium lanthanum zirconate (LLZO), wherein the latter is co-doped with at least one trivalent M^{3+} ion on the lanthanum site, wherein the trivalent M^{3+} ion has an ionic radius that is smaller than that of La^{3+} , and a higher lithium content (superstoichiometric lithium content) is present in comparison to a stoichiometric garnet structure, with the provision that if M^{3+} represents yttrium, an additional trivalent M^{3+} ion, which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} , is co-doped on the lanthanum site.

According to a preferred embodiment, the present invention thus relates to an aluminum-doped lithium ion conductor having the general chemical formula:



wherein

M^{3+} : represents one or more trivalent cations with an ionic radius smaller than La^{3+} , with the exception of Al^{3+} ,

M^{2+} : represents one or more divalent cations,

M^{1+} : represents one or more monovalent cations, with the exception of Li^+ ,

M^{4+} : represents one or more tetravalent cations, with the exception of Zr^{4+} ,

M^{5+} : represents one or more pentavalent cations,

M^{6+} : represents one or more hexavalent cations,

$$0.1 \leq x < 1$$

$$0 < y < 2$$

$$0 \leq y' < 0.2$$

$$0 \leq y'' < 0.2$$

$$0 \leq y' + y'' < 0.2$$

$$0 \leq z < 0.5$$

$$0 \leq z' < 0.8$$

$$0 \leq z'' < 0.5$$

$$0 \leq \delta < 2,$$

wherein

$u > 0$ for a superstoichiometric lithium content, preferably $u \geq 0.2$,

with the provision that if M^{3+} represents yttrium, an additional trivalent M^{3+} ion, which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} , is co-doped on the lanthanum site.

The general chemical formula (I) given above involves an aluminum-doped lithium lanthanum zirconate (LLZO).

The formulation “based on a garnet structure” means that the known basic structure is present each time, wherein, however, deviations from the basic structure known from the prior art may exist. These can be, for example, in addition, dopings with other elements that are known from the prior art. The term thus comprises all compounds falling under the general heading of garnet structure or garnet-like structure.

$0.1 \leq x$ means $x = 0.1$ and $0.1 < x$, wherein $0.1 < x$ preferably means values for x that are 0.11 or greater; and $x < 1$ preferably means values for x that are 0.99 or smaller.

$0 < y$ preferably means values for y that are 0.001 or higher and $y < 2$ preferably means values for y that are 1.99 or less.

$0 \leq y'$ means $y' = 0$ and $0 < y'$, wherein $0 < y'$ preferably means values for y' that are 0.01 or higher; and $y' < 0.2$ preferably means values for y' that are 0.19 or less.

$0 \leq y''$ means $y'' = 0$ and $0 < y''$, wherein $0 < y''$ preferably means values for y'' that are 0.01 or higher; and $y'' < 0.2$ preferably means values for y'' that are 0.19 or less.

$0 \leq y'+y''$ means $y'+y'' = 0$ and $0 < y'+y''$, wherein $0 < y'+y''$ preferably means values for $y'+y''$ that are 0.01 or higher; and $y'+y'' < 0.2$ preferably means values for $y'+y''$ that are 0.19 or less.

$0 \leq z$ means $z = 0$ and $0 < z$, wherein $0 < z$ preferably means values for z that are 0.01 or higher; and $z < 0.5$ preferably means values for z that are 0.49 or less.

$0 \leq z'$ means $z' = 0$ and $0 < z'$, wherein $0 < z'$ preferably means values for z' that are 0.01 or higher; and $z' < 0.8$ preferably means values for z' that are 0.79 or less.

$0 \leq z''$ means $z'' = 0$ and $0 < z''$, wherein $0 < z''$ preferably means values for z'' that are 0.01 or higher; and $z'' < 0.5$ preferably means values for z'' that are 0.49 or less.

$u > 0$ preferably means values for u that are 0.01 or higher.

$u \geq 0.2$ means $u = 0.2$ and $u > 0.2$, wherein $u > 0.2$ preferably means values for u that are 0.21 or higher.

According to one embodiment, the aluminum-doped lithium lanthanum zirconate (LLZO) according to the above chemical formula (I) thus has a lithium content that is higher in comparison to a stoichiometric garnet structure and that lies at $u > 0$, preferably $u \geq 0.2$. A stoichiometric lithium content would be present for $u = 0$. The latter is determined by the quantity of Al^{3+} and M^{1+} , M^{2+} , M^{5+} and M^{6+} : $\text{Li}_{7-3x+y'+2y''-z'-2z''}$. A stoichiometric lithium content in the aluminum-doped lithium ion conductor, preferably lithium lanthanum zirconate (LLZO) is not desired according to the invention and is thus excluded.

It has been found that it is advantageous if the quantity x of aluminum amounts to $0.1 \leq x < 1$, referred to one formula unit of the lithium lanthanum zirconate (LLZO), preferably $0.14 \leq x < 1$, referred to one formula unit of the lithium lanthanum zirconate (LLZO), in formula (I), in order to obtain sufficient lithium vacancies (V_{Li}) for stabilizing the cubic

modification of doped lithium lanthanum zirconate (LLZO) at room temperature. The following also is particularly preferred: $0.1 \leq x < 0.5$, and still more preferred is $0.14 \leq x < 0.5$.

In order to simplify and for better understanding, in the present description, the lithium lanthanum zirconate (LLZO) is usually drawn on as a representative example for explaining an aluminum-doped lithium ion conductor. It is understood, however, that embodiments for any other aluminum-doped garnet-based lithium ion conductors shall be valid in the same way. In the following, the aluminum-doped, garnet-based lithium ion conductor is also simply called just a lithium ion conductor or aluminum-doped lithium ion conductor.

The numerical or quantitative data for the individual components of the lithium ion conductor that are specified without units are understood as [pfu], i.e., atoms per formula unit of the aluminum-doped lithium ion conductor, in particular of the aluminum-doped lithium lanthanum zirconate (LLZO).

The super-valent doping of an aluminum-doped lithium ion conductor, in particular of lithium lanthanum zirconate (LLZO), i.e., a doping with ions that have a higher valence than the ion to be replaced is of great importance for generating lithium vacancies, which finally lead to the stabilizing of the cubic modification with higher ion conductivity at room temperature.

