CHEMICALLY CONTROLLED SINTERING AND MICROSTRUCTURAL DEVELOPMENT IN CERAMICS

KEMIJSKO NADZOROVANO SINTRANJE IN RAZVOJ MIKROSTRUKTURE V KERAMIKI

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The sintering step in manufacturing most ceramic articles is dominated by the chemical reactions which occur during firing. Such chemical reactions may be caused by chemical heterogeneity of the constituents of the ceramic body, small amounts of additives or impurities. Even in chemically equilibrated multicomponent systems the capillary forces may cause dehomogenisation and influence the sintering mechanism. Reaction sintering in the $BaTiO_3$-$CaZrO_3$-TiO_2 system is described as an example of a system where controlled chemical heterogeneity may optimise the electrical properties. Sintering of $PbZr_{1-x}Ti_xO_3$ ceramic is described as an example of chemical dehomogenisation due to capillary forces.

Key words: reaction sintering, ceramic microstructure, barium titanate, lead zirconate-titanate, sintering mechanisms

Proces sintranja v proizvodnji večine keramičnih izdelkov določajo kemijske reakcije, ki potekajo med žganjem. Kemijske reakcije lahko povzročajo heterogenost sestavin keramike, majhne količine dodatkov ali nečistoče. Celo v kemijsko uravnoteženih večkomponentnih sistemih lahko kapilarne sile povzročijo dehomogenizacijo in vplivajo na mehanizem sintranja. Delo obravnava reakcijsko sintranje v sistemu $BaTiO_3$-TiO_2-$CaZrO_3$ kot primer procesa, pri katerem lahko z nadzorovano kemijsko heterogenostjo optimiziramo električne lastnosti keramike. Sintranje $PbZr_{1-x}Ti_xO_3$ keramike obravnavamo kot primer sistema, pri katerem se kemijsko homogena trdna raztopina med sintranjem prehodno dehomogenizira. Fenomen vpliva na mehanizem sintranja in električne lastnosti piezokeramike.

Ključne besede: reakcijsko sintranje, keramična mikrostruktura, barijev titanat, svinčev cirkonat-titanat, mehanizmi sintranja

1 INTRODUCTION

1.1 SWOT analysis of advanced technical ceramics

SWOT analysis (S = strength, W = weakness, O = opportunities, T = threat) is a frequently used method for evaluation of the potential of a particular activity. Such analysis applied to the manufacture of ceramic articles may give the following answers: (Many other arguments may be added).

S: Ceramics are the oldest artificial materials invented by mankind. In last 50 or 60 years the applicability of ceramics increased enormously. As a result, the market growth in many segments in recent decades maintained a level of 8-10 % per year, which is far above many other industrial activities.

W: The weaknesses of ceramics are well known: The producers and consumers complain of insufficient reproducibility, insufficient reliability and insufficient cost effectiveness of ceramic products.

O: Experts agree on the great yet unexploited technical potential of ceramics.

T: There are several obstacles which limit opportunities in the ceramic field. To be competitive and assure high performance products, high investments in knowledge and manufacturing equipment are necessary.

In the following, we examine reasons for shortcomings of ceramics, listed in "W". In this article, we concentrate on sintering.

Sintering is the final step in the ceramic fabrication process. It decisively influences the properties of products made from powders by sintering and represents the last chance of optimising the product.

Sintering theories are based on physical arguments such as the tendency for reduction in free surface energy and on simplified assumptions such as simple particle shapes (spheres) and simple particle arrangements (two or a limited number of spheres).

The general validity of sintering theories developed in pioneering works by Frenkel[1], Ivensen[2], Kucyznski[3], Kingery[4], Coble[5], Johnson[6] and others was proven by numerous experiments. Sintering theories are primarily concerned with material transport mechanisms and the kinetics of the sintering process. Knowledge of both are of fundamental importance for designing a cost effective manufacturing process for ceramic and powder metal articles with optimal properties.

However, the value of sintering theories in the manufacturing practice of specific ceramic products is limited due to the fact that theoretical assumptions about sintering processes are not valid in practice[7]. Fundamental studies assume (I) a pure, a homogeneous, single component starting powder, (II) uniform, small, spherical grains, (III) homogeneous body before sintering, and (IV) sintering at constant temperature. In contrast, practitioners in industrial production deal with (I) impure powders, usually inhomogeneous mixtures, (II) powders with a wide distribution of particle sizes, agglomerated to various degree, (III) with non-uniform density distri-

bution, and (IV) sintering at practically non-isothermal conditions.

Among serious inconsistencies between the assumptions underlying theoretical and basic experimental research on sintering phenomenon, chemical reactions at sintering temperature among constituents in the sintered body play an important role.

