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[NZP]: A new family of ceramics with low thermal expansion and tunable properties

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Abstract

Ceramic materials belonging in the sodium zirconioum phosphate (NZP), family were prepared and characterized, with the view to identify a ceramic material, that may be used as honeycomb material in three way catalysts (TWC). Two different families were studied.

The first one belongs to the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$ (x = 0–1). This system was chosen because $CaZr_4P_6O_{24}$ contracts while $BaZr_4P_6O_{24}$ expands on heating. The material for $x = 0.25$ has a thermal expansion coefficient value close to zero and its flexural strength varies between 36 and 50 MPa for porosity of 17–28%. However, this system is quite unstable in acidic environments.

Another NZP system, namely $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ (x = 0–0.4) was investigated. The effect of the addition of Si substituting P was studied. As x increases, the thermal expansion coefficient decreases. For $x = 0.22$, the material is chemically stable and has a TEC value close to zero. Its porosity was quite high (36–47%) combined with flexural strength in the range of 20–40 MPa.

Additionally, it was proved that materials with adequate physical and mechanical properties can be produced at relatively fast firing schedules. Optimum calcination time is 4 h and optimum sintering time is 8 h.

Keywords: NZP ceramics; Thermal shock resistance; Thermal expansion; Powders solid state reaction

1. Introduction

Sodium zirconium phosphate, $NaZr_2P_3O_{12}$, was first discovered and studied in the mid-seventies, due to its fast ionic conductivity. Several compounds belonging to the so-called orthophosphate group of $NaZr_2(PO_4)_3$ (NZP) family have emerged as a new class of low expansion ceramic materials.[1–3]

These materials exhibit a flexible hexagonal crystal structure formed by PO_4 tetrahedra sharing corners along the c-axis with ZrO_6 octahedra.[4,5] The alkali atoms (Na, Ca, Ba, Mg, K, Sr, etc.) are located in the holes between the ZrO_6 octahedra.[6] The open, but also strongly bonded, structure allows the high mobility of the alkali ion tunneling through the PO_4-ZrO_6 polyhedra chain.[1,4,5] As a result there is an enormous number of 212 formula types of compounds containing one to five different cations, belonging to the family.[5,6]

The NZP compounds are lately receiving attention for their potential to be used in high anti-thermal shock applications, automobile industry, space, telescope technology, etc. Also, they can be used as catalyst supports, fast ionic conductors, hosts for immobilizing radioactive waste etc.[1,5,7,8] A very important feature of those materials is the possibility to be designed with controlled thermal expansion coefficient. Additionally, some NZP members present high mechanical strength, good chemical stability, high melting point, great hardness and radiation resistance.[5] In some cases the crystal lattice presents a highly anisotropic behavior. When anisotropy exists, it has a detrimental effect on mechanical strength because it causes micro stresses and consequently microcracks.[9,10]

The attractive thermal expansion properties mentioned above have risen the interest of several researchers. Among the members studied, $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ has attracted interest as a low thermal expansion ceramic with good mechanical properties at high temperature and chemical stability. Although, general studies on the relation of ion substitution to structure and properties (e.g. thermal expansion) have been carried out, no detailed approach to $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ mechanical and chemical properties has been made by now.[11–13]

In the present work, two different NZP formulas were investigated namely $Ca_{1-x}Ba_xZr_4P_6O_{24}$ and $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$.

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The aim was to investigate the materials derived from these formulas with the substitution of Ca by Ba in the first and the partial substitution of P by Si in the later.

2. Experimental procedure

Several compounds were prepared in the $Ca_{1-x}Ba_xZr_4P_6O_{24}$ (CB) family. They were produced by solid state reaction and the compounds present were identified by X-ray diffraction. The materials were characterized with respect to expansion behavior, mechanical strength and porosity. Finally, their chemical stability was studied under acidic and alkaline conditions.

$Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ (BS) system was studied with the view to find a material suitable for applying as ceramic substrate (honeycombs) at catalytic converters. The material must meet application's requirements, such as: low thermal expansion (TEC $\approx 0 \times 10^{-6}\,°C^{-1}$), high flexural strength ($\geq$18 MPa), high porosity ($\geq$30%) and chemical stability when exposed to corrosive and oxidizing conditions.

After being produced by solid state reaction, the BS compounds were identified by X-ray diffractometer (XRD) and characterised concerning their thermal expansion behavior, mechanical strength and porosity. SEM images of the material were also taken and studied. Finally, optimization of the two steps production process was carried out resulting to a remarkable reduction of calcination and sintering time.

2.1. Preparation of the powders

Silicon doped barium zirconium phosphates were synhtesized by reaction sintering of stoichiometric amounts of $CaCO_3$, $BaCO_3$ (Fluka, 98.5% purity), ZrO_2 (UNITEC), $(NH_4)H_2PO_4$ (Merck, 99% purity) and SiO_2 (Alfa). Appropriate amounts of the reactants were used in order to prepare the compositions $Ca_{1-x}Ba_xZr_4P_6O_{24}$ (x = 0–1) and $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ (x = 0–0.4). The starting powders were mixed by wet-milling with acetone and alumina balls for 24 h. The produced mixtures after drying were calcined at 900 °C for various calcining times. Phase identification was performed by X-ray diffractometer (Siemens, D-500). Afterwards, the precursor powders were ball milled again and extruded as rods.

2.2. Extrusion of rods

The powders were mixed with 8%, (w/w) cellulose (MHPC 20000), 2%, (w/w) sodium stearate and distilled water. The mass produced, was extruded as rods. The samples were dried and fired at 1400 °C, for various sintering times.

2.3. Evaluation-characterization

The study of the samples included: (i) four point bending strength measurements (INSTRON 8562), (ii) thermal expansion behavior (dilatometry DIL 402, Netzch), (iii) porosity calculated by Archimidis method and (iv) microstructural analysis using SEM (Jeol-6300).

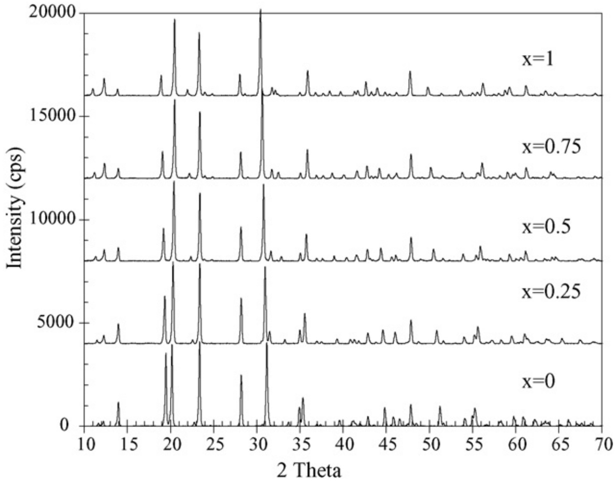

Fig. 1. XRD patterns for $Ca_{1-x}Ba_xZr_4P_6O_{24}$.

3. Results and discussion

3.1. The system $Ca_{1-x}Ba_xZr_4P_6O_{24}$

3.1.1. Crystal structure

The XRD patterns of all compositions prepared are shown in Fig. 1. In all cases a single-phase material was formed having the NZP structure. Crystal changes accompanying the Ca substitution with Ba are obvious in Fig. 1, where a gradual shift of the peaks at smaller angles for higher amounts of Ba is observed. Unit cell expands towards one direction while it contracts along another according to a more detailed study. Based on the XRD data, and with the aid of a least squares unit cell refinement (LSUCR) computer program, the lattice parameters of the hexagonal unit cell of the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$ were determined (Fig. 2). Parameter a decreases and parameter c increases when the concentration of Ba increases. The overall unit cell volume increases as Ba increases. This happens because the ionic radius of Ba^{2+} (0.135 Å) is greater than the ionic radius of host ion Ca^{2+} (0.099 Å) leading to a larger cell.

