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Synthesis, sintering and thermal expansion of porous low expansion ceramics

Stefano Maschio[a,*], Alessandro Bachiorrini[a], Elio Lucchini[b], Sergio Brückner[a]

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via del Cotonificio 108, 33100 Udine, Italy
[b] Dipartimento di Ingegneria dei Materiali e Chimica Applicata, Università di Trieste, Via A. Valerio 2, 34127 Trieste, Italy

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Abstract

In this paper we report on the preparation and characterization of porous ceramic substrates in the group of $NaZr_2(PO_4)_3$, $CaZr_4(PO_4)_6$, $SrZr_4(PO_4)_6$ and $BaZr_4(PO_4)_6$ with low thermal expansion coefficients. The starting powders were obtained by a sol–gel process and attrition milling both before and after calcination. The resulting sintered bodies exhibited high porosity also after further thermal treatments at high temperature. On the other hand their thermal expansion coefficient (CTE) is low over the range 25–1000 °C. In particular the blend between $NaZr_2(PO_4)_3$ and $SrZr_4(PO_4)_6$ has a CTE close to zero in the whole temperature range. According to these properties the above mentioned materials seem to be potential candidates as ceramic substrates for catalytic applications in combustion reactions since they maintain a high level of micrometric porosity when operating at temperatures exceeding 1000 °C.

Keywords: Powders-chemical preparation; Sintering; Porosity; Thermal expansion; $NaZr_2(PO_4)_3$; $CaZr_4(PO_4)_6$; Phosphates

1. Introduction

Ceramic substrates are used in catalytic applications according to their good chemical inertness and high melting temperatures.[1–5] Such substrates are often subjected to sudden temperature changes therefore they must tolerate thermal shocks without catastrophic ruptures.[6] A low thermal expansion coefficient is required in order to minimize dramatic degradations of the materials in use.[7] Several single phased materials have low thermal expansion coefficient, but those containing the PO_4 and ZrO_6 groups known as (NZP) family of materials are particularly interesting[8–21] also as catalyst support.[22,23] In particular we share the opinion of Limaye et al.[10] who wrote that “The interesting properties of such materials are mainly attributed to their crystal structure, which consists of flexible and strongly bonded, three dimensional networks of PO_4 tetrahedra and ZrO_6 octahedra interconnected through corners sharing and developing a rigid, stable hexagonal lattice containing structural holes which can be partially or fully (depending on the composition) occupied by several ions such as Na^+, Ca^{++}, Sr^{++}, Ba^{++}. The reason of the low thermal expansion behaviour is due to strongly bonded polyhedra, presence of holes which absorb thermal vibrations and anisotropy in axial thermal expansion of the lattice”.

An important feature of those materials is the tailorability of their thermal expansion coefficients. In fact materials having a CTE of required value over any desired temperature range can be prepared by selecting suitable composition in (NZP) family. For instance Limaye et al.[10] demonstrated that CZP, $CaZr_4(PO_4)_6$ and SZP, $SrZr_4(PO_4)_6$ have opposite thermal anisotropy in their respective cell axes. In particular, in the former, the *a*-axis contracts on heating while the *c*-axis expands, in the latter a reverse situation occurs, i.e. the *a*-axis expands on heating while the *c*-axis contracts. The same opposite thermal anisotropy can be detected by comparing $NaZr_2(PO_4)_3$ (NZP) and $BaZr_4(PO4)_6$ (BZP).[10,11,15] Briefly NZP behaves like CZP whereas SZP behaves like BZP. It is evident that by coupling proper quantities of these components one can obtain solid solutions giving rise to materials having “tailored” thermal expansion coefficient.

Porosity is actually another fundamental requirement for good performance of ceramic substrates for solid–gas reac-

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[*] Corresponding author.

E-mail addresses: stef.maschio@uniud.it (S. Maschio), bachiorrini@uniud.it (A. Bachiorrini), lucchini@units.it (E. Lucchini), bruckner@uniud.it (S. Brückner).

