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PREPARATION OF POROUS CERAMIC MATERIALS BASED ON $CaZrO_3$

PRIPRAVA POROZNE KERAMIKE NA OSNOVI $CaZrO_3$

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The present study was devoted to an investigation of the synthesis conditions and the influence of Sn ions on the production of a $CaZrO_3$ porous structure. Porous ceramics based on $CaZrO_3$ with a SnO addition were prepared by means of pressureless sintering. The study presents the influence of the type of the starting materials and the firing procedures on the microstructures of the $CaZrO_3$ materials. Two different firing procedures were applied. The samples were obtained from pure chemical reagents $CaCO_3$ or CaO and ZrO_2. SnO was added in the mass fraction of 2 %. The prepared materials were investigated in terms of phase composition with the XRD. The microstructure was analyzed using the SEM/EDS and mercury porosimetry methods. It was found that using $CaCO_3$ in a one-step firing process at 1650 °C with a soaking time of 10 h allowed us to obtain porous zirconate ceramics with a porosity of about 44 %. The second synthesis, where CaO was used, allowed us to obtain a porosity of about 36 %. During the firing solid solutions containing Sn ions in $CaZrO_3$ and ZrO_2 were formed. No other compounds containing Sn ions were identified. It was found that these ions played a significant role in the formation of a stable porous microstructure. The final materials mainly consisted of $CaZrO_3$ and a small amount of ZrO_2. The obtained porous $CaZrO_3$ materials with an excellent oxidation and alkali resistance in a wide temperature range could be potential candidates for the use as membranes and filters.

Keywords: calcium zirconate, porous ceramics, solid solution

Ta študija je namenjena preiskavi razmer pri sintezi in vplivu ionov Sn na izdelavo porozne strukture $CaZrO_3$. Porozna keramika na osnovi $CaZrO_3$ z dodatkom SnO je bila pripravljena s sintranjem brez tlaka. Študija predstavlja vpliv vrste izhodnega materiala in procesa žganja na mikrostrukturo materiala $CaZrO_3$. Uporabljena sta bila dva načina žganja. Vzorci so bili izdelani iz čistih kemijskih sestavin $CaCO_3$ ali CaO in ZrO_2. Masni delež dodanega SnO je bil w = 2 %. Fazna sestava pripravljenega materiala je bila analizirana z rentgensko difrakcijo. Mikrostruktura je bila analizirana s SEM/EDS in s porozimetrijo z živim srebrom. Ugotovljeno je, da uporaba $CaCO_3$ v enostopenjskem postopku žarjenja 10 h na 1650 °C omogoča pridobitev porozne cirkonske keramike s poroznostjo okrog 44 %. Druga sinteza, kjer je bil uporabljen CaO, omogoča doseganje poroznosti okrog 36 %. Med žganjem je nastala trdna raztopina, ki je vsebovala ione Sn v $CaZrO_3$ in v ZrO_2. Ni bila ugotovljena nobena druga sestavina, ki bi vsebovala ione Sn. Navedeno je, da ti ioni igrajo pomembno vlogo pri nastanku stabilne porozne mikrostrukture. Končni materiali so vsebovali pretežno $CaZrO_3$ in majhno količino ZrO_2. Dobljen porozni keramični $CaZrO_3$-material z odlično odpornostjo proti oksidaciji in alkalijam v širokem temperaturnem intervalu je lahko potencialni kandidat za uporabo v obliki membrane in filtrov.

Ključne besede: kalcijev cirkonat, porozne keramike, trdna raztopina

1 INTRODUCTION

Zirconate materials with a perovskite structure are interesting for many engineering fields, especially for high-temperature structural applications. Due to their characteristics they can be applied in the sensors, mechanical filters or coatings used at high temperatures and in corrosive environments. It is interesting to obtain porous materials based on calcium zirconate ($CaZrO_3$).