3.1.2. Thermal behavior

The crystal changes mentioned above have a pronounced effect on the thermal behavior of the material. The larger Ba^{2+} ions are located in the holes between the ZrO_6 octahedra, reducing the free space available for thermal movement thus causing expansion. The thermal expansion curves of the $Ca_{1-x}Ba_xZr_4P_6O_{24}$ system are shown in Fig. 3, and the TEC values at 600 °C are tabulated in Table 1. Indeed, the $CaZr_4P_6O_{24}$ end member has a negative coefficient of thermal expansion while the $BaZr_4P_6O_{24}$ end member has a positive coefficient.

Table 1
Thermal expansion coefficient of $Ca_{1-x}Ba_xZr_4P_6O_{24}$

x	0	0.25	0.5	0.75	1
TEC ($\times 10^{-6}\,°C^{-1}$) at 600 °C	−4	0.8	1.9	2.0	1.8

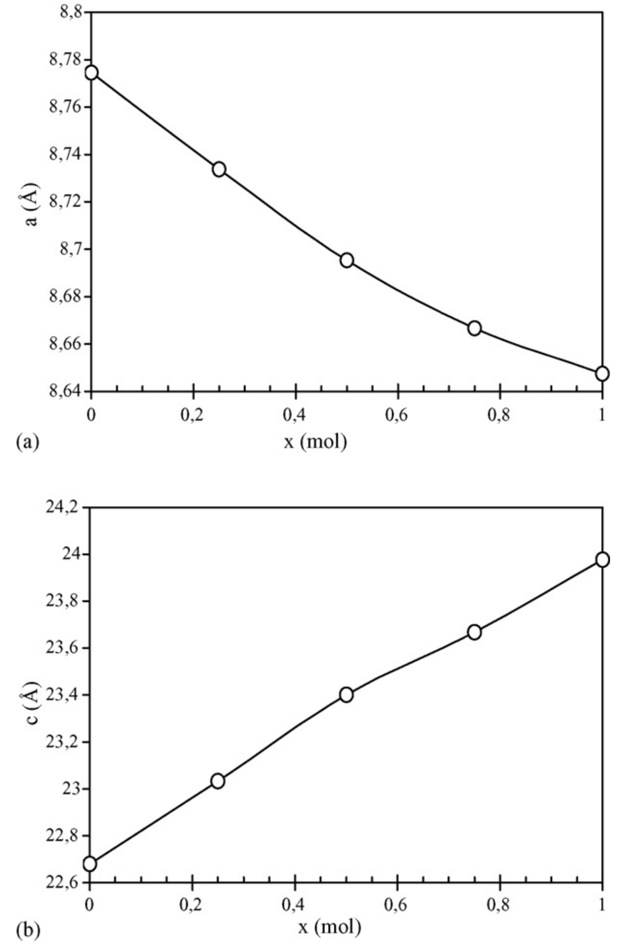

Fig. 2. (a) Lattice parameters of the hexagonal unit cell of the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$. (b) Lattice parameters of the hexagonal unit cell of the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$.

As x increases, TEC also increases indicating that materials can be designed within CB system with tunable thermal expansion behavior. The composition with $x = 0.25$ (CB25) has a TEC value very close to zero.

