# MONOCLINIC ZIRCONIA SINTERED BODIES PREPARED VIA TWO-STEP SINTERING AND CHARACTERISATION OF SELECTED MECHANICAL PROPERTIES

[#]WÓJTOWICZ B., PYDA W., ŁABUZ A.

*AGH University of Science and Technology, Faculty of Material Science and Ceramics,
Department of Ceramics and Refractories, A. Mickiewicz Av. 30, 30-065 Kraków, Poland*

[#]E-mail: wojtowic@agh.edu.pl

*In the paper we examine some mechanical properties of the unstabilised zirconia sinters, such as Vickers hardness and fracture toughness. The sinters were prepared using two step sintering technique. It is the first time, when two step sintering is used to process unstabilised zirconia nanopowders. As a preparatory experiment, a microstructure evolution of the sinters was determined in order to select the temperatures $T_1$ and $T_2$ of two step sintering. The samples were sintered below the monoclinic to tetragonal transformation temperature, using several $T_1$ and $T_2$ combinations and different sintering times. The sinters were compared in terms of density, grain size, Vickers' hardness and fracture toughness. The samples were sintered to full density, showing a grain size of 95 nm, Vickers hardness of 11 GPa and fracture toughness of 5.32 MPa·m$^{0.5}$.*

## INTRODUCTION

Due to very high thermal and chemical resistivity and mechanical properties, zirconia based polycrystals are the very interesting materials. They are resistant to a majority of acids and bases and have a melting point of 2680°C. Due to the transformation toughening mechanism, fracture toughness of tetragonal zirconia polycrystals (TZP) is supreme in a group of ceramic materials and reaches values as high as 15 MPa·m$^{0.5}$ in case of ceria partially stabilized zirconia [1] or more. This is accompanied by very high values of Weibull modulus exceeding 10 [2]. Zirconia is strongly defected in an anionic sublattice, so it can be used as solid electrolyte in SOFCs (Solid Oxide Fuel Cells). Low thermal conductivity and high chemical resistance are responsible for the usage of fully stabilized zirconias in thermal barrier coatings [3].

Zirconia can exist in 4 different crystallographic structures: monoclinic (up to about 1180°C), tetragonal (from 1180°C to 2400°C), cubic (from 2400°C to the melting point), and high pressure tetragonal (ortho-rhombic), existing under pressures higher than 3 GPa and in Mg-PSZ and Mg-Y-PSZ materials [4]. There is a large difference in densities between monoclinic and tetragonal phases, 5.7 g·cm$^{-3}$ (value based on helium picnometry results) and 6.1 g·cm$^{-3}$, respectively. It is the greatest virtue of this material in the context of transformation toughening, but also the greatest drawback when the transformation is not controlled. The phase transformation from the tetragonal to monoclinic polymorph can be caused by crack propagation: the local increase in the material specific volume can close the crack up, greatly increasing fracture toughness of the material [5]. On the other hand, the density difference of the tetragonal and monoclinic phases makes it very difficult to obtain unstabilised zirconia sinters. Therefore, zirconia is typically stabilized with a number of metal oxides such as ceria, yttria, magnesia or calcia to obtain fully tetragonal (TZP), or cubic (CSZ), sinters with outstanding mechanical or electrical properties.

The stabilized zirconia polycrystals tend to degrade in a process called ageing, in which stabilizing oxide is lost from the material structure in humid environment and at elevated temperatures [6]. This causes the tetragonal to monoclinic phase transformation, resulting in cracking and lowering the mechanical properties of the material. Therefore, there is a need to either develop technologies of stabilized zirconia manufacturing which prevents the degradation process, or to develop an effective sintering method for unstabilised monoclinic zirconia material of acceptable properties.

There were several attempts to produce the unstabilised zirconia sinters. Some of them were successful, and they required complicated sintering schedules, involving different gas atmospheres or vacuum at every stage of sintering (Sense et al.[7], Gareth and Ruth [8]), complex powder preparation methods or expensive equipment, such as hot pressing (Skandan [9]).

he promising approach for nanopowder consolidation has been given by Cheng and Wang [10], which can be applied for unstabilised zirconia nanpowders. It comprises two steps of pressureless heating at carefully selected temperatures to control both densification and grain growth processes, and therefore is called as two step sintering (TSS). In the first step, a sample is continuously heated, until it reaches density of 75 - 90 % of theoretical density [11], and then it is rapidly cooled by several dozen or even more than a hundredth centigrade. The second step comprises sintering at a lowered temperature for an elongated period of time (several to over a dozen hours, in some cases even several dozen hours). The first step is related with rapid densification, during the second step the porosity of the sinter is slowly eliminated to restrain grain growth. The result of the two step sintering is a dense material with the fine microstructure and good mechanical properties, as shown i.a. in our previous publications [12, 13].

