

Novel Glass Ceramics for Electronic Applications

Roland Langfeld, Miriam Kunze, Martin Letz
(SCHOTT AG, Hattenbergstrasse 10, D-55122 Mainz, Germany)

Abstract: Glass-ceramic materials based on lithium aluminium silicate found widespread applications as a zero-expansion material in optics or as a temperature resistant material for fireplaces and oven cook stoves. We will present recent developments of two new types of glass-ceramics based on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) and within the LiSiCon structure, produced by a melting and ceramization route, which reveal promising Li-ion conductivities in the range of 10^{-3} S/cm at room temperature. Additionally glass-ceramics with nano-grain ferroelectric or para-electric crystalline phases are presented as a new dielectric material for high-performance electrical capacitors.

Key words: glass; glass-ceramic; dielectric properties; capacitors; ion conductivity; solid state electrolytes; lithium-ion battery

CLC number: TQ171 Document code: A Article ID: 1674-3962(2015)07-0558-07

新型微晶玻璃在电子领域的应用

Roland Langfeld, Miriam Kunze, Martin Letz
(肖特公司, 德国美因茨 D-55122, Hattenberg 街 10 号)

摘要: 硅酸锂铝微晶玻璃材料作为零膨胀材料在光学领域, 以及作为耐高温材料在壁炉和烤炉方面的应用都极为广泛。介绍了通过熔化陶瓷化法生产的以 $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) 为主, 并以 LiSiCon 结构为主的两种新型微晶玻璃的最新进展, 这两种微晶玻璃在室温下 10^{-3} S/cm 范围内都显示出了良好的 Li 离子导电性能。此外, 还介绍了含纳米晶铁电体或顺电晶相的微晶玻璃, 这种微晶玻璃应用于高性能电容器所用新型介电材料上。

关键词: 玻璃; 微晶玻璃; 介电性能; 电容器; 离子导电性; 固态电解质; 锂离子电池

1 Introduction

Bulk glass-ceramics which are obtained from a melt via a true amorphous glassy phase are partially crystallized glasses. Such glass-ceramics are usually highly homogeneous since they obtain their material homogeneity from a glass production which for example for optical glasses are known to be very uniform and free of pores over large production volumes. The growth of particular crystalline phases is initialized via a controlled nucleation mechanism and guided via control of a time temperature profile to ensure proper crystal growth. In this way depending on the application sizes of crystallites from 10 nanometer to several micrometer with relatively sharp size distributions can be obtained. The crystal volume in such glass-ceramic materials can range from 30 vol% up to 98 vol%.

It is possible to tailor material properties by using material properties of one or more crystalline phases and combi-

ning it with the material properties of the residual glassy phase. In this way a composite material is obtained which is homogeneous on macroscopic length scales.

The most common types of such bulk glass-ceramic materials are the lithium aluminium silicate glass-ceramics. In these systems the physical property of the crystalline phase is determined by the negative thermal expansion of some high quartz solid solution crystalline phases and other silicate phases in a particular temperature range. In combination with the positive thermal expansion of the residual glass phase this can be balanced out to materials with a thermal expansion which is very close to zero. These glass-ceramics are known under the brand names CeranTM for cook stoves, RobaxTM for transparent fire place windows and ZerodurTM. The latter one is used as a substrate for astronomic mirrors and finds nowadays increasing use in high precision applications like metrology and microlithography. In ZerodurTM the coefficient of thermal expansion can be optimized down to a level of a few ppb/K ($=10^{-9}$ K⁻¹).

More recent material development is trying to synthesize crystal phases with particular electronic properties in glass-ceramics. One possibility which is described in more detail in section 1 is the growth of highly alkaliion conducting crystals

Received date: 2015-05-12

Corresponding author: Roland Langfeld; PhD., Email:
roland.langfeld@schott.com

DOI: 10.7502/j.issn.1674-3962.2015.07.10

in a glass-ceramic. In this way materials are developed which can find applications in e. g. Li ion batteries. When semi-conducting crystalline phases are grown electronic conductivity can be achieved. Such materials can find applications as high temperature stable oxide thermoelectric materials^[1-2] and are stable under normal atmosphere to multiple thermal cycling up to temperatures of 700 °C and more.

On the side of highly insulating electronic materials also a number of developments are present. By crystallizing polar crystal phases like fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) or $\text{Li}_2\text{Si}_2\text{O}_5$ ^[3] in an oriented way one can obtain glass-ceramics with piezoelectric properties^[4-5]. Some of these phases have superior properties at high temperatures above 500 °C over existing ceramic and single crystalline material solutions and can find applications e. g. as high temperature pressure sensors.

Recently SCHOTT has commercialized three new glass-ceramic materials as dielectrics for electronic applications. These are Poweramic™_P2200 which is based on a nanocrystalline ferroelectric crystalline phase and Poweramic™_N150 and Poweramic™_GHz_33 which are both based on a paraelectric titanate based crystalline phase. These dielectrics for high power applications and for mobile applications are described in more detail in section 2.