Chemical reactions in many ceramic systems occur among the constituents which are not in equilibrium at high temperatures and form new compounds or solid solutions. When the sintering process involves purposely chemically heterogeneous mixtures which are supposed to react during the sintering operation, one uses the term "reaction sintering". Examples are $BaTiO_3$ capacitor ceramics or ZnO based varistor ceramics. Most ceramic products are made of a basic compound with a small amount of additives which are intended to accelerate densification, suppress grain growth or modify the physical properties of the fired ceramics. The role of additives was frequently analysed, for example in [8] and [9]. In general, the additives may accelerate sintering by forming a liquid phase or control the microstructure by forming solid second phases which pin grain boundaries and impede grain growth. More subtle effects, which, however, profoundly influence the sintering process, are segregation at the grain boundaries, change of lattice defect concentration and diffusion constants when additives form a solid solution with the major component and a change in the ratio of grain boundary energy to free surface energy.

It is clear that the design of the sintering process, based on theoretical physical arguments only, must be modified by taking into account the possible chemical reactions.

In the following section, we report the results of research conducted in our laboratory on the effects of various aspects of chemical reactions on sintering. Specifically, we report effects of chemical heterogeneity on the sintering process in multicomponent systems. We demonstrate that even in single phase systems chemical dehomogenisation/homogenisation takes place. The aim of the review is to stress the importance of knowledge of chemical phenomena which occur during sintering of ceramics in designing and controlling the sintering process.

2 REACTION SINTERING IN THE BaTiO₃-CaZrO₃-TiO₂ SYSTEM

The term "reaction sintering" or "reactive sintering" is used to describe a sintering process in which a chemical reaction in the starting powder mixture and the densification of the ceramic body occur in the same heating operation. Depending on the material system and processing variables (particle size, temperature, pressure, etc.) the two processes, reaction and densification, can occur simultaneously, in sequence or as some mixture of these.
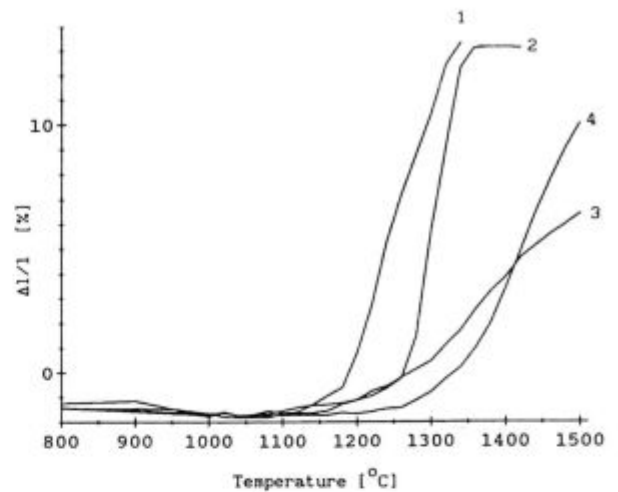

Figure 1: Dilatometric curves for $BaTiO_3$ - 2 mol % TiO_2 (1), $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ (2), $BaTiO_3$ - 8 mol % $CaZrO_3$ (3) and $CaZrO_3$ (4).
Slika 1: Krivulje krčenja za mešanice $BaTiO_3$ - 2 mol % TiO_2 (1), $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ (2), $BaTiO_3$ - 8 mol % $CaZrO_3$ (3) in $CaZrO_3$ (4).
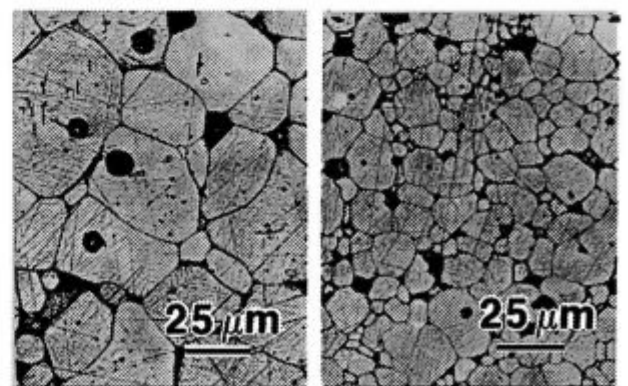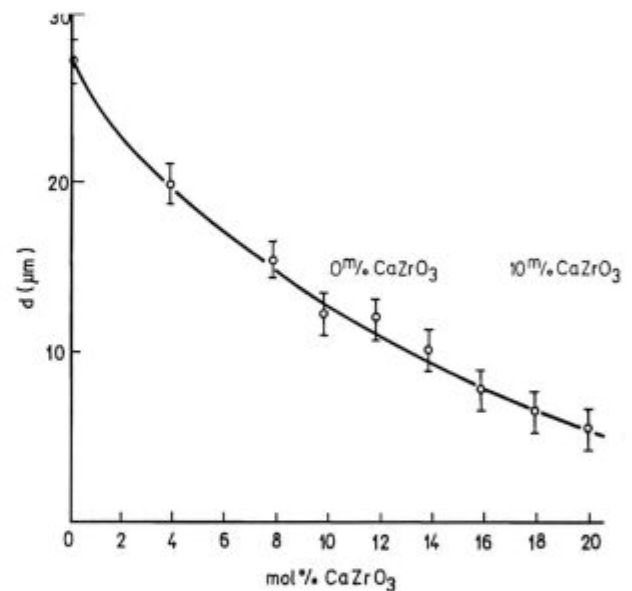

