Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 33 (2013) 991–1000

www.elsevier.com/locate/jeurceramsoc

Development of a model for the sintering of PZT multilayer ceramics and their dielectric properties

Tobias Kühnlein [a,*], Alfons Stiegelschmitt [b], Andreas Roosen [b], Martin Rauscher [a]

[a] *Robert Bosch GmbH, Manufacturing, Operations and Engineering, Bamberg, Germany*
[b] *University of Erlangen-Nuremberg, Department of Materials Science, Glass and Ceramics, Germany*

Received 27 June 2012; received in revised form 28 October 2012; accepted 31 October 2012
Available online 3 December 2012

Abstract

Piezoelectric multilayer ceramics are increasingly used in sophisticated applications for high-precision positioning systems. The reproducibility of the piezo-electrical properties is of major importance for the manufacture of high quality products. This study focuses on the variation of the sintering parameters and its effect on the poling behaviour as a contribution to the establishment of an understanding of PZT multilayer processing. To cover the complexity of the sintering process, the experiments were conducted with the design of experiments method. As parameters the sintering temperature, the holding time, the airflow in the furnace and the lead oxide atmosphere were investigated. As target variables the grain size, density and mass loss were investigated. In the following the correlations between the target variables and the sintering parameters were discussed and summarised in a model. The ceramic properties were correlated to the dielectric properties and the influence of the poling process was evaluated.

Keywords: PZT; Sintering; Multilayer; Microstructure-final; Dielectric properties

1. Introduction

Lead zirconate titanate (PZT) ceramics are today widely used in industrial sensor and actuator applications, such as for pressure and ultrasonic sensors and actuators for fuel injection, due to their excellent piezoelectric properties.[1–3] The application-specific adjustment of the material properties is achieved by the ratio of zirconate to titanate and by doping.[4] Depending on the size of the incorporated ions, a soft or hard PZT is obtained by doping.[5] A high strain PZT ceramic is achieved by doping with Sr, K and Nb. This so called PZT–SKN reaches elongations up to 2‰ and is therefore well suited for high strain applications.[4,6]

The sintering process defines basically the microstructure, which in turn defines the electrical and mechanical properties of the multilayer, even though the result depends on the composition of the PZT and electrode material. During the sintering process the parameters temperature, time and the atmosphere have to be controlled to adjust the sintering density, shrinkage, mass loss and grain size.[7,8] Typical sintering temperatures for the co-firing of PZT multilayers lie in the range of 950–1150 °C, which depends on the stability of the electrode material and the liquid phase content in the ceramic during densification.[2]

The sintering of PZT is a complex process due to the melting and evaporation of PbO starting at low temperatures of around 890 °C. Therefore different methods exist to prevent a depletion of the Pb in the PZT. A PbO excess can be added to the PZT, which generates a liquid phase during sintering and enhances the densification.[9] For such ceramics the overall sintering process can be described by the liquid phase sintering theory.[10,11] For stoichiometric PZT an encapsulation with a Pb containing atmospheric powder, in which the Pb has a higher partial pressure than in PZT, is often used.[8] In this case the sintering follows the solid state sintering regime.

For PZT multilayers which are co-fired with inner electrodes consisting of Ag and Pd, an additional influence of the electrode material on the sintering has to be considered. Donnelly et al.[12] found reactions between Pb and Pd in the temperature range up to 800 °C, which lead to the formation of a thin $PdPbO_2$ layer between the electrode and the ceramic. In contrast, Zuo

* Corresponding author at: Am Börstig 2, 96052 Bamberg, Germany. Tel.: +49 951 181 4797; fax: +49 711 811 501 4797.
E-mail address: tobias.kuehnlein@de.bosch.com (T. Kühnlein).

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.10.018

et al.[13] observed the stability of this phase far above 800 °C. The decomposition of this Pd/Pb compound depends on the Ag/Pd ratio, and starts between 525 °C for $Ag_{0.9}/Pd_{0.1}$ and 730 °C for $Ag_{0.55}/Pd_{0.45}$.[2] However, the electrode–PbO reaction affects the final microstructure since these reaction products are present during liquid phase sintering, which starts below 800 °C.[9,14] Another interaction between ceramic and electrode is the Ag migration into the ceramic. Laurent et al.[15] assumed an Ag diffusion via the gas phase into the ceramic; as a result the Ag concentration in the PZT is independent of the existence of a $PdPbO_2$ diffusion barrier between electrode and ceramic. The Ag^+ ions are supposed to be incorporated into the PZT lattice on Pb^{2+} sites,[16,17] but can also be enriched at the grain boundaries, depending on the Ag content in the ceramic,[18] both resulting in an enhanced grain growth. Due to the reported variation between Ag/Pd printed and non-metallised PZT multilayer ceramics, this influence on the PZT microstructure will be investigated in detail.