2 Li ion conducting glass-ceramics for battery applications

2.1 Solid state batteries

Due to an increasing demand on energy and accordingly energy storage devices during the last 50 years new battery concepts were established. In the main focus are the lithium-ion and lithium-metal battery concepts. Examples of these systems are besides the conventional lithium-ion battery, lithium-sulfur, and lithium-air batteries^[6-8]. These various battery cell setups can be realized by either using a liquid or solid electrolyte. However, the basic setup for an all solid state battery is similar to a liquid electrolyte battery (cf. Fig. 1) except

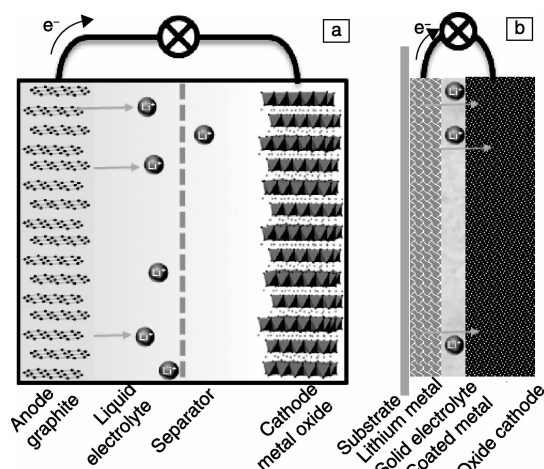


Fig. 1 Schemes of lithium-ion battery with a liquid electrolyte (a) and lithium-metal battery with solid electrolyte (b) during discharge

for the electrolyte state of aggregate. The advantages using solid electrolytes between the anode and the cathode in lithium-ion and lithium-metal batteries instead of a liquid electrolyte are manifold: increasing safety by preventing leakage and flammability of the electrolyte, avoiding aging and gassing of the cell due to dissolution and degradation of the electrolyte, lithium dendrite formation, which result in short circuits and more severe incidents, increase of cell operating temperatures, larger electrochemical stability window, and increase of lifetime^[9-16].

2.2 Electrolytes for solid state batteries

To realize a lithium ion charge transport based solid state battery with the given advantages besides good electrode materials a well performing solid electrolyte or solid ion conductor is necessary. The key features of a solid ion conductor include^[17-19]: ① a high ionic conductivity ($\sigma > 10^{-4}$ S/cm) with a high lithium ion transference number t_+ ($t_+ \sim 1$); ② electrochemical stability between 0 ~ 6 V vs. $\text{Li}^+/\text{Li}^\circ$; ③ chemical stability against the electrode materials and ambient atmosphere, and ④ a negligible interface resistance between the solid electrolyte and the electrode materials.

Based on these properties a large number of solid ion conductors were synthesized and investigated during the last 20 to 50 years, which can be divided into inorganic and organic lithium ion conducting materials (Fig. 2). The organic materials are the polymers within the field of polyelectrolytes^[20] and polymer electrolytes^[21], while the inorganic solid ion conductors are either glasses, ceramics or glass-ceramics.

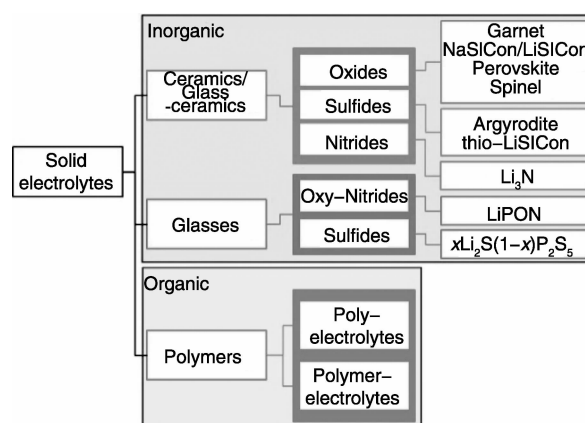


Fig. 2 Classes of solid electrolytes for lithium ion conduction for various lithium-ion battery applications

For all inorganic material classes oxides and sulfides are intensively studied in terms of their lithium conductivity in dependence on temperature as well as the electrochemical and chemical stability^[17, 22-26]. In Fig. 3 conductivities of the various lithium ion conductors are presented. Also pointed out is the optimal region of conductivity for battery applications in a temperature range between $-40 \sim 80$ °C. These criteria are fulfilled by some ceramic and glass-ceramic materials based on oxides like garnets, LiSiCon (Lithium Super Ion Conductor) and NaSiCon (Sodium (Na) Super Ion Conductor), and sulfides, especially argyrodites and thio-LiSiCon. Besides the in-

tensive material development, which took place, there is a need to produce these materials not only in laboratory scale but also in industrial dimensions. Hence, the main aim for these materials is not only fulfilling the above mentioned requirements according to their application, but an inexpensive and stable material, which can be produced in industrial scale.

