THE INFLUENCE OF PREPARATION TECHNOLOGY ON LUMINESCENCE PROPERTIES OF Y-TZP AND $ZrSiO_4$ CERAMICS

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The photoluminescence spectra of the $ZrSiO_4$ and 3Y-TZP ceramics excited by laser irradiation with the wavelength of 325 nm are presented. The phase composition of the ceramics is determined by using X-ray diffraction measurements. The spectra are recorded in visible region at the room temperature. The shape of the blue-green emission spectra depends on technological parameters, such as the applied pressure and the sintering temperature.

INTRODUCTION

Zirconia toughened ceramics induced a great commercial success due to their high ionic conductivity [1, 2], fracture toughness [3], hardness [3], compressive strength and wear-resistance. Due to its availability and reasonable price, the zircon ($ZrSiO_4$) raw material serves usually for a preparation of zirconia (ZrO_2) powders. As luminescence methods are rarely used for investigating physical properties of ceramics, the published information on the emission of ZrO_2 or $ZrSiO_4$ ceramics is not particularly extensive. Besides, the published data on the emission of zirconia ceramics report different results depending on the purity and mechanical straining of the material. A particular attention is paid to the influence of the excitation wavelength on the luminescence of the monoclinic, tetragonal and cubic zirconia [4 - 11].

In this paper the influence of preparation conditions on luminescence properties of both yttria doped tetragonal zirconia ceramics (Y-TZP) and $ZrSiO_4$ ceramics is investigated. The influence of the sintering temperature and applied compacting pressure on the photoluminescence spectra is studied. In order to identify centers of the luminescence, the phase composition of all ceramics has been examined.

EXPERIMENTAL PART

Powders for preparation of zirconia ceramics were produced by coprecipitation. The calculated amounts of $ZrOCl_2$ and YCl_3 were dissolved in water. The $ZrOCl_2$ doped with YCl_3 or the synthetic $ZrSiO_4$ were coagulated by aqueous ammonia. The coagulate was washed until the absence of Cl^- ions was proved. Then the coagulate was dried in air and calcinated at the temperature of 650 °C. The compacts, in the form of tablets of 5 mm in diameter and 3-4 mm in thickness, were prepared either from the $ZrSiO_4$ ball-milled powder or from the fine 3Y-TZP (tetragonal zirconia polycrystals stabilized with 3 mol% Y_2O_3) ball-milled powder by pressing in the Zeiss-Jena oil press. The ball-milling time ranged from 2 to 6 hours. The compacting pressure ranging from 50 MPa to 175 MPa was applied for several seconds. Then, the compacts were sintered in air, at temperatures from 1000 °C to 1400 °C for 2 to 6 hours in an electric furnace. The temperature was measured by a Pt-PtRh thermocouple and stabilized with the accuracy of ±2 °C. Below 700 °C , the heating rate was 12 °C min^{-1}. Above 700 °C, the heating rate was decreasing with increasing temperature down to 5 °C min^{-1}. After the sintering, a free cooling of samples ($\approx$1.5 °C min^{-1}) to the room temperature followed.

The luminescence of $ZrSiO_4$ ceramics was excited by He-Cd laser radiation with a wavelength of 325 nm through a WG1 filter at room temperature. The luminescence of 3Y-TZP ceramics was excited both with the laser through a WG1 filter and with the mercury discharge lamp HBO through a UG 5 filter (λ = 365 nm). The photoluminescence radiation was recorded by a computer-controlled gridding spectrophotometer PG S-2 with a No 45993 grid containing 651 nickings per mm. For both $ZrSiO_4$ and Y-TZP prepared under various conditions, the spectra recorded in the visible range are given in figures 1 - 4.

The phase analysis of selected samples was done by using the method of X-ray diffraction analysis by the Zeiss HZG-4 diffractometer applying CuK_α radiation (λ = 0.15418 nm) while the K_β component was filtered off by a Ni filter. The radiation was measured by a scintillation detector, in a 2 angle interval ranging from

18 deg. to 77 deg. with a shift speed of 2 deg min^{-1}. The diffraction records are given in figures 5 *a*, *b*. In Table 1 and 2, the corresponding indexing is shown. The last column of the tables shows the ratio (%) of a particular maximum intensity to the highest maximum intensity.

