Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Microwave properties and structure of La–Ti–Si–B–O glass-ceramics for applications in GHz electronics

Hubertus P. Braun[a,b,c,*], Arshad Mehmood[d], Martun Hovhannisyan[c], Huairuo Zhang[e], Damoon Sohrabi Baba Heidary[g,i], Clive Randall[g,i], Michael T. Lanagan[h,i], Rolf Jakoby[d], Ian M. Reaney[f], Martin Letz[c], Hans-Joachim Elmers[a,b]

[a] Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 7, 55128 Mainz, Germany
[b] Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany
[c] SCHOTT AG, Hattenbergstrasse 10, 55122 Mainz, Germany
[d] Institute for Microwave Engineering and Photonics, Technical University of Darmstadt, Merckstrae 25, 64283 Darmstadt, Germany
[e] National Institute of Standards and Technology, Functional Nanostructured Materials Group, 100 Bureau Drive, Gaithersburg, MD 20899, USA
[f] Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, United Kingdom
[g] Department of Materials Science & Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[h] Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA 16802, USA
[i] Center for Dielectrics & Piezoelectrics, Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 9 August 2016
Received in revised form
28 November 2016
Accepted 29 November 2016
Available online xxx

Keywords:
Dielectric glass-ceramics
Titanate-based glass-ceramics
Microwave materials
GHz materials
Dielectric-loaded antenna materials

ABSTRACT

A dielectric bulk glass-ceramic of the La_2O_3–TiO_2–SiO_2–B_2O_3 system is developed which is able to fulfill the requirements for dielectric loading-based mobile communication technologies. It is shown that the given dielectric requirements can be fulfilled by glass-ceramic materials without being dependent on ceramic processing techniques. The material exhibited permittivity values of $20 < \varepsilon_r < 30$, quality factor 2000 GHz < Qf < 10,000 GHz and a temperature coefficient of resonance frequency $-100 < \tau_f < +180$ ppm/K. A zero τ_f material with a Qf value of 9500 GHz and $\varepsilon_r = 21.4$ could be achieved at a ceramming temperature $T_{cer} = 870\,^{\circ}C$. The material is aimed to provide an alternative to existing, commercially used sintered ceramic materials. Further focus is laid on the investigation of the dominant dielectric loss mechanisms in the GHz frequency range and how they are correlated with the microstructure.

1. Introduction

Dielectric oxide ceramics have revolutionized the microwave wireless communication industry by reducing size and cost of filter, resonator and antenna components in various applications ranging from cellular phones to global positioning systems [1]. This is apparent by the increasing number of smart phones combining the use of multiple microelectronic components of different operating frequencies on a limited spatial area (GSM/UMTS/LTE, GPS, WLAN, Bluetooth). Miniaturization is a critical factor for hand-held devices and can be directly observed in the decrease of size and weight of the devices in recent years. The required performance increase for future technologies (e.g. 5G) can be achieved by the use of MIMO-based antenna systems [2] (MIMO: multiple-input and multiple-output). Miniaturization and MIMO can be realized by the use of dielectric loading-based implementation solutions. While for cavity filters, exceptionally low-loss materials (Qf > 100,000 GHz) are necessary [3], dielectric loading-based wireless communication technologies (MIMO, GPS, multiresonant dielectric resonator antennas) as for example dielectrically loaded antennas (DLA) can utilize dielectrics with higher losses (Qf > 5000 GHz, $\varepsilon_r > 20$, $|\tau_f| < 20$ ppm/K), as their antenna efficiency is mainly dominated by metallization losses [4]. A quite large number of commercially available ceramics with excellent dielectric properties already exists [3], but due to their manufacturing process (sintering) they show some disadvantageous non-electronic properties which cause problems for their use in DLA applications [5,6]:

- Porosity (problematic for metallization processes).
- Blank inhomogeneity/non-uniformity (performance deterioration).

* Corresponding author. Present address: Robert Bosch GmbH, Postfach 30 02 20, 70442 Stuttgart, Germany.
E-mail address: h.braun86@gmx.de (H.P. Braun).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.048
0955-2219/

Table 1
Microwave properties and JCPDS code for the relevant crystal phases in the La_2O_3–TiO_2–SiO_2–B_2O_3 system.