According to the invention, therefore, a super-valent doping with aluminum is present on the lithium site ($\text{Li}^+ \rightarrow \text{Al}^{3+} + 2 \text{V}_{\text{Li}}$; two Li vacancies are generated per Al^{3+}). As already mentioned, the doping with aluminum is of advantage in comparison to niobium, based on the low cost of raw materials, in particular in comparison to tantalum or gallium, as well as due to the good redox stability. Since, however, unlike in the doping with tantalum or niobium, the doping with aluminum takes place directly on the lithium site, an exact balancing of the lithium-aluminum ratio is necessary in order to obtain the correct phase: An increase in the lithium content would lead to the fact that the dopant aluminum would be partially displaced again from the crystal structure, so that the cubic

lithium lanthanum zirconate (LLZO) would no longer be stabilized sufficiently at room temperature. A simple increase in the lithium content by using a larger quantity of lithium initial component thus is out of the question.

This circumstance is particularly critical, since an increased lithium content is desirable in order to compensate for the vaporization of Li_2O at the high synthesis temperatures, on the one hand, (independent of the production process: reactive sintering, sol-gel, spray pyrolysis, melt), and, on the other hand, in order to improve the sintering properties of the material (Rangasamy E. et al., 2012, loc.cit.). In the production of lithium lanthanum zirconate (LLZO) by way of a melting process, the phase composition reacts in a particularly sensitive manner to a change in the aluminum-lithium ratio. Even a slight change in the lithium content, such as may occur for fluctuations in production, leads to a massive shift in the phase content relating to the undesired tetragonal lithium lanthanum zirconate (LLZO). This is also shown in the examples for the present invention.

The present invention solves this problem of lithium sensitivity of the aluminum-doped lithium ion conductor, in particular aluminum-doped lithium lanthanum zirconate (LLZO) by a specific co-doping strategy for the aluminum-doped lithium ion conductor, which stabilizes the cubic phase against a higher lithium content, in particular a superstoichiometric lithium content.

The co-doping strategy according to the invention comprises the doping of an aluminum-doped lithium ion conductor, in particular an aluminum-doped lithium lanthanum zirconate (LLZO), with one or more trivalent M^{3+} cations on the lanthanum site, whose ionic radius according to Shannon (Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Cryst.* 32, 1976, 751-767) is smaller than the ionic radius of the La^{3+} cation.

The use of trivalent cations of the lanthanides as M^{3+} , is preferred; these correspond to the named condition for the ionic radius, i.e., the group composed of cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium,

dysprosium, holmium, erbium, thulium, ytterbium and lutetium. Actinides, such as for example, thorium and protactinium, could also be used, since they satisfy the condition of a smaller ionic radius than La^{3+} . Based on their radioactivity, however, one should refrain from using them. Also, other trivalent cations, which fulfill the requirement that they have a smaller ionic radius than La^{3+} , such as, for example, yttrium, scandium, bismuth and indium, can be used. Most particularly preferred is the combination of gadolinium and yttrium. However, the invention is not limited thereto.

The presence of yttrium alone as trivalent M^{3+} cation is generally excluded in the present invention, since it does not achieve the object according to the invention. It has been found that the use of yttrium alone as M^{3+} does not display the desired stabilization, since the quantity of Y^{3+} necessary for stabilization is not fully introduced on the lanthanum site. With increasing yttrium content, the formation of undesired secondary phases sharply increases (see Figure 2 of the present invention and the explanations therefor). As will be described in detail, with the use of yttrium in comparison to gadolinium, Figure 1 shows a deviation of the lattice parameter from Vegard's Law (linear relationship between degree of doping and lattice parameter). This behavior should probably be attributed to the binding structure of the yttrium that is different in comparison to the binding structure of the lanthanides, which is characterized by the absence of f-orbitals in the case of yttrium. Therefore, if M^{3+} is yttrium, an additional trivalent M^{3+} ion that has an ionic radius that is smaller than that of La^{3+} and that is different than Y^{3+} must be co-doped on the lanthanum site.

If yttrium should be present in the aluminum-doped lithium ion conductor, it is particularly advantageous if yttrium is used in a quantity such that $\text{Y}^{3+} < 0.2$ per formula unit of the aluminum-doped lithium ion conductor. The stabilization of the cubic phase can be promoted in this way.

Of the trivalent cations of the lanthanides as M^{3+} , gadolinium is particularly preferred. Thus, the use of at least 0.1 mol of gadolinium as trivalent cation per formula unit of the aluminum-doped lithium ion conductor, in particular aluminum-doped lithium lanthanum zirconate (LLZO) is particularly advantageous. In other words, in the above formula (I),

the trivalent M^{3+} cation is particularly preferred to be gadolinium and the following is then valid for y : $y > 0.1$ [pfu]. Then $y = 0.11$ or greater is particularly preferred. Aluminum is especially well stabilized as dopant thereby in the garnet structure, whereby the cubic phase remains also in the case of a lithium excess.

In another particularly preferred embodiment, a combination of Gd^{3+} and Y^{3+} is present for M^{3+} in the aluminum-doped lithium ion conductor, and the following preferably applies: $Y^{3+} < 0.2$ per formula unit of the aluminum-doped lithium ion conductor and $Gd^{3+} > 0.1$ per formula unit of the aluminum-doped lithium ion conductor.

For the use of the described ion-conducting lithium lanthanum zirconate (LLZO) as electrolyte in a battery with a lithium anode, it is preferred if the trivalent M^{3+} cations that are used for the doping on the lanthanum site are not polyvalent. In other words, M^{3+} ions, which may have a valence other than trivalent, such as, for example, Ce^{3+}/Ce^{4+} , are thus preferably not used for M^{3+} in the present invention when a lithium anode is present in a battery to be used. Also, other anode materials may reduce polyvalent cations.

The selection of the dopants for the lanthanum based on their smaller ionic radius is a completely novel concept and it follows a completely different approach than in the entire prior art: The procedure known from the prior art is aliovalent doping (doping with ions of a different valence (e.g., $Zr^{4+} \rightarrow Ta^{5+} + V_{Li}$ or $Zr^{4+} \rightarrow Y^{3+} + Li^{+}$) in order to influence the lithium vacancy concentration (V_{Li}). In contrast to this, according to the invention, an isovalent doping (doping with ions of the same valence) is carried out with a smaller trivalent cation (M^{3+} for La^{3+}), wherein the lithium vacancy concentration (V_{Li}) is not directly influenced, but is stabilized by the change in the lattice geometry of the aliovalent dopant aluminum that is present in the crystal structure. This can also be referred to as "second-order doping". Therefore, unlike what is usual in the prior art, instead of the lithium vacancy concentration (V_{Li}), influence is brought to bear directly on the lattice geometry.

