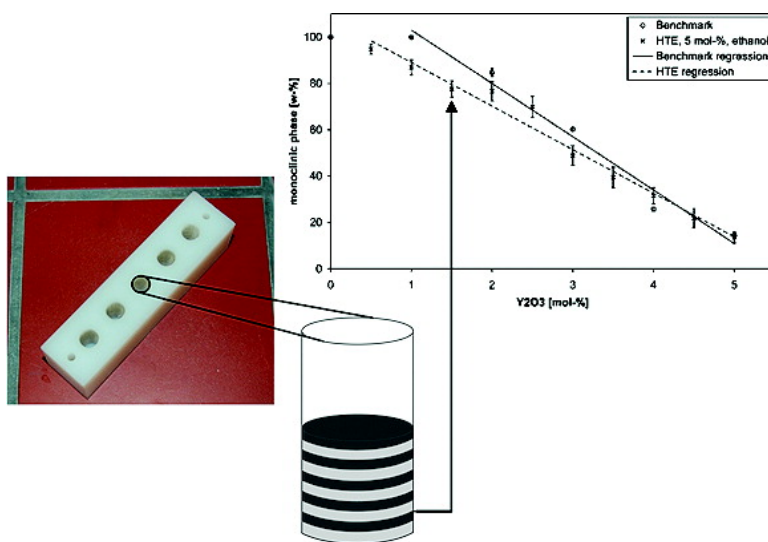


High-Throughput Synthesis and Characterization of Bulk Ceramics from Dry Powders

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High-Throughput Synthesis and Characterization of Bulk Ceramics from Dry Powders

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A high-throughput experimental (HTE) setup using conventional powders as raw materials was developed to synthesize and characterize ceramic bulk samples avoiding the customary liquid- or vapor-phase synthesis routes. Its functionality was verified using the well-known binary material system $\text{ZrO}_2\text{--Y}_2\text{O}_3$. Libraries of 0.5 mol % yttria zirconia were prepared using varying boundary systems as well as a number of liquid mixing aids. Automated powder X-ray diffraction (XRD) was applied to check the monoclinic phase content retained after heat-treatment on various positions for each sample. This phase information was used for comparison with a reference library comprising conventionally prepared samples by means of a regression analysis and mean deviation of monoclinic phase percentage. Out of the eight HTE libraries, three showed a significant comparability to the reference library.

Introduction

High-throughput experimentation (HTE) has been defined as “a set of techniques for creating a multiplicity of compounds and then testing them for activity”,¹ and since its adaptation to materials science, this technology has seen extensive use in both academia and industry for the improvement of known substances as well as the development of new ones.²

The first applications of HTE in the engineering of ceramic materials were in the field of thin-film processing,^{3–5} and this synthesis route remains the most frequently used for HTE applications of ceramics in electronics^{6–9} and catalysis^{10,11} as well as various others.^{12,13}

Numerous workers have reported on the use of liquid precursors for HTE investigation of ceramic bulk libraries, where they synthesized respective libraries by ceramic ink-jet printing,^{14–16} via a complex forming reaction,^{12,17–19} by means of a sol–gel or hydrothermal reaction^{18,20} or by drying aqueous solutions of metal salts.²¹ Furthermore, Yang and Evans applied acoustic deposition for the preparation of HTE libraries from dry powders.²² Nevertheless, this technique was only used on coarse metallic powders.²³ None of the processing routes mentioned is suitable for the most common powder metallurgical synthesis for ceramic materials, which consists of the conditioning, shaping, and heat-treatment of dry ceramic powders.

Consequently, this paper reports on an HTE procedure to synthesize and examine ceramic bulk libraries using fine-grained ($d_{50} \sim 0.5\mu\text{m}$), dry powders as starting materials. The experimental results from this procedure are thus directly comparable to results from conventionally synthesized bulk samples, and the setup described here can therefore act as a means to quickly and reliably scan large material systems

to identify potentially active areas suitable for conventional dry powder processing on laboratory and commercial scales.