The synthesis conditions and properties of $CaZrO_3$ can be modiefied with an addition of selected ions, such as scandium, indium, gallium, yttrium, aluminum, magnesium, etc. $CaZrO_3$ doped with Al_2O_3, Y_2O_3 and MgO is an oxygen-ion conductor. Undoped $CaZrO_3$ is a p-type semiconductor used at low temperatures (< 1200 °C). Moreover, trivalent cations, e.g., indium, scandium, gallium change the conduct of $CaZrO_3$ and in this state it acts as a proton conductor.[1–6]

Suzuki et al.[7] investigated porous, In-doped $CaZrO_3$/MgO composites with respect to the CH_4-sensitivity in air. The samples were prepared from a high-purity natural dolomite, ZrO_2, In_2O_3 and LiF. To obtain porous composites the samples were sintered in air at 1300 °C. It was found that the porous composite, consisting of $CaZrO_3$, MgO and $CaIn_2O_4$ (amount fraction x = 10 % of In_2O_3), was characterized by the porosity of 57 %. A higher porosity (60 %) of the samples was obtained with an addition of x = 5 % of In_2O_3; these samples were composed only of the $CaZrO_3$ and MgO phases. The In-doping decreased the CH_4-sensitivity in argon, but it was effective at improving the CH_4-sensitivity in air.[7] The $CaZrO_3$/MgO composites without In obtained with the one-step heat treatment were also characterized by a high porosity of 30–50 % which depended on the sintering temperature.[8]

The method of preparing the MgO-$CaZrO_3$-β-Ca_2SiO_4 porous materials with an interconnected porosity and a controlled size in the range of micrometers was presented in[9]. Dolomite-zirconia mixtures were used to obtain porous materials for refractory applications. The samples were fired in the temperature range from 800 °C to 1740 °C. After the final sintering at 1740 °C the porosity was at a significant level due to the decarbonization process associated with the loss of CO_2.[9]

Individual properties of $CaZrO_3$ and SnO_2 may lead to an assumption that the Sn-doped $CaZrO_3$ has a stable porous structure. Therefore, it is interesting to study the synthesis process, the influence of the Sn ions on it and the structure of $CaZrO_3$ ceramics.

2 EXPERIMENTAL WORK

$CaZrO_3$ porous ceramics were prepared by means of a conventional solid-state reaction method. Calcium carbonate ($CaCO_3$), zirconium dioxide (ZrO_2) and tin oxide (SnO) were used as the starting raw materials. The characteristics of the starting raw materials are presented in **Table 1**. The firing was carried out in two ways: $CaCO_3$ was used with the first firing method (designation: ICZSn) and CaO was used with the second one (designation IICZSn). The compositions of the materials were designed taking into account the $CaCO_3$ or CaO to ZrO_2 ratio corresponding to the $CaZrO_3$ stoichiometry. SnO was added in the mass fraction of 2 %. The oxides were mixed together for 2 h. The homogenized mixtures were pressed into pellets (a diameter 20 mm, a thickness 10 mm) at a pressure of 70 MPa. The synthesis of the two series of the samples was carried out with pressureless sintering as shown in **Figure 1**. The pellets were heated up to 1650 °C with different hating rates, held at this temperature for 10 h and then cooled down in the furnace. Because $CaCO_3$ was used in the first firing, the samples were heated at two different heating rates: 2 °C/min up to 1000 °C and 5 °C/min up to the final temperature.

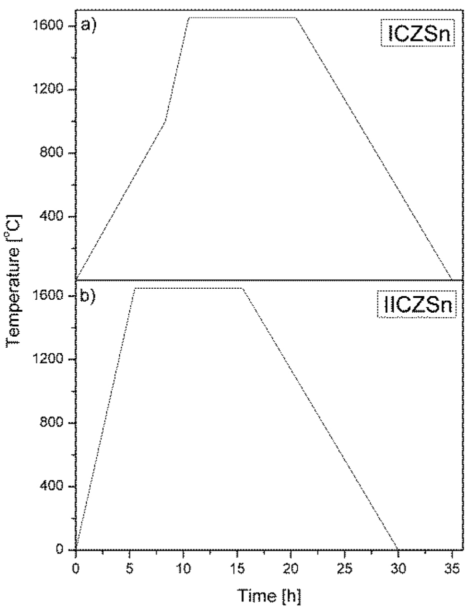

Figure 1: Firing curves: a) ICZSn, b) IICZSn
Slika 1: Krivulje žganja: a) ICZSn, b) IICZSn