In this paper we present the results concerning preparation of dense, unstabilised zirconia sinters by using two step sintering. Some mechanical properties of the sinters are also shown .

This is the first attempt to apply the Cheng and Wang approach of sintering to consolidation of unstabilised zirconia nanopowder.

## EXPERIMENTAL

Zirconia powder used in experiments was composed of 30 % monoclinic and 70 % tetragonal nanoparticles of a mean grain size of 15 nm, and prepared by hydrothermal treatment of hydrous zirconia gel at 240°C for 8 h under 3.3 MPa in a stainless steel autoclave equipped with a PTFE container. The gel was precipitated from a zirconyl chloride solution ($ZrOCl_2 \cdot 8H_2O$ pure) with ammonia (a.p., POCH), and washed with distilled water several times to remove leftovers of ammonia and chlorine ions. No mineralizes or environment modificators were applied to the crystallization process. The morphology of the nanopowder and its phase composition are shown in Figure 1. Sizes of zirconia nanoparticles were derived both from the TEM images (JEM-1011, Jeol) and the XRD pattern (X'Pert plus, PANalitycal).

A lubricant was used to prepare the nanopowder for pressing and it was 10 wt. % water emulsion of F-15 oil delivered by Naftochem. The powder with 2 wt. % of emulsion was uniaxially pressed under 300 MPa into pellets of 6 mm in diameter and about 2 mm in height. The density of green compacts was 50 % of theoretical density, and the pellets were partially translucent. The amount of lubricant added and the forming pressure were selected experimentally, taking as an optimizing criterion the density of the samples calcined at 500°C for 1 h.

Density of the pellets was determined when the samples were heated to 600, 700, 800, 900, 1000, 1100 and 1150°C with a heating rate of 5°C/min) and cooled with the furnace. The geometric method was used. The evolution of crystallite sizes accompanying the temperature increase was determined using the XRD method.

On the basis of the density measurements, the temperatures $T_1$ of 1000°C, 1050°C or 1100°C and $T_2$ of 900°C, 950°C, or 1000°C were selected for the two step sintering. The sintering times were 2 h, 6 h or 10 h, and a heating rate of 5°C/min to $T_1$ was applied. After the sintering, the samples were characterized in terms of densification, and hardness and fracture toughness by using the Archimedes' and Vickers' (Palmqvist crack model [14]) methods, respectively. The grain size was measured by measuring the size of 100 grains in the SEM image on the as received surface of the samples (FEI Nova 200 NanoSEM). The phase composition was determined by the XRD method.
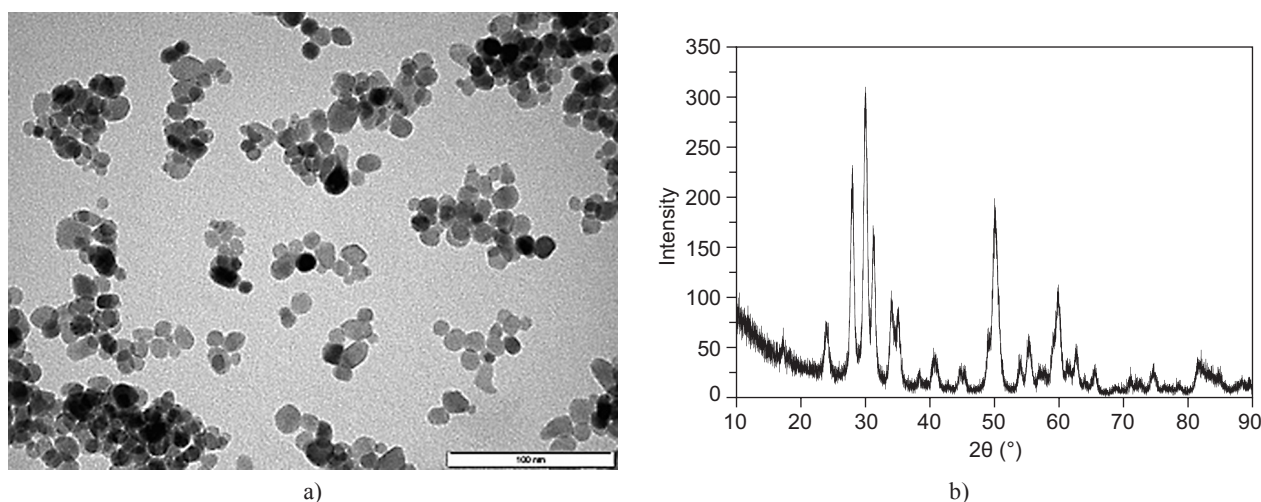