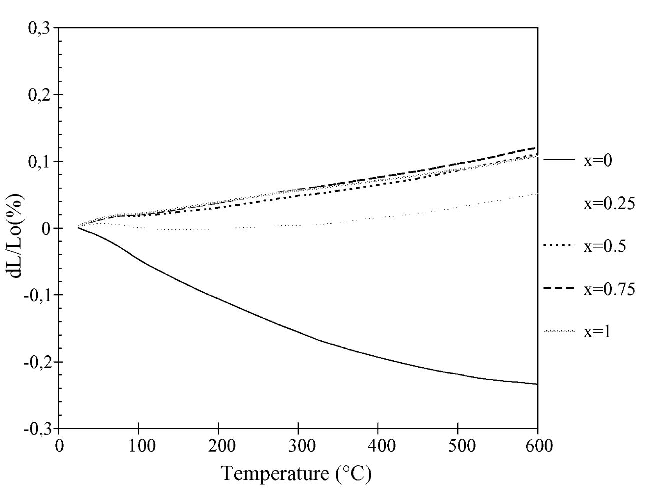

Fig. 3. Thermal expansion curves for $Ca_{1-x}Ba_xZr_4P_6O_{24}$.

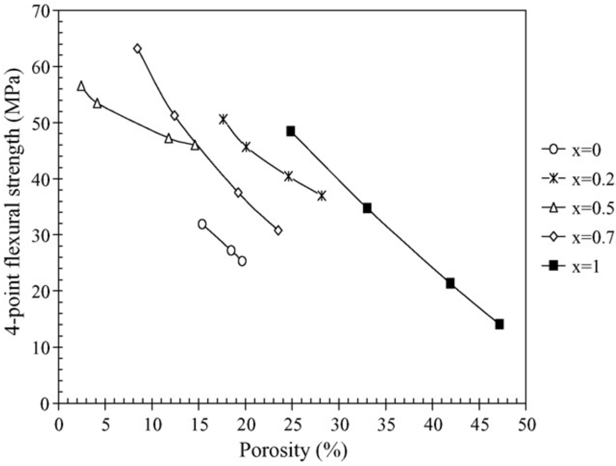

Fig. 4. Flexural strength vs. porosity for $Ca_{1-x}Ba_xZr_4P_6O_{24}$.

3.1.3. Flexural strength

Flexural strength measurements (Fig. 4) show that the CB0 end member is characterized by high flexural strength at low porosity as compared to the CB100, which has better flexural strength even at much higher porostity (~double). The mechanical improvement of the barium rich compounds is probably due to the crystal lattice distortion when larger ionic radius Ba^{2+} cations substitute smaller Ca^{2+} cations. Among the intermediate compositions, $Ca_{0.75}Ba_{0.25}Zr_4P_6O_{24}$ is characterized by high strength values (36–50 MPa for porosity 17–28%), compared to the other compositions of the system. Therefore, it can be concluded that this composition represents a potential candidate material since it fulfills the requirements set for the application.

3.1.4. Chemical stability of the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$

Chemical stability tests proved that this system is quite unstable in acidic environments. Specifically, chemical stability tests performed in 1:1 H_2SO_4 solution showed that $Ca_{1-x}Ba_xZr_4P_6O_{24}$ lost 20.28% of its mass in 24 h at room temperature. This happens probably due to the dissociation of the phosphates in the presence of hydrogen ions to phosphine, PH_3. The system is also unstable in strong alkaline environment. A mass loss of 17.18% was measured when the material was exposed in 10N NaOH solution for 24 h at room temperature. The CB system was also tested in oxidative conditions performing both TG-DTA and thermal treatment experiments. Both experiments confirmed that CB system is chemically stable in oxidative conditions and no mass loss was measured. This material therefore can be used only in cases of absence of strong acidic or alkaline conditions. Such acidic conditions can be imposed in three way catalysts (TWC) only in the case of the catalyst regeneration in the presence of acids.