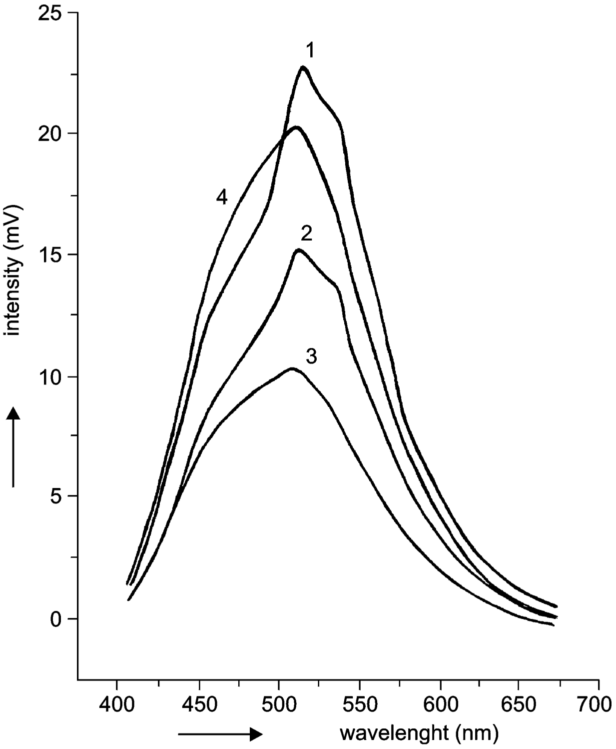

Figure 1. Influence of the applied pressure on the luminescent spectra of $ZrSiO_4$ ceramics.
1 – 50 MPa, 2 – 91 MPa, 3 – 125 MPa, 4 – 175 MPa. The sintering temperature is 1300 °C. The sintering time is 3 hours.

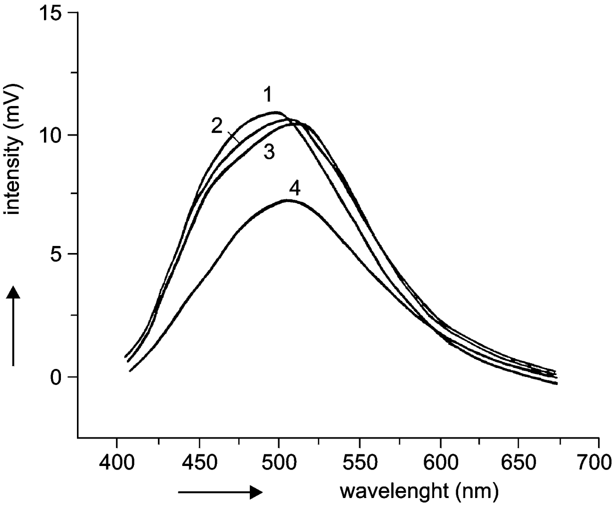

Figure 2. Influence of the firing temperature on the luminescent spectra of $ZrSiO_4$ ceramics.
1 – 1000 °C, 2 – 1200 °C, 3 – 1300 °C, 4 – 1400 °C. The applied pressure is 125 MPa. The sintering time is 3 hours.

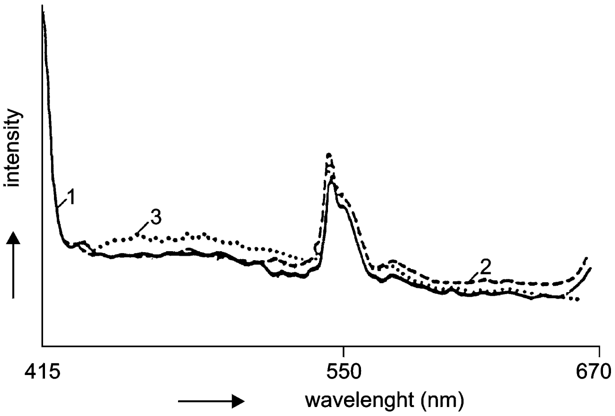

Figure 3. Influence of the applied pressure on the luminescent spectra of 3Y-TZP ceramics.
1 – 91 MPa, 2 – 121 MPa, 3 – 175 MPa. The sintering temperature is 1400 °C. The sintering time is 3 hours.