a)



b)

Figure 1.  TEM image (a) and XRD pattern (b) of zirconia nanopowder. The size indicator in corresponds to 100 nm.

## RESULTS AND DISCUSSION

The overall data of the microstructure evolution of green compacts is shown in Table 1. The results of density measurements and the XRD patterns are shown in Figures 2 and 3, respectively. Density, Vickers' hardness and fracture toughness of the two step sintered samples are presented in Table 2.

On the basis of the results of Table 2, the following samples were selected for SEM observations: (i) the sample with the highest fracture toughness (1050°C/950°C/6 h), (ii) sample with the highest hardness (1100°C/1000°C/6 h), (iii) sample with the highest density (1150/1050°C/10 h). SEM images of the as received surface with no grinding and polishing are shown in Figure 4.

The XRD patterns allow us to conclude that, at the temperatures of about 700°C and higher, there is only the monoclinic zirconia polymorph present in the sinters due to crystallite growth. When the crystallite size exceeds some value, which is clearly below 15 nm, the metastable tetragonal grains transform into the stable, monoclinic form. The data of Table 1 and Figure 2 indicate that crystallite growth begins at the temperatures of 500°C or even lower, enabling consolidation of the compacts by sintering. The density measurements of the green compacts and the compacts heated at 500°C (Figure 2) suggest that the volume shrinkage begins at even lower temperatures. The course of the density and crystallite size curves (Figure 2) are very similar up to the point of the offset sintering temperature, which is below 1100°C. At the higher temperature, the samples stop to shrink when crystallites grow further, indicating that crystallite (grain) growth commences to inhibit densification.

Taking into consideration the density measurement results and the literature suggestions [8], the $T_1$ temperature of the two step sintering should be present between 900°C and about 1050°C. First, the $T_1$ temperature of 1050°C and the $T_2$ temperature of 100°C lower than $T_1$ were chosen, and the sintering was conducted for 2 h, 6 h
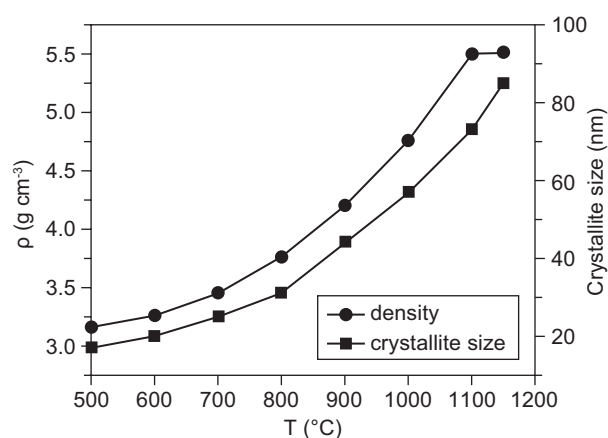


Figure 2. Density and crystallite size of compacts as a function of temperature for heating with constant rate of 5°C/min.

Table 1. Green compacts characteristics as a function of temperature (*m* – monoclinic, *t* – tetragonal).