Since Al^{3+} and Li^+ compete for the same lattice sites, with a superstoichiometric lithium content, aluminum is displaced from the lithium lanthanum zirconate (LLZO) structure. The desired cubic modification is no longer sufficiently stabilized thereby and tetragonal lithium lanthanum zirconate (LLZO) is partially formed. This is also shown and substantiated in the examples for the present invention.

Due to the partial replacement of La^{3+} by one or more trivalent M^{3+} cations, whose ionic radius is smaller than that of La^{3+} , the unit cell of the lithium lanthanum zirconate (LLZO) structure shrinks (see also Figure 1). Since the Al^{3+} cation with an ionic radius according to Shannon (Shannon, R. D., 1976, loc. cit.) of 67.5 pm in octahedral coordination or 53.5 pm in tetrahedral coordination is smaller than the Li^+ cation with an ionic radius according to Shannon (Shannon, R. D., 1976, loc. cit.) of 90 pm in octahedral coordination or 76 pm in tetrahedral coordination, the incorporation of Al^{3+} is promoted in the case of a smaller unit cell. It is thus preferred that the lattice constant a of the cubic lithium lanthanum zirconate (LLZO) modification is smaller than 12.965 Å. Preferably, this means 12.964 Å or smaller. Due to this stabilization of Al^{3+} in the lithium lanthanum zirconate (LLZO) structure, in a surprising way, superstoichiometric quantities of lithium are also now possible without forming tetragonal lithium lanthanum zirconate (LLZO).

This effect is stronger, the more La^{3+} is replaced by one or more trivalent M^{3+} cations, whose ionic radius is smaller than that of La^{3+} . However, with too great a degree of doping, undesired, poorly ion-conducting secondary phases may occur, for which reason, the quantity y of M^{3+} in formula (I) is limited to $0 < y < 2$, referred to one formula unit of the aluminum-doped lithium lanthanum zirconate (LLZO).

In addition, a small portion of the La^{3+} can be optionally replaced by one or more divalent M^{2+} cations and one or more monovalent M^{1+} cations. In this way, however, the number of lithium vacancies is reduced and tetragonal lithium lanthanum zirconate (LLZO) can form. Therefore, too high a percentage of M^{2+} and M^{1+} on the lanthanum site should be avoided, and the sum of the monovalent and divalent cations M^{2+} and M^{1+} is thus limited to < 0.2 .

In order to increase the lithium vacancy concentration, in addition to the super-valent doping with aluminum on the lithium site, zirconium can also be partially replaced by one or more pentavalent M^{5+} cations or one or more hexavalent M^{6+} cations. In this case, the quantity z' of pentavalent cations should be smaller than 0.8, the quantity of hexavalent cations z'' should be less than 0.5, each time referred to one formula unit of the aluminum-doped lithium lanthanum zirconate (LLZO). Too many vacancies in the lithium sublattice can lead to a reduction in conductivity as well as promote the formation of foreign phases (e.g., pyrochlore). Also, zirconium can be partially replaced by other tetravalent M^{4+} cations. This occurs, e.g., due to the contamination of Zr raw materials with Hf^{4+} . Doping can take place also, however, in a targeted manner with tetravalent cations, such as Si^{4+} and Ge^{4+} , on the zircon site, in order to influence, for example, the sintering properties of the material. However, this does not influence the lithium vacancy concentration.

The co-doping strategy according to the invention therefore comprises a combination both of super-valent doping with aluminum on the lithium site as well as isovalent doping with one or more trivalent M^{3+} cations on the lanthanum site, the ionic radius of these trivalent M^{3+} cations being smaller than that of La^{3+} ; and optionally with one or more monovalent M^{1+} cations and optionally with one or more divalent M^{2+} cations on the lanthanum site; as well as optionally with one or more tetravalent M^{4+} cations, with optionally one or more pentavalent M^{5+} cations, and optionally with one or more hexavalent M^{6+} cations on the zirconium site. In this way, aluminum-doped lithium lanthanum zirconate (LLZO) with superstoichiometric lithium content is obtained and the stability and preference for the cubic modification is assured.

The co-doping strategy according to the invention provides the use of trivalent M^{3+} cations, the ionic radius of which is smaller than that of the La^{3+} , as isovalent dopant on the lanthanum site. An aliovalent doping with M^{3+} on the zirconium site ($Zr^{4+} \rightarrow M^{3+} + Li^+$) opposes the generation of lithium vacancies and is thus not desired. Therefore, a ratio preferably of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+}) < 1.5$, preferably $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+}) < 1.35$, is adjusted. In this ratio, M^{3+} is always present and is thus not 0. M^{1+} , M^{2+} , M^{4+} , M^{5+} and M^{6+} are optionally

present and in each case may also be 0. Preferably, the ratio of $(\text{La}^{3+} + \text{M}^{3+} + \text{M}^{2+} + \text{M}^{1+})/(\text{Zr}^{4+} + \text{M}^{6+} + \text{M}^{5+} + \text{M}^{4+} + \text{M}^{3+})$ can lie in the range of 1.49 to 1.0, more preferably in the range of 1.35 to 1.0. In the examples, values and a sample calculation for this ratio are specified. The ratio is therefore adjusted to the specified value in order to avoid the formation of foreign phases in a doping on the lanthanum site.

A melting method is the preferred method for the production of large quantities of the ion-conductive garnet. Sol-gel reactions and spray pyrolysis are disadvantageous, because these consume large quantities of solvent. Also, a reactive sintering, i.e., a heating below the melting point of the initial components, is disadvantageous, since, due to the large surface, a strongly corrosive Li_2O atmosphere is produced, which attacks the oven material and contact materials.

When a melting method is used for the production, however, it should be taken into consideration that lithium-containing melts are very aggressive, so that a melting cannot be carried out in platinum or platinum-rhodium crucibles. A melting in a platinum crucible leads to an attack on the crucible material, and, in the produced product, to clearly detectable quantities of the precious metal. This results in turn in a clear percentage of electronic conductivity via precious metals, which acts overall in a detrimental manner.

The production by melting down and homogenizing is thus preferably carried out in an inductively heated skull crucible, by which means the above-mentioned disadvantages will be avoided.

Another possibility for production by melting technology is the use of a vitreous carbon crucible. Since these crucibles, however, become oxidized in oxygen-containing atmospheres at the required high temperatures, the production must take place under a protective gas atmosphere (nitrogen or argon). This mode of production therefore makes sense only for smaller amounts; it would be disadvantageous, however, for large-scale production, since it is associated with additional costs.