Figure 2: Average grain size vs. composition in $BaTiO_3$ - 2 mol % TiO_2 - $CaZrO_3$ ceramics sintered 1 hour at 1360°C.
Slika 2: Poprečna velikost zrn v odvisnosti od sestave keramike $BaTiO_3$ - 2 mol % TiO_2 - $CaZrO_3$, sintrane 1 uro pri 1360°C.

In ceramic fabrication practice, reaction sintering is usually avoided. The complexity of the processes caused by the chemical potential on one hand and the tendency to decrease the surface energy on the other renders the process difficult to control reproducibly. So, for example, in the manufacturing of soft Mn-Zn ferrites, the oxides are first calcined to form spinel solid solutions and then sintered. On the other hand, reactive sintering offers the possibility to optimise the properties of sintered products which are intentionally not in chemical equilibrium. Such is the case with several types of functional ceramics, for example varistors or high permittivity ceramic capacitors.

Frequently used compositions for ceramic capacitors are based on the solid solutions $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$. If Zr is incorporated into $BaTiO_3$ the maximum of the permittivity curve (at the Curie point) is shifted from 130°C to room temperature, whereas the non-ferroelectric $CaTiO_3$ broadens this maximum. $CaTiO_3$ has only limited solubility in $BaTiO_3$ and small undissolved particles of $CaTiO_3$ act as grain-growth inhibitors in the ferroelectric matrix[10].

$(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ capacitor ceramic is usually prepared by reaction sintering of $BaTiO_3$ - $CaZrO_3$ mixed powders. $BaTiO_3$ and $CaZrO_3$ are not compatible at high temperatures. During sintering, chemical reaction takes place resulting in formation of $(Ba,Ca)(Ti,Zr)O_3$ and $(Ca,Ba)TiO_3$ solid solutions[11]. The sintering kinetics and microstructural development of $BaTiO_3$-$CaZrO_3$ formulations are influenced by the kinetics of the chemical reaction, particularly at lower temperatures, i.e. in the initial sintering stage.

Research in our laboratory[12,13] showed that the particular batch of $BaTiO_3$ used started to shrink at around 1100°C and sintered considerably in the temperature region 1300-1350°C (Fig. 1). $CaZrO_3$, being more refrac-

tory, started to shrink at around 1250°C and sintered to high density in the temperature region 1450-1500°C. A $BaTiO_3$ - 8 mol % $CaZrO_3$ mixture started to shrink at approximately the same temperature as $BaTiO_3$. However, after a few % shrinkage the kinetics slowed down and temperatures higher than 1500°C were needed for densification. The sinterability of the $BaTiO_3$-$CaZrO_3$ mixture was improved by avoiding solid state diffusion. A small addition of TiO_2 (2 mol %), causing the formation of a low melting $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ eutectic at around 1310°C, strongly improved the sinterability of the mixture. Temperatures between 1300-1350°C were sufficient to achieve high density. The microstructures of dense $BaTiO_3$ - 2 mol % TiO_2 and $BaTiO_3$ - 10 mol % $CaZrO_3$-2 mol % TiO_2 ceramics sintered at 1360°C are shown in Fig. 2. The microstructures also show that $CaZrO_3$ strongly reduces the exaggerated grain growth which is common phenomenon in $BaTiO_3$ - TiO_2 ceramics.