Table 1: Specification of the starting materials
Tabela 1: Pregled izhodnih materialov

	Reagents		
	$CaCO_3$ (POCH)	ZrO_2 (Acros Organics)	SnO (Aldrich Chemistry)
Pure (%)	98.5	98.5	97
Median particle size (μm)	41.83	4.53	23.66

The phase composition of the sintered samples was examined using the powder X-ray diffraction (XRD) technique at room temperature. The measurements were performed with a Panalytical X'Pert-Pro diffractometer using Cu-$K\alpha$ radiation at a 2θ angle ranging from 10 ° to 90 °. The obtained data were analyzed using the X'Pert Pro Highscore Plus software. The open porosity of the sintered samples was measured using the water-displacement method based on Archimedes' principle. The pore-size distribution was analyzed with the mercury-intrusion method (Porosimeter PoreMaster 60, Quantachrome Instruments). A cylindrical-pore model was used for the calculation. The changes in the microstructure of the products were discussed on the basis of SEM observations (NovaNanoSem 200) accompanied by an EDS chemical analysis of micro-areas.

3 RESULTS AND DISCUSSION

Figure 2 shows the XRD analysis of the samples. The X-ray diffraction patterns of ICZSn and IICZSn indicated that $CaZrO_3$ in the amounts of 95 % and 99 %, respectively, was the main phase. Cubic ZrO_2 stabilized with calcium oxide (4 %) and monoclinic ZrO_2 (1 %) were identified in ICZSn. Furthermore, when CaO was used as the starting material (IICZSn) only cubic ZrO_2 (1 %) was determined. No phases containing tin were identified. This may indicate that the SnO_2-ZrO_2 solid solution was created in accordance with reference[10]. An effective ionic radius of Sn^{4+} (0.069 nm) is close to Zr^{4+} (0.072 nm) and considerably lower than Ca^{2+} (0.112 nm).[11]

It is worth mentioning that, in the Sn-O system, tin oxide is present in various forms, such as SnO, SnO_2, Sn_2O_3, Sn_3O_4 and Sn_5O_6. Only SnO and SnO_2 are stable. Above 270 °C, SnO decomposes into Sn_3O_4 and metallic tin in accordance with Equation (1):

$$4SnO \rightarrow Sn_3O_4 + Sn(l) \tag{1}$$

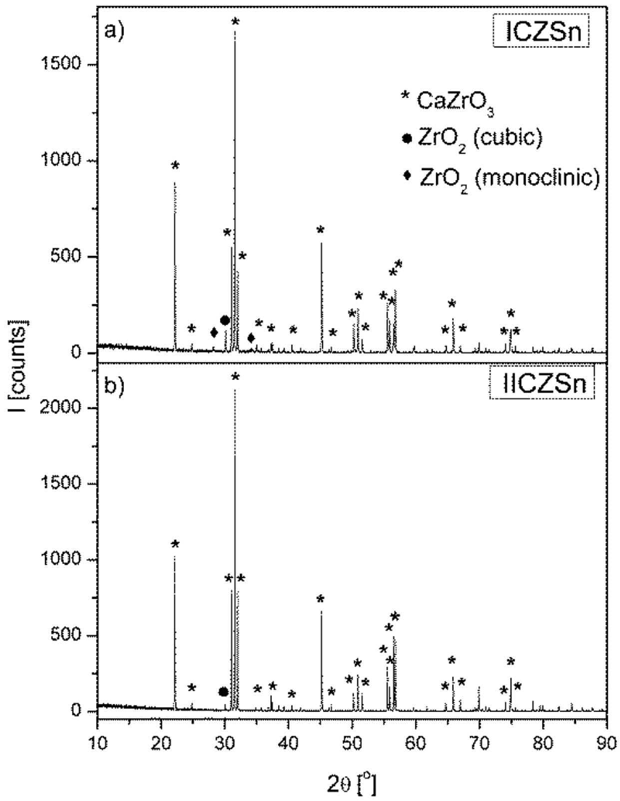

Figure 2: X-ray diffraction patterns of the samples prepared with a solid-state reaction: a) ICZSn, b) IICZSn
Slika 2: Rentgenski difrakcijski posnetek vzorcev, pripravljenih z reakcijo v trdnem: a) ICZSn, b) IICZSn

