Journal of
Ceramic Science
and Technology

Contacting Methods for C12A7 Electride Ceramic

K. Waetzig[*1], A. Rost[1], J. Schilm[1], M. Tajmar[2], A. Michaelis[1]

[1]Fraunhofer IKTS, Institute for Ceramic Technology and Systems,
Winterbergstrasse 28, D-01277 Dresden, Germany
[2]Institute of Aerospace Engineering, Technische Universität Dresden, D-01307 Dresden, Germany

Abstract

C12A7:e⁻ ($[Ca_{24}Al_{28}O_{64}]^{4+}4e^-$) ceramic is a material with high electrical conductivity and low work function, so that this ceramic is suitable as an electron-emitting material. Although the bulk material indicates these extraordinary properties, the surface of the ceramic is insulating. Therefore, a metallization film is needed to realize an electrical contact with low ohmic losses for the application of the material. In this study, we investigated three different metal pastes (Pt, Au and Cusil-ABA®) for contacting the surface and measured the reduction of the resistance during the firing process of the pastes. The resistance of the contacted C12A7:e⁻ was determined as a function of the temperature under nitrogen atmosphere. Additionally, the oxidation behaviour of the electride was observed based on increasing resistance when the material was heated in air.

The lowest resistance was measured with Ag-based braze (Cusil-ABA®), however, cracking of the contacted ceramic was observed. Alternatively, contacting with Au reached a specific resistance of 5.4 Ω cm (T = 800 °C).

Keywords: Electron emitter, conductive ceramic, C12A7, calcium aluminate, metallization, contacting

I. Introduction

In 1964, the mineral mayenite ($Ca_{12}Al_{14}O_{33}$) was discovered near Mayen (Germany) and used as an additive for calcium aluminate cement[1], and the structure of $12CaO \cdot 7Al_2O_3$ (named "C12A7") was described. It consists of twelve crystallographic cages per unit cell forming a framework of $[Ca_{24}Al_{28}O_{64}]^{4+}$ cages [2; 3]. Two free oxygen ions per unit cell are accommodated in this cage structure and can be substituted by four F⁻, Cl⁻ or OH⁻ ions [4] as well as H⁻ [5] or even by electrons[3]. Depending on the type of occupying ions, the C12A7 exhibits the properties of an electride with high electronic conductivity or as an ionic conductor. For preparing electron-doped C12A7:e⁻, different pathways starting with mayenite are known: 1) Single crystals of mayenite can be easily grown by means of the floating zone technique [6] and the Czochalski process[7] or 2) Mayenite powder can be prepared based on the solid state reaction of $CaCO_3$ and $Al(OH)_3$. In the latter case the resulting powder can be shaped by conventional pressing to ceramic green bodies [3, 8] and subsequently sintered. In both cases the reduction of the mayenite single crystal or the ceramic green body (including sintering) into the electron-doped state takes place in a graphite environment under flowing nitrogen at temperatures between 1 000 and 1 200 °C for 24 h (C12A7:$2O^{2-}$ + 2 CO $\xrightarrow{\Delta}$ C12A7:4e⁻ + 2 CO_2) [9,10]. The driving force for the reduction is the instability of the oxygen ions in the cages, which results in the formation of O_2^- and O^- radicals [11], which