Comparison of the relative linear shrinkage of $BaTiO_3$ - 2 mol % TiO_2 and $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ compacts as a function of time for isothermal sintering at 1260°C (Fig. 3) clearly indicated the differences in the sintering mechanism. $BaTiO_3$ - 2 mol % TiO_2 sintering kinetics in the initial stage can be described by an equation for first order kinetics $\Delta l/l = kt^n$ in which n is constant over the whole temperature range of sintering. In contrast, for $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ the graphical representation of $\ln(\Delta l/l_0)$ vs. $\ln t$ shows a change in slope, indicating two different densification regions with different n - values. The densification process is especially disturbed in the first stage of sintering at lower temperatures (Fig. 4) due to the chemical reaction between $BaTiO_3$ and $CaZrO_3$. When heated, $BaTiO_3$ and $CaZrO_3$ react to form a $(Ba,Ca)(Ti,Zr)O_3$ solid solution. The equilibrium solid solution limit is
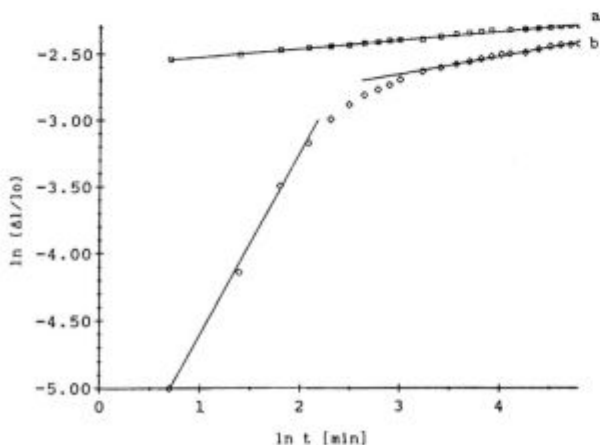
Figure 3: Comparison of the relative linear shrinkage of $BaTiO_3$ - 2 mol % TiO_2 (a) and $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ (b) compacts as a function of time for the isothermal sintering at 1260°C.
Slika 3: Primerjava med relativnim skrčkom oblikovancev iz $BaTiO_3$ - 2 mol % TiO_2 (a) in $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ (b) v odvisnosti od časa izotermnega sintranja pri 1260°C.
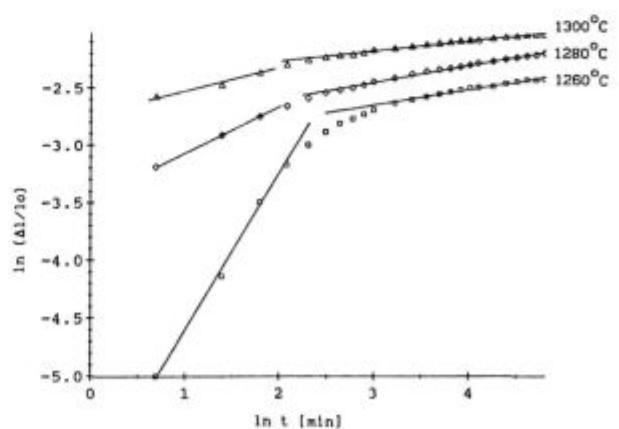
Figure 4: The relative linear shrinkage of $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ samples as a function of time for the isothermal sintering temperatures of 1260°C, 1280°C and 1300°C.
Slika 4: Relativni linearni skrček oblikovancev iz $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ v odvisnosti od časa pri izotermnem sintranju pri 1260°C, 1280°C in 1300°C.
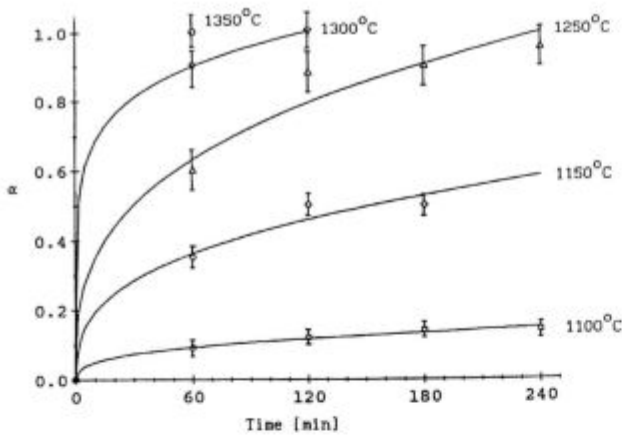
Figure 5: Degree of reaction (α) as a function of time for $BaTiO_3$ + $CaZrO_3 \rightarrow BaZrO_3 + CaTiO_3$ at various temperatures.
Slika 5: Stopnja reakcije (α) v odvisnosti od časa za reakcijo $BaTiO_3$ + $CaZrO_3 \rightarrow BaZrO_3 + CaTiO_3$ pri različnih temperaturah.

Figure 6: Comparison of the reaction rate $d\alpha/dt$ and densification rate $d\alpha'/dt$ ($\alpha = \rho' \cdot \rho_o/\rho_{th} \cdot \rho_o$) for $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ samples at 1260°C.
Slika 6: Primerjava med reakcijsko hitrostjo $d\alpha/dt$ in hitrostjo zgoščevanja $d\alpha'/dt$ ($\alpha' = \rho' \cdot \rho_o/\rho_{th} \cdot \rho_o$) oblikovancev iz $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ pri 1260°C.

around 16 mol % $CaZrO_3$. Larger amounts of $CaZrO_3$ cause formation of barium zirconate phase with some Ca and Ti in solid solution and a calcium titanate phase with some dissolved $BaTiO_3$[10,14]. In a 1:1 mole ratio $BaTiO_3$ - $CaZrO_3$ mixture the reaction was detectable by XRD analysis after only 1 hour's heating at 1100°C. The two characteristic X-ray reflections of $CaTiO_3$ at $2\theta = 59.052$ (d = 1.563) and $2\theta = 47.401$ (d = 1.918) were used for identification of $CaTiO_3$ and to determine the amount of $CaTiO_3$ formed during the reaction.