Above 450 °C Sn_3O_4 melts incongruently into Sn and SnO_2.[12,13]

The SEM micrographs of the samples are presented in **Figures 3** to **6**. The chemical compositions of the samples were confirmed with the EDS measurements (**Tables 2** and **3**). These allowed us to identify the most probable phase compositions of individual grains, $CaZrO_3$ (dark grey grains – point 1) and ZrO_2 (light grey phase – point 2). **Figures 4** and **6** present different forms of ZrO_2. In ICZSn, ZrO_2 created clearly identifiable

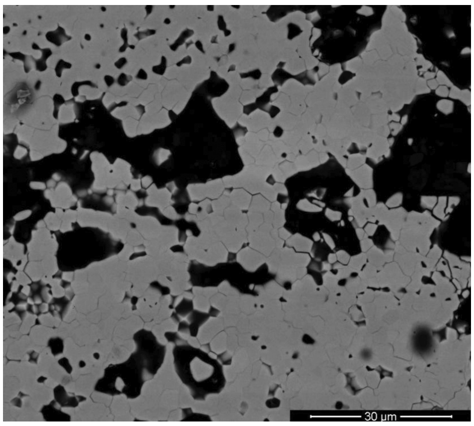

Figure 3: SEM micrograph of the ICZSn microstructure
Slika 3: SEM-posnetek mikrostrukture ICZSn

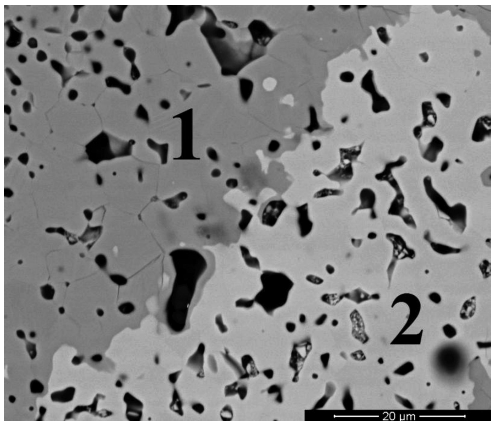

Figure 4: SEM micrograph of the ICZSn sample with marked points where the EDS analysis was performed
Slika 4: SEM-posnetek mikrostrukture vzorca ICZSn z označenima točkama, kjer je bila izvršena EDS-analiza

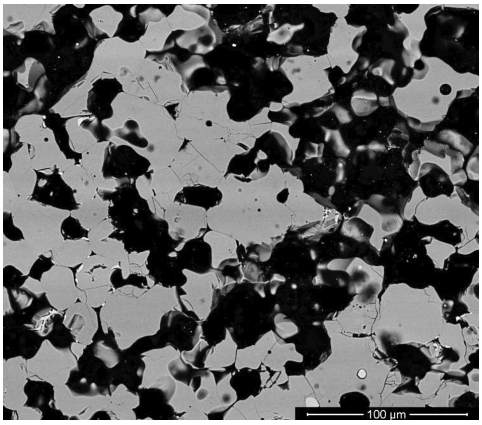

Figure 5: SEM micrograph of the IICZSn microstructure
Slika 5: SEM-posnetek mikrostrukture IICZSn

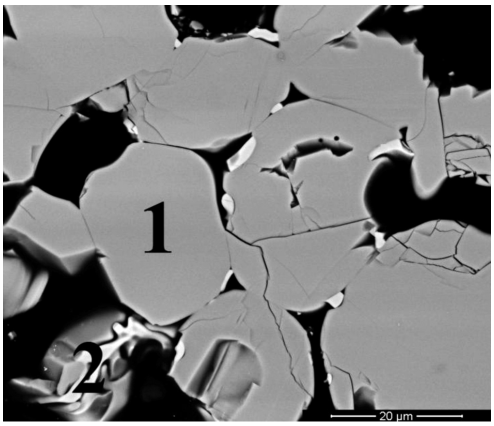

Figure 6: SEM micrograph of the IICZSn sample with marked points where the EDS analysis was performed
Slika 6: SEM-posnetek mikrostrukture vzorca IICZSn z označenima točkama, kjer je bila izvršena EDS-analiza

areas. In IICZSn, ZrO_2 occurred as individual inclusions. This can be explained with a higher concentration of ZrO_2 in the ICZSn samples (5 %). Furthermore, it can be established that the Sn ions incorporated in $CaZrO_3$ and