The invention therefore also relates to a method for producing an aluminum-doped lithium ion conductor, wherein the production is carried out with the use of a melting method, preferably in a skull crucible.

A skull crucible is constructed from a plurality of metal pipes through which coolant flows, with slot-like intermediate spaces between the metal pipes, and with an induction coil surrounding the metal pipes from outside, wherein the metal pipes are preferably short-circuited together. For the production by way of a melting method, for example, by melting and homogenizing the initial materials with the use of a skull crucible and cooling of the melt, either by direct solidifying or a targeted, controlled cooling, or by quenching, followed by a temperature treatment (ceramicizing treatment), refer to DE 199 39 780 A1, DE 199 39 782 C1 and DE 10 2014 100 684 A1.

Aluminum-doped lithium ion conductors, in particular an aluminum-doped lithium lanthanum zirconate (LLZO) that is or are produced via a melting method, is or are characterized in that in addition to the crystalline ion-conducting garnet, an amorphous phase in which lithium and/or aluminum and/or M^{3+} are enriched may also be present. This has the advantage that the softening point or melting point of this amorphous phase is lower than that of the lithium lanthanum zirconate (LLZO), for which reason the sintering properties are improved. This means, for example, lower sintering temperatures and denser sintering.

The subject of the invention is also a powder composed of the aluminum-doped lithium ion conductor according to the present invention, which has a particle size in the range of $d_{50} = 0.1 \mu\text{m}$ to $30 \mu\text{m}$. The particle size was determined by a laser particle-size analyzer (CILAS).

In addition, the present invention relates to a sintered aluminum-doped lithium ion conductor, preferably produced with the use of the above-mentioned powder, wherein the sintered aluminum-doped lithium ion conductor has a lithium ion conductivity of more than 10^{-5} S/cm .

In addition, the present invention relates to the use of the aluminum-doped lithium ion conductor, preferably in the form of a powder, in batteries or rechargeable batteries, preferably lithium batteries or lithium rechargeable batteries, in particular separators, cathodes, anodes, or solid electrolytes.

The aluminum-doped lithium ion conductor according to the invention, preferably in the form of lithium ion conducting powder materials, alone or together with additional battery materials, for example, sintered into a purely inorganic, ceramic membrane, or as electrolyte, incorporated as a filler in a polymer electrolyte or in polyelectrolytes, in rechargeable lithium ion batteries, in particular in solid-state lithium ion batteries (all-solid-state batteries (ASSB)). On the one hand, use as a separator is possible in this case: Introduced between the electrodes, it protects them from an undesired short circuit and in this way assures the functionality of the entire system. To do this, the corresponding composite can either be introduced as a layer onto one or both electrodes or it can be integrated into the battery as a free-standing membrane, as a solid-state electrolyte. On the other hand, a co-sintering or compounding with the electrode materials is possible: In this case, the solid-state electrolyte accomplishes the transport back and forth of the relevant charge carriers (lithium ions and electrons) to the electrode materials and to the conducting electrodes, each time depending on whether the battery is being directly charged or discharged.

As additional applications of the material according to the invention, use in gas sensors and as ion-selective membranes in chemical processes is also conceivable.

The advantages of the present invention are of many layers:

In a surprising way, it was established that the cubic modification of an aluminum-doped lithium ion conductor based on a garnet structure, preferably an aluminum-doped lithium lanthanum zirconate (LLZO), is then obtained particularly when co-doping takes place with at least one trivalent M^{3+} ion on the lanthanum site, wherein the trivalent M^{3+} ion has an ionic radius that is smaller than that of La^{3+} , with the provision that the trivalent

M^{3+} ion does not represent only yttrium. Doping only with aluminum on the lithium site is not sufficient for stabilization of the cubic modification in the case of a superstoichiometric lithium content, so that a sufficient stabilization of the cubic modification is obtained only in combination with an isovalent doping with one or more trivalent M^{3+} cations, the ionic radius of which is smaller than that of La^{3+} , on the lanthanum site. Only the cubic modification leads to a desired high conductivity of more than 10^{-5} S/cm.

The doping of the lithium ion conductor with aluminum based on a garnet structure is of advantage, due to the low costs for raw materials as well as the known good redox stability in comparison to other elements. In addition, the doping of aluminum on the lithium site leads to an increased number of lithium vacancies (two Li vacancies are generated per Al^{3+}).

Furthermore, in comparison to a stoichiometric garnet structure, a higher lithium content is possible in the aluminum-doped lithium ion conductor based on a garnet structure. This is particularly advantageous, since an increased lithium content, on the one hand compensates for the vaporization of Li_2O in the case of the high temperatures during the production, and, on the other hand, the sintering properties of the material are improved.

Optionally, one or more additional monovalent M^{1+} cations (except for Li^+) and one or more divalent M^{2+} cations can be doped on the lanthanum site. However, this reduces the lithium vacancy concentration. Therefore, the sum of the monovalent M^{1+} cations (except for Li^+) and divalent M^{2+} cations is limited to less than 0.2, referred to one formula unit of the aluminum-doped lithium lanthanum zirconate (LLZO). The advantage of the use of monovalent M^{1+} cations (except for Li^+) and also divalent M^{2+} cations is that the sintering properties can be improved thereby.

With the use of monovalent ions, except for lithium, preferably those ions are used that have a lesser mobility than the lithium ion, thus, e.g., K^+ or Cs^+ , in order not to adversely affect the use as lithium ion conductors in batteries.

With the use of divalent ions, preferably those ions that are not polyvalent are used, thus, e.g., alkaline-earth cations, in order not to adversely affect the use as lithium ion conductors in batteries.

Optionally, in addition, one or more pentavalent M^{5+} cations and one or more hexavalent M^{6+} cations can also be doped on the zirconium site, in order to increase the lithium vacancy concentration. Also, a portion of the Zr^{4+} cations can be replaced by one or more tetravalent M^{4+} cations, such as Si^{4+} and Ge^{4+} . However, the lithium vacancy concentration remains uninfluenced by this.

Preferably, lanthanides and combinations of lanthanides and other trivalent cations that fulfill the requirement that they have an ionic radius that is smaller than La^{3+} are used for the trivalent M^{3+} cations. Most particularly preferred is gadolinium and the combination of gadolinium and other trivalent cations that fulfill the requirement that they have an ionic radius that is smaller than La^{3+} , for example yttrium.