The aim of the presented work was to validate the HTE setup using the common material system $\text{ZrO}_2\text{--Y}_2\text{O}_3$.^{24–30} Yttria-doped zirconia is used nowadays for its mechanical strength (Y-TZP) and for its electrochemical potential resulting from oxygen vacancies due to charge mismatch of Y cations on Zr lattice sites (Y-PSZ). The importance of a homogeneous distribution of Y_2O_3 in the ZrO_2 has long been known and is the reason for the wet-chemical production technology of modern Y-TZP powders.^{25,30} Unfavorable for HTE procedures, the diffusion of yttrium in zirconia takes place only slowly and is further limited by the need for low sintering temperature to avoid rapid grain growth.³⁰ With the material requiring essentially homogeneous powder compacts, Y-TZP can be considered as a “worst case example” with regard to interdiffusion and can be used for a proof of principle of a successful, dry powder based HTE setup.

Experimental Details

Dry Powder HTE Setup. The core of the HTE procedure was a laboratory robot (Accelerator VLT-100, Chemspeed Technologies, Augst, Switzerland) equipped with a solid dosing unit. The respective powders were dosed into bore-holes of 10 mm diameter in custom-made containers with a height and width of 30 mm and a length of 120 mm (see Figure 1). The containers were machined from ultrahigh molecular weight polyethylene (UHMW-PE) to minimize abrasion due to the ceramic powders. A steel fixture fixed up to four containers for mixing in a conventional planetary mill (Pulverisette, Fritsch, Idar-Oberstein, Germany). The mill allowed for 2 fixtures to be inserted, hence a maximum of 40 samples could be mixed in parallel. The solid dosing unit took part in mixing by dosing the powder fractions in five layers each, according to Figure 2.

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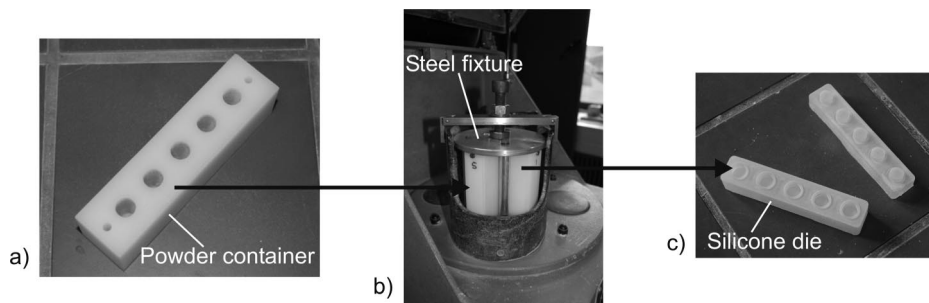


Figure 1. Custom-made powder container (a) and steel fixture in conventional planetary mill, allowing up to four powder containers to be installed in parallel (b). For pressing, powders are transferred to silicon dies (c).

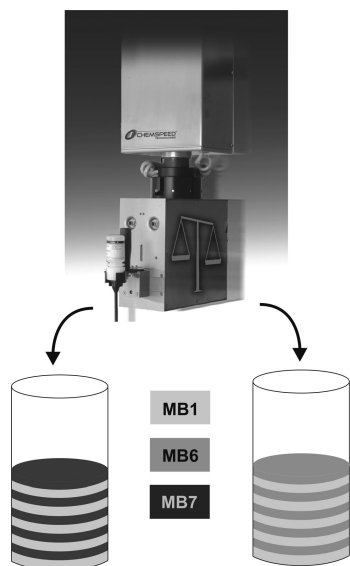


Figure 2. Scheme of the layered dosing performed by the solid-dosing unit to assist powder mixing (MB = masterbatch).

Powder compact shaping and densification took place in a conventional cold-isostatic press (KIPP200ES, Paul Weber, Remshalden-Brunbach, Germany). For pressing, the powders were transferred in a parallel manner into silicone dies adapted to the powder containers that could take up and shape five samples at a time. The small number of samples here, arose solely out of the fact that a press with a very small chamber was used in the experiments. In principle, this procedure allows for higher amounts of samples to be pressed in parallel using a bigger pressing chamber. Thus, pressing does not constitute a bottleneck for the presented setup.

All analytic procedures were based on powder X-Ray diffraction (XRD) on a D8 Discovery (Bruker AXS, Karlsruhe, Germany) equipped with a Göbel mirror, general analysis diffraction detector system (GADDS), and an xyz -stage allowing for the sequential treatment of up to 25 samples per experimental run in the present setup. Samples resulting out of the HTE setup were tablet-shaped and had a diameter of about 10 mm as a green body and about 9 mm in the sintered state. Ten independent XRD-patterns were recorded on various locations on any single sample surface using a spotsize of approximately 1 mm in diameter.