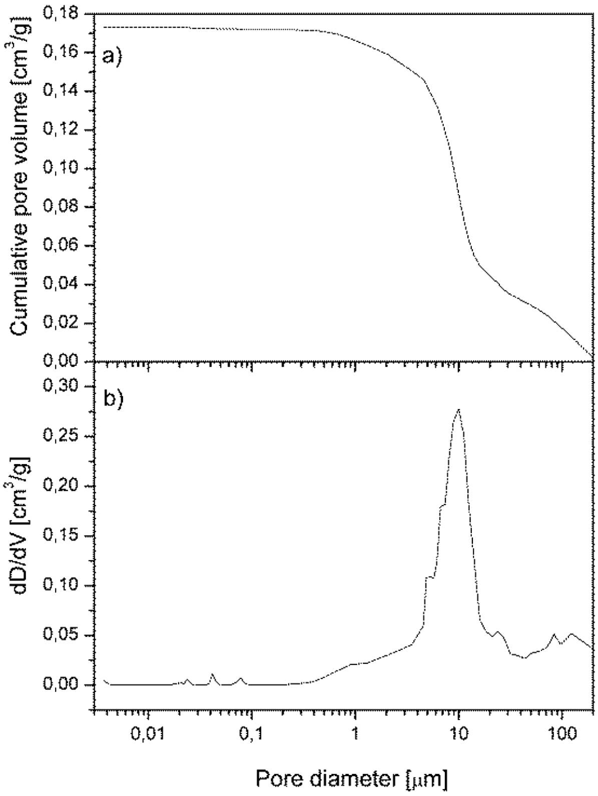

Figure 7: a) Cumulative pore-volume changes and b) pore-size distribution (pore-frequency curve) of the ICZSn sample
Slika 7: a) Kumulativna sprememba volumna por in b) razporeditev velikosti por (krivulja frekvence por) vzorca ICZSn

ZrO_2 are in different amounts. The SEM/EDS investigations confirmed the results of the XRD analysis. The average diameter of the $CaZrO_3$ grains changed from about 5–15 μm for ICZSn to 50 for IICZSn. The grain growth was associated with the type of the used raw material ($CaCO_3$-ICZSn or CaO-IICZSn). Moreover, when only small amounts of ZrO_2 were observed in the samples (IICZSn – 1 %) the Sn ions were incorporated into the $CaZrO_3$ structure.

Table 2: Average chemical compositions (EDS) of $CaZrO_3$ and ZrO_2 grains according to **Figure 4**
Tabela 2: Povprečna kemijska sestava (EDS) $CaZrO_3$ in ZrO_2 zrn, skladno s **sliko 4**

Point	Amount fraction, *x*(ICZSn)/%			
	O	Zr	Sn	Ca
1	53.9	23.8	0.4	21.9
2	57.9	33.6	0.7	7.8

Table 3: Average chemical compositions (EDS) of $CaZrO_3$ and ZrO_2 grains according to **Figure 6**
Tabela 3: Povprečna kemijska sestava (EDS) $CaZrO_3$ in ZrO_2 zrn, skladno s **sliko 6**

Point	Amount fraction, *x*(IICZSn)/%			
	O	Zr	Sn	Ca
1	51.1	24.5	0.9	23.5
2	62.2	29.9	0.2	7.7