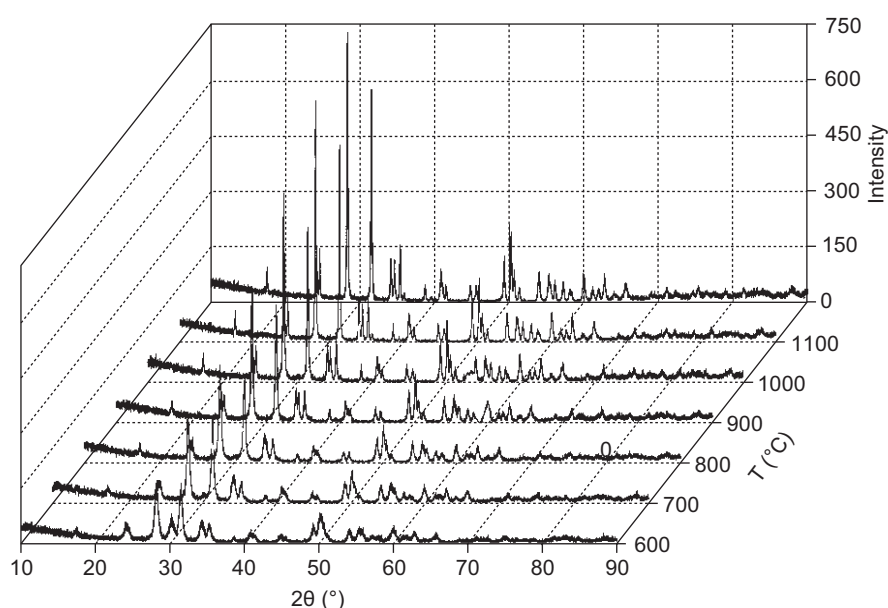| No. | T (°C) | Density (g/cm³) | Phase composition | | Density (%) | Crystallite size (nm) |
|---|---|---|---|---|---|---|
| | | | *m* (wt. %) | *t* (wt. %) | | |
| 1 | 500 | 3.16 | 70 | 30 | 54.57 | 17 |
| 2 | 600 | 3.26 | 80 | 20 | 56.59 | 20 |
| 3 | 700 | 3.45 | 100 | 0 | 60.52 | 27 |
| 4 | 800 | 3.76 | 100 | 0 | 65.96 | 31 |
| 5 | 900 | 4.42 | 100 | 0 | 77.54 | 44 |
| 6 | 1000 | 4.66 | 100 | 0 | 81.75 | 57 |
| 7 | 1100 | 5.50 | 100 | 0 | 96.49 | 73 |
| 8 | 1150 | 5.51 | 100 | 0 | 96.66 | 85 |



Figure 3. XRD patterns of zirconia compacts heated at indicated temperatures.

Table 2.  Density, Vickers' hardness and fracture toughness of samples after two step sintering.

| No. | $T_1$ (°C) | $T_2$ (°C) | t (h) | Density (%) | HV (GPa) | $K_{IC}$ (MPa·m$^{0.5}$) | Grain size (nm) |
|---|---|---|---|---|---|---|---|
| 1 | 1050 | 950 | 2 | 92.67 ± 0.21 | 8.93 ± 0.37 | 2.76 ± 0.33 | – |
| 2 | 1050 | 950 | 6 | 93.25 ± 0.16 | 10.93 ± 0.14 | 5.32 ± 0.12 | 95 ± 11 |
| 3 | 1050 | 950 | 10 | 94.43 ± 0.11 | 9.88 ± 0.27 | 3.67 ± 0.25 | – |
| 4 | 1100 | 1000 | 2 | 96.26 ± 0.05 | 9.86 ± 0.21 | 4.45 ± 0.11 | – |
| 5 | 1100 | 1000 | 6 | 97.32 ± 0.14 | 11.30 ± 0.09 | 4.05 ± 0.21 | 194 ± 25 |
| 6 | 1100 | 1000 | 10 | 97.41 ± 0.23 | 10.64 ± 0.22 | 3.47 ± 0.14 | – |
| 7 | 1150 | 1050 | 2 | 96.31 ± 0.12 | 10.77 ± 0.14 | 4.31 ± 0.10 | – |
| 8 | 1150 | 1050 | 6 | 98.56 ± 0.04 | 10.92 ± 0.25 | 3.48 ± 0.15 | – |
| 9 | 1150 | 1050 | 10 | 100 | 11.10 ± 0.11 | 3.25 ± 0.21 | 215 ± 27 |
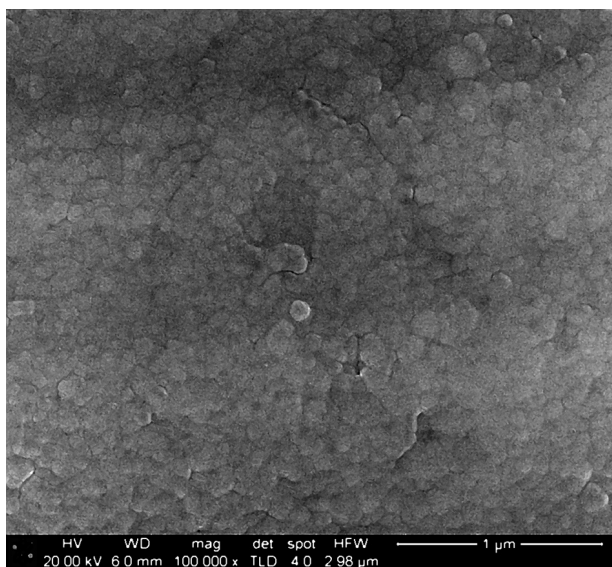