Preparation of Masterbatches. Yttrium (III) oxide (Y_2O_3 , REacton, Alfa-Aesar, Karlsruhe, Germany) and monoclinic zirconium oxide (ZrO_2 , Carpenter/Z-Tech, Bow, NH, USA) were used as raw materials to synthesize 7 powder masterbatches (also referred to as MB1–7 in this paper) containing

0, 1, 2, 3, 4, 5, and 10 mol % Y_2O_3 by wet processing in a conventional manner by approximately 5 h of attrition-milling in ethanol, where the milling procedure was stopped when a certain predefined median value (d_{50}) of the grain size distribution was reached. The batches were 150 g each, and the milling took place in ethanol using 1200 g of grinding balls (diameter 3 mm, yttria-toughened zirconia, Tosoh, Tokyo, Japan). All the batches were dried and homogenized after being milled.

Homogeneity Investigations. Preliminary experiments were conducted to ensure the quality of the parallelized mixing procedure with respect to the powder homogeneity of the samples. The masterbatches MB1 (0 mol % Y_2O_3) and MB6 (5 mol %) as well as MB1 and MB7 (10 mol %) were used as boundary systems to mix samples of 600 mg mass with a concentration of 3 mol % Y_2O_3 (referred to as 0-5/3 and 0-10/3 henceforth) using the mixing approach mentioned above with varying mixing parameters. Reference samples were pressed directly from MB4 (3 mol % Y_2O_3). All homogeneity measurements were performed on green samples.

Ten XRD patterns were recorded on different areas of each sample in the range of 20 – 50° 2θ . They were evaluated, yielding ten independent Y_2O_3 concentrations \overline{c}_Y for each sample. A mean value c_Y was formed and compared to the mean Y_2O_3 content value of the reference sample $\overline{c}_Y^{\text{reference}}$

$$\Delta c_Y = \frac{|\overline{c}_Y - \overline{c}_Y^{\text{reference}}|}{\overline{c}_Y^{\text{reference}}} \times 100\% \quad (1)$$

The normalized standard deviation (coefficient of variance)

$$CVar(c_Y) = \frac{\sqrt{\frac{1}{9} \sum_{i=1}^{10} (c_{Y,i} - \overline{c}_Y)^2}}{\overline{c}_Y} \times 100\% \quad (2)$$

was taken as the measure for the homogeneity of the sample.

The Y_2O_3 content was determined using the commercial software *PolySNAP*²⁶ that allowed for the quantitative analysis of XRD patterns using full pattern matching, which meant that the whole pattern was worked upon point-by-point. Patterns of pure yttria and zirconia were accessed by the program, and all the analyzed patterns were numerically composed out of those two database patterns. Hence, the program calculated a fraction of the analyzed pattern that was accounted for by the presence of Y_2O_3 . This fraction was displayed in so-called scale percent. Even though a

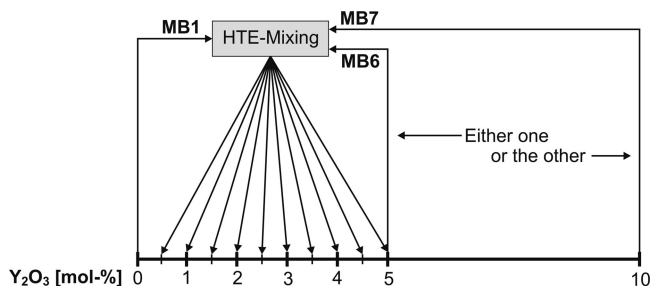


Figure 3. Scheme of the HTE-library synthesis from masterbatches (MBs) 1, 6, and 7 containing 0, 5, and 10 mol % Y_2O_3 , respectively.

correlation between the reported scale percent and the actual yttria content in mole percent existed,²⁷ it has to be stated that this correlation was dispensable for the analysis described above, as neither of the parameters of interest expressed by eqs 1 and 2 was absolute in nature. Therefore, all yttria concentrations in this paper will be reported in scale percent. For more concise information on PolySNAP, especially the underlying mathematics, the reader is referred to the work of Gilmore et al.^{27,28}

Library Preparation. The HTE-libraries consisted of ten samples of 600 mg mass each. Every library ranged from 0 to 5 mol % Y_2O_3 with a resolution of 0.5 mol %. MB1 and MB6 as well as MB1 and MB7 were used for the preparation as shown schematically in Figure 3. Libraries will be referred to as 0-5 and 0-10, respectively, in this paper. Additionally, mixing aids were applied for the parallel mixing of the libraries mentioned above. They were varied between ethanol, cyclohexane, acetone, and no mixing aid.