In addition to the influence of the microstructure, which is a result of the materials composition and its processing including firing, the resultant electrical properties are affected by the poling parameters.[4,19,20] The electric field which is applied to the ceramic aligns the domains up to a certain degree in the direction of the electric field. The degree of orientation depends on the grain size and doping.[21] The resultant remanent polarisation leads to pronounced piezoelectric and dielectric properties.

The aim of the present work is to improve the understanding of co-firing PZT multilayer ceramics with inner metal electrodes. Many studies have been published on the sintering of bulk PZT ceramics, but only a few papers have been published co-fired multilayers. The focus has been drawn on the electrode–ceramic interactions[12,22,23] and less on the sintering parameters and their influence on microstructure development. In this study the influence of a small variation of the sintering parameters on the ceramic properties, such as density, mass loss and grain size, is evaluated. To get access to the complex interactions during the sintering process, the experiments were conducted and analysed by using the design of experiments. Therewith it is possible to evaluate the effect of single process parameters on the overall sintering result. The interrelations between microstructural properties and dielectric characteristics of the multilayers were discussed. Furthermore, the poling behaviour is investigated to study possible variations in the microstructure which may alter the dielectric properties. The found regression results were validated by using published results on PZT ceramics. The DoE results are used in an engineering point of view to achieve information about the importance of different processing variables and their variation on the final PZT properties sintered in a technical large scale sintering process. These discussions result in a sintering profile to reduce the variations in the dielectric properties.

2. Experimental

For the investigations, a commercial soft PZT ceramic doped with Sr, K and Nb and an excess of Pb (CeramTec AG, Lauf a.d. Pegnitz, Germany) was used. The composition of the tape cast material was $0.98Pb_{1.02}(Zr_{0.53}Ti_{0.47})O_3–0.02Sr(K_{0.25}Nb_{0.75})O_3$. RFA analysis (S4 Explorer, Bruker AXS GmbH, Karlsruhe, Germany) detected the presence of small impurity amounts of Al_2O_3, SiO_2 and Fe_2O_3 with concentrations of 0.019 Ma.%, 0.021 Ma.% and 0.026 Ma.%, respectively. The particle size distribution (1190, CILAS, Orleans, France) of the PZT material used is shown in Fig. 1.

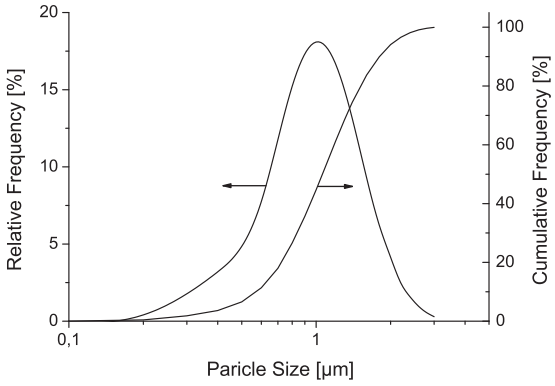

Fig. 1. Particle size distribution of the PZT material used.

The inner electrodes were screen printed on the green tape using an $Ag_{0.7}/Pd_{0.3}$ paste. After drying, several hundred single layers were stacked in such a way that the electrodes were attached to alternating the opposite surfaces by rotating every second layer by 180°. Additionally, dummy specimens without any metallisation were built up in the same way using the same PZT material. To evaluate the differences in the principle thermophysical behaviour between multilayer specimens printed with Ag/Pd paste and the pure PZT multilayers, mass loss and shrinkage measurements were conducted. The shrinkage was determined by means of a dilatometer (Dil402, Netzsch-Gerätebau GmbH, Selb, Germany). The same time-temperature profile with a heating rate of 5 K/min up to a temperature of 1035 °C, followed by a holding time of 2 h was used for all measurements with debinded PZT samples. The mass loss development of the pure PZT samples and metallised multilayers was evaluated thermogravimetrically (Simultaneous Thermal Analysis STA 429, Netzsch-Gerätebau GmbH, Selb, Germany) using a heating rate of 1 K/min until 550 °C, followed by 5 K/min until 1025 °C with a holding time at the peak temperature of 9 h.

The sintering experiments were conducted using a design of experiments (DoEs) (Software Cornerstone, Applied Materials Inc., Santa Clara, USA). The debindered specimens were sintered according to a full factorial 2^3 DoE plan with a centre point. In the DoE the parameters peak temperature T_{top}, holding time t_{hold} and air flow Q were varied with two settings for each. The centre point is adjusted to the mean value of the three influencing factors. The sintering settings are shown in Table 1. Additionally, the specimens were sintered in different PbO atmospheres in each sintering run; Fig. 2 illustrates these sintering conditions. Half of the specimens were placed within a distance of 20 mm to each other, i.e., air with a low PbO partial pressure p_{PbO} surrounding the samples. The other specimens were