are able to react with CO from the graphite environment by leaving electrons bonded in the crystal structure. Owing to this functionalization reaction, the properties of C12A7 can be changed by electron doping from an insulator to a conductor. The electron-doped C12A7:e⁻ exhibits a low work function with > 0.6 eV at room temperature, which means that this electride material can be used as a stable electron emitter under normal environmental conditions [12, 13, 14]. Furthermore, the C12A7:e⁻ exhibits high electronic conductivity between 100 and 1500 S cm⁻¹ at room temperature, which is comparable to the conductivity of a transition metal such as manganese [15, 16]. This high conductivity was measured on C12A7:e⁻ single crystals and correlates with a concentration of electron carriers between 10^{20} and 10^{21} cm⁻³ [17]. Compared to single crystals, polycrystalline C12A7:e⁻ glass ceramic or ceramic has considerably lower conductivity of ~4 S/cm (300 K) and a decreased concentration of electron carriers with $8 \cdot 10^{19}$ cm⁻³ [9, 18]. Although it is known that the conductivity can be influenced strongly by grain boundaries, the decreased conductivity of the polycrystalline C12A7:e⁻ in comparison to single crystals is not clearly understood. After preparation, the C12A7:e⁻ has an insulating surface, so the surface should be cleaned or contacted in a special way. Therefore Ar⁺ sputtering and annealing were developed to overcome the insulating layer and to obtain fully conductive C12A7:e⁻ [7]. However, this method is only successful if you handle the material after cleaning in the same vacuum unit. Exposure of cleaned surfaces to other atmospheres would again result in unwanted insulating surface

layers. Hence in order to receive a stable ceramic-based and usable electride, it is necessary to have metallization films on the surfaces, which are able to penetrate or destruct the insulating zones and realize a reliable ohmic contact.

We studied the development of electric contacts between the C12A7:e⁻ bulk material with an insulating surface and different metals by applying metal pastes and firing them under nitrogen. Afterwards the oxidation behaviour in air was observed by heating up the contacted specimen and measuring the change in electrical resistance.

II. Experimental

Glass ceramic powder was prepared by mixing $CaCO_3$ and Al_2O_3 in a stoichiometric ratio of 12 to 7. The powder mixture was heated up in an alumina crucible at a temperature of 1 450 °C for 1 h and the melt was quenched on a brass block. The clear glass was milled in ethyl alcohol together with an organic binder. The slurry was dried using a rotary evaporator and the resulting powder was shaped by uniaxial pressing to give round discs. The discs with 20 mm diameter were debindered in air at a temperature of 800 °C and sintered at 1 200 °C for 5 hours in a graphite crucible under flowing nitrogen. The sintering skin was removed by grinding the two surfaces of the discs. The phase composition of powder and ceramic was determined by means of X-ray diffraction using a D8 Advance (Bruker AXS Ltd.). The sintering characteristic of the pressed powder was analyzed using a thermomechanical analyzer TMA-60H (Shimadzu Corp., Japan). For the contacting process three different pastes (Table 1) were applied on the two sides of the C12A7:e⁻ and connected with two interwoven platinum wires on each paste layer. The sample is placed on three ceramic spacers with a thermocouple located in the middle of this set-up in order to monitor the two-wire type electric measurement. The set-up was placed in a tube furnace (LINSEIS Messgeräte GmbH, Germany). During the firing process of the pastes and the formation of an electric contact, the tube was flushed with nitrogen for 3 h (60 L/h), heated up with 5 K/min to different maximum temperatures. During the heat treatment a constant current of 0.01 A was applied to the samples and the resulting voltage was monitored. After cooling down with 10 K/min, the measurement was performed again under nitrogen to measure the resulting resistance of the contacted C12A7:e⁻ ceramic and in a third cycle under air to observe the change in resistance.

III. Results and Discussion

The preparation of C12A7:e⁻ ceramics started with the melting and quenching of glass, which was black in colour (Fig. 1). After grinding and milling of the glass, the sintering characteristic of the resulting and pressed powder was measured (Fig. 2). Thereby, a volume expansion at a temperature of about 850 °C was observed (Fig. 3). The sintering shrinkage of the compacted powder started at about 1 020 °C and was followed by a maximum of the shrinkage rate at 1 210 °C. After sintering under nitrogen atmosphere, the discs were completely crystallized as the C12A7 phase (Fig. 3), coloured black (Fig. 4) and reached 96 % of the theoretical density (2.676 g/cm³).