The degree of reaction α as a function of time for the reaction $BaTiO_3 + CaZrO_3 \rightarrow BaZrO_3 + CaTiO_3$ at various temperatures is shown in Fig. 5. At lower temperatures (1100°C) α remains under 20 % even after prolonged heating. A considerably higher degree of reaction was achieved by heating the mixture of $BaTiO_3$ and $CaZrO_3$ at 1250°C and higher. The relationship $\alpha = f(t)$ at various temperatures has been evaluated using different mathematical expressions, theoretically derived for various models. The best fit was achieved with Jander's equation[15]:

$$[1 - (1 - \alpha)^{1/3}]^2 = kt,$$

which describes three dimensional diffusion[16]. It may be concluded that the diffusion mechanism is rate controlling.

The reaction kinetics $d\alpha/dt$ were compared with the sintering kinetics $d\alpha'/dt$. The densification parameter α' ($\alpha' = \rho - \rho_o/\rho_{th} - \rho_o$) was calculated from dilatometric measurements in the temperature region 1200-1300°C (Fig. 6).

Comparison of the reaction rates with the densification rates at various temperatures confirmed the priority of chemical reaction in the first stage of sintering, and densification in the second stage (at higher temperatures). Sintering conditions have a strong influence on the microstructural development. A slower heating rate
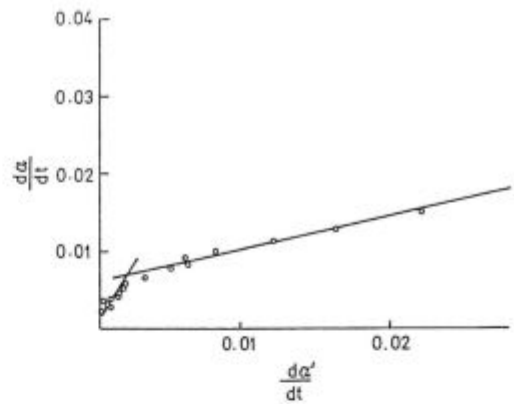
(1°/min) leads to the development of a coarse microstructure with a broad grain size distribution, whereas more rapid heating (5° or 10°C/min.) results in a finer microstructure with a narrower grain size distribution. The results may be explained on the basis of the kinetic studies. A fast heating rate favours reaction sintering with hindered grain growth, whereas a slow heating rate favours chemical reaction which takes place at lower temperatures than densification. The heterogeneous structure with phase separations in the initial sintering stage favours discontinuous grain growth and a broad grain size distribution.

Microstructural development also depends on the solid state diffusion rate during heating. A small excess of TiO_2, causing a liquid phase eutectic at sintering temperature, promotes grain growth, especially at slow heating rates. When $BaTiO_3$ with a small excess of BaO was used, grain growth during sintering was considerably hindered, especially when a slow heating rate was used.

Coarsening of the microstructure as a result of prolonged firing is accompanied by dielectric property changes. Different compositions of $BaTiO_3$ - $CaZrO_3$ based ceramics were fired at 1360°C for 15, 60, 480 minutes and the resulting dielectric properties were measured (Table 1). Whereas an ε value below the Curie temperature decreases with increasing firing time, the peak at the Curie temperature increases in value and broadens. Changes in the intensity and broadness of the peak are accompanied by coarsening of the microstructure. The coarse microstructure shows a more pronounced T_C shift and higher permittivity, while the room temperature permittivity is lowered. Maximum values of permittivity were obtained with the composition 84 mol % $BaTiO_3$ - 16 mol % $CaZrO_3$ near to the limit of solid solubility in the system.

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Table 1: Dielectric properties of $BaZrO_3$ based ceramics with 2 mol % TiO_2 addition vs. soaking rime at 1360°C (at 1 kHz)

Composition	90 m/o $BaTiO_3$-10 m/o CZ			84 m/o $BaTiO_3$-16 m/o CZ			80 m/o $BaTiO_3$-20 m/o CZ		
time (min)	15	60	480	15	60	480	15	60	480
$\varepsilon_{25°C}$	4753	4270	2030	4045	7200	10694	2780	3105	5210
$tg\delta.10^4$	107	105	200	79	92	130	45	74	105
Tc(°C)	60	60	70	20	25	35	-20	-15	-10
ε_{max}	6350	7820	8960	4600	7200	10767	3820	4650	6619
$\Delta C/C$ (%)	/	/	/	-31,0 +14,0	-48,20	-71,2 +0,7	/	/	/

Chemically inhomogeneous ceramics in metastable ceramic equilibrium make it possible to make, by careful control of firing conditions, the temperature stable dielectric materials. This is ascribed to specific core-shell grain structure[17]. The relatively flat temperature characteristic of dielectric constant of $BaTiO_3$-$CaZrO_3$ based ceramics is determined by the superposition of the two permittivity/temperature maxima, those of $BaTiO_3$ core at ~ 120°C and (Ca,Zr) doped $BaTiO_3$ shell with maximum at lower temperature. Core-shell structure is discernible in TEM micrograph in Fig. 7. In the formation of the shell, reactive liquid phase plays important role, since the shell is formed by precipitation of dissolved matter on $BaTiO_3$ nuclei. Prolonged sintering provokes chemical homogenisation by solid state diffusion giving rise to increased permittivity and increased temperature dependence of permittivity.