Subsequent to mixing, cold-isostatic pressing was performed at 400 MPa for 2 min. The heat-treatment cycle was chosen following the work of Lange²⁹ with a heating ramp of 2 K/min. Subsequently, the temperature was kept at 1500 °C for 2 h and then cooled to room temperature at 10 K/min. Sintering took place under atmospheric conditions.

Additionally, a reference library was produced in the same concentration range as the HTE libraries. This was done by directly pressing and sintering samples from the masterbatches MB1–6.

Library Characterization. The phase information was gathered using the polymorph method³¹ and thus the peak intensity ratio

$$X_M = \frac{I(111)_M + I(11\bar{1})_M}{I(111)_M + I(11\bar{1})_M + I(111)_{C,T}} \quad (3)$$

where the subscripts M, C, and T are used for monoclinic, cubic, and tetragonal, respectively.

Applying the correction term for the monoclinic–tetragonal zirconia system

$$W_M = \frac{PX_M}{1 + (P - 1)X_M} \quad (4)$$

and $P = 1.311$, a weight fraction of monoclinic phase could be calculated.^{32,33} It is important to note that the {111} peaks of the tetragonal and the cubic ZrO_2 phases can not be resolved easily.³³ Consequently, only monoclinic phase content is reported here. The phase analysis was done on

Table 1. Results of the Homogeneity Tests Done on Green Samples with Constant Concentration of 3 mol % Y_2O_3 ^a

samples	mixing parameters		\bar{c}_Y [scale-%]	$\Delta\bar{c}_Y$ [%]	CVar (c_Y) [%]	
	time [s]	rotating speed [rpm]				
reference	n.a.	n.a.	4.2	n.a.	3.8	
0-5/3	60	340	5.2	23	2.9	
0-10/3	60	340	5.5	29	9.1	
0-5/3	10	340	4.6	8	2.1	
0-10/3	10	340	6.3	49	11.7	
0-5/3	600	80	4.4	5	10.7	*
0-10/3	600	80	4.4	5	17.7	*
0-5/3	10	80	3.5	17	36.4	
0-10/3	10	80	6.0	42	16.5	
0-5/3	60	80	5.2	22	27.4	
0-10/3	60	80	3.2	26	39.6	

^a Values of c_Y , Δc_Y , and CVar (c_Y) were evaluated according to eqs 1 and 2. Asterisks mark the lines that hold the mixing parameter values used in HTE-library preparation.

sintered HTE libraries as well as on the reference library. Each pattern was recorded in the range of 20–50° 2θ .

In the following, each sample's 10 phase composition values were checked for normal distribution by the Kolmogorov–Smirnov test. Furthermore, a comparison between the reference library and the HTE libraries was performed. For this purpose, linear regression lines were fitted for monoclinic phase content using a least-squares method. The resulting regression coefficients β_0 (intercept) and β_1 (slope) of the HTE libraries were compared to those of the reference library using two T -type test statistics with null-hypotheses $H_{0,1}$, $\beta_{0,\text{reference}} = \beta_{0,\text{HTE}}$, and $H_{0,2}$, $\beta_{1,\text{reference}} = \beta_{1,\text{HTE}}$ and alternative hypotheses $H_{A,1}$, $\beta_{0,\text{reference}} \neq \beta_{0,\text{HTE}}$, and $H_{A,2}$, $\beta_{1,\text{reference}} \neq \beta_{1,\text{HTE}}$. Acceptance of $H_{0,1}$ represented equality of intercepts and acceptance of $H_{0,2}$ parallelism. In the case of acceptance of both null-hypotheses, coincidence of the reference and the HTE regression models could be deduced.

To allow for a quantitative comparison between the reference and each HTE library, first a mean monoclinic phase content was calculated from the phase concentration values of each library member. For each HTE-library member that had a counterpart in the reference library, a difference was formed between its mean monoclinic phase content and the monoclinic content of the reference library member with the same yttria concentration. Finally, the arithmetic mean of the aforementioned differences was used as a measure for the distance between the reference and the respective HTE library (mean deviation).