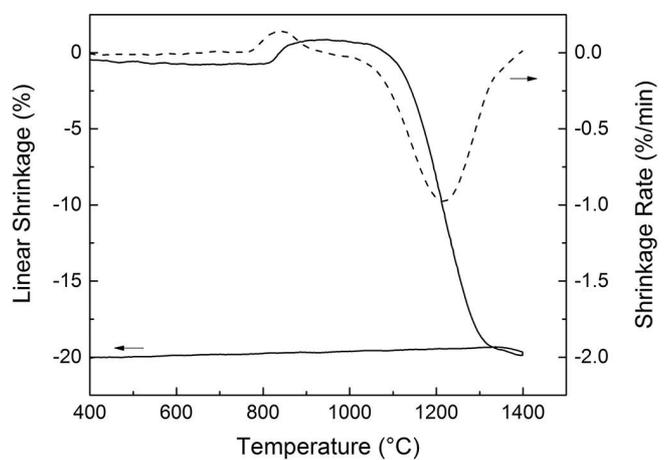**Fig. 1:** Cracked glass-ceramic disc of C12A7 composition after melting and quenching.

Fig. 2: Sintering characteristic of C12A7 powder prepared by melting, quenching and milling.
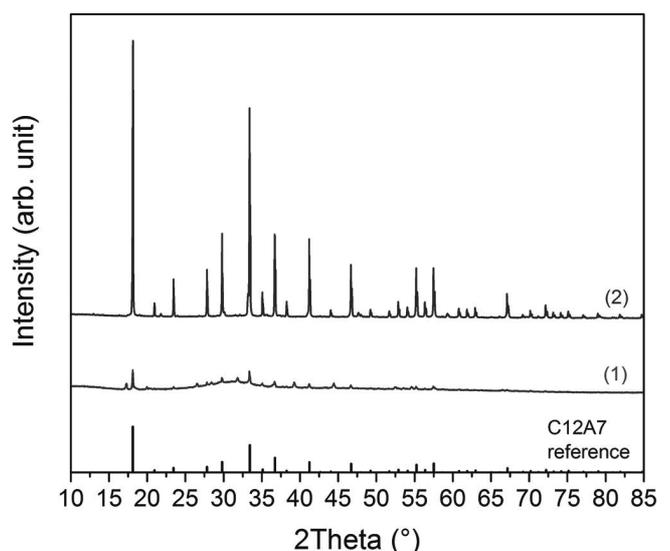

Fig. 3: X-ray diffraction pattern of (1) powder of glass-ceramic after melting, quenching and milling and (2) pulverized ceramic disc after sintering made of this glass-ceramic powder compared to C12A7 reference data of PDF 01 – 078 – 0910.

Table 1: Properties of pastes used for contacting C12A7 electride:

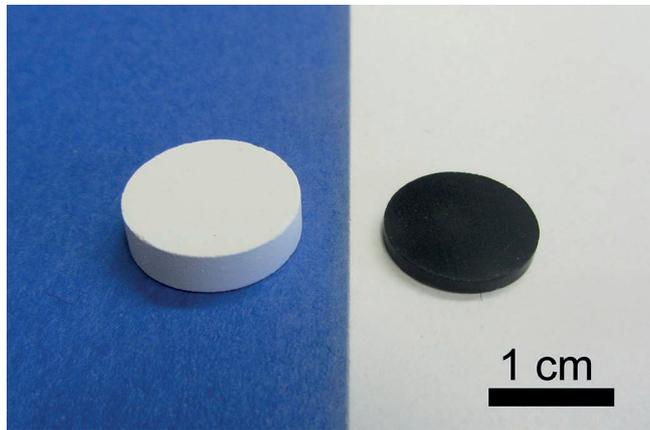| Paste name	Provider	Composition	Melting point
Pt	self-made by IKTS	100 % Pt powder with organic binder and dispersant	1 768 °C
Au	self-made by IKTS	100 % Au powder with organic binder and dispersant	1 064 °C
Cusil-ABA®	Wesgo Metals	63 % Ag, 1.75 %Ti, 35.25 % Cu	815 °C

Fig. 4: Pressed green body made of C12A7 powder before sintering (left) and sintered C12A7:e⁻ ceramic (right).