a)
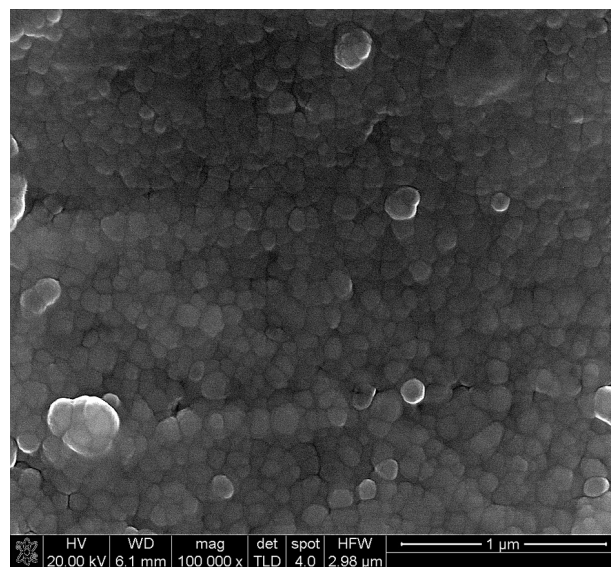


b)
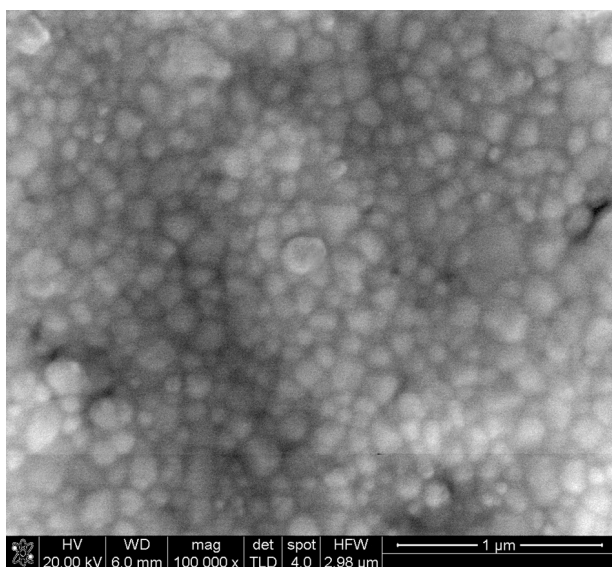


c)

Figure 4.  SEM images of as-received surface of sintered samples: a) 1050°C/950°C/6 h, b) 1100°C/1000°C/6 h, c) 1150/1050°C/10 h.

or 10 h. After that, the $T_1$ and $T_2$ was increased twice by 50°C, leading to the density exceeding in each case the density threshold of 90 % suggested to be reached at $T_1$ [e.g. 8].

All sinters consisted of the pure monoclinic phase as confirmed by XRD measurements. The density values from about 93 % to full density, Vickers' hardness from about 9 GPa to about 11 GPa and fracture toughness from 2.62 MPa·m$^{0.5}$ to over 5.32 MPa·m$^{0.5}$, were measured. The former value of fracture toughness exceeds that reported for alumina sinters (4 - 4.5 MPa·m$^{0.5}$) [12].