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tions operating at high temperatures; it should be stable on use and densification must be minimized.[2–4] The main problem of most ceramic materials is that some densification may occur after a number of cycles at high temperature. It causes the reduction of the surface area and, as a consequence, lowers the catalytic activity. Coarsening and densification can be limited by lowering the operating temperature or by the use of ceramic substrates less prone to sintering at high temperature. It is known that materials of the NZP family, made of anisotropically expanding structures, undergo extensive microcracking on cooling after sintering and show characteristic hysteresis in bulk thermal expansion behaviour.[16,20,24] More in detail, Cloer et al.[20] demonstrated that the thermal expansion coefficient of some NZP samples can be similar in magnitude, but opposite in sign if the CTE measurements are made by dilatometer or X-ray. Microcracking starts when the grains exceed a critical size which is related to the maximum thermal expansion difference.[25] It follows that grain size control is essential in order to preserve the stability of density and/or porosity of the sintered materials since it is known that materials having small grains are often more stable than those characterized by large grains. It is therefore important to synthesize materials of desired porosity coupled with grains of size, possibly, below the critical value.

In two recent papers[26,27] we demonstrated that reactive powders, leading to monolithic ceramic bodies can be prepared by denitration or coprecipitation of relative chemical precursors. Their ability to sinter can be then modified by adjusting calcinations steps and attrition milling processes.

In this work, following a similar procedure, we have produced powders of NZP, CZP, SZP and BZP using the sol–gel technique followed by calcination and some attrition milling processes in order to evaluate the influence of processing conditions on the sinterability of powders and porosity of the sintered materials. Two mixtures of different powders were also prepared and their thermal expansion were measured over the range 25–1000 °C. The goal of this experiment was the preparation of materials with an average CTE as close as possible to zero in the given temperature range and with a high porosity after sintering.

2. Experimentals

$NaNO_3$ (Riedel de Haen 99.5%), $Sr(NO_3)_2$ (Aldrich Chem. 99%), $Ca(NO_3)_2{\cdot}4H_2O$ (Aldrich Chem. 98%), $Ba(NO_3)_2$ (Aldrich Chem. 99%), $ZrO(NO_3)_2{\cdot}xH_2O$ and $NH_4(H_2PO_4)$ (Aldrich Chem. 98%) were the starting salts used in the sol–gel method.

As a first step, a 0.3 M solutions of Na, Ca, Sr, or Ba precursors were prepared by dissolving the calculated amount of the respective nitrates in deionized water, using a magnetic stirrer. In such solutions was also dissolved the zirconyl nitrate and, when the solution became clear, the monobasic ammonium phosphate was finally added. After stirring for 4 h, the sols, having a milky white colour, were aged for 24 h at room temperature. During this time the sols became gels which were then thermally treated in an oven at 80 °C for 12 h.

Dry gels were coarsely ground and again thermally treated at 300 °C for 1 h in order to remove the volatiles. They were then attrition milled for 1 h in a plastic container with zirconia/yttria (3 mol%) spheres at 300 cycle/min using isopropanol as dispersing medium. The milled powders were dried in an oven at 80 °C and calcined at 700 °C for 1 h. This thermal treatment was chosen according to the results of previous tests performed with a STA equipment (Netzsch ecc.) After calcinations, the powders were again attrition milled for 3 h as in the first milling, dried again, sieved through a 63 μm sieve and stored under vacuum.

Attrition milling causes wear of the milling balls which contaminates the powders. The evaluation of contamination by yttria was done by weighting the balls before and after the milling and was considered negligible (below 0.5wt.%) since the starting precursors have a similar purity.

We prepared also two selected mixtures of the aforementioned powders, i.e. CZP was blended with BZP and NZP with SZP. In this case too the homogenization of the required amounts of calcined powders was done by 3 h attrition milling using the same conditions as for the pure products. The amounts of each single phase powder was calculated using the equation:

$$v_i\alpha_i + v_j\alpha_j = 0$$

v_i and v_j being the fractional volumetric amounts of the powders i, j ($i =$ NZP or CZP and $j =$ SZP or BZP) and α_i and α_j their experimental average thermal expansion coefficients measured between 25 and 1000 °C. Using data obtained by the dilatomatric tests, and reported in the results and discussion section, the two mixtures assume the following stoichiometric compositions: $Ca_{0.4}Ba_{0.6}Zr_4(PO_4)_6$ and $Na_{0.86}Sr_{0.14}Zr_2(PO_4)_3$.