These C12A7:e⁻ ceramics were dry-ground on the surface to eliminate the sintering skin. For measuring the resistance, an electric contact of the surface has to be realized. Therefore, three different types of contacting pastes were selected (Table 1). Two pure metal pastes of platinum and gold were self-prepared with a binder and a dispersant, which can be debindered under nitrogen. The third tested paste was a commercial active filler metal named Cusil-ABA® with a high content of silver and copper activated with TiH_2. This paste is provided for brazing ceramic-ceramic or ceramic-metal bonds at temperatures below 1 000 °C, so that an application is limited to a maximum of 800 °C. After applying the pastes onto the C12A7 ceramics, the contact was realized by firing under nitrogen up to different temperatures depending on the sintering conditions of the metal-based pastes.

Fig. 5 indicates the temperature-dependent resistance of coated C12A7-ceramic during the firing process of the pastes. The pure metal pastes of Au and Pt show comparable characteristics of the curves and achieve a resistance below 200 Ω cm only above 450 °C. After cooling down, the resulting resistance of both samples was between 10 and 30 Ω cm. In contrast, the ceramic with Cusil-ABA® paste starts with a lower resistance of about 40 Ω cm before firing. This paste is comparable to a conductive silver lacquer, which has a low content of organics and therefore exhibits conductive particle-particle contacts already in the non-fired state. After firing, this paste achieved a resistance of 1 Ω cm above 300 °C and 4 Ω cm after cooling down. Directly after firing under nitrogen the resistance of C12A7:e⁻ ceramics was measured again in the same atmosphere as a function of the temperature (Fig. 6, Table 2). The samples contacted with gold reached a minimum of resistance with 5.4 Ω cm at 800 °C. At the same temperature the Pt contact indicates a lower resistance of 3.9 Ω cm, but

with Cusil-ABA® the resistance is decreased to 1.1 Ω cm. The cooling down curve is slightly increased for all metallizations. This could be indicated by an onset of degradation (e.g. formation of cracks and loss of contact) or a slightly oxidation of the C12A7 electride with residual oxygen in the nitrogen atmosphere.
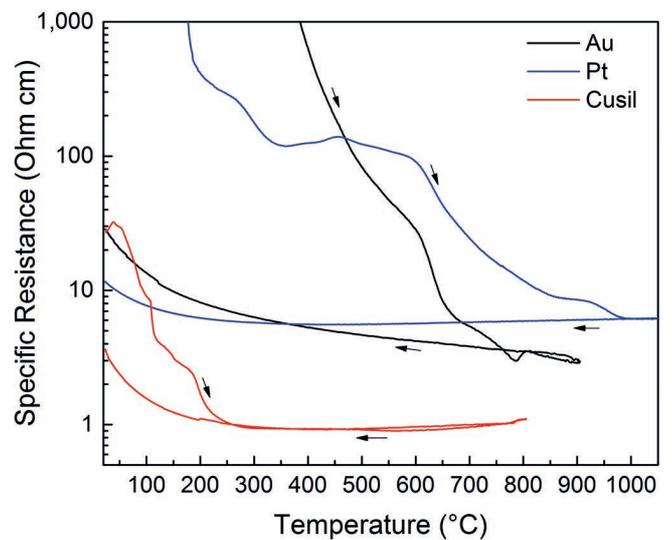