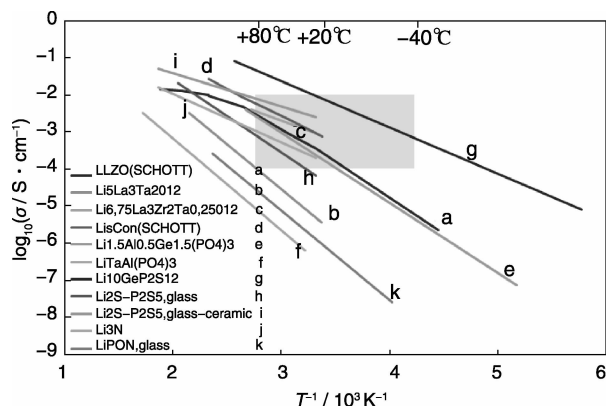


Fig. 3 Comparison of lithium conductivity of various solid ion conducting materials. The light gray area points out the necessary conductivity for industrial applications in a temperature range between $-40\text{ }^{\circ}\text{C}$ up to $80\text{ }^{\circ}\text{C}$ [24, 28–29, 36, 39, 47–50]

2.3 Sulfidic solid lithium ion conductors

The sulfidic solid lithium ion electrolytes are intensively studied during the last 20 years and are a new class of lithium ion conductors compared to oxidic systems. Typical examples of the lithium ion conductors based on sulfides are $x\text{Li}_2\text{S}_{(1-x)}\text{P}_2\text{S}_5$ glasses and glass-ceramics [27–28]. Conductivities of these materials are about $10^{-5} \sim 10^{-3}\text{ S/cm}$ at room temperature. Another material in the field of sulfides, the thio-LiSiCon material [29] like $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, shows the highest lithium ion conductivity measured at room temperature: $12 \times 10^{-3}\text{ S/cm}$ [24]. Unfortunately, this material does have a high germanium content, which results in a costly electrolyte material unstable against lithium metal. Besides these disadvantages the sulfidic systems are not stable against water and air and consequently they can only be prepared under inert atmosphere. Preparation routes under defined atmospheres, like e. g. argon, are milling procedures in planetary mills and melting in quartz glass ampoules. Hence, the raw materials are inexpensive but due to controlled atmospheres requirements during syntheses these materials are cost intensive and limited in production yield. However, this limits the use of these materials for the production of the various lithium-(ion) batteries.

2.4 Oxidic solid lithium ion conductors.

In the last 40 to 50 years lithium based solids came into the focus as materials for solid electrolytes. Typical oxidic solid electrolytes for this task are garnet, LiSiCon, and NaSiCon structured materials. The garnets have a molecular formula $\text{Li}_{1+x-y}\text{M}^{\text{II}}\text{M}^{\text{III}}\text{M}_{2-x-y}^{\text{IV}}\text{M}_{2-y}^{\text{V}}\text{O}_{12}$, where M^{II} is Mg, Ca, Sr, Ba, Zn; M^{III} is La, Al, Ga, In; M^{IV} is Zr, Hf, Ti, Sn; M^{V} is Nb, Ta, Zr, Hf, Sn, (Ti). The first lithium filled garnet ma-

terials, $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ and $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$, were reported by Thangadurai and co-workers with a lithium ion conductivity of $\sim 10^{-6}\text{ S/cm}$ [30]. This material was further optimized for battery applications and the main focus for garnet structured material lies on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [31]. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ has a conductivity σ in the low temperature modification (tetragonal phase) in the range of $\sigma = 6 \times 10^{-7}\text{ S/cm}$, which can be increased up to $\sigma = 4 \times 10^{-4}\text{ S/cm}$ using different dopants like e. g. Al, Ta or Nb stabilizing the high temperature modification (cubic phase) [32–35].

Classical syntheses of this material are carried out by solid state reaction, sol-gel and Pechini-method, co-precipitation and hot pressing. For all these methods at least one high temperature treatment between $900\text{ }^{\circ}\text{C}$ and $1150\text{ }^{\circ}\text{C}$ is necessary to achieve the correct crystalline structure with a high ionic conductivity [32, 36–40]. Disadvantages of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ material produced by the given syntheses are low yields combined with a high expenditure of time and sometimes not 100% pure cubic phase. Furthermore, only powder material with a small particle size and consequently a small crystal size can be achieved.

However, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ material additionally can be produced via a melting and crystallization route using SCHOTT Skull melting technology. The resulting material is white to slightly yellow colored and has a highly ordered crystalline phase with 100 % cubic garnet modification. This material is a glass-ceramic with about 10% glassy phase and 90% crystalline phase (Fig. 4a) and shows a conductivity σ of $3 \sim 5 \times 10^{-4}\text{ S/cm}$ (cf. Fig. 3 curve a). No impure phases can be detected and powder samples in kg scale as well as dense bulk-samples can be prepared via melting production route. Furthermore SCHOTT garnet glass-ceramic is stable against lithium metal and electrochemically stable up to 6 V vs. $\text{Li}^+/\text{Li}^{\circ}$. With these properties the SCHOTT LLZO is an excellent material suitable as electrolyte in solid lithium metal batteries.

Besides the garnet system, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, solid lithium ion conductors with NaSiCon or LiSiCon structure ($\text{Li}_{1+x-y}\text{M}_y^{\text{V}}\text{M}_x^{\text{III}}\text{M}_{2-x-y}^{\text{IV}}(\text{PO}_4)_3$, where M^{III} is Al, Cr, Fe; M^{IV} is Ge, Ti, Zr; M^{V} is Nb, Ta) can reach conductivities in the range of 10^{-3} S/cm at increased temperatures (cf. Fig. 3). From the crystallographic point of view LiSiCon and NaSiCon are isostructural with each other and below only the term “LiSiCon” will be used. This class of materials was introduced for energy storage applications by Thangadurai and co-workers [41]. Since then the material was intensively studied and developed [42–44]. Typically, these materials have a high amount of germanium and/or titanium. Hence, solid ion conductors with a high germanium and titanium content have high conductivities, up to $6 \times 10^{-4}\text{ S/cm}$, but are not chemically stable against lithium metal. The Ge^{IV} and Ti^{IV} are reduced to Ge^{III} and Ti^{III} by lithium metal, respectively, and the material discolors and shows an increase of the internal resistance. Additionally the germanium containing materials are expensive due to their high raw material costs.