Powders were uniaxially pressed at 200 MPa into cylindrical or rectangular specimens and sintered in air for various times and at various temperatures ranging from 1200 to 1500 °C. The density of the green samples was determined by the ratio between weight and volume while that of sintered bodies was evaluate d by the Archimede's method after having previously sealed sample surfaces with paraffin.

X-ray diffraction data were recorded on an XRG 300 Inel powder diffractometer equipped with CPS 120 detector. Monochromatic Co $K\alpha_1$ was obtained by setting 35 kV and 20 mA as operating conditions. Dilatometric behaviour in air was evaluated by a Netzsch alumina dilatometer at a heating rate of 10 °C/min up to a temperature of 1000 °C. Three samples were analysed for each composition. Microstructures were examined by an Assing Stereoscan scanning electron microscope (SEM).

3. Results and discussion

In a recent paper[27] we have described the effects of attrition milling, before calcinations, on powders of Al_2O_3 and 12Ce-TZP produced via denitration or via coprecipitation. In that work, we demonstrated that a pre-calcination milling reduces their crystallization temperature and improves their sinterability after further millings relative to the same powders which were milled only after calcination. Such effects can be summarized as a high reactivity of particles during all the thermal treatments which lead to monolithic fired materials.

In the present research, powders of all compositions crystallize as single phase after 1 h at 700 °C, their X-ray diffraction patterns being in agreement with the respective JCPDS files.[28–31] This result confirms the benefits obtainable by an attrition milling carried out before powders' crystallization. A similar crystallization temperature (688 °C) was determined by Lynch et al.,[13] in the production of NZP powders, in our case, however, all the powders prepared according to the present procedure display the same behaviour.

The second column of Table 1 lists the relative density of the green samples and supports the above results in terms of powders rheology. A low calcination temperature limits agglomeration and powders can be pressed into specimens having relatively high density. In the present research, green specimens have relative densities ranging from 57 to 62%, which are rather high values for an uniaxial pressing procedure. Differences between the various compositions, see Table 1, are probably due to the coarse method used for the measurement.

The densification of samples does not follow the trend observed in other materials[27] and no high density was reached in all cases we examined in this work.

The third and fourth columns in Table 1 list respectively real and relative densities of all samples after sintering for 2 h at 1300 °C. Higher sintering temperature or longer ageing times do not further sinter, indicating that porosity remains high in all the samples prepared. Furthermore, we have observed that prolonged thermal treatment caused only grain growth and, in parallel, different type of porosity. In fact, samples sintered 2 h at 1300 °C showed the same density as those sintered 6 h at the same temperature, the difference being their larger grain size and the enlarged pores dimension which remains of micrometric size. Fig. 1a and b report the SEM microstructures of two samples of NZP fired 2 and 6 h, respectively at 1300 °C. The grain size is

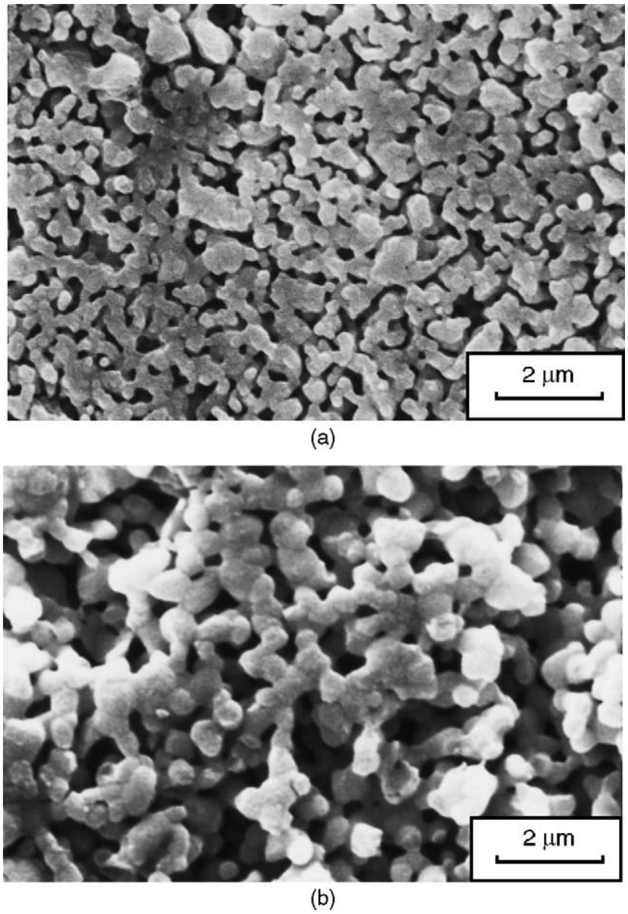

Fig. 1. SEM microstructures of NZP materials after sintering at 1300 °C: (a) 2 h, (b) 6 h.