Fig. 5: Specific resistance of C12A7:e⁻ ceramics contacted with three different metal pastes during firing under nitrogen atmosphere.
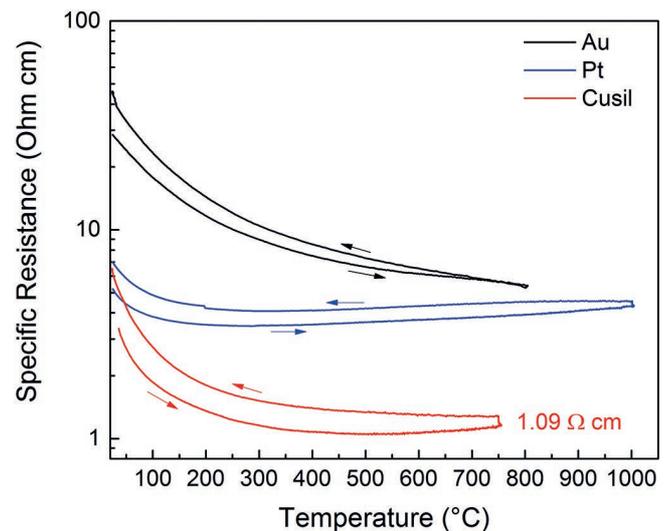

Fig. 6: Specific resistance of C12A7:e⁻ ceramics contacted with three different metal pastes under nitrogen atmosphere (additional measurement after firing process).

The stability of the C12A7:e⁻ electride against oxidation was tested by heating up the contacted samples during measurement of the resistance in air (Fig. 7). At first the samples contacted with Cusil-ABA® showed an increase in the resistance at temperatures above 500 °C, indicating

Table 2: Resistance and specific resistance of C12A7:e⁻ ceramic using different types of metallization pastes:

|	Au			Pt			Cusil-ABA®		
T	R	ρ	σ	R	ρ	σ	R	ρ	σ
°C	mΩ	Ω cm	S/cm	mΩ	Ω cm	S/cm	mΩ	Ω cm	S/cm
30	2 663	27.5	0.04	484	5.0	0.20	326	3.36	0.30
100	1 736	17.9	0.06	372	3.8	0.26	151	1.56	0.64
200	1 133	11.7	0.09	341	3.5	0.28	106	1.09	0.91
300	868	9.0	0.11	337	3.5	0.29	91	0.94	1.06
400	726	7.5	0.13	341	3.5	0.28	89	0.92	1.09
500	645	6.7	0.15	349	3.6	0.28	90	0.93	1.08
600	597	6.2	0.16	360	3.7	0.27	88	0.91	1.10
700	565	5.8	0.17	368	3.8	0.26	93	0.96	1.04
800	527	5.4	0.18	380	3.9	0.26	106	1.09	0.91
900				395	4.1	0.25			
1000				417	4.3	0.23			
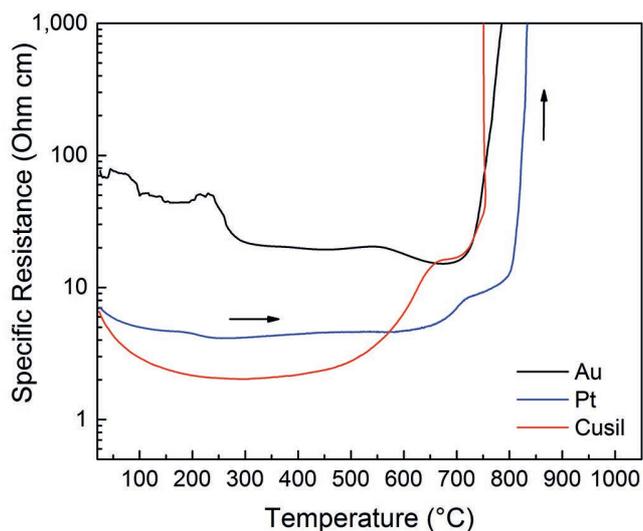
Fig. 7: Specific resistance of C12A7:e⁻ ceramics contacted with three different metal pastes during the oxidation in air. The fluctuations in the curve with gold metallization are not clearly understood, but could be correlated with the loss of contact between metal and ceramic indicated by initial cracks.