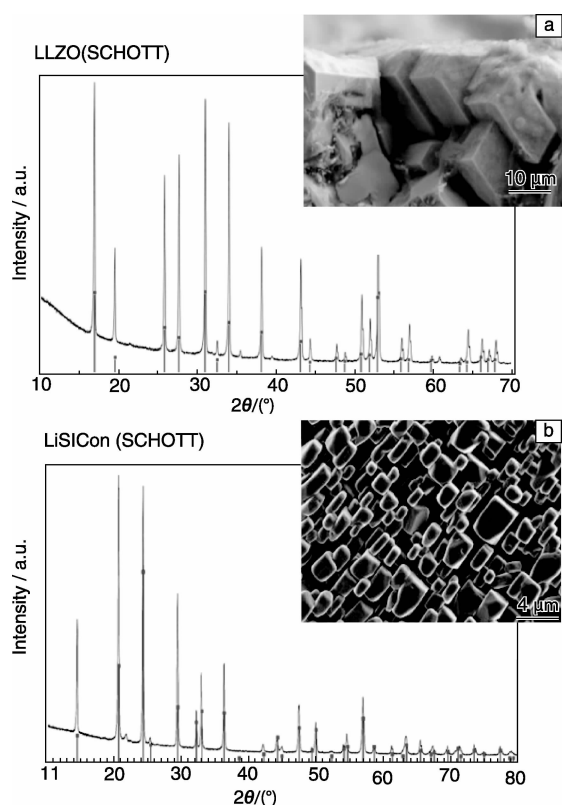


Fig. 4 XRD and SEM measurements of LLZO synthesized by skull melting technology (a) and LiSiCon prepared by classical glass-ceramic route (b), Both synthesized at SCHOTT

Preparation routes of LiSiCon materials are the classical glass-ceramic route, sol-gel procedures and milling processes^[45–46]. The latter are, like for the garnet ion conductor, expensive and not efficient. For the classical glass-ceramic processing the oxidic raw materials are melted and afterwards the glass is placed in a furnace for the ceramization according to an optimized temperature profile. The ion conducting LiSiCon glass-ceramic by SCHOTT has a quite high grain core lithium ion conductivity of about 1×10^{-3} S/cm at room temperature (cf. Fig. 3 curve d). The XRD data show a pure crystalline phase of the material and the crystallites themselves are homogeneous (Fig. 4b). Therefore it is an outstanding electrolyte candidate for solid state lithium ion batteries used at ambient temperatures. This material can be handled at ambient atmosphere and is as well as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ -glass-ceramic electrochemically stable up to 6 V vs. $\text{Li}^+/\text{Li}^\circ$. SCHOTT lithium ion conductor with LiSiCon structure can be manufactured in kg amounts, which is up-scalable, and inexpensive.

3 Glass-ceramic with nano-grain ferroelectric crystalline phases

Crystal systems with ferroelectric crystalline phases are well known as dielectrics. Ceramic BaTiO_3 plays a major role as a dielectric in capacitors. It has a large dielectric

constant and is used frequently in consumer applications in multilayer capacitors with low voltages and high capacities. However the saturation polarization together with the hysteresis loop of a ferroelectric usually do not allow to apply such ferroelectric ceramic material in high power applications. The reason is the dielectric loss mechanism which occurs when ferroelectric domain walls are moved within crystalline grains. The situation changes when nanocrystalline materials are used with crystalline grains which are of order of the size of the ferroelectric domains. In this case the material response to large field strength changes towards a para-electric behavior and the area of the hysteresis loop becomes very small. Obtaining nano-grain ceramics is very difficult since sintering is often accompanied by grain growth which leads to crystalline grains of several micrometer diameter even when nano-grain powder are used to start the ceramization process. An ideal way to obtain nano-grain structures are glass-ceramics obtained via a true glassy phase. Glass-ceramics with BaTiO_3 as a main crystalline phase are well known since many years^[51]. In recent years there was a lot of activity in this field. In the group of Yong Zhang a number of very systematic investigations have been made which deal with the glass stability, the oxidation state and also the dielectric breakdown strength as a function of material composition^[52–55]. The barium strontium titanate glass-ceramic system is investigated in detail by a group from the US who find very high values of dielectric constants which are however always accompanied by high dielectric loss^[56].