The use of gadolinium as trivalent cation is particularly preferred, wherein at least 0.1 mol of gadolinium per formula unit of the aluminum-doped lithium ion conductor, in particular aluminum-doped lithium lanthanum zirconate (LLZO) is preferably present. In chemical formula (I), y would then be > 0.1 for Gd^{3+} , and preferably y would be 0.11 or greater. This is particularly advantageous, since aluminum is especially well stabilized as dopant thereby in the garnet structure, whereby the cubic phase remains also in the case of a lithium excess.

With use of the described lithium ion conductor as electrolyte in a battery with a lithium anode, it is preferred if the trivalent M^{3+} cations that are used for the doping on the lanthanum site are not polyvalent, i.e., they can only exist as trivalent. Also, other anode materials may reduce polyvalent cations.

Therefore, according to the invention, a concept that is completely different than that in the prior art is realized. Instead of the usual doping with ions of different valence with direct influence on the number of lithium vacancies (V_{Li}), according to the invention, a

combination of aliovalent doping and isovalent doping will be carried out, wherein a doping on the lanthanum site with ions of the same valence, but smaller diameter, brings about the change in the lattice geometry in the desired direction. This “doping of the second order” leads to a reduction in the unit cell of the lithium lanthanum zirconate (LLZO) structure, which promotes the incorporation of Al^{3+} on the lithium site. The more that La^{3+} is replaced by one or more trivalent M^{3+} cations with smaller ionic radius, the clearer the effect becomes; this replacement can be limited, however, due to the formation of disadvantageous secondary phases. The quantity y of M^{3+} in formula (I) is thus limited to $0 < y < 2$, referred to one formula unit of the aluminum-doped lithium lanthanum zirconate (LLZO).

This is successfully carried out by adjusting the lattice constant a in a targeted manner by the selected percentage of smaller M^{3+} cations; i.e., preferably $a < 12.965 \text{ \AA}$, so that the cubic modification is obtained. This stabilization of Al^{3+} makes possible, in an unexpected way, the use of superstoichiometric quantities of lithium without the tetragonal modification being formed.

The stability of the cubic phase is further improved by the co-doping with a smaller ion on the lanthanum site during a thermal post-treatment; the formation of undesired secondary phases is not observed.

It is particularly preferred that a ratio of $(\text{La}^{3+} + \text{M}^{3+} + \text{M}^{2+} + \text{M}^{1+})/(\text{Zr}^{4+} + \text{M}^{6+} + \text{M}^{5+} + \text{M}^{4+} + \text{M}^{3+}) < 1.5$ is adjusted, whereby, with a doping on the lanthanum site, the formation of foreign phases can be avoided.

Preferably, the aluminum-doped lithium ion conductor according to the invention, in comparison to a stoichiometric garnet structure, has a higher lithium content and a ratio of cubic to tetragonal crystal phase of $>90 \%$ to $<10\%$ (e.g., 90.1% or more of cubic crystal modification to 9.9% or less of tetragonal crystal modification), preferably $>95\%$ to $<5\%$ (e.g., 95.1% or more of cubic crystal modification to 4.9% or less of tetragonal crystal modification), particularly preferred $>98\%$ to $<2\%$ (e.g., 98.1% or more of cubic crystal modification to 1.9% or less of tetragonal crystal modification).

The production of the lithium ion conductor of the present invention preferably takes place via a melting method. In general, solvents can be avoided in this way. The use of a skull crucible for the production is thereby preferred. An aluminum-doped lithium ion conductor produced via a melting method, the conductor being based on a garnet structure, in particular an aluminum-doped lithium lanthanum zirconate (LLZO) advantageously has, in addition to the crystalline ion-conducting garnet, an amorphous phase in which lithium and/or aluminum and/or M^{3+} are enriched.

Description of the drawings

Several aspects in connection with the present invention will be described in more detail based on the appended drawings, without this limiting the invention. In the drawings:

Figure 1 shows the lattice constant of the cubic Al-doped lithium lanthanum zirconate (LLZO) modification as a function of the dopant concentration of gadolinium (Gd) and yttrium (Y); and

Figure 2 shows excerpts, arranged one above the other, of x-ray diffraction (XRD) diffractograms of Examples 14, 15, 16 and 18.

In Figure 1, the lattice constant in [Å] of the cubic, Al-doped lithium lanthanum zirconate (LLZO) modification (y-axis) is plotted against the dopant concentration in [pfu] of gadolinium (Gd) and yttrium (Y) (x-axis). The lattice constant decreases linearly with the replacement of La^{3+} by the smaller Gd^{3+} ion (Vegard's Law). The deviant behavior in the case of the yttrium doping shows that the desired reduction in the lattice constant due to yttrium alone cannot be reliably achieved.

In order to investigate the yttrium doping in detail, for structural clarification, XRD x-ray diffractograms were taken of the compositions according to Examples 14, 15, 16 and 18. In Figure 2, excerpts of 4 XRD x-ray diffractograms of each of Examples 14, 15, 16 and 18 are now shown arranged one above the other. The compositions of the Examples are

specified in Table 1. The XRDs show the increase in the foreign phase LiYO_2 with increasing yttrium content in the Examples 14, 15, and 16. The excerpts of XRDs that are shown with small scattering angles make it clear that with increasing yttrium content, in addition to the desired cubic LLZO modification (solid lines), an undesired secondary phase (dashed lines)—that was identified as LiYO_2 —also is found to be increased. In the case of co-doping of Gd^{3+} with small quantities of Y^{3+} (Example 18), the formation of this secondary phase is not observed.

Therefore, Figure 1 shows that gadolinium (Gd), for example, is particularly well suitable for doping on the lanthanum site. Other elements with smaller ionic radius than the La^{3+} ion, such as the lanthanides, for example, lead to comparably advantageous results. The lattice constant can be successfully adjusted to the desired value in this way, whereby a stabilization of the Al-doped lithium lanthanum zirconate (LLZO) in the cubic modification is obtained in a targeted manner. In contrast thereto, Figures 1 and 2 show that yttrium alone is not suitable for this purpose, and thus, the use of yttrium alone was excluded from the teaching according to the invention.

The present invention will be explained in more detail below on the basis of examples, but without limitation thereto.

