

THE EFFECTS OF γ -IRRADIATION ON THE ELECTROKINETIC AND THERMAL BEHAVIOUR OF ZIRCONIUM HYDROXIDE

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Abstract

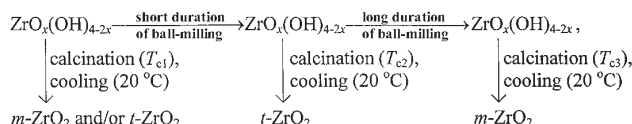
Zirconium hydroxide particles produced by rapid precipitation at pH 10.4, 7 or 2 were subjected to γ -irradiation up to a final dose of 20 MGy. The effects of the γ -irradiation were examined by X-ray powder diffraction, laser Raman spectroscopy, differential scanning calorimetry and microelectrophoretic measurements. It was found that γ -irradiation had no influence on the behaviour of zirconium hydroxide during calcination and subsequent cooling. The results of microelectrophoretic measurements showed that γ -irradiation influences the surface properties of zirconium hydroxide as a function of the precipitation pH. Zirconium hydroxide precipitated at pH 2 proved to be the most susceptible to γ -irradiation, while the same γ -irradiation had very little (if any) effect on the surface properties of zirconium hydroxide precipitated at pH 10.5. After γ -irradiation, the electrophoretic mobility of zirconium hydroxide precipitated at pH 2 was increased at both low and high pH, thereby indicating an increase in its adsorption capacity. The analogy observed between the pH-dependence of the effects of γ -irradiation on the electrokinetic behaviour of zirconium hydroxide and the influence of ball-milling on the thermal behaviour of zirconium hydroxide [8] suggested that the susceptibility of amorphous zirconium hydroxide increases with decrease of the precipitation pH.

Keywords: DSC, γ -irradiation, laser Raman, microelectrophoresis, XRD, zeta-potential, zirconium hydroxide, ZrO_2

Introduction

Zirconia powder is a very important material with different applications in advanced ceramics [1]. Catalysts based on ZrO_2 have been used in hydrogenation, isomerization and dehydration reactions [2–4]. The activity and selectivity of the catalysts obtained depend significantly on the preparation procedure. In practice, zirconium hydroxide (hydrous zirconia) is usually used as a precursor phase in the production of zirconia powders. The properties of the materials obtained depend greatly on the preparation conditions under which zirconium hydroxide, as a green body, is produced. The preparative conditions used to obtain zirconium hydroxide, such as the pH of precipitation [5], the duration of precipitation [6] and the type of zirconium salt from which the zirconium hydroxide is

produced [7], influence the phase composition of the ZrO_2 products. Davis [5] found that precipitation at high or low pH favours the formation of metastable t - ZrO_2 after calcination between 400 and 600°C, while in neutral medium the same thermal treatment yields m - ZrO_2 . Štefanić *et al.* [8] showed that, regardless of the pH of precipitation, the influence of mechanical treatment on the thermal behaviour of zirconium hydroxide can be illustrated by means of Scheme I.



Scheme I

where T_{c1} , T_{c2} and T_{c3} are the temperatures of crystallization, mutually related by $T_{c1} < T_{c3} < T_{c2}$. Specifically adsorbed anions, e.g. sulfate, influence the process of zirconium hydroxide calcination [9]. It has been found that sulfate-modified zirconia exhibits an increased activity and selectivity in the skeletal isomerization of alkenes [10–12].

Besides solid-state calcination, the crystallization of ZrO_2 can be achieved by the hydrothermal treatment of zirconium hydroxide suspensions, and possibly by the ball-milling of zirconium hydroxide [13]. Štefanić *et al.* [14] reported that the rates of hydrothermal crystallization are at a minimum near the isoelectric point at pH~7, where the solubility of zirconium hydroxide is the lowest, and increase as the pH departs from the isoelectric point. It was concluded that the hydrothermal crystallization of zirconium hydroxide proceeds via a dissolution/precipitation mechanism [14].