C12A7:e⁻ ceramic was metallized with Au paste. After firing and cooling down, no delamination or cracking of the metallized samples was observed (Fig. 9).
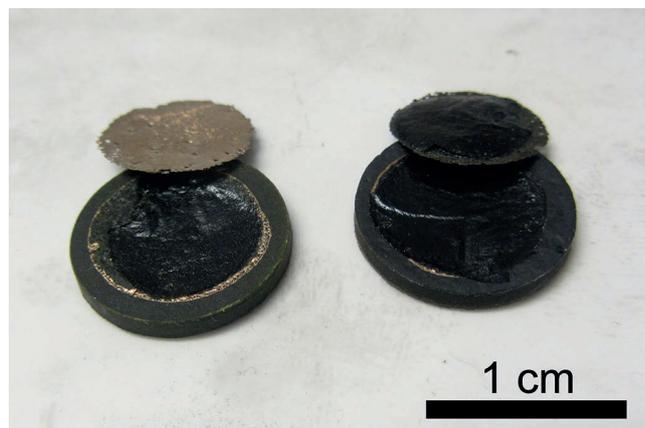

Fig. 8: Delamination after the metallization with Cusil-ABA® (Ag-based paste) and firing of the paste. The metallized paste seems to adhere to C12A7:e⁻ ceramic, but the stresses during cooling down lead to cracking of the ceramic.

the beginning of oxidation processes. An extreme increase in the resistance is observed for all types of samples at temperatures above 700 °C. This indicates that C12A7:e⁻ is stable in air below a temperature of 700 °C.

The measurement of resistance under nitrogen indicates that the Ag-containing paste (Cusil-ABA®) contacts the C12A7:e⁻ ceramic with the lowest ohmic resistance. Therefore the Cusil-ABA® was applied to the ceramic and fired under nitrogen to realize surface-contacted discs. Although the metallization seems to contact the ceramic, after one day the layer of metal contact was lost because of cracking of the ceramic (Fig. 8). This observation means that the metallization was under excessively high tensile stress, which induced crack formation in the ceramic. With the same procedure, the

Fig. 9: Successful metallization of gold on C12A7:e⁻ ceramic.

IV. Conclusions

The C12A7:e⁻ ceramic is a well-conducting material, but has an insulating surface. Therefore the surface has to be metallized to obtain a usable electric contact of the ceramic. Three different pastes (Au, Pt and Ag-based Cusil-ABA®) were applied to the ceramic and fired under nitrogen. With the use of Au- and Pt-based metallization, a resistance of the C12A7:e⁻ < 6.2 Ω cm was measured at a temperature of 800 °C. The lowest resistance was achieved with the Cusil-ABA® paste (106 mΩ; 1.1 Ω cm) at the same temperature. Unfortunately, the Cusil-ABA®-based contacts introduced stress in the ceramic and resulted in a failure of the ceramic by cracking. Therefore the Au contact should be used alternatively to Cusil-ABA® with regard to lower stress and the higher price of Pt. A specific resistance of 5.4 Ω cm (T = 800 °C) was realized with Au contacting. In future, long-term measurements have to be investigated to study the behaviour of the metallization with cycling temperature load under inert atmosphere.

Acknowledgement

References

[1] Boysen, H., Lerch, M., Stys, A., Senyshyn, A.: Structure and oxygen mobility in mayenite ($Ca_{12}Al_{14}O_{33}$): a high-temperature neutron powder diffraction study, *Acta Cryst.*, **B63**, 675 – 682, (2007).

[2] Bartl, H., Scheller, T.: The structure of $7CaO \cdot 12Al_2O_3$, in german, *Neues Jahrb. Mineral. Monatsh.*, **35**, 547 – 552, (1970).

[3] Hosono, H.: Functioning of traditional ceramics $12CaO \cdot 7Al_2O_3$ utilizing built-in nano-porous structure, *Sci. Tech. Adv. Mater.*, **5**, 409 – 416, (2004).

[4] Jeevaratnam, J., Glasser, F.P., Dent Glasser, L.S.: Anion substitution and structure of $12CaO \cdot 7Al_2O_3$, *J. Am. Ceram. Soc.*, **47**, 105 – 106, (1964).