Exemplary embodiments

Examples of compositions with the percentage of lithium lanthanum zirconate (LLZO) in the cubic modification, referred to the total quantity of lithium lanthanum zirconate (LLZO) are specified in Table 1 below. The composition is specified as atoms per formula unit (pfu) of the aluminum-doped lithium lanthanum zirconate (LLZO). The percentage of lithium lanthanum zirconate (LLZO) in the cubic modification was determined from the XRD data by Rietveld analysis and is given as:

$$\text{LLZO}_{\text{cubic}} / \text{LLZO}_{\text{tetragonal}} + \text{LLZO}_{\text{cubic}},$$

wherein the analysis was produced in wt.%.

Table 1:

Ex.	Li ⁺	Al ³⁺	La ³⁺	Gd ³⁺	Y ³⁺	Zr ⁴⁺	Hf ⁴⁺	Si ⁴⁺	Ta ⁵⁺	Ba ²⁺	Sr ²⁺	K ⁺	$\frac{(La^{3+} + M^{3+} + M^{2+} + M^{1+})}{(Zr^{4+} + M^{3+} + M^{2+} + M^{1+})}$	Percentage of cubic LLZO [wt.%]	Conductivity [S/cm]
1*	6.4	0.2	3			2							1.50	100.0	1.4E-04
2*	6.4	0.2	3			1.96			0.04				1.50	100.0	8.9E-05
3*	6.6	0.2	3			2							1.50	70.1	8.4E-05
4*	6.6	0.2	2.8			2					0.2		1.50	29.5	3.0E-5
5*	6.4	0.2	2.2	0.8		2							1.07	100.0	2.8E-05
6*	6.4	0.2	2.73	0.27		2							1.32	100.0	8.8E-05
7*	6.4	0.2	2.4	0.6		2							1.15	100.0	4.2E-05
8	6.8	0.2	2.4	0.6		2							1.15	100.0	9.0E-05
9	7.6	0.2	2.2	0.8		2							1.07	100.0	6.4E-05
10	7.2	0.2	2.1	0.9		2							1.03	100.0	7.8E-05
11	6.8	0.4	2.7	0.3		2							1.30	100.0	6.3E-5
12	7.2	0.4	2.7	0.3		1.97		0.03					1.30	100.0	1.0E-04
13*	7.2	0.15	2.8		0.2	2							1.36	40.0	3.8E-05

*.....Examples not according to the invention

Ex.	Li ⁺	Al ³⁺	La ³⁺	Gd ³⁺	Y ³⁺	Zr ⁴⁺	Hf ⁴⁺	Si ⁴⁺	Ta ⁵⁺	Ba ²⁺	Sr ²⁺	K ⁺	$\frac{(La^{3+} + M^{3+} + M^{2+} + M^{1+})}{(Zr^{4+} + M^{3+} + M^{2+} + M^{1+})}$	Percentage of cubic LLZO [wt.%]	Conductivity [S/cm]
14*	6.8	0.2	2.7		0.3	2							1.30	100.0	1.0E-04
15*	7	0.2	2.6		0.4	2							1.25	100.0	1.2E-04
16*	7	0.2	2.5		0.5	2							1.20	100.0	1.0E-04
17	7	0.2	2.7	0.25	0.05	1.99		0.01					1.30	100.0	7.9E-5
18	6.7	0.2	2.7	0.25	0.05	2							1.30	100.0	2.5E-4
19	7	0.3	2.7	0.25	0.05	2							1.30	100.0	1.5E-4
20	6.7	0.15	2.7	0.25	0.05	1.98	0.02						1.30	100.0	1.5E-4
21	6.7	0.2	2.68	0.25	0.05	1.99		0.01		0.02			1.30	100.0	n.d.
22	7.5	0.4	2.60	0.3	0.05	1.97		0.03				0.05	1.28	100.0	5.3E-5

*.....Examples not according to the invention

Examples 8 to 12 and 17 to 22 are according to the invention.

Exemplary compositions and the corresponding percentage of lithium lanthanum zirconate (LLZO) in the cubic modification (determined by Rietveld analysis of the XRD data, referred to the total percentage of lithium lanthanum zirconate (LLZO)) are shown in Table 1. Examples 1 to 7 and 13 to 16 are not according to the invention. In Examples

1 to 4, the lanthanum site is not co-doped by another smaller trivalent M^{3+} cation. In Examples 5 to 7, the lithium is present in stoichiometric quantity. In Examples 13 to 16, co-doping is carried out with yttrium alone, whereby the doping with yttrium alone as M^{3+} is excluded according to the invention, since in small quantity, it cannot ensure the stabilization of the cubic modification (Example 13), or in higher concentration, in fact, even though the cubic modification is stabilized, at the same time, however, the formation of undesired secondary phases is brought about (Examples 14-16 or Figure 2).

The raw materials were mixed corresponding to the compositions according to Table 1 and filled into a skull crucible open at the top. The mixture had to be pre-heated first in order to obtain a certain minimum conductivity. A burner heating was used for this purpose. After reaching the coupling temperature, the further heating and homogenizing of the melt were achieved by high-frequency coupling via an induction coil. In order to improve the homogenizing of the melts, stirring was conducted with a water-cooled stirring device. After complete homogenization, direct samples were removed from the melt (rapid cooling), while the remainder of the melt was slowly cooled by switching off the high frequency.

The material produced in this way can be converted into a glass-ceramic material with garnet-like primary crystal phase either by direct solidification from the melt or by quenching, followed by a temperature treatment (ceramicizing). The samples removed directly from the melt, independently of how they were cooled, showed a spontaneous crystallization, so that a downstream ceramicizing treatment could be dispensed with. Samples were produced from the thus-obtained glass ceramics for impedance spectroscopy to determine the conductivity, as well as for X-ray diffraction (XRD) investigations. In order to avoid a degradation of the samples upon contact with water, the sample preparation was conducted in an anhydrous manner.

The ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+}) < 1.5$ is fulfilled in Examples 5 to 22, whereby, however, only Examples 8 to 12 and 17 to 22 are according to the present invention. In further detail, the ratio is calculated as follows:

This shall be explained explicitly based on Example 11:

$$\text{La}^{3+} = 2.7 \text{ pfu}$$

$$\text{M}^{3+} : \text{Gd} = 0.3 \text{ pfu}$$

$$\text{Zr}^{4+} = 2 \text{ pfu}$$

$$\text{M}^{6+}, \text{M}^{5+}, \text{M}^{4+}, \text{M}^{2+}, \text{M}^{1+} \text{ is not present; therefore, } \text{M}^{6+} = \text{M}^{5+} = \text{M}^{4+} = \text{M}^{2+} = \text{M}^{1+} = 0 \text{ pfu}$$

$$\text{This then results: } (2.7 \text{ pfu} + 0.3 \text{ pfu} + 0 \text{ pfu} + 0 \text{ pfu}) / (2 \text{ pfu} + 0 \text{ pfu} + 0 \text{ pfu} + 0 \text{ pfu} + 0.3 \text{ pfu}) = (3 \text{ pfu}) / (2.3 \text{ pfu}) = 1.30$$

The following explanations can be given for the above-given Examples 1 to 22:

The stoichiometric lithium lanthanum zirconate (LLZO) composition in Example 1 leads to the formation of 100% cubic lithium lanthanum zirconate (LLZO). In this case, Example 2 shows that with additional doping with a pentavalent cation on the Zr site, the cubic structure remains. However, a small increase in the lithium content (from 6.4 to 6.6 pfu) has already had as a consequence a decrease in the content of cubic lithium lanthanum zirconate (LLZO) to 70.1 wt.% (see Example 3). Therefore, the explained effects occur, according to which an increased Li content would lead to the fact that the dopant aluminum is partially displaced again from the crystal structure, so that the cubic lithium lanthanum zirconate (LLZO) is no longer stabilized sufficiently at room temperature.

The addition of divalent M^{2+} cations with a stoichiometric lithium content already leads to the formation of the undesired tetragonal modification (see Example 4).

Examples 5 to 12 are compositions with gadolinium and aluminum doping. In the case of stoichiometric composition (Examples 5 to 7), the cubic modification is obtained, independent of the quantity of gadolinium.

However, based on an isovalent co-doping on the lanthanum site, as shown in Examples 8 to 12 according to the invention, due to the gadolinium co-doping,

it is now possible in an unexpected way to also obtain the cubic modification with a superstoichiometric lithium content.

In this case, the aluminum content can be varied (Examples 11 and 12), and also doping can be conducted additionally on the zirconium site without obtaining the undesired tetragonal modification of the lithium lanthanum zirconate (LLZO).

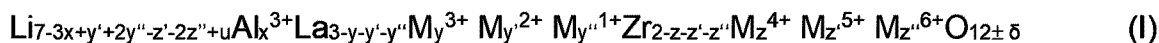
Examples 13-16 are compositions with yttrium and aluminum doping. If the quantity of yttrium is too small (Example 13), cubic lithium lanthanum zirconate (LLZO) is only partially obtained. With higher yttrium content, the effect is also shown here that, despite superstoichiometric Li content, the cubic modification of lithium lanthanum zirconate (LLZO) is obtained (Examples 14 to 16). However, with these yttrium contents, the formation of undesired secondary phases increases (see Figure 2).

Examples 17 to 20 are compositions with gadolinium, yttrium, and aluminum doping. In all of these examples, despite the superstoichiometric Li content, the cubic modification of lithium lanthanum zirconate (LLZO) is obtained. Due to the lower yttrium content, however, no undesired secondary phases occur (see Figure 2). In this case, both the lithium content (see Examples 17 and 18) as well as the aluminum content (see Examples 17 and 19) can be varied without forming the tetragonal modification of the lithium lanthanum zirconate (LLZO), despite the superstoichiometric Li content. Also, small quantities of zirconium may be substituted (Examples 17 and 20).

Examples 21 and 22 are compositions with gadolinium (or gadolinium and yttrium) and aluminum doping, and which additionally contain small quantities of divalent M^{2+} cations (Example 21) and monovalent M^{1+} cations (Example 22) on the lanthanum site. Such co-dopings with subvalent cations lead to the formation of the undesired tetragonal modification of the lithium lanthanum zirconate (LLZO) in the case of aluminum-doped lithium lanthanum zirconate (LLZO), even with stoichiometric lithium content (Example 4). By co-doping with gadolinium or gadolinium and yttrium on the lanthanum site, the formation of the undesired tetragonal modification, in an unexpected way, does not occur any longer.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An aluminum-doped lithium ion conductor based on a garnet structure comprising lanthanum, which is an aluminum-doped lithium lanthanum zirconate (LLZO), wherein the LLZO is co-doped with at least one trivalent M^{3+} ion on the lanthanum site, wherein the trivalent M^{3+} ion has an ionic radius that is smaller than that of La^{3+} , and a higher lithium content is present in comparison to a stoichiometric garnet structure, wherein the aluminum-doped lithium ion conductor has the general chemical formula:



wherein:

M^{3+} : represents one or more trivalent cations with an ionic radius smaller than La^{3+} , with the exception of Al^{3+} ,

M^{2+} : represents one or more divalent cations,

M^{1+} : represents one or more monovalent cations, with the exception of Li^+ ,

M^{4+} : represents one or more tetravalent cations, with the exception of Zr^{4+} ,

M^{5+} : represents one or more pentavalent cations,

M^{6+} : represents one or more hexavalent cations,

$$0.1 \leq x < 1$$

$$0 < y < 2$$

$$0 \leq y' < 0.2$$

$$0 \leq y'' < 0.2$$

$$0 \leq y' + y'' < 0.2$$

$$0 \leq z < 0.5$$

$$0 \leq z' < 0.8$$

$$0 \leq z'' < 0.5$$

$$0 \leq \delta < 2,$$

wherein:

$u > 0$ for a superstoichiometric lithium content,

with the proviso that if M^{3+} represents yttrium, an additional trivalent M^{3+} ion, which is different than Y^{3+} and has an ionic radius that is smaller than that of La^{3+} , is co-doped on the lanthanum site.

2. The aluminum-doped lithium ion conductor according to claim 1, wherein:
 $u \geq 0.2$.

3. The aluminum-doped lithium ion conductor according to claim 1 or 2,
wherein:

$0.1 \leq x < 0.5$, in each case referred to one formula unit of the aluminum-doped lithium ion conductor based on the garnet structure in formula (I).

4. The aluminum-doped lithium ion conductor according to claim 3, wherein:
 $0.14 \leq x < 0.5$, in each case referred to one formula unit of the aluminum-doped lithium ion conductor based on the garnet structure in formula (I).

5. The aluminum-doped lithium ion conductor according to any one of claims 1 to 4, wherein:
the molar quantity of Y^{3+} is < 0.2 per formula unit of the aluminum-doped lithium ion conductor based on the garnet structure in formula (I).

6. The aluminum-doped lithium ion conductor according to any one of claims 1 to 5, wherein:

the molar ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+})$ is < 1.5 , wherein M^{3+} is not zero, but M^{6+} , M^{5+} , M^{4+} , M^{2+} and M^{1+} may be zero in each case.