At SCHOTT we improved the glass stability of the system for large scale economic production and obtained a glass-ceramic with a true nano-grain structure. The result of this nano-grain structure on the hysteresis loop is shown in Fig. 5. At identical field strength a ceramic BaTiO_3 shows a large hysteresis, while the nano-grain glass-ceramic material only has a very small in

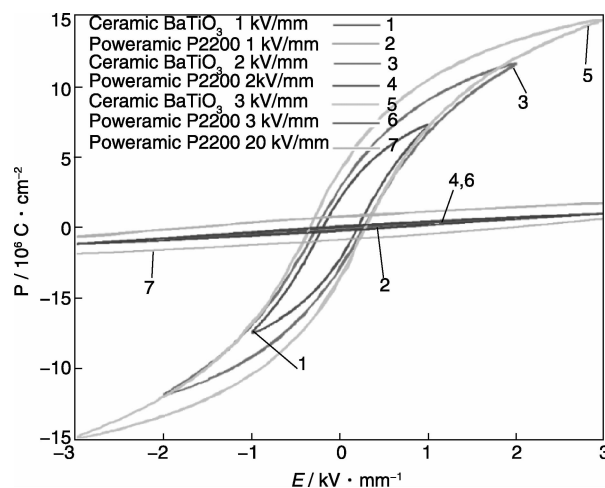


Fig. 5 The Polarization is plotted as a function of applied electric field. A comparison of the hysteresis of ceramic BaTiO_3 with the hysteresis of the PoweramicTM P2200 glass-ceramic containing nano-grain BaTiO_3 is shown

barely visible, hysteresis. Only at a field strength of 20 kV/mm which cannot be reached in the ceramic material, a small hysteresis loop becomes observable. The polarization is still far from saturation. In a glass-ceramic the starting point is a truly amorphous material, a transparent glass. A controlled nucleation and crystal growth leads to a nano-grain structure.

In Fig. 6 we compare the structure of the SCHOTT Poweramic P2200 glass-ceramic to the structure of a ceramic (Fig. 6a) from a commercial 20 kV high power capacitor. In the ceramic a large number of pores is clearly visible with diameters of several micrometer. In contrast to that the Poweramic P2200 glass-ceramic (Fig. 6b) is free of pores and shows in the inset a structure only when magnified to the nanometer scale. The final crystallites have diameters in the order of 30 nm. This nanocrystalline structure in the ferroelectric material BaTiO_3 leads to a close to para-electric behavior^[57] which means that the material is still far from saturation when a field strength of 20 kV/mm is applied (Fig. 5). The resulting dielectric constant is around $\epsilon = 220$ and shows a positive temperature coefficient. With increasing temperature the capacity of such a capacitor increases with 2200 ppm/K and the dielectric loss decreases well below 1% when the temperature increases. The maximum operating temperature of such a capacitor is around 200 °C since above 200 °C the permittivity of the P2200 material decreases strongly with increasing temperature. The temperature dependence of the dielectric properties is shown in Fig. 7.

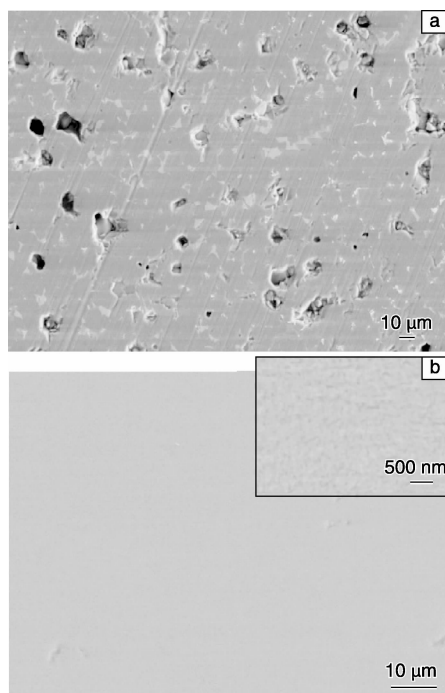


Fig. 6 SEM images of a ceramic from a commercial 20 kV capacitor (a) in comparison to a PoweramicTM glass-ceramic (b). The pore free nature of the glass-ceramic can clearly be seen. The inset of (b) shows the nanometer scale where a first structure becomes visible with individual crystallites of the order of 30 nm

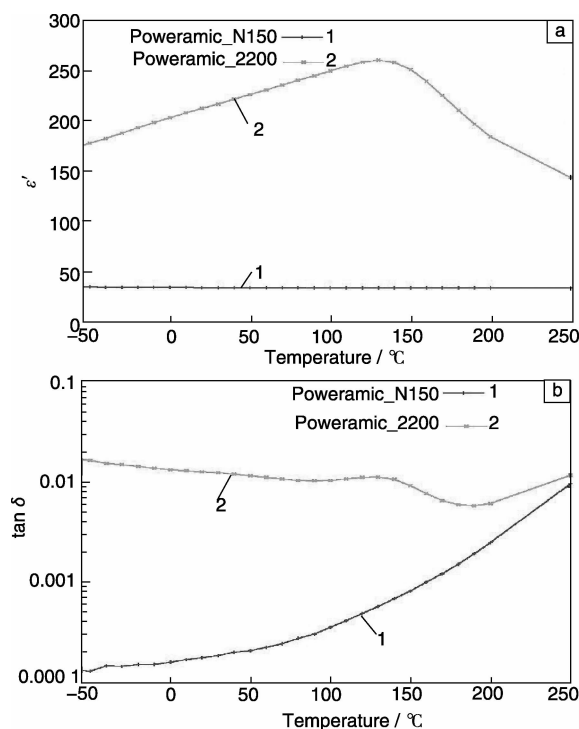


Fig. 7 Comparison of the dielectric properties of the SCHOTT glass-ceramic materials. In (a) the dielectric constant measured at 1 kHz is shown as a function of temperature. While the para-electric material (curve 1, PoweramicTM N150) is practically temperature independent, the BaTiO_3 glass-ceramic (curve 2, PoweramicTM P2200) shows a maximum around 150 °C. In (b) the dielectric loss is shown. For the BaTiO_3 glass-ceramic system the loss decreases with increasing temperature