[5] Hayashi, K.: Heavy doping of H⁻ ion in $12CaO \cdot 7Al_2O_3$, *J. Solid State Chem.*, **184**, 1428 – 1432, (2011).

[6] Ebbinghaus, S.G., Krause, H., Syrowatka, F.: Floating zone growth of large and defect-free $Ca_{12}Al_{14}O_{33}$ single crystals, *Cryst. Growth Des.*, **13**, 2990 – 2994, (2013).

[7] Toda, Y., Kubota, Y., Hirano, M., Hirayama, H., Hosono, H.: Surface of room-temperature-stable electride $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$: preparation and its characterization by atomic-resolution scanning tunneling microscopy, *ACS Nano*, **5**, 1907 – 1914, (2011).

[8] Hosono, H., Abe, Y.: Occurrence of superoxide radical ion in crystalline $12CaO \cdot 7Al_2O_3$ prepared via Solid-state reactions, *Inorg. Chem.*, **26**, 1192 – 1195, (1987).

[9] Kim, S.-W., Hayashi, K., Hirano, M., Hosono, H.: Electron carrier generation in a refractory oxide $12CaO \cdot 7Al_2O_3$ by heating in reducing Atmosphere: conversion from an insulator to a persistent conductor, *J. Am. Ceram. Soc.*, **89**, 3294 – 3298, (2006).

[10] Trofymluk, O., Toda, Y., Hosono, H., Navrotsky, A.: Energetics of formation and oxidation of microporous calcium Aluminates: A new class of electrides and ionic conductors, *Chem. Mater.*, **17**, 5574 – 5579, (2005).

[11] Hayashi, K., Ueda, N., Hirano, M., Hosono, H.: Effect of stability and diffusivity of extra-framework oxygen species on the formation of oxygen radicals in $12CaO \cdot 7Al_2O_3$, *Solid State Ionics*, **173**, 89 – 94, (2004).

[12] Williams, J.D., Sanmartin, J.R., Rand, L.P.: Low work-function coating for an entirely propellantless bare electrodynamic tether, *IEEE Transactions on plasma science*, **40**, 1441 – 1445, (2012).

[13] Drobny, C., Nürmberger, F., Tajmar, M.: Development of a compact hall thruster with a C12A7 low-power hollow cathode, *Proc. of the Space Propulsion Conference*, Paper 3124751, Rome, March 2 – 6, (2016).

[14] Toda, Y., Kim, S.W., Hayashi, K., Hirano, M., Kamiya, T., Hosono, H., Haraguchi, T., Yasuda, H.: Intense thermal field electron emission from room-temperature stable electride, *Appl. Phys. Lett.*, **87**, 254103, (2005).

[15] Somiya, S. (Ed.), Handbook of Advanced Ceramics, 2nd edition, Elsevier Inc., 466 – 467, (2013).

[16] Matsuishi, S., Toda, Y., Miyakawa, M., Hayashi, K., Kamiya, T., Hirano, M., Tanaka, I., Hosono, H.: High-density electron anions in a nanoporous single Crystal: $[Ca_{24}Al_{28}O_{64}]^{4+}(4e^-)$, *Science*, **301**, 626 – 629, (2003).

[17] Lobo, R.P.S.M., Bontemps, N., Bertoni, M.I., Mason, T.O., Poeppelmeier, K.R., Freeman, A.J., Park, M.S., Medvedeva, J.E.: Optical conductivity of Mayenite: from insulator to metal, *J. Phys. Chem. C*, **119**, 8849 – 8856, (2015).

[18] Kim, S.-W., Matsuishi, S., Miyakawa, M., Hayashi, K., Hirano, M., Hosono, H.: Fabrication of room temperature-stable $12CaO \cdot 7Al_2O_3$ electride: a review, *J. Mater. Sci.: Mater. Electron.*, **18**, S5 – S14, (2007).