Table 1
Measured properties of the materials studied and reference data

Material	Green materials, ρ (%)	Fired materials, ρ (g/cm^3)	Fired materials, ρ (%)	CTE α			
				Present research	Ref. 20[a]	Ref. 9[a]	Ref. 10[a]
$NaZr_2(PO_4)_3$ (NZP)	58	2.30	72	−0.62	−3.00	–	–
$CaZr_4(PO_4)_6$ (CZP)	60	2.60	80	−2.70	–	−2.11	–
$SrZr_4(PO_4)_6$ (SZP)	61	2.63	79	1.88	–	3.2	3.16
$BaZr_4(PO_4)_6$ (BZP)	57	2.55	75	1.73	–	–	3.37
$Ca_{0.4}Ba_{0.6}Zr_4(PO_4)_6$ (CZP + BZP)	62	2.77	83	2.20	–	–	–
$Na_{0.86}Sr_{0.14}Zr_2(PO_4)_3$ (NZP+SZP)	58	2.49	77	0.21	–	–	–

The second column lists the relative densities of the green materials uniaxially pressed into cylinders at 200 MPa. The third and the fourth columns list respectively real and relative densities of the different materials sintered 2 h at 1300 °C. The fifth column reports average experimental thermal expansion coefficients (CTE) of the different materials sintered for 2 h at 1300 °C measured between 20 and 1000 °C ($\times 10^{-6}$ °C^{-1}). Columns 6–8 report some literature data.

[a] Temperature range, 25–500 °C.

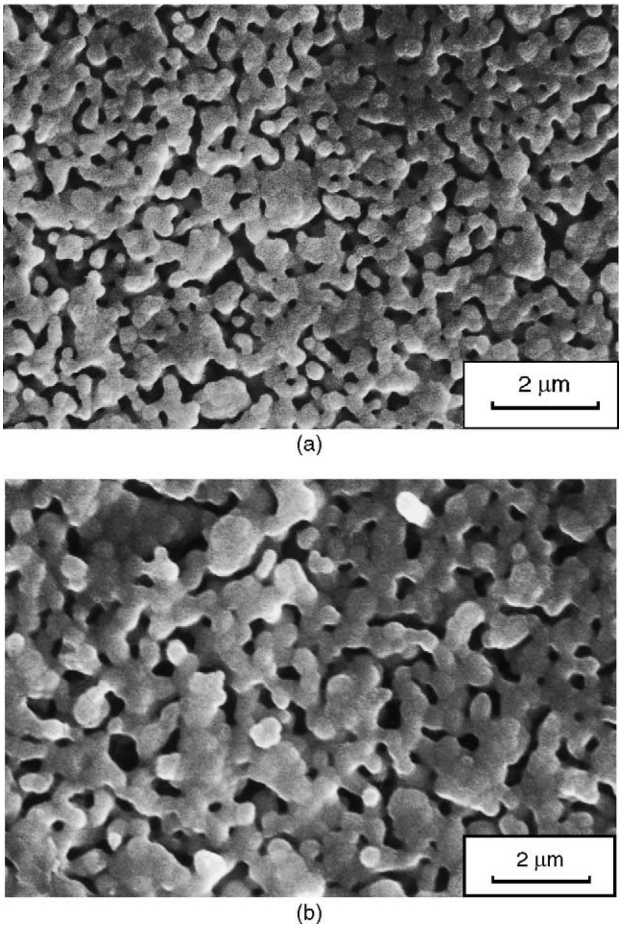

Fig. 2. SEM microstructures of SZP materials after sintering at 1300 °C: (a) 2 h, (b) 6 h.