All statistical tests were performed on a level of significance of $\alpha = 0.05$.

Results and Discussion

Table 1 shows the results of the homogeneity investigations to determine the mixing quality of the parallelized approach. It is evident that the sample's mean yttria content was supposed to be as close as possible to the respective reference value. Additionally, a small variation of the content within one sample was achievable as it signified a high homogeneity. The results show that both demands could not be met together. Two small values could only be achieved for 0-5/3 when mixing for 10 s at 340 rpm. But, the respective 0-10 mixture showed rather bad results. Additionally, the

Table 2. Results of the Regression Analysis and Mean Deviation Values of Monoclinic Phase Content^a

library	regression analysis				mean deviation [wt %]	
	β_0	β_1	r^2	equal intercepts parallelism		
reference	125.97	-22.99	0.98	n.a.	n.a.	
0-5, dry	107.20	-18.90	0.97	$H_{A,1}$	$H_{0,2}$	8.53
0-10, dry	103.50	-12.20	0.98	$H_{A,1}$	$H_{A,2}$	n.a. ^b
0-5, acetone	109.20	-19.50	0.98	$H_{A,1}$	$H_{0,2}$	5.36
0-10, acetone	100.90	-13.50	0.98	$H_{A,1}$	$H_{A,2}$	n.a. ^b
0-5, ethanol	107.80	-18.80	0.98	$H_{A,1}$	$H_{0,2}$	7.79
0-10, ethanol	102.30	-12.00	0.97	$H_{A,1}$	$H_{A,2}$	n.a. ^b
0-5, cyclohexane	104.60	-18.30	0.99	$H_{A,1}$	$H_{A,2}$	n.a. ^b
0-10, cyclohexane	99.60	-11.70	0.95	$H_{A,1}$	$H_{A,2}$	n.a. ^b

^a The accepted hypotheses are given for the regression analysis (H_0 null-hypothesis, H_A alternative hypothesis). Hypotheses were tested using T -type statistics on a level of significance of $\alpha = 0.05$. ^b Only in the case of acceptance of $H_{0,2}$ could a normal distribution of the deviations of means be assumed. Therefore, only in these cases, a mean deviation value was calculated.

high mixing intensities lead to increased wear of the powder containers and the formation of big coagulates. A good matching of the mean values and an acceptable variance could be achieved for both samples at 600 s of mixing time and 80 rpm. Therefore, these mixing parameters were chosen for the ensuing HTE-library preparation.

Table 2 gives the regression data as well as the mean deviation values where applicable. The linear regression was suitable to explain most of the variance as can be seen from the coefficients of determination (r^2) of all libraries. Neither for the 0-10 libraries nor the 0-5 library using cyclohexane as a mixing aid could equality of intercepts or parallelism be detected. In the case of cyclohexane as a mixing aid, a detrimental effect due to its nonpolar nature was likely to exist. Besides this, it can be assumed that the concentration range between the two boundary systems for the 0-10 libraries was too wide to allow for sufficient homogenization using the parallelized mixing approach.

Three libraries out of the group of 0-5 libraries showed parallelism. Their respective means of deviation were all in the same order of magnitude. The system without any liquid mixing additives was preferable though, as the dosing and the drying of the mixing aid took approximately one extra day within the synthesis cycle.

Figure 4 shows the Y_2O_3 concentration versus the monoclinic phase content for the three statistically relevant HTE libraries compared with the reference. The most interesting composition is in the area of 3 mol % which typically gives the best mechanical performance in view of strength and fracture toughness.^{29,36} The HTE libraries' results of Figure 4 show that the phase content of 60% monoclinic phase corresponding to 3 mol % Y_2O_3 in the reference system is met at 2–2.5 mol % Y_2O_3 in the investigated HTE systems. In other words, the monoclinic phase content of 60% can be deduced with an experimental error of about 0.5–1 mol % Y_2O_3 content. This result can be considered sufficient in order to evaluate the Y_2O_3 - ZrO_2 system in general. The error in Y_2O_3 content would be revealed in subsequent experimental cycles, when "zooming in" on the optimum concentration by lowering the amount of samples and applying more conventional laboratory approaches.