Phase	ε_r	Qf [GHz] (f_{meas})	τ_f [ppm/K]	Ref.	JCPDS (ICCD)
$La_4Ti_9O_{24}$	37	24,800 (8 GHz)	+15	[24,11]	00-036-0137
$La_2Ti_2SiO_9$	28	29,500 (5 GHz)	+23	[25]	01-082-1490
TiO_2 (rutile)	104	44,000 (4 GHz)	+450	[26,1]	01-086-0148
$LaBO_3$	12.5	53,000 (12 GHz)	N/A	[27,28]	00-012-0762
$LaSiBO_5$	N/A	N/A	N/A	N/A	01-077-0989
SiO_2 (glass)	3.8	67,000 (9 GHz)	<0	[29]	

- Batch-to-batch variation of the dielectric properties ($\Delta\varepsilon_r/\varepsilon_r \approx 1$–2%).

At low frequency ranges dielectric resonators become larger which intensifies these manufacturing-related problems. Especially for the frequency range below 2 GHz, which is important for mobile communications large blank geometries are necessary [7]. For these applications glass-ceramic materials can be a suitable alternative to sintered ceramic materials. Glass-ceramic-based dielectrics tend to have comparatively higher dielectric losses due to the residual glassy phase, but provide superior structural properties to sintered ceramics. As glass-ceramics are initially produced from a homogeneous liquid glass melt, they are intrinsically pore-free and provide a better material homogeneity and reproducibility. First work on glass-ceramic-based dielectrics for DLA applications was made in the Bi_2O_3–Nb_2O_5–SiO_2–B_2O_3 system by Mirsaneh et al. [8,4], but the dielectric requirements could not be sufficiently fulfilled. In this work the development of a dielectric glass-ceramic material with suitable dielectric properties (Qf = 9500 GHz, ε_r = 21.4, τ_f = −1 ppm/K) is presented.

2. Material development and characterization

2.1. Motivation for the choice of the La_2O_3–TiO_2–SiO_2–B_2O_3 system

The dielectric properties of glass-ceramic material system dominantly determined by the dielectric properties of the existing crystalline phases, which were investigated in literature (e.g. [1]) under consideration of the requirements of the aimed application ($\varepsilon_r > 20$, $Qf > 5000$ GHz and $|\tau_f| \leq 20$ ppm/K). In the ternary system La_2O_3–TiO_2–SiO_2, two optimal crystalline phases ($La_4Ti_9O_{24}$ and $La_2Ti_2SiO_9$, see Table 1) exist, which show sufficiently high ε_r and Qf, in combination with a small positive τ_f. The τ_f values are optimal for the use in glass-ceramic materials, as the residual glassy phase generally has a negative τ_f [1,9] and both phases can thereby compensate to an overall τ_f close to zero. TiO_2 (rutile) and $LaBO_3$ are minor phases (<20 wt%) for some glass compositions/ceramming programs. TiO_2 (rutile) has excellent dielectric properties [10] but also an extremely high τ_f. $LaBO_3$ crystallizes from the excess B_2O_3 and La_2O_3 which is not used in the major crystalline phases. To enhance the glass forming ability of the system (avoid devitrification), a combination of the two network former oxides SiO_2 and B_2O_3 was added. This enables a glass composition in the field of crystallization of the two target crystalline phases. Nevertheless, the aim is always a one-crystalline-phase material with main content of $La_4Ti_9O_{24}$ or $La_2Ti_2SiO_9$, as multiple-phase materials always tend to have a higher dielectric losses [11]. Unfortunately SiO_2 and B_2O_3 only have a low ionic polarizability due to their strong covalent bonds, but also they have a comparatively low dielectric loss [12,1]. The amount of SiO_2 and B_2O_3 was kept to a minimum to achieve a maximum amount of crystalline phase respectively minimum amount of residual glass phase content after the ceramming process.