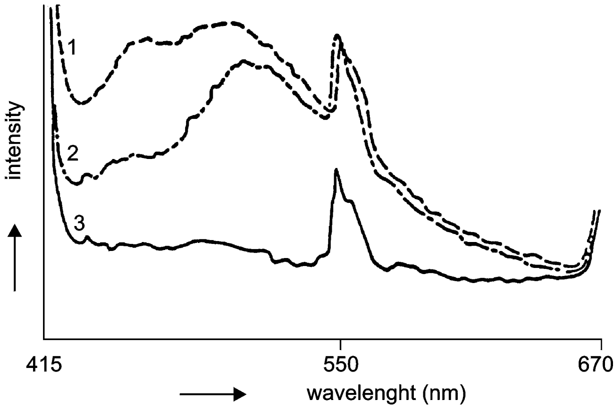

Figure 4. Influence of the firing temperature on the luminescent spectra of 3Y-TZP ceramics.
1 – 1200 °C, 2 – 1300 °C, 3 – 1400 °C. The applied pressure is 125 MPa. The sintering time is 3 hours.

Table 1. X-ray powder diffraction data for $ZrSiO_4$ ceramics.

Hkl	d_{exp} (nm)	d_{theor} (nm)	I / I_0	d^* (nm)
101	0.4462	0.4401	31	0.434
200	0.3314	0.3307	100	0.330
211	0.2675	0.2652	8	0.2650
220	0.23383	0.23381	17	0.2336
202	0.22168	0.22200	10	0.2217
301	0.20668	0.20688	33	0.2066
103	0.19141	0.19118	22	0.1908
321	0.17523	0.17538	22	0.1751
312	0.17827	0.17147	90	0.1712
400	0.16502	0.16533	32	0.1651
411	0.15655	0.15494	7	0.1547
004	0.14968	0.14978	6	0.1495
420	0.14775	0.14787	22	0.1477
332	0.13822	0.13827	30	0.1381
204	0.13645	0.13644	18	0.1362
501, 431	0.12915	0.12915	8	0.1290
224	0.12620	0.12612	15	0.1259
413	0.12494	0.12505	4	0.1245

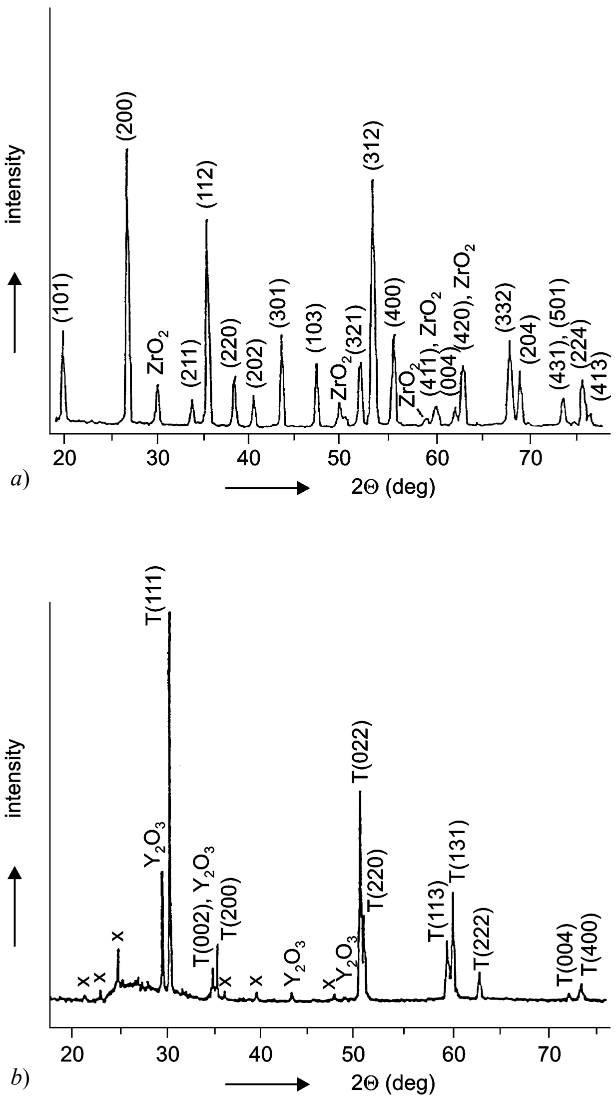

Figure 5. X-ray diffraction patterns of *a*) $ZrSiO_4$ ceramics. The firing temperature is 1300 °C. The applied pressure of 50 MPa, *b*) 3Y-TZP ceramics. The firing temperature is 1400 °C. The applied pressure is 91 MPa.