3.2. The system $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$

3.2.1. Crystal structure

The chemical instability of the CB system was the reason that the research was focused on another NZP system, namely

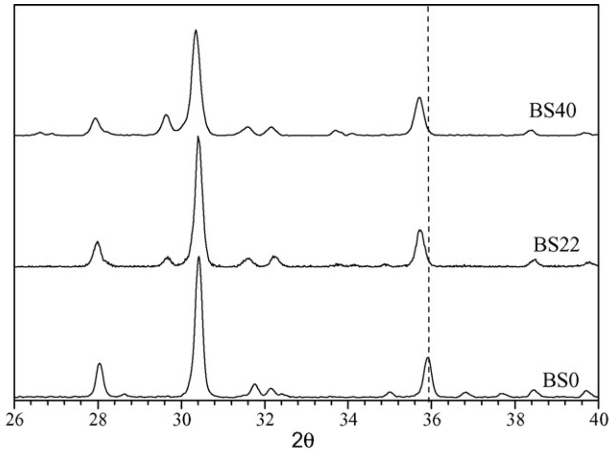

Fig. 5. XRD patterns for $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$.

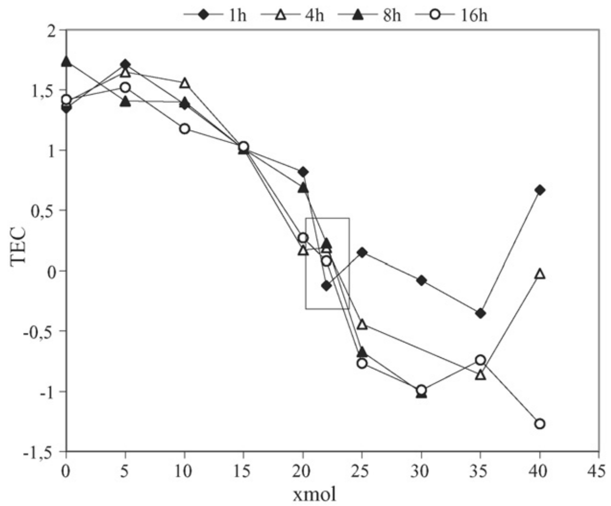

Fig. 6. TEC ($\times 10^{-6}$ °C^{-1}), at 600 °C, for $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$.

$Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ ($x = 0$–0.4). It was estimated that partial substitution of *P* by Si probably has a beneficial effect on chemical stability. The $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ (BS) system has the same hexagonal crystal structure as the whole NZP family. The XRD patterns of three compositions prepared ($x = 0, 0.22, 0.40$) are shown in Fig. 5. Although, in all cases a single-phase material was formed having the NZP structure, the peaks formed were not present at the same angles. The discontinuous line in Fig. 5 highlights this difference, which is a slight shift of the peaks towards smaller angles. This shift is higher as the percentage of silicon in the system increases.

Based on crystal chemistry, the replacement ions Si^{4+} (ionic radius:0.04 nm) occupy the P^{5+} (ionic radius:0.031 nm) positions while the extra Ba^{2+} take up the trigonal prismatic geometry sites. Silicon accomodation at the openings of the NZP structure causes the stretching of the unit-cell leading to shorter crystal distances as noticed at X-ray patterns. A previous study[14] has noted an increase of the unit cell volume, which also happens, due to this substitution.

3.2.2. *Thermal expansion*

The thermal expansion curves of the $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ system are shown in Fig. 6. The $BaZr_4P_6O_{24}$ end member has a positive coefficient of thermal expansion. As *x* increases, TEC decreases. The composition with $x = 0.22$ has a TEC value closest to zero. It should be noted that even though TEC values shift from positive to negative as *x* increases, they always remain in the region of -1.5 to 1.5×10^{-6} °C^{-1}.

In Fig. 6, it is clear that TEC values are gradually decreased at higher silicon content. The pure barium zirconium phosphate material (BS0), exhibited a TEC of $+1.5 \times 10^{-6}$ °C^{-1}. For $x = 0.22$, a TEC value almost zero was measured at 600 °C, but for higher silicon amounts the materials exhibite a contractive behavior at high temperatures (e.g. $\mathrm{TEC}^{600C}_{BS35} \approx -1.0 \times 10^{-6^{\circ}}\mathrm{C}^{-1}$). It is recorded that larger ionic radii or fewer interstitial ions result in lower thermal expansion[3]. Among the members studied, BS22 was pointed out since it presents an almost zero thermal expansion, irrespective to the firing conditions. This is an indication that the material presents an isotropic behavior and thus, it is reliable for use at various thermal conditions. A more detailed study on its thermal behavior was carried out, over a wide temperature range of 50–1200 °C (Fig. 7). The samples measured, had been fired following four different firing schedules. The dilatometric curves lay in a zone of $\pm 0.05 \times 10^{-6}$ °C around zero and prove that this is an ideal material for use at tough conditions, since it shows strong resistance to thermal shock.