4 Glass-ceramic with a paraelectric crystalline phase

Similarly, we can create glass-ceramics with a paraelectric phase. Glass-ceramics with paraelectric phases were first considered for GHz applications^[58-59] using BiNbO_4 as a crystalline phase. Contrary to^[58-59] we use paraelectric phases in the Ba-Ti-Al-system which also allow adjustment of the temperature coefficient of the dielectric constant to exactly zero. In this way a glass-ceramic with a paraelectric phase can come close to an ideal dielectric. The dielectric loss is nearly two orders of magnitude lower than the one of the BaTiO_3 glass-ceramic and a balancing between two different crystalline phases allows an adjustment of the temperature coefficient of the dielectric constant close to zero. In Fig. 7 we show the temperature dependence of the dielectric properties of such a material. The pore free micro-structure leads to a very high breakdown strength of 85 kV/mm measured on 200 μm thick discs.

The low dielectric loss of such paraelectric glass-ceramics ranges well into the GHz frequency range where a number of microwave electronic applications are present. Together with the excellent material homogeneity of glass-ceramics which is derived from optical glass production, now a material is availa-

ble which allows accurate design of filters and antenna elements with MHz accuracy for GHz applications. SCHOTT is currently commercializing such a glass-ceramic system under the brand name PoweramicTM_GHz_33.

5 Conclusion

SCHOTT developed LLZO and LiSiCon-type glass-ceramics with promising properties as solid state electrolytes for Li-ion batteries, which can be produced by a melt and ceramization route without using expensive raw materials like germanium.

PoweramicTM glass-ceramics with either para-electric or ferroelectric properties, offer solutions in high power electronics where large thermal loads are also affecting passive components like capacitors. The high dielectric breakdown strength of a pore free material obtained via a glass production process can lead to capacitors which have an energy storage density exceeding the one of current capacitor solutions by a factor of 10.

Acknowledgements The authors thank the German federal ministry of education and research (BMBF) for funding within the project GLANZ, promotion sign 03X4623A.