3 SINTERING OF MONOPHASE COMPLEX CERAMICS: SINTERING OF $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT)

In analysing sintering phenomena, it is important to realise that chemical reactions may influence the densification mechanism even in chemically homogenous compounds.

In recent years, considerable progress in the processing of ceramics has been achieved by improving the quality of powders. Attention is paid to wet-chemical methods of powder preparation, which assure fine particle size, controlled morphology, high purity and high homogeneity. Improved homogeneity is particularly desirable in complex multicomponent ceramics.

It is frequently stressed that wet chemical methods, such as coprecipitation or sol-gel methods, assure chemical homogeneity "on a molecular" level. However, this homogeneity may be temporarily lost during the sintering operation due to the very nature of the sintering process.

Kuczynski et al[18] pointed out that the vacancy gradient set up between sintered particles by the sharp curvature of the neck between particles can, under favourable conditions, produce considerable segregation in a completely homogenised solid solution. When the diffusion coefficients of constituent atoms in solid solution are different (which is frequently the case), the neck area be-

comes enriched in the faster diffusing atoms, at least in the early stage of sintering when the vacancy gradient due to the smallness of the radius of neck curvature is large. Such segregation must be a transient phenomenon, since segregation gives rise to a chemical potential gradient arising from the concentration gradient between the neck and regions adjacent to the neck, and acts in a direction opposite to the chemical potential gradient due to the neck curvature. When the radius of curvature of the neck increases, the chemical potential which causes the dehomogenization decreases. With accumulation of faster diffusing atoms in the neck, the concentration gradient also increases and the maximum segregation is reached. After this, the chemical potential gradient due to the concentration gradient predominates and back diffusion from the neck to other regions occurs. As a result, homogeneity is re-established.

Kuczynski et al[18] demonstrated segregation in Cu-In and Cu-Ag alloys. Mishra et al[19] demonstrated dehomogenization of Au-Ag alloy and concluded that the initial neck growth as well as segregation take place by surface
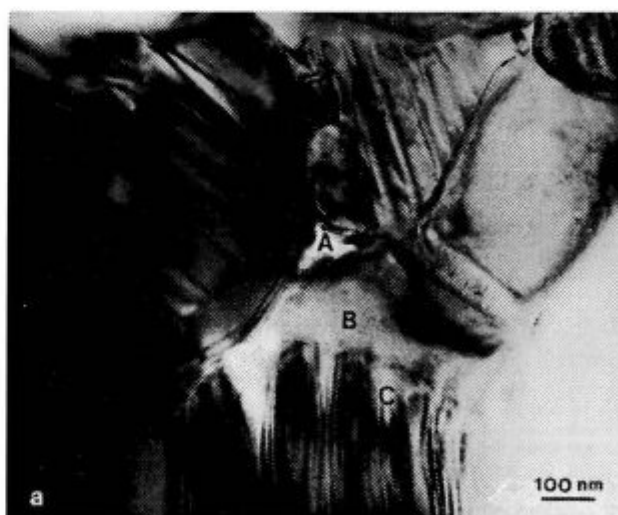

Figure 7: TEM photomicrograph of $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ ceramic, sintered 2 hours at 1260°C showing (A) solidified TiO_2 - rich phase at grain corners and along grain boundaries, (B) Ca- and Zr- modified domain free region and (C) ferroelectric $BaTiO_3$ grain core.

Slika 7: TEM posnetek keramike iz $BaTiO_3$ - 2 mol % TiO_2 - 8 mol % $CaZrO_3$ keramike, sintrane 2 uri pri 1260°C. Posnetek kaže (A) strjeno talino, bogato na TiO_2 med zrni in vzdolž zrn, (B) s Ca in Zr bogat rob zrn brez domen in (C) ferroelektrično $BaTiO_3$ jedro z domenami.
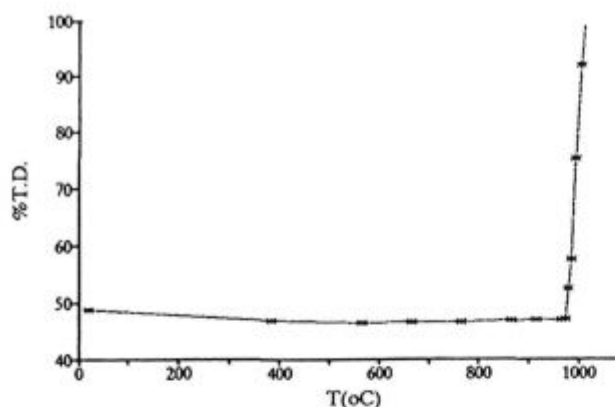
Figure 8: Sintering curve of $Pb(Zr_{0.5}Ti_{0.5})O_3$ compact in air, pressed at 100 MPa. Heating rate: 10°C/minute.
Slika 8: Krivulja zgoščevanja oblikovanca iz $Pb(Zr_{0.5}Ti_{0.5})O_3$, stisnjenega s tlakom 100 MPa. Hitrost segrevanja 10°C/min.