very low in both specimens, i.e. nearly 0.2 µm in the former and nearly 0.5 µm in the latter. The same behaviour was observed in the other materials examined. In particular Fig. 2a and b show the microstructures of SZP after sintering for 2 h and for 6 h at 1300 °C. It is possible to see that also in these samples grains are very small being nearly 0.1 µm after 2 h and nearly 0.4 µm after 6 h. We have observed that NZP and SZP have grains of similar magnitude, but in the second one their size remains lower than in the former for same thermal treatments. Similar microstructures and similar trends were observed in CZP, BZP and in the two other mixtures prepared in the present work, corresponding micrographs are not reported for brevity. Sintering at 1400 °C for 2 and 6 h did not improve density relative to tests performed at lower temperatures. Thermal treatments at temperatures above 1500 °C caused a partial lost of substances and the transformation of the single phases, obtained by calcinations, into double or multiphase materials as a function of the starting components. Monoclinic zirconia is present in all specimens sintered at temperatures above 1500 °C. This phase grows on cooling after sintering and causes extended micro- and macrocracks, as function of the thermal treatment, in the materials which cannot be characterized as pellets.[32–34] However, this should be not a serious drawback since it is known that, if used as ceramic substrates for solid–gas combustion reactions, temperature values above 1400 °C, normally, do not represent common working conditions and could be reached only in some extraordinary circumstances, generally causing the degradation of the catalysts as well as of the ceramic support.

The poor sinterability of the powders could be due to their high reactivity which leads to a complete crystallization at low temperature (700 °C). Later on, the pressed samples, during the initial stage of the sintering, develop the growth of the starting NZP, CZP, SZP and BZP structures and consequently microstructures show very small grains and pores of similar size. When occurring in the NZP family of materials, the grow of such highly open and rigid crystal structure causes a low mobility of grains reducing cannibalism between them as revealed by their monosized distribution. This reduces the densification driving force to very low values. It follows that densification is difficult and, consequently, porosity remains high even after very long treatments at high temperature. The increase of the sintering temperature and/or time leads only to modest changes of the initial microstructure as it can be seen by examining Figs. 1a, b and 2a, b where it is shown that the grain growth at 1300 °C is very low. If we consider that we have seen a similar trend of grain growth also at 1400 °C, we are prone to say that grain growth kinetic is very low at any temperature and for all the compositions examined in the present work.

An important topic of the present research is the influence of microcracking, which occurs during cooling after sintering in the NZP family and the porosity of the sintered materials. Yamai and Ota,[25] reported the grain size–microcracking relation for several low thermal expansion ceramics. They have demonstrated that microcracking occurs when the grain size exceed a certain critical size, resulting in the lowering of the strength, Young modulus and thermal expansion coefficient. The critical size they determined ranged from 2 µm for $CaZr_4(PO_4)_6$ to >100 µm for $SrZr_4(PO_4)_6$. It seems reasonable to expect values of comparable magnitude also for the materials prepared by us, that were not considered in their research. In all our materials grains remain below the dimension of 1 µm even after the most severe sintering conditions, the largest grains measured in our materials are therefore below the smallest critical size determined by Yamai and Ota. We may safely conclude that, although microcracking cannot be totally excluded, nevertheless it should only slightly affect the porosity of materials.

Fig. 3 displays the experimental thermal expansion, in terms of $\Delta l/l_0$ versus temperature, of the different materials prepared. Average CTE values, between room temperature and 1000 °C are reported in the fifth column of Table 1. Thermodilatometric tests, between room temperature and 1000 °C, showed that both NZP and CZP shrink on heating, whereas SZP and BZP do expand. The thermal behaviour of such materials has been already explained by other researchers and results obtained in the present work are