The electrokinetic or zeta-potential determined whether repulsive or attractive forces operate at the hydroxide–water interface. Depending on the pH of the solutions, hydrous oxides can exchange both anions and cations. In the pH region near the isoelectric point, agglomeration and sedimentation occur, resulting in a minimum in the solubility and in the ion-exchange capacity [15, 16]. The bulk and surface properties of metal oxides or hydroxides can also be changed by the action of ionizing radiation. Such radiation can cause an increase or decrease in the rates of adsorption and desorption, and changes in surface reactions that can bring about a catalysis effect [17]. For example, increases in the oxygen and hydrogen adsorption capacity and an enhancement of catalytic activity for the hydrogen–deuterium exchange reaction can be caused by the γ -irradiation of silica gels [18]. Davranov *et al.* [19] found that ionic centres $>O^-$, formed after the γ -irradiation of γ - Al_2O_3 , were able to initiate the polymerization of some organic monomers. Eley and Zammitt [20] investigated the isotopic exchange reaction between hydrogen and deuterium on the surface of γ - Al_2O_3 after γ -irradiation of the adsorbent. It was concluded that the surface free valencies were responsible for the catalytic activity of the γ -irradiated γ - Al_2O_3 . Kang *et al.* [21] found that the electrical conductivity in the system ZrO_2 –10 mol% Gd_2O_3 gradually increased with increase of the irradiation time. It was concluded that the irradiation of the material induced electrical conductivity due to an increased number of oxygen vacancies.

The effects of radiation on the properties of zirconia ceramics have been investigated in several papers [21–24]. On the other hand, the effects of radiation on the behaviour of zirconium hydroxide, a precursor in the production of zirconia, have been much less extensively investigated. In a previous paper [8], we investigated the influence of mechanical treatment on the thermal behaviour of zirconium hydroxides precipitated at different pH values. It was found that the susceptibility of zirconium hydroxide to the influence of ball-milling increases with decrease of the precipitation pH.

In the present work, we focus on the influence of γ -irradiation on the properties of zirconium hydroxide particles precipitated at various pH values. The results are compared with those of mechanical treatment, reported previously [8].

Experimental

Zirconium hydroxide was precipitated at pH 10.4, 7 or 2 from a solution of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by the addition of NaOH under vigorous stirring. The precipitates were subsequently washed with doubly distilled water, using a Sorvall RC2-B ultra-speed centrifuge (max. 20000 r.p.m.) and dried for 24 h at 70°C. After drying, the powders precipitated at pH 7 were ground in an agate mortar for 2 min to ensure a higher yield of metastable *t*- ZrO_2 in the product of crystallization [6]. The samples obtained (notation Z10, Z7 and Z2) were subjected to γ -irradiation at a dose rate of 5.6 Gy s⁻¹ up to a final dose of 20 MGy, using a cobalt-60 source at the Rudjer Bošković Institute. A part of each sample was left as a standard probe.

The phase compositions of the irradiated and non-irradiated samples were investigated at room temperature by using X-ray powder diffraction (a Philips MPD 1880 diffractometer with monochromatized CuK_α radiation and a graphite monochromator) and laser Raman spectroscopy (a Dilor Z24 triple monochromator with the 514.5 nm line of a Coherent Innova-100 argon laser as excitation source). Laser Raman spectra were recorded with a relatively small laser power (30 mW) in order to prevent a possible laser beam influence on the spectra recorded. The samples were prepared for laser Raman recording by deposition into a recess in a lead plate. This procedure ensured better heat transfer during the recording of laser Raman spectra.

The zeta-potentials of the irradiated and non-irradiated samples were determined as a function of pH, using a PenKem S3000 automated instrument for microelectrophoresis (PenKem Inc., Bredford Hills, N. Y., USA). The measurements were performed by immersing 100 mg zirconium hydroxide samples in 100 ml of 10⁻³ M NaCl solution. The pH of the suspension was regulated by the addition of NaOH or HCl solution. The zeta-potential was calculated from the electrophoretic mobility by using Henry's equation [25]:

$$u_e = \frac{2\varepsilon\zeta}{3\eta} f_1(\kappa a) \quad (1)$$

where u_e is the electrophoretic mobility, ε is the permittivity of the medium, η is the viscosity, ζ is the elektrokinetic (zeta) potential, a is the particle radius, κ is the recip-

rocal double layer thickness and $f_1(\kappa a)$ is a function dependent on the particle size and shape. We assumed a high ratio between the particle radius and the double layer thickness, giving $\kappa a > 1$ and $f_1(\kappa a) = 3/2$. In this case, the relation between the electrophoretic mobility and the zeta-potential becomes

$$\zeta / \text{mV} = 12.8 \cdot 10^8 u_e / \text{m}^2 \text{V}^{-1} \text{s}^{-1} \quad (2)$$