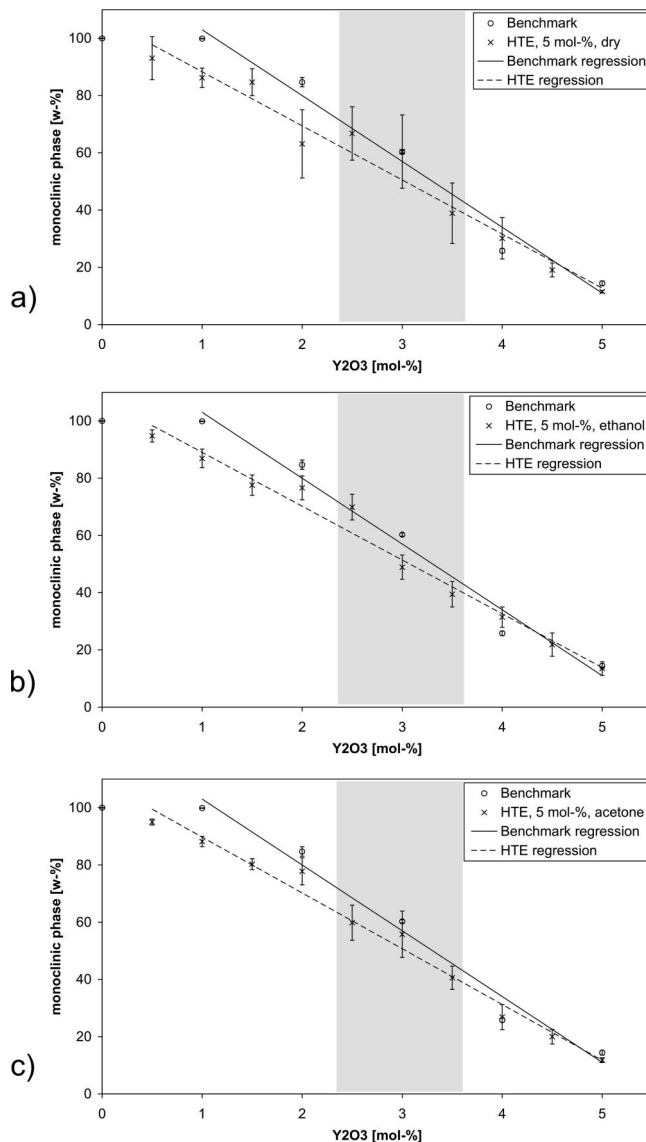


Figure 4. Y_2O_3 concentration vs monoclinic phase content for 0-5 libraries with (a) no liquid mixing aid, (b) ethanol as a mixing aid, and (c) acetone as a mixing aid. The reference values as well as both regression lines are given for comparison. Scattering is shown as standard deviation. The grey area is the concentration range of commercial Y-TZP.

As a first approximation toward the diffusion behavior relevant to the homogenization, one can estimate as a model a finite point source of matter (M moles) diffusing into an infinite volume of zero initial concentration. The concentration is given as a special solution to Fick's second law of diffusion

$$C(r, t) = M \frac{\exp\left(-\frac{r^2}{4Dt}\right)}{8(\pi Dt)^{3/2}} \quad (5)$$

where r is the radius, t is the time, and D is the diffusion coefficient.³⁴ On the basis of this solution, the peak width at half-height can be calculated to be

$$r = \sqrt{2.77Dt} \quad (6)$$

and taken as an estimator for the homogenization potential through diffusion. For the sintering temperature of 1500 °C,

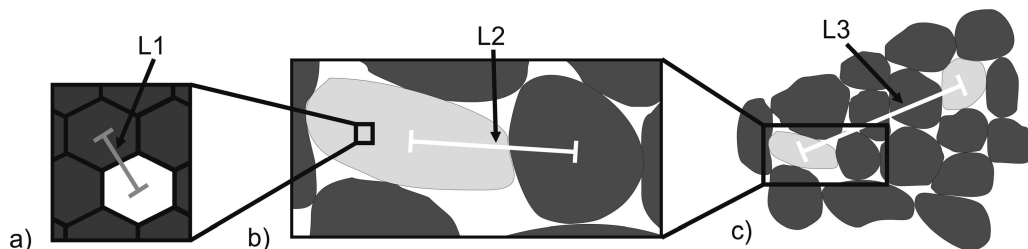


Figure 5. (a) Scheme of microstructure with an yttria grain (bright) and several zirconia grains (dark) in an exemplified green body. (b and c) Scheme of agglomerates containing yttria and zirconia (light grey) as well as zirconia only (dark). Characteristic lengths for homogenization through diffusion are in the order of magnitude of (a) one grain size (L1), (b) the agglomerate size (L2), and (c) the average distance between two agglomerates of likewise concentration (L3). Note that $L1 < L2 \leq L3$ always. Specifically, $L2 \ll L3$ for small overall concentrations of yttria.