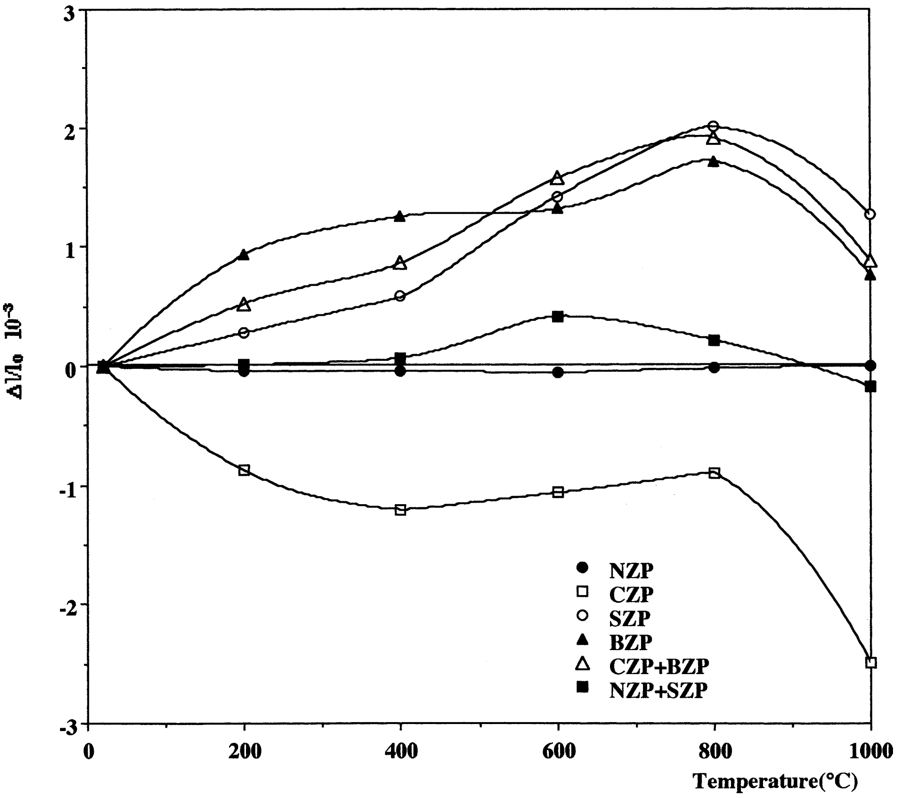

Fig. 3. Experimental thermal expansion $\Delta l/l_0$ of the different materials between 25 and 1000 °C.

in qualitative agreement with published data.[8,9,10,14,20,21] Numerical differences are probably due to the different thermal range in which average thermal expansion was evaluated, to small zirconia (yttria) contaminations introduced by attrition milling into the powders and to the fact that our materials contain submicronic grains which reduce the microcracking effect on the behaviour observed during thermal expansion.[20,25] Experimental thermal expansion data and average CTE data of the materials obtained by sintering the two mixtures of monophasic powders prepared by us are also shown in Fig. 3 and in Table 1.

In agreement with literature data,[8,9,10,14] X-ray diffraction patterns showed the presence of single phase materials not only after calcinations, but also after the sintering for all samples prepared in the present research.

The equation reported in the experimental section, used for the calculation of the amounts of single phased powders that we blended to prepare mixtures of materials having opposite thermal expansion behaviour, in order to produce zero expansion ceramics, assumes unchanging phases during sintering. In this work, during sintering, powders transform from two-phased-mixtures into monophasic monolithic materials. It follows that compositions calculated with the given equation represent only a first approach on the way for the production of materials having an average CTE equal to zero, the ultimate criterion being obviously of empirical nature. We observe that samples containing CZP and BZP exhibit a relatively high value of the average CTE, whereas samples containing NZP and SZP exhibit a value close to zero between 25 and 1000 °C.

4. Concluding remarks

Powders produced by sol–gel technique followed by calcination and attrition milling can lead to monophasic sintered materials in the production of NZP, CZP, SZP and BZP. Pressed powders produce porous materials after sintering at temperatures above 1300 °C for 1 h or more. Increase of the ageing time at high temperature, during sintering procedures, does not enhance density, but it rather enlarges the grain size and changes the type of porosity. Sintering at temperatures above 1500 °C causes decomposition of the components and induce the formation of monoclinic zirconia which, in turns, degrade the samples due to the development of micro and macrocracks. The grain size of the samples remains very low even after long sintering time at 1400 °C therefore minimizing the influence of microcracking on the properties of the materials.

The thermal behaviour of such materials has been evaluated between 25 and 1000 °C and is in qualitative agreement with published data.

The blend between powders containing NZP and SZP, calculated on the ground of their average CTE and using volumetric amounts of the components, exhibits CTE values close to zero between 25 and 1000 °C thus confirming that the procedure used for the calculation of powders mixtures is suitable for the production of materials characterized by zero CTE within any thermal range of interest.

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