3.2.3. *Porosity-flexural strength*

The use of $(NH_4)H_2PO_4$ as a phosphorous precursor, results in highly porous structures. Indeed, when $(NH_4)H_2PO_4$ is heated up to 400–900 °C it dissociates and volatile ammonia is produced. This phenomenon is responsible for the significantly high porosity of the samples (>42%).

The results of the porosity versus flexural strength tests (Fig. 8) show that in general, porosity increased at higher amounts of silicon. Flexural strength, on the other hand, lies in the range of 19–25 MPa, for the intermediate compositions ($0.5 \le x \le 0.25$). The combination of such a high porosity with

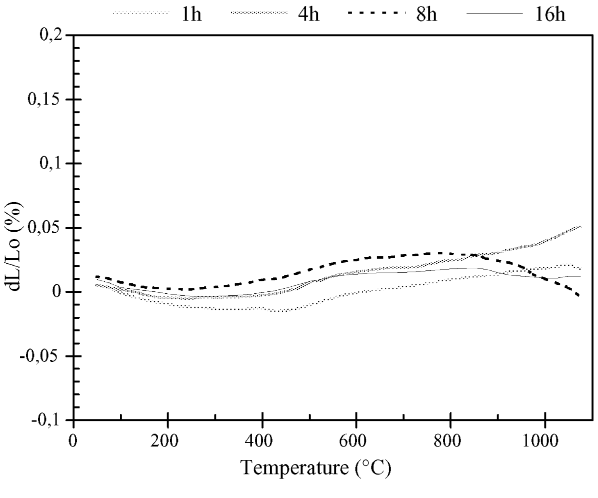

Fig. 7. Thermal expansion of BS22 sintered for 1, 4, 8 and 16 h.