Figure 9: Density of $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics as a function of temperature and time of isothermal heating runs in an air atmosphere.
Slika 9: Gostota $Pb(Zr_{0.5}Ti_{0.5})O_3$ keramike v odvisnosti od temperature in časa pri izotermnem segrevanju v atmosferi zraka.

diffusion, whereas back diffusion occurs by a combination of surface and volume diffusion.

It may be expected, due to capillary forces in the early sintering stage, that the dehomogenization effect occurs in complex ceramic systems as well. It should be particularly pronounced in sintering of nanosized powders, where surface diffusion plays an important role. The segregation-homogenisation phenomenon should be reflected in densification curves.

To demonstrate the effect, we examined the sintering of fine sol-gel prepared powders of lead zirconate - lead titanate solid solution, $Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZT)[20].

Fig. 8 shows the densification curve of a $Pb(Zr_{0.5}Ti_{0.5})O_3$ compact, made of fine powder prepared by alkoxide sol-gel synthesis. The very rapid densification above ~950°C does not support the expected solid state sintering mechanism. Instead, the sudden and steep increase in sintering rate and the well crystallised grains are indicative of liquid phase sintering. The liquid phase may be the PbO-PZT eutectic above ~840°C; however, the presence of PbO could not be detected by XRD or TEM in the starting powder.

The isothermal densification curves, presented in Fig. 9, show anomalous behaviour in the temperature region 750-800°C. The anomaly is an extended "induction" period in the densification curves at 750 and 800°C. Anomalous densification of PZT in the initial sintering stage may be explained by preferential diffusion of PZT constituents.

Accumulation of faster diffusing species in the necks between the particles, triggered by surface curvature, causes an increased tendency for backward diffusion, sustained by the concentration gradient. Formation of the thermodynamically nonequilibrium phase and its subsequent annihilation interferes with the normal densification process, being reflected as an induction period. Further densification commences only after neck curvature decreases and the material homogenises again.
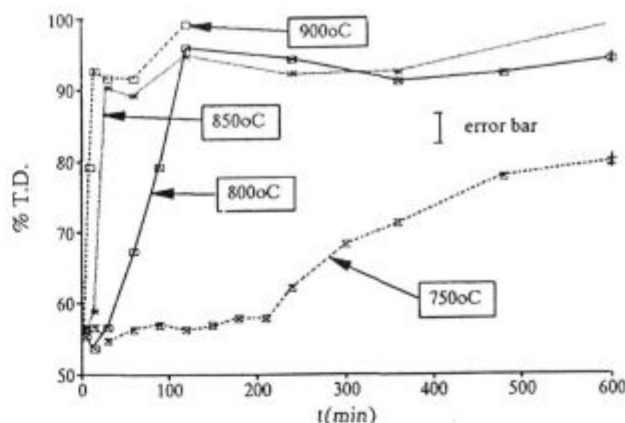
At low sintering temperatures, material transport takes place predominantly by surface diffusion and, when possible, by vapour transport. PZT is known for the high vapour pressure of PbO[21]. To the author's knowledge, surface diffusivities of Pb, Zr and Ti ions in PZT have not been reported. Slinkina and Doncov[22], using radioactive tracers, measured the effective self-diffusion coefficients in polycrystalline 99 % dense $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics. The effective diffusion coefficient of Pb^{2+} was 5 - 40 times higher than that of O^{2-} and almost two orders of magnitude higher than D_{Ti} and D_{Zr},
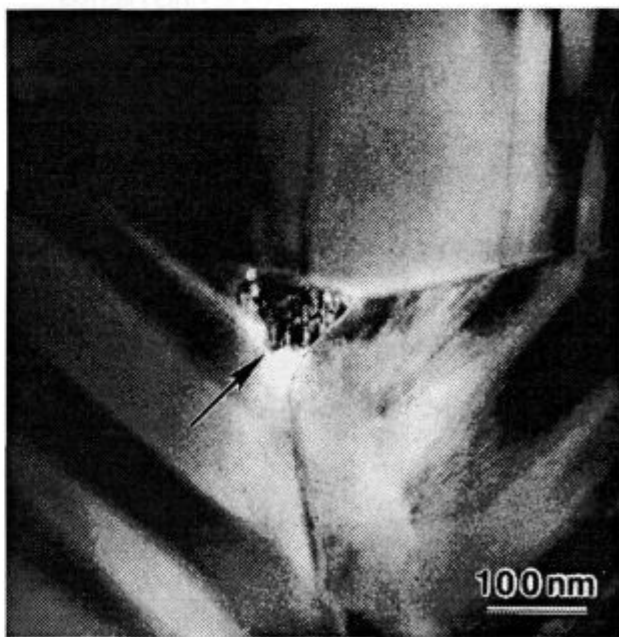