diffusivity values of $D_B \approx 2 \times 10^{-18} \text{ m}^2/\text{s}$ (bulk diffusion) and $D_{GB} \approx 2 \times 10^{-12} \text{ m}^2/\text{s}$ (grain boundary diffusion) have been reported for diffusion of yttrium in yttria stabilized zirconia.³⁵ We assume the diffusion of yttrium to be rate-limiting in the investigated system. Using a sintering time of $t = 7200 \text{ s}$ (the time used in this work), one can calculate $r_B \approx 0.2 \mu\text{m}$ in the case of bulk diffusion and $r_{GB} \approx 200 \mu\text{m}$ for grain boundary diffusion. It can be claimed comprehensively that the latter value is an upper limit for the size of potential agglomerates that have made it through the mixing and pressing procedures into the green sample. Furthermore, the calculated radius in the case of bulk diffusion is on the same order of magnitude as the average grain size of the powders used ($d_{50} \sim 0.5 \mu\text{m}$). Hence as a first approximation, homogenization in the system is imaginable as a series connection of grain boundary diffusion with a characteristic length in the order of magnitude of the agglomerate size and bulk diffusion with a characteristic length in the order of magnitude of the grain size.

In spite of the theoretical considerations above, none of the libraries correlated with the reference behavior in the very low Y_2O_3 regime, which itself was in accordance with the respective phase diagram.²⁴ This phenomenon can be valued as a hint to the existence of agglomerates that survived the mechanical offense posed by the mixing and pressing. These agglomerates had the same yttria concentration for all samples of a library, namely the concentration of the respective masterbatch. However, the frequency of yttria-rich agglomerates per sample became lower, when moving toward the zirconia-rich side of the library, thus hindering more complete homogenization due to longer diffusion paths necessary. It can be followed that a third characteristic length in the homogenization process is the average distance between yttria-rich agglomerates. The authors suspect heat treatment in the presence of a liquid phase to be necessary for a homogenization in cases where the latter characteristic length is very high. For materials synthesized by a solid phase reaction, it seems necessary to minimize the relative concentration difference between the respective masterbatches.

To shed more light upon the question of mixing quality wavelength or energy dispersive X-ray spectroscopy mappings are necessary. Unfortunately, this technology was not accessible for the authors of this work. Nevertheless, the values of diffusion coefficients derived above show the possibility of homogenization during heat treatment.

The degree of automation involved in the setup reported here makes it possible to minimize the influence of human

error on the accuracy and precision of the experiments. Also, the complete cycle from powder to evaluated results including the dosing, mixing, shaping, and sintering was completed in approximately 3 days, the longest intervals of which were for sintering and the XRD analysis. Both of these procedures ran unsupervised, and further green body preparation could be performed meanwhile. Furthermore, the dosing robot and the parallel mixer can work on up to 40 samples at once in the present setup. Therefore, it is possible for one laboratory assistant to analyze a complete binary material system within 1 week.

Conclusions

It has been shown that high-throughput experimentation is applicable to ceramic bulk materials and that the automated synthesis and characterization procedure presented here is a functioning HTE system. Within one experimental run, the material system $\text{ZrO}_2\text{-Y}_2\text{O}_3$ could be scanned in the concentration region between 0 and 5 mol % of Y_2O_3 with a resolution of 0.5 mol %. Due to the importance of homogeneity of Y_2O_3 in ZrO_2 and the low interdiffusion rate in the material system used, the results stand as a proof of principle that our setup is a valuable help for development and optimization of material systems resulting out of solid state reactions. Even better results can be expected in metallic or liquid phase sintered ceramic systems, because of much higher interdiffusion rates during heat treatment.

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Supporting Information Available. Mean monoclinic phase contents, scattering values, and deviation of means for all samples of all libraries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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