7. The aluminum-doped lithium ion conductor according to claim 6, wherein: the molar ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+})$ is < 1.35 , wherein M^{3+} is not zero, but M^{6+} , M^{5+} , M^{4+} , M^{2+} and M^{1+} may be zero in each case.

8. The aluminum-doped lithium ion conductor according to any one of claims 1 to 6, wherein: the molar ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+})$ lies in the range of 1.49 to 1.0.

9. The aluminum-doped lithium ion conductor according to claim 8, wherein: the molar ratio of $(La^{3+} + M^{3+} + M^{2+} + M^{1+})/(Zr^{4+} + M^{6+} + M^{5+} + M^{4+} + M^{3+})$ lies in the range of 1.35 to 1.0.

10. The aluminum-doped lithium ion conductor according to any one of claims 1 to 9, wherein: the one or more trivalent M^{3+} cations comprise cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, scandium, bismuth, indium, or any combination thereof.

11. The aluminum-doped lithium ion conductor according to claim 10, wherein: the one or more trivalent M^{3+} cations comprise gadolinium, niobium, yttrium, or any combination thereof.

12. The aluminum-doped lithium ion conductor according to claim 11, wherein:

the one or more trivalent M^{3+} cations comprise a combination of gadolinium and an additional trivalent cation.

13. The aluminum-doped lithium ion conductor according to claim 12, wherein the additional trivalent cation is yttrium.

14. The aluminum-doped lithium ion conductor according to any one of claims 1 to 13, wherein:

one of the trivalent M^{3+} cations represents gadolinium and at least 0.1 mol of gadolinium is present per formula unit of aluminum-doped lithium ion conductor based on a garnet structure.

15. The aluminum-doped lithium ion conductor according to any one of claims 1 to 14, having a lattice constant of $a < 12.965 \text{ \AA}$.

16. The aluminum-doped lithium ion conductor according to any one of claims 1 to 15, wherein:

the trivalent M^{3+} cation is not polyvalent.

17. The aluminum-doped lithium ion conductor according to any one of claims 1 to 16, having an amorphous phase, in which lithium and/or aluminum and/or M^{3+} are enriched.

18. The aluminum-doped lithium ion conductor according to any one of claims 1 to 17, wherein:

in comparison to a stoichiometric garnet structure, the aluminum-doped lithium ion conductor has a higher lithium content and has a ratio of cubic to tetragonal crystal phase of greater than 9 : 1.

19. The aluminum-doped lithium ion conductor according to claim 18, wherein:
the ratio of cubic to tetragonal crystal phase is greater than 19 : 1.
20. The aluminum-doped lithium ion conductor according to claim 19, wherein:
the ratio of cubic to tetragonal crystal phase is greater than 49 : 1.
21. The aluminum-doped lithium ion conductor according to any one of claims 1 to 20, which has an ion conductivity of more than 10^{-5} S/cm.
22. A powder, composed of the aluminum-doped lithium ion conductor as defined in any one of claims 1 to 21, which has a particle size in the range of $d_{50} = 0.1 \mu\text{m}$ to $30 \mu\text{m}$.
23. A method for producing an aluminum-doped lithium ion conductor as defined in any one of claims 1 to 21, wherein:
the method comprises a step of melting initial materials of the aluminum-doped lithium ion conductor.
24. The method according to claim 23, wherein:
the method is carried out in a skull crucible.
25. Use of the aluminum-doped lithium ion conductor as defined in any one of claims 1 to 21 or of the powder as defined in claim 22 in batteries, capacitors or rechargeable batteries.
26. The use of claim 25, wherein the batteries are lithium batteries or lithium rechargeable batteries.

27. Use of the aluminum-doped lithium ion conductor as defined in any one of claims 1 to 21 or of the powder as defined in claim 22 in separators, cathodes, anodes, or solid electrolytes.

Fig.1

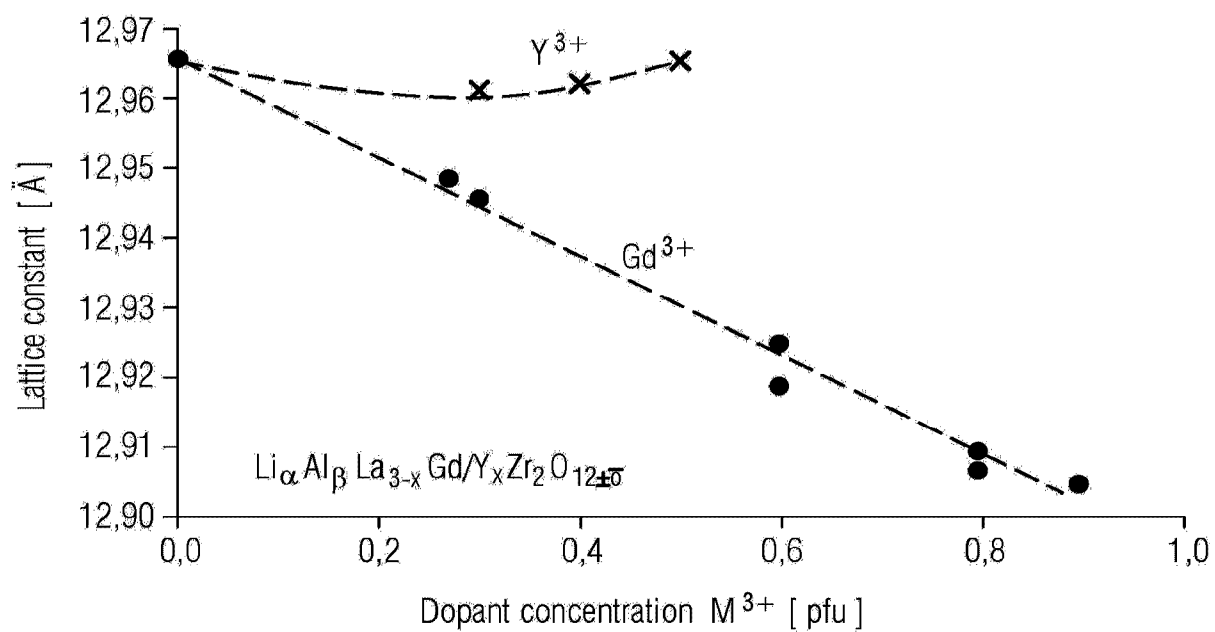


Fig. 2