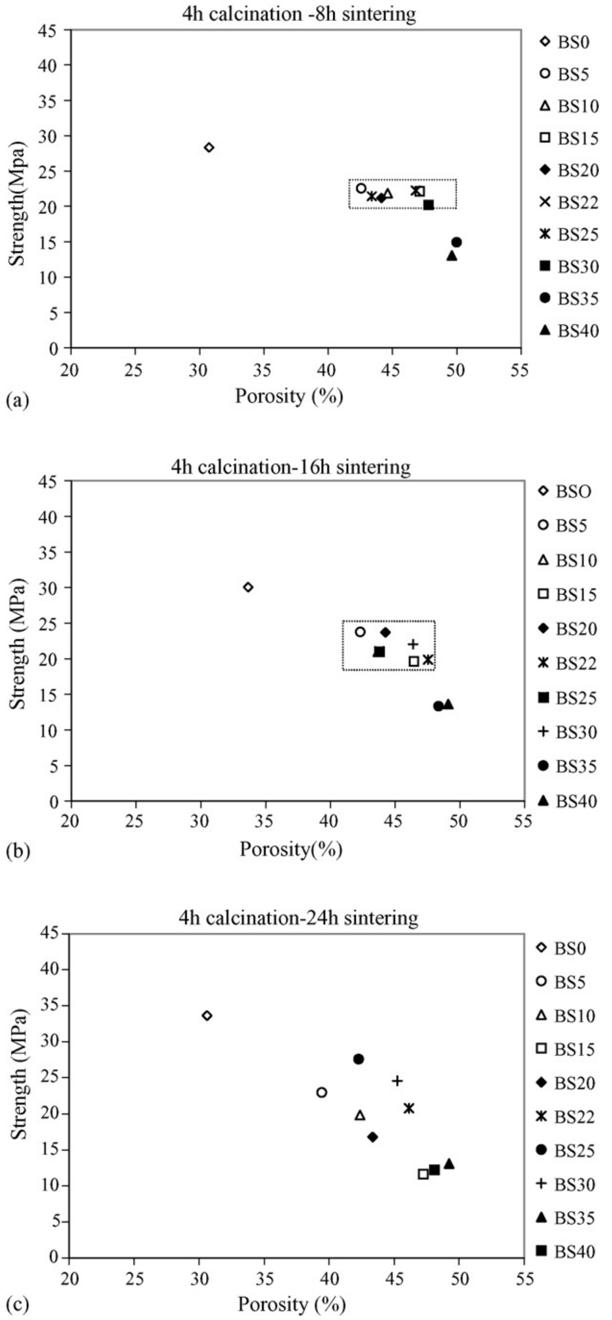

Fig. 8. (a) Flexure strength porosity at different firing times. (b) Flexure strength vs. porosity at different firing times. (c) Flexure strength porosity at different firing times.

high flexural strength values proves that materials in the BS system are very strong. Especially, $Ba_{1.22}Zr_4P_{5.56}Si_{0.44}O_{24}$ has a flexural strength of 24 MPa for a porosity of 47%. It should be noted, that cordierite, which is the ceramic generaly used for the construction of catalytic substrates, has a four point flexural strength of about 18 MPa for a porosity of only 30%. A comparison between BS22 and cordierite leads to the conclusion that BS22 presents 25% higher strength combined with 36% higher porosity.

The effect of sintering time on physical properties was also studied. Several samples were fired for 4 or 16 h and their flexural strength values range in a very narrow zone irrespective of porosity (Fig. 8a and b). On the contrary, when they were fired for 24 h this zone was rather wide (Fig. 8c). This indicates that the material after firing for 24 h is probably over fired. As Si amount increases the refractoriness of the samples also increases leading to increased porosity.

Table 2
Chemical stability tests on $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ and $Ca_{1-x}Ba_xZr_4P_6O_{24}$

	% Mass loss			
	1:1 H_2SO_4	CH_3COOH	10N NaOH	Thermal treatment
$Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ $x = 0.4$	0.9	0.03	10.12	0.01
$Ca_{1-x}Ba_xZr_4P_6O_{24}$ $x = 0.25$	20.28	0.05	17.18	0.03

3.2.4. *Chemical stability of the $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ system*

Chemical stability tests were carried out for the system $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$. Initially, the material was tested under identical conditions as in the $Ca_{1-x}Ba_xZr_4P_6O_{24}$ system. The results indicate that $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ is much more stable than $Ca_{1-x}Ba_xZr_4P_6O_{24}$. After 24 h, in 1:1 H_2SO_4 solution a mass loss of 0.9% was recorded as compared to 20.28% for the $Ca_{1-x}Ba_xZr_4P_6O_{24}$ system (Table 2). When the material was tested under 10N NaOH solution a mass loss of 10.12% was recorded as compared to 17.18% for the $Ca_{1-x}Ba_xZr_4P_6O_{24}$ material. $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ samples were also tested in more dilute solutions (1N H_2SO_4, 1N NaOH). After 24 h an insignificant mass loss was measured under H_2SO_4 attack. However, a mass loss in the order of 1% was measured under NaOH attack. Because of its apparent chemical stability it is clear that ceramics in the BS system can be used in three way catalysts.