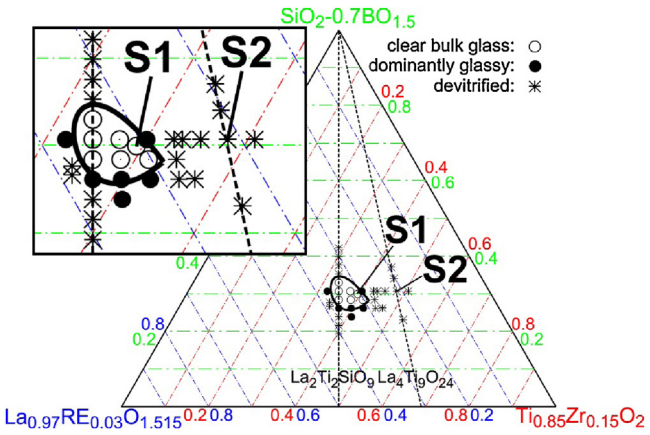

Fig. 1. Pseudo-ternary diagram to visualize the glass-forming area, the black dashed lines correspond to La:Ti ratios of 1:1 ($La_2Ti_2SiO_9$) resp. 4:9 ($La_4Ti_9O_{24}$).

2.2. Glass melting and ceramming process

The glass samples were melted from milled dry powders according to the batch composition inside a one-liter Pt–Ir alloy crucible. The melts are cast into size-adjustable steel molds. From each melt 4 glass bars of 2 cm × 5 cm × 23 cm size could be made, which were then cut into suitable geometries for subsequent measurements. The high volume and the possibility to stir the melt ensured homogeneous samples. The melting temperature T_m varied between 1450 °C and 1650 °C. A typical melting procedure can be summarized as:

- Insertion of raw materials in 5 g steps at T_m − 100 °C (typically 1500 °C), until batch is melted.
- Oxygen bubbling and stirring (to achieve oxidizing melting conditions) with 27 l/h for 30 min at T_m − 50 °C (typically 1550 °C).
- Keeping time at the high temperature chamber furnace for t_k = 30 min at T_m (typically 1600 °C).
- Casting into steel mold (on room temperature, placed on graphite plates to improve heat conduction).
- Cooling in the cooling furnace to prevent crack formation (preheated at T_g − 20 °C) with 20 K/h until room temperature.

The glass transition temperature of S1 was measured to T_g = 768 °C via DTA at a heating rate of 200 K/h. First compositional attempts were made with La:Ti ratios close to the stoichiometry of the $La_4Ti_9O_{24}$ phase (e.g. sample S2, see Fig. 1). These glasses showed a strong devitrification tendency (see Fig. 2) and therefore the composition was moved closer to the stoichiometry of the $La_2Ti_2SiO_9$ phase. An important concept to stabilize glass formation in multicomponent systems is the principle of glass frustration [13]. The increase of the number of different cations/components leads to a "geometrical frustration" which increases disorder of the system and thereby retards the formation of an ordered crystalline state [14], respectively stabilizes the disordered amorphous glassy phase. Fig. 1 shows a pseudo-ternary compositional diagram and a comparatively small glass-forming area. TiO_2 was partially substituted by ZrO_2 and La_2O_3 by other rare earth oxides (RE: CeO_2, Nd_2O_3, Sm_2O_3, Gd_2O_3) to create additional disorder and thereby improve the glass-forming properties of the system. A Ti substitution with 10–20% Zr and a La substitution with 1–5% RE showed the best results. Samples containing Gd_2O_3 showed the best stability against devitrification. The composition S1 (30.71 $La_{0.97}Gd_{0.03}O_{1.5}$–39.37 $Ti_{0.85}Zr_{0.15}O_2$–17.32 SiO_2 – 12.60 $BO_{1.5}$, see Fig. 2) showed optimum glass-forming abilities (purely amorphous) in combination with sufficiently good dielectric properties after the ceramming process. The used raw materials are high purity

Please cite this article in press as: H.P. Braun, et al., Microwave properties and structure of La–Ti–Si–B–O glass-ceramics for applications in GHz electronics, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.11.048