The thermal behaviour of the samples was investigated by using a Perkin Elmer model 7 differential scanning calorimeter (DSC). The samples were heated up to 600°C at a scanning rate of 20°C min⁻¹. During the measurements, nitrogen was used as a purging gas and circulating water as a coolant. The instrument was coupled with a personal computer loaded with a program for processing of the DSC curves obtained. The molar values of the crystallization and dehydration enthalpies (ΔH_c and ΔH_d) were calculated by the same procedure as previously [8, 13].

The phase compositions of the samples heated inside the DSC instrument were investigated at room temperature by means of laser Raman spectroscopy with a laser power of 50 mW. The volume fractions of *m*-ZrO₂ (v_m) and *t*-ZrO₂ (v_t) were estimated from the equations proposed by Clarke and Adar [26]:

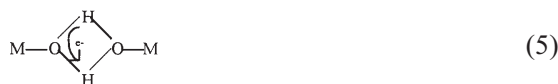
$$v_m = \frac{I_m^{178} + I_m^{189}}{F(I_t^{148} + I_t^{267}) + I_m^{178} + I_m^{189}} \quad (3)$$

$$v_t = 1 - v_m \quad (4)$$

where I_m and I_t are, respectively, the intensities of the *m*-ZrO₂ and *t*-ZrO₂ Raman-active modes at the wavenumbers given as superscripts, while F is a factor close to unity (0.97).

Results and discussion

Radiation effects in solid materials depend strongly on the chemical nature of these materials [27]. In the case of amorphous metal hydroxides, which may contain a significant amount of 'free' water, the effect of water radiolysis must also be taken into account. The γ -irradiation of water causes chemical changes, e.g. formation of the radicals e_{hydr}^- , OH and H, the molecules H₂ and H₂O₂, and the ion H₃O⁺ [22, 28]. The formation of e_{hydr}^- , OH and H is favoured on the action of γ -irradiation, whereas particle irradiation favours the molecular products. The formation of OH is characteristic of all metal hydroxides and is not dependent on the crystal structure. However, the crystal lattice type does influence the stabilization of OH. In the brucite-type structure, for example, OH is stabilized by vacancies, while in Sr(OH)₂ and Ba(OH)₂ the stabilization of OH by the formation of hydrogen-bonds with hydroxyl ions is suggested [29]. In this case formation of a paramagnetic centre of the type



takes place in the metal hydroxide (M =metal), in which the unpaired electron is delocalized in the loop including two equivalent atoms of hydrogen. The above-mentioned, general statements also apply to zirconium hydroxide particles.

In the present work, the results of phase analysis revealed that all the samples (irradiated and non-irradiated) were amorphous (Table 1). The broad amorphous maximum present in the X-ray powder diffraction patterns remained approximately the same after γ -irradiation of the zirconium hydroxide particles.

Table 1 Results of XRD and laser Raman phase analysis and pH_{iep} values of zirconium hydroxide particles

| Sample | pH | γ -Irradiation/ MGy | Phase composition | pH_{iep} |
|---------------|------|-------------------------------|-------------------|--------------------------|
| Z10 | 10.4 | 0 | amorphous | 6.1 ± 0.2 |
| Z10- γ | 10.4 | 20 | amorphous | 5.8 ± 0.3 |
| Z7 | 7 | 0 | amorphous | 7.0 ± 0.1 |
| Z7- γ | 7 | 20 | amorphous | 7.7 ± 0.1 |
| Z2 | 2 | 0 | amorphous | 7.0 ± 0.1 |
| Z2- γ | 2 | 20 | amorphous | 6.2 ± 0.1 |

The pH values of the isoelectric points (pH_{iep}) of the zirconium hydroxide particles, determined from microelectrophoretic measurements, are given in Table 1. The pH_{iep} values of the non-irradiated samples Z10, Z7 and Z2 are in the range of values found in the literature [30, 31] for hydrous zirconia.