3.2.5. *Investigation of firing parameters*

The production of NZP, requires two steps of firing. Previous studies[15,16] report that NZP production requires several hours of calcination (900 °C) and sintering (1400 °C). However, long calcination and sintering processes can be an economical drawback for a new material. Thus, it was thought necessary to identify minimal calcination and sintering times. This was obtained by combining different calcination and sintering schedules and characterizing the resulting samples in terms of phases present and physical and mechanical properties. In Fig. 9a, no significant difference of the phases present can be identified after a calcination times of 4, 8, 16 h. Similarly, in Fig. 9b, the NZP phase is formed after 4 h sintering time. Thermal expansion coefficient is not significantly affected by sintering time (TEC $\approx 0 \times 10^{-6}\,°C^{-1}$) but flexural strength and porosity are optimally combined when the sample has been sintered for 8 h. In conclusion, the calcining time proposed is 4 h, while the proposed sintering time is 8 h.

4. Conclusions

(A) During this study an extended investigation of the system $Ca_{1-x}Ba_xZr_4P_6O_{24}$ ($x = 0$–1) was performed and it was

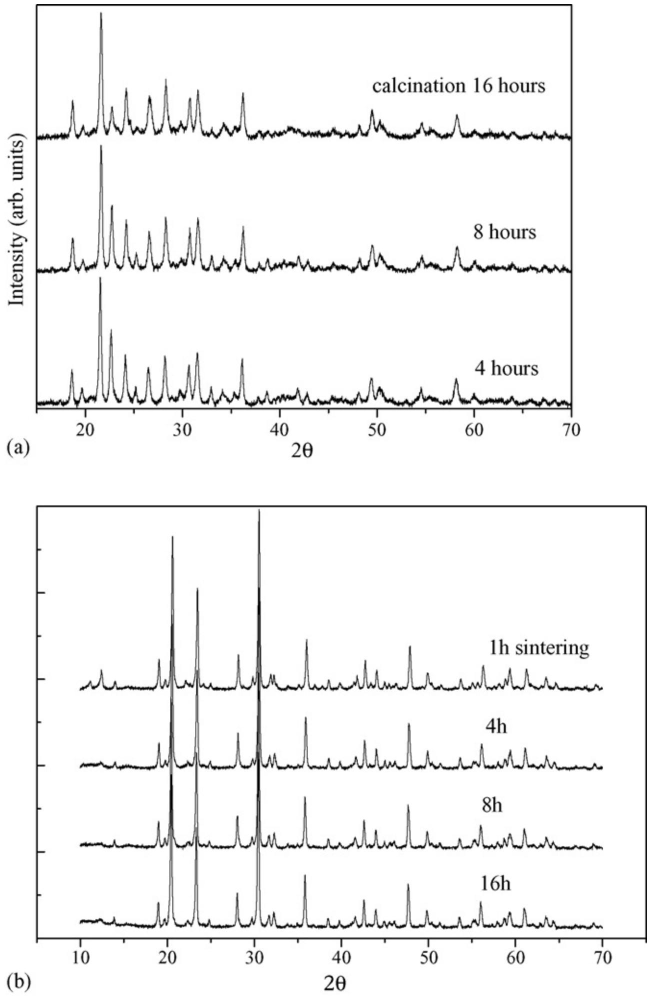

Fig. 9. (a) X-ray diffraction diagrams for $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}(x = 0.22)$. (b) X-ray diffraction diagrams for $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ $(x = 0.22)$.

proven that for $x = 0.25$ the system shows almost zero thermal expansion, high flexural strength combined with high porosity. However, chemical stability tests proved that this system is quite unstable in acidic or alkaline environments. This material, therefore, can be used only in cases of weak corrosive conditions.

(B) The research then was focused in another NZP system, namely $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ $(x = 0–0.4)$. It was concluded that chemically stable ceramic materials with tunable properties can be derived from the $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ (BS) system. The composition BS22 is a high-performance ceramic material, ideal to be used as a catalyst substrate, due to: (i) high resistance to thermal shocks because of its ultra low thermal expansion behavior at all sintering temperatures and (ii) high porosity (36–49%) depending on sintering conditions combined with high flexural strength (17.5–40 MPa).

(C) It was estimated that for $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ system the optimum calcination time is 4 h and the optimum sintering time is 8 h.

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