Figure 10: TEM micrograph of $Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramic, sintered at 900°C for 1 hour. Arrow points to Pb-rich inclusion among 3 perovskite grains (Courtesy G. Dražič).
Slika 10: TEM posnetek $Pb(Zr_{0.5}Ti_{0.5})O_3$ keramike, sintrane pri 900°C 1 uro. Puščica kaže vključek, bogat s Pb, med 3 perovskitnimi zrni (posnetek G. Dražič).

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which were close to each other. Nakamura, Chandratreya and Fulrath[23] and Kosec and Kolar[24] reported that during the formation of PZT from $PbTiO_3$ and $PbZrO_3$, titanium ions diffuse much faster than zirconium ions. The vapour pressure transport of PbO into the necks is also possible. To maintain electrical neutrality, diffusion of cations is accompanied by a simultaneous flow of oxygen ions, or through gas-phase transport. Faster diffusion of Pb and Ti, caused by high neck curvature in the initial sintering stage of fine-grained PZT compacts, causes accumulation of Pb and Ti or Zr in the necks, and corresponding depletion of both species in other regions of PZT grains. According to the phase diagram[25], PZT may be Pb deficient up to 2 mol % PbO; however, PbO does not dissolve in PZT. The simplified equation derived by Kuczynski et al[18], makes it possible to estimate the maximal excess concentration of the faster diffusing species in the neck area.

In simplified form, Kuczynski's equation reads:

$$\rho_c = \frac{2\gamma\Omega C}{\Delta CkT}$$

where

ρ_c critical neck radius necessary to reverse the neck curvature driven atoms outward flow to concentration gradient driven inward flow

γ surface energy

Ω mean atomic volume

$\Delta C/C$ relative concentration gradient between neck area and grain interior

k Baltzman's constant

T temperature

Neck radius is related to particle diameter (2a) and neck diameter (2x) by expression

$$\rho_c = \frac{x^2}{4a}$$

Assuming surface energy $\cong 1$ J/m^2, mean atomic volume 10^{-29} m^3, and kT (at 1000 K) $1,4.10^{-20}$ J, one can estimate the maximal excess concentration of the faster diffusing specie in the neck area. With 200 nm size particles and neck diameter 140 nm, the calculated excess concentration is 8 mol %. In view of crudity of assumptions, the result seems reasonable.

The proposed explanation of the PZT sintering anomaly was supported by the following experimental observations:

(1) XRD patterns of PZT after the early sintering stage confirmed the presence of tetragonal and rhombohedral phases, whereas in the starting PZT powder only reflections of the tetragonal phase were present. $Pb(Zr_xTi_{1-x})O_3$ solid solution exhibits a phase transformation from the tetragonal to rhombohedral structure at x ~ 0.53. The appearance of rhombohedral phase indicates the shift in PZT composition. After prolonged sintering, the rhombohedral phase disap-

peared, confirming homogenisation to the initial composition with x = 0.5.

(2) After the early sintering stage, PbO inclusions in the microstructure were observed by SEM and TEM examinations (Fig. 10). Enrichment of PbO in the necks as compared with the grain interior was confirmed by quantitative EDX analysis in the transmission electron microscope. On further heating, PbO inclusions redissolved.

The findings of the work presented disprove the correctness of solid state sintering models assumed for PZT by several researchers. The transient presence of PbO, which forms a eutectic in the early sintering stage, provokes liquid phase sintering. This has several important consequences, for example that microstructural development in PZT must be sensitive to the heating schedule. Probably the most important result from this investigation is that the dehomogenization phenomenon with the transient existence of metastable phases is likely to be a frequent occurrence in the initial stage of sintering of multicomponent ceramics. It is particularly to be expected in sintering of fine powders with a high driving force for sintering.

4 SUMMARY

The critical issues in mastering ceramic processing to assure the reliability and reproducibility of ceramic bodies are well known. These are (a) appropriate raw materials (purity, finess, grain size distribution), (b) correct shaping of homogenous bodies without macro defects and (c) suitable sintering parameters (T, t, dT/dt, etc.) But of particular importance for the reliable manufacturing process is a knowledge and control of chemical reactions at high temperatures. This in turn demands knowledge of high temperature phase relations, knowledge of reaction kinetics and availability of data such as (1) systematic trends in the periodic system, (2) the nature and strength of chemical bonds, (3) thermodynamics $(\Delta G,\gamma)$ and (4) kinetic parameters (diffusion coefficients). In short, to achieve optimal properties of ceramic products and to assure competitiveness demands a high professional knowledge and appropriate equipment.

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