Table 2. X-ray powder diffraction data for 3Y-TZP ceramics.

Hkl	d_{exp} (nm)	d_{theor} (nm)	I / I_0	d* (nm)
111	0.2979	0.2976	100	0.2949
002	0.2607	0.2603	10	0.2584
200	0.2498	0.2565	15	0.2542
202	0.18241	0.18272	50	0.1804
220	0.18106	0.18138	20	0.1771
113	0.15619	0.15656	15	0.1551
311	0.15441	0.15489	30	0.1535
222	0.14839	0.14882	6	0.1471
004	0.12976	0.13017	3	0.1291
400	0.12780	0.12826	5	0.1270

RESULTS AND DISCUSSION

The measurement of the photoluminescence spectra has shown that all examined ceramic samples exhibit an emission in the blue-green range of the spectrum. Both the form and the intensity of the spectrum are functions of the composition and of technological parameters of samples. In the range of 400 to 600 nm, the intensity of the spectrum changes with the compacting pressure and sintering temperature. However, a systematic dependence of the intensity on both parameters has not been observed. In $ZrSiO_4$ ceramics, the sintering temperature influences the structure of the observed broad band only slightly in the temperature range of 1000 °C - 1300 °C (figure 2). The minimum intensity of the photoluminescence is observed for samples compacted with a pressure of 125 MPa. A different influence (figure 3) of the sintering temperature on the photoluminescence spectra was observed for the Y-TZP ceramics at an applied pressure of 125 MPa and a sintering temperature ranging from 1200 °C to 1400 °C . After sintering at 1400 °C, the 3Y-TZP ceramics show only the characteristic emission peak near 540 nm and the emission spectrum is rather independent of the applied compacting pressure (figure 4). The independence of the luminescence spectra both of the compacting pressure and of the time of sintering (3 – 6 hours) results probably from the full stabilization of the tetragonal zirconia phase at this temperature (1400 °C).

The diffraction measurements show that both investigated materials crystallize in the tetragonal system. The corresponding indexing is shown in tables 1 and 2. The values of lattice parameters of both $ZrSiO_4$ ceramics, $a = b = 0.661(2)$ nm, $c = 0.599(2)$ nm, and 3Y-TZP ceramics, $a = b = 0.513(1)$ nm, $c = 0.520(1)$ nm, correspond to the published data [12,13]. The investigated $ZrSiO_4$ ceramics contain besides the $ZrSiO_4$ phase also some traces of the cubic ZrO_2 phase and probably also of the SiO_2 phase. However, the peaks of SiO_2 are superimposed on the more intensive $ZrSiO_4$ peaks. The 3Y-TZP ceramic is fully stabilized in the tetragonal phase. Both lattice parameters and phase compositions of the ceramics are independent of the compacting pressure and sintering temperature.

Minimum porosity was obtained for a ball-milling time of 4 hours with a ball diameter of 10 mm, applied pressure of 125 MPa and sintering temperature of 1400 °C for 3 hours. At these conditions, the experimental density of both types of ceramics is equal to 98-99 % of the theoretical density (5.943 g cm^{-3} for 3Y-TZP ceramics and 4.646 g cm^{-3} for $ZrSiO_4$ ceramics).

CONCLUSIONS

Both the investigated samples of the $ZrSiO_4$ and Y-TZP ceramics and the zirconia toughened ceramics examined recently [8-11] exhibit a blue-green luminescence in the range of 400 nm to 600 nm.