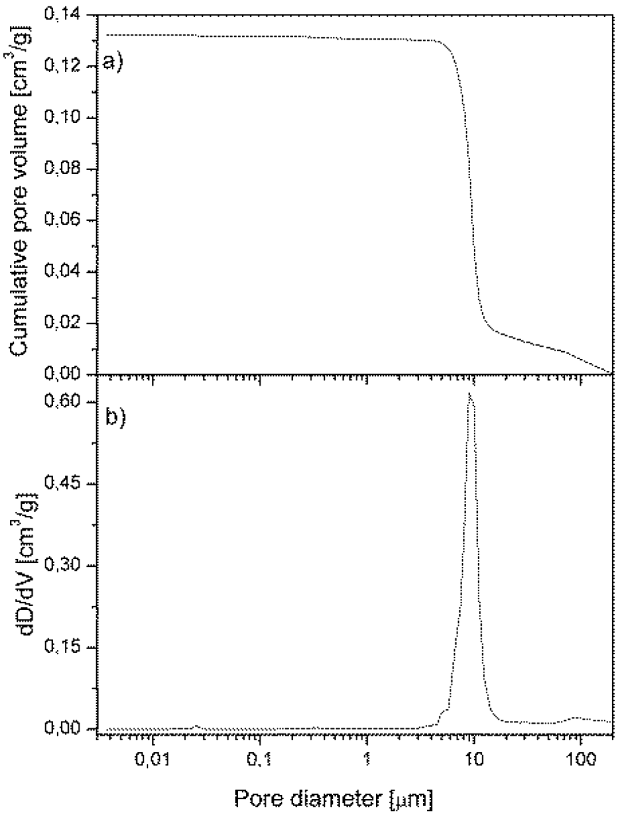

Figure 8: a) Cumulative pore-volume changes and b) pore-size distribution (pore-frequency curve) of the IICZSn sample
Slika 8: a) Kumulativna sprememba volumna por in b) razporeditev velikosti por (krivulja frekvence por) vzorca IICZSn

Table 4: Properties of ICZSn and IICZSn materials determined with mercury porosimetry
Tabela 4: Lastnosti materialov ICZSn in IICZSn, določene s porozimetrijo z živim srebrom

	Cumulative pore volume mm^3/g	Median pore diameter μm	Bulk density g/cm^3	Porosity %
ICZSn	173.6	10	2.49	43.2
IICZSn	132.3	9	2.84	37.6

The total pore volume and the median pore diameter of the samples analyzed with the mercury-intrusion method are shown in **Figures 7** and **8** and summarized in **Table 4**. The figures show slightly different types of curves but having the same mean pore size. The ICZSn sample (**Figure 7**) was characterized by one main pore population of about 10 μm in diameter. Two other populations were also distinctly detectable: of less than 0.1 μm and of about 100 μm. In contrast, the IICZSn sample had a very narrow pore-size distribution with the mean size of 9 μm (**Figure 8**). This proved that, in this case, the pores were more uniform and monomodal. This difference may have resulted from the $CaCO_3$ decarbonization which occurred, as generally known, in the 600–950 °C temperature range. During the heating,

$CaCO_3$ decomposed into CaO (solid) and CO_2 (gas) according to Equation (2). The formed CaO reacted with ZrO_2 creating $CaZrO_3$.

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \tag{2}$$

The porosity measured in accordance with Archimedes' principle varied from 44 % to 35 % for ICZSn and IICZSn, respectively, being in good agreement with the results of the mercury-intrusion analysis.

These porous materials, being comprised of $CaZrO_3$ and a small amount of ZrO_2 have an excellent oxidation and alkali resistance in a wide temperature range. The presented materials can be used as filters, membranes and insulation materials. Moreover, an incorporation of Sn ions in the $CaZrO_3$ and ZrO_2 structure can lead to obtaining unique electrical properties.

4 CONCLUSIONS

The article focuses on porous $CaZrO_3$ materials with SnO additions. The presented results describe the influence of the starting raw materials and the firing procedure on the final properties of the $CaZrO_3$ ceramics. It is shown that using $CaCO_3$, in comparison with CaO, allowed us to obtain a material with the porosity exceeding 40 %. A porous structure can be controlled by the synthesis conditions.

During the firing solid solutions containing Sn ions were formed in $CaZrO_3$ and ZrO_2. The final materials ICZSn and IICZSn were composed of about 95 % and 99 % of $CaZrO_3$, respectively, and ZrO_2. No free CaO or Sn-containing inclusions (expect for the $CaZrO_3$ solid solution) were detected with the performed XRD and SEM/EDS analyses. Porous $CaZrO_3$ materials could be potential candidates for the use as membranes and filters. Moreover, a $CaZrO_3$ structure with incorporated Sn ions can reveal unique electrical properties.

Acknowledgement

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