Maximum grain size of the monoclinic zirconia sinters does not exceed 250 nm (Table 2), but even in the case of the smallest grain size of 95 nm the grain growth ratio (grain size in sinter divided by powder grain size) is about 6, indicating the fast grain boundary diffusion in temperatures as low as 950°C. It is remarkable, that the best hardness and fracture toughness were reached in the samples sintered at lower temperatures and during shorter times than the samples sintered to full density. The sample sintered at 1050°C/950°C for 6 h showed the Vickers' hardness of close to 11 GPa (which is

comparable with some ytria stabilized zirconia materials, such as NOBORAN), the highest (5.32 MPa·m$^{0.5}$) fracture toughness and the grain size of 95 nm, what makes this sample the best one in terms of mechanical properties, despite of low density of 93 % presented. The sample sintered to the theoretical density was very brittle, second to the least resistant on fracture toughness. All the samples, in that the grain size was measured, had the narrow grain size distribution as shown by a standard deviation of ± 10 % (Table 2). This can be the result of the narrow particle size distribution of the starting zirconia nanopowder and very homogeneous densification of the green samples.

In each series of the two step sintering, the porosity was noticeably removed at $T_2$. This effect was the biggest in the case of the samples sintered at the highest temperatures: the samples sintered for 10 h reached the theoretical density, and the samples sintered for 2 h and 10 h differed in porosity by 3.5 %. In two other series, the effect was similar: the difference between density of the samples sintered for 2 h and 10 h in both cases was about 1.5 %. Therefore, the samples sintered at lower $T_1$ and $T_2$ temperatures should be sintered at $T_2$ for even longer times to enable higher densification without further grain growth. It is remarkable, that the combination of good hardness and fracture toughness is achieved during the middle sintering time of 6 h. Concerning above, to improve both hardness and fracture toughness, the samples should be sintered at $T_2$ lower than 950°C for the period of time longer than 10 h.

## CONCLUSIONS

The two step sintering technique can be successfully used for processing of unstabilised zirconia nanopowders. In the experiment presented, full densification was achieved in the case of zirconia sample sintered at $T_1$ higher than suggested in literature: the density of the $T_1$ sintered samples was larger than 90 %. This indicates that the density range of (75 - 90) %, which should be reached at $T_1$, is either necessary to reconsider, or is not appropriate in all cases. However, the samples of unstabilised zirconia nanopowder sintered at $T_1$, in which samples reached the density from the range suggested in the literature, have the best combination of mechanical properties. It is clear that the proper selection of both $T_1$ and $T_2$ sintering temperatures and time of the sintering has great influence on properties of the unstabilised zirconia consolidated using the two step sintering technique, but such a selection is difficult and depends on the properties of green sample.

Despite the fact that some zirconia samples has reached the full density, the best fracture toughness and Vickers' hardness are obtainable in the case of materials of lower densities. The highest fracture toughness, which is higher than fractures toughness of typical alumina, is probably related to the combination of small grain size and porosity, but the toughening mechanism has not been examined. Probably, further increase of the above-mentioned mechanical properties, especially fracture toughness, is possible by using two step sintering in lower temperatures to ensure the presence of a fraction of tetragonal zirconia grains and hot isostatic pressing (HIP) of the resultant sinters.

## REFERENCES

1. Sharma S.C, Gokhale N.M., Dayal R., Lal, R.: Bull. Mater. Sci. 25, 1 (2002).
2. Stawarczyk B., Ozcan M., Trottmann A., Hammerle C.H., Roos M..: J. Mech. Behav. Biomed. Mater. 10, 34 (2012).
3. Troczynski T., Cockcroft S., Wong H.: Adv. Cer. Mat. 122 (1996).
4. Haberko K., Pyda W., Muraś M., Bućko M.M.: Ceramica Acta 168 (1989).
5. Garvie R.C., Hannik R.H., Pascoe R.T.: Nature (London) 258 (1975).
6. Kobayashi K., Kuwajima H., Masaki T.: Solid State Ionics 3/4 (1981).
7. Sense K.: J. of Am. Cer. Soc. 44, 465 (1961).
8. Garret H., Ruth R.: Am. Cer. Soc. Bull. 47, 578 (1965).
9. Skandan G.: Nanostr. Mat. 5, 2 (1995).
10. Chen I.W., Wang X.H.: Nature 2000, 404 (2000).
11. Maca K., Pouchly V., Zalud P.: J. Eur. Ceram. Soc. 30 (2010).
12. Wójtowicz B., Pyda W.: Composites: theory and practice 12, 2 (2012) .
13. Wójtowicz B., Pyda W.: Ceramic Materials 63, 4 (2011).
14. Niihara K.: J. Mater. Lett. 2, 221 (1983).