Because the blue-green luminescence does not depend on the stabilizing oxide in zirconia ceramics [10] and appears also in $ZrSiO_4$ ceramics, both the emission spectrum of the $ZrSiO_4$ ceramics and that of the TZP ceramics probably result from the luminescence of Zr^{4+} ions in an asymmetric (tetragonal) oxygen surrounding. The influence of technological parameters (the compacting pressure and sintering temperature) is manifested in a change of the intensity of the emission band and in a change of its structure. Both the lattice parameters and phase composition of the ceramics are independent of the applied pressure and sintering temperature. After a sintering at 1400 °C, the emission spectrum of the 3Y-TZP ceramics is independent of the applied pressure and of the sintering time. A full stabilization of the tetragonal zirconia phase at this temperature after 3 hours is therefore supposed. As to obtain a stable blue-green luminescence in $ZrSiO_4$ ceramics the compacting pressure of 125 MPa and the sintering temperature of 1300 °C are recommended. After a sintering at 1400 °C, the experimental density of both types of ceramics is equal to 98-99 % of the theoretical density.

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VPLYV TECHNOLÓGIE PRÍPRAVY NA LUMINISCENČNÉ VLASTNOSTI Y-TZP A $ZrSiO_4$ KERAMÍK

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Práca sa zaoberá vplyvom lisovacieho tlaku a teploty výpalu na fotoluminiscenčné spektrá a fázové zloženie tetragonálnych zirkoničitých keramík dopovaných s 3 mol.% Y_2O_3 (3Y-TZP) a zirkónových ($ZrSiO_4$) keramík. Transformačne spevnené zirkoničité keramiky sú technicky významné svojou vysokou húževnatosťou, tvrdosťou, pevnosťou v tlaku, oteruvzdornosťou a vysokoteplotnou superiónovou vodivosťou. Pre svoju dostupnosť a rozumnú cenu zirkón sa často používa ako surovina na prípravu ZrO_2 práškov a na výrobu zirkoničitých keramík.

Prášky komponent keramík sa mleli v guličkovom mlyne 2 až 6 hodín. Lisovací tlak sa menil v medziach 50 až 175 MPa a pôsobil po niekoľko sekúnd. Pripravené tabletky sa vypaľovali na vzduchu, pri teplote z intervalu 1000 °C až 1400 °C, počas 3 až 6 hodín. Luminiscencia sa budila pri izbovej teplote laserom s vlnovou dĺžkou 325 nm cez WG 1 filter. Pre porovnanie sa budili niektoré vzorky aj ortuťovou výbojkou cez UG 5 filter (λ = 365 nm). Fotoluminiscenčné spektrá sa snímali vo viditeľnej oblasti spektrometrom PG S-2. Fázová analýza sa robila pomocou difraktomeru Zeiss HZG-4 a CuK_α žiarenia.

Obidva typy keramík emitujú v modrozelenej oblasti spektra (400 - 600 nm). Tvar a intenzita fotoluminiscenčných spektier závisia od zloženia a technológie prípravy vzoriek. Vplyv lisovacieho tlaku a teploty výpalu na luminiscenčné spektrá zirkónových keramík je ukázaný na obrázkoch 1 a 2. Vplyv lisovacieho tlaku a teploty výpalu na luminiscenčné spektrá zirkoničitých keramík je ukázaný na obrázkoch 3 a 4. Po výpale pri 1400 °C fluorescenčné spektrum zirkoničitých keramík bolo nezávislé od lisovacieho tlaku a doby výpalu (obr. 4), čo naznačuje, že v týchto keramikách je tetragonálna fáza plne stabilizovaná.

Obidva typy keramík kryštalizujú v tetragonálnom systéme a ich hustota dosahuje 98 až 99 % teoretickej hustoty. Minimálna porozita sa pozoruje pri 4-hodinovom mletí s guličkami o priemere 10 mm, lisovacom tlaku 125 MPa a teplote výpalu 1400 °C. Difrakčné záznamy oboch typov keramík sú uvedené na obrázkoch 5 *a, b.* Indexovanie čiar a ich relatívne intenzity udávajú tabuľky 1 a 2.

Pretože modrozelená luminiscencia nezávisí od stabilizačného oxidu v zirkoničitých keramikách a objavuje sa aj v zirkónových keramikách, predpokladáme, že táto luminiscencia Zr^{4+} iónov súvisí s ich asymetrickým (tetragonálnym) kyslíkovým okolím.