References

- [1] Lingner J, Letz M, Jakob G. SrTiO₃ Glass-Ceramics as Oxide Thermoelectrics[J]. *Journal of Materials Science*, 2013 (48): 2 812-2 816.
- [2] Jost M, Lingner J, Letz M, *et al.* Thermoelectric Properties of p-Type Bi₂Sr₂Co₂O₉ Glass-Ceramics[J]. *Semiconductor Science and Technology*, 2014(29): 124 011 – 124 014.
- [3] Halliyal A, Safari A, Bhalla A S, *et al.* Grain-Oriented Glass-Ceramics for Piezoelectric Devices[J]. *Journal of the American Ceramic Society*, 1984(67): 331 – 335.
- [4] Davis M J, Vullo P, Mitra I, *et al.* Ferroelectric and Nonferroelectric (Polar) Piezoelectric Glass-Ceramics[J]. *Journal of the American Ceramic Society*, 2008 (91): 2 878 – 2 885.
- [5] Patschger M, Wischnewski W, Rüssel C. Cry Eng Com[M]. 2012 (14): 7 368 – 7 373.
- [6] Bruce P G, Freunberger S A, Hardwick L J, *et al.* Li-O₂ and Li-S Batteries with High Energy Storage[J]. *Nature Materials*, 2012 (11): 19 – 29.
- [7] Tarascon J Marie, Armand M. Issues and Challenges Facing Rechargeable Lithium Batteries[J]. *Nature*, 2001 (414): 359 – 367.
- [8] Kim J G, Son B, Mukherjee S, *et al.* A Review of Lithium and Non-Lithium Based Solid State Batteries[J]. *Journal of Power Sources*, 2015(282): 299 – 322.
- [9] Sloop S E, Kerr J B, Kinoshita K. The Role of Li-Ion Battery Electrolyte Reactivity in Performance Decline and Self-Discharge[J]. *Journal of Power Sources*, 2003(119 – 121): 330 – 337.
- [10] Xu K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries[J]. *Chemical Reviews*, 2004(104): 4 303 – 4 417.
- [11] Campion C L, Li W, Lucht B L. Thermal Decomposition of LiPF₆-Based Electrolytes for Lithium-Ion Batteries[J]. *Journal of the Electrochemical Society*, 2005(152): A2327 – A2334.
- [12] Zhang S S. A Review on Electrolyte Additives for Lithium-Ion Batteries[J]. *Journal of Power Sources*, 2006(162): 1 379 – 1 394.
- [13] Weppner W. All-Solid State Battery in Encyclopedia of Electrochemical Power Sources Edited by Garche Jürgen, Elsevier[M]. 2009: 162 – 168.
- [14] Nazri G A, Pistoia G (eds.). Chapter IV-Electrolytes in Lithium Batteries: Science and Technology[J]. *Springer Science, New York*, 2009.
- [15] Gores H J, Barthel J, Zugmann S, *et al.* Liquid Nonaqueous Electrolytes in Handbook of Battery Materials Edited 2nd ed. by Daniel C, Besenhard J, Weinheim: Wiley-VCH[M]. Weinheim, 2011 (Vol. 2): 525 – 626.
- [16] Quartarone E, Mustarelli P. Electrolytes for Solid-State Lithium Rechargeable Batteries: Recent Advances and Perspectives[J]. *Chemical Society Reviews*, 2011 (40): 2 525 – 2 540.
- [17] Thangadurai V, Weppner W. Recent Progress in Solid Oxide and Lithium Ion Conducting Electrolytes Research[J]. *Ionics*, 2006 (12): 81 – 92.
- [18] Takada K. Progress and Prospective of Solid-State Lithium Batteries[J]. *Acta Materialia*, 2013 (61): 759 – 770.
- [19] Birke P, Weppner W. Solid Electrolytes in Handbook of Battery Materials Edited 2nd ed. by Daniel C, Besenhard J, Weinheim: Wiley-VCH[M]. Weinheim, 2011 (Vol. 2): 657 – 692.
- [20] Cramer C, Schönhoff M. Ion Conduction in Solid Polyelectrolyte Complex Materials[J]. *Advances in Polymer Science*, 2014(255): 97 – 138.
- [21] Gray F M, Armand M. Polymer Electrolytes in Handbook of Battery Materials Edited 2nd ed. by Daniel C, Besenhard J, Weinheim: Wiley-VCH[M]. Weinheim, 2011 (Vol. 2): 627 – 656.
- [22] Knauth P. Ceramic and Polymeric Solid Electrolytes for Lithium-Ion Batteries[J]. *Solid State Ionics*, 2009(180): 911 – 916.
- [23] Fergus J W. Ceramic and Polymeric Solid Electrolytes for Lithium-Ion Batteries[J]. *Journal of Power Sources*, 2010(195): 4 554 – 4 569.
- [24] Kamaya N, Homma K, Yamakawa Y, *et al.* A Lithium Superionic Conductor[J]. *Nature Materials*, 2011 (10): 682 – 686.
- [25] Hayashi A, Noi K, Sakuda A, *et al.* Superionic Glass-Ceramic Electrolytes for Room-Temperature Rechargeable Sodium Batteries[J]. *Nature Communications*, 2012 (3): 1 – 5.
- [26] Cao C, Li Z Bin, Wang X L, *et al.* Recent Advances in Inorganic Solid Electrolytes for Lithium Batteries[J]. *Frontiers in energy research*, 2014(2): 1 – 10.
- [27] Hayashi A, Minami K, Tatsumisago M. Development of Sulfide Glass-Ceramic Electrolytes for All-Solid-State Lithium Rechargeable Batteries[J]. *Journal of Solid State Electrochemistry*, 2010 (14): 1 761 – 1 767.
- [28] Mizuno F, Hayashi A, Tadanaga K, *et al.* New, Highly Ion-Conductive Crystals Precipitated from Li₂S – P₂S₅ Glasses[J]. *Advanced Materials*, 2005 (17): 918 – 921.
- [29] Kanno R, Murayama M. Lithium Ionic Conductor Thio-LISICON: The Li₂S-GeS₂-P₂S₅ System[J]. *Journal of Electrochemical Society*, 2001 (148): A742 – A746.
- [30] Thangadurai V, Kaack H, Weppner W J F. Novel Fast Lithium Ion Conduction in Garnet-Type Li₅La₃M₂O₁₂ (M = Nb, Ta)[J]. *Journal of the American Ceramic Society*, 2003(86): 437 – 440.

- [31] Murugan R, Thangadurai V, Weppner W. *Fast Lithium Ion Conduction in Garnet-Type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$* [M]. *Angewandte Chemie*, Int Edition, 2007 (46): 7 778 – 7 781.
- [32] Geiger C A, Alekseev E, Lazic B, *et al.* Crystal Chemistry and Stability of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Garnet: A Fast Lithium-Ion Conductor [J]. *Inorganic Chemistry*, 2011 (20): 1 089 – 1 097.
- [33] Ohta S, Kabayashi 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]. *Journal of Power Sources*, 2011 (196): 3 342 – 3 345.
- [34] Rangasamy E, Wolfenstine J, Sakamoto J. The Role of Al and Li Concentration on the Formation of Cubic Garnet Solid Electrolyte of Nominal Composition $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [J]. *Solid State Ionics*, 2012 (206): 28 – 32.
- [35] Thangadurai V, Narayanan S, Pinzaru D. Garnet-Type Solid-State Fast Li Ion Conductors for Li Batteries: Critical Review [J]. *Chemical Society Reviews*, 2014(43): 4 714 – 4 727.
- [36] Awaka J, Kijima N, Hayakawa H, *et al.* Synthesis and Structure Analysis of Tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with the Garnet-Related Type Structure [J]. *Journal of Solid State Chemistry*, 2009 (182): 2 046 – 2 052.
- [37] Li Y, Han J, Wang C, *et al.* Optimizing Li^+ Conductivity on a Garnet Framework [J]. *Journal of Materials Chemistry*, 2012 (22): 15 357 – 15 361.
- [38] Allen J L, Wolfenstine J, Rangasamy E, *et al.* Effect of Substitution (Ta, Al, Ga) on the Conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [J]. *Journal of Power Sources*, 2012 (206): 315 – 319.
- [39] Kokal I, Somer M, Notten O H L, *et al.* Sol-Gel Synthesis and Lithium Ion Conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with Garnet-Related Type Structure [J], *Solid State Ionics*, 2011 (185): 42 – 46.
- [40] Wolfenstine J, Rangasamy E, Allen J L, *et al.* High Conductivity of Dense Tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [J]. *Journal of Power Sources*, 2012 (208): 193 – 196.
- [41] Thangadurai V, Shukula A K, Gopalakrishnan J. New Lithium-Ion Conductors Based on the NASICON Structure [J]. *Journal of Materials Chemistry*, 1999(9): 739 – 741.
- [42] Abrahams I, Hadzefejzovic E. Lithium Ion Conductivity and Thermal Behaviour of Glasses and Crystallised Glasses in the System $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ [J]. *Solid State Ionics*, 2000 (134): 249 – 257.
- [43] Xu X, Wen Z, Wu X, *et al.* Lithium Ion-Conducting Glass - Ceramics of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3 - x\text{Li}_2\text{O}$ ($x = 0.0 - 0.20$) with Good Electrical and Electrochemical Properties [J]. *Journal of the American Ceramic Society*, 2007 (90): 2 802 – 2 806.
- [44] Narváez-Semanate J L, Rodrigues A C M. Microstructure and Ionic Conductivity of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ NASICON Glass-Ceramics [J]. *Solid State Ionics*, 2010 (181): 1 197 – 1 204.
- [45] Takahashi K, Ohmura J, Im D, *et al.* A Super High Lithium Ion Conducting Solid Electrolyte of Grain Boundary Modified $\text{Li}_{1.4}\text{Ti}_{1.6}\text{Al}_{0.4}(\text{PO}_4)_3$ [J]. *Journal of the Electrochemical Society*, 2012 (159): A342 – A348.
- [46] Xu X, Wen Z, Gu Z, *et al.* Preparation of Nanostructured $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ Glass-Ceramics by a Citrate Process [J]. *Chemistry Letters* [J], 2005 (34): 512 – 513.
- [47] Mariappan C R, Gellert M, Yada C, *et al.* Grain Boundary Resistance of Fast Lithium Ion Conductors: Comparison between a Lithium-Ion Conductive Li-Al-Ti-P-O-Type Glass Ceramic and a $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ Ceramic [J]. *Electrochemistry Communications*, 2012 (14): 25 – 28.
- [48] Alpen U V, Rabenau A, Talat G H. Ionic Conductivity in Li_3N Single Crystals [J]. *Applied Physics Letters*, 1977 (30): 621 – 623.
- [49] Lapp T, Skaarup S, Hooper A. Ionic Conductivity of Pure Li_3N , a Stable Thin-Film Lithium Electrolyte: Lithium Phosphorus Oxynitride [J]. *Solid State Ionics*, 1983(11): 97 – 103.
- [50] Yu X, Bates J B, Jellison Jr G E, *et al.* A Stable Thin-Film Lithium Electrolyte: Lithium Phosphorus Oxynitride [J]. *Journal of the Electrochemical Society*, 1997 (144): 524 – 532.
- [51] Herczog A. Microcrystalline BaTiO_3 by Crystallization from Glass [J]. *Journal of the American Ceramic Society*, 1964(47): 107 – 115.
- [52] Chen J, Zhang Y, Deng C, *et al.* Effect of the Ba/Ti Ratio on the Microstructures and Dielectric Properties of Barium Titanate-Based Glass-Ceramics [J]. *Journal of the American Ceramic Society*, 2009(92): 1 350 – 1 353.
- [53] Chen J, Zhang Y, Deng C, *et al.* Improvement in the Microstructures and Dielectric Properties of Barium Strontium Titanate Glass-Ceramics by $\text{AlF}_3/\text{MnO}_2$ Addition [J]. *Journal of the American Ceramic Society*, 2009(92): 1 863 – 1 866.
- [54] Huang J, Zhang Y, Ma T, *et al.* Applied Physics Letters [M]. 2010(96): 0 429 021 – 0 429 023.
- [55] Zhang Y, Huang J, Ma T, *et al.* Sintering Temperature Dependence of Energy-Storage Properties in (Ba, Sr) TiO_3 Glass-Ceramics [J]. *Journal of the American Ceramic Society*, 2011(94): 1 805 – 1 810.
- [56] Gorzkowski E P, Pan M J, Bender B, *et al.* Glass-Ceramics of Barium Strontium Titanate for High Energy Density Capacitors [J]. *Journal of Electroceramics*, 2007(18): 269 – 276.
- [57] Mc Neal M P, Jang S J, Newnham R E. The Effect of Grain and Particle Size on the Microwave Properties of Barium Titanate BaTiO_3 [J]. *Journal of Applied Physics*, 1998(83): 3 288 – 3 297.
- [58] Mirsaneh M, Leisten O P, Zalinska B, *et al.* Circularly Polarized Dielectric-Loaded Antennas: Current Technology and Future Challenges [J]. *Advanced Functional Materials*, 2008(18): 2 293 – 2 300.
- [59] Zalinska B, Mirsaneh M, Reaney I M. BiNbO_4 Based Glass-Ceramic Composites for Microwave Applications [J]. *Journal of the American Ceramic Society*, 2009(92): 1 981 – 1 985.

(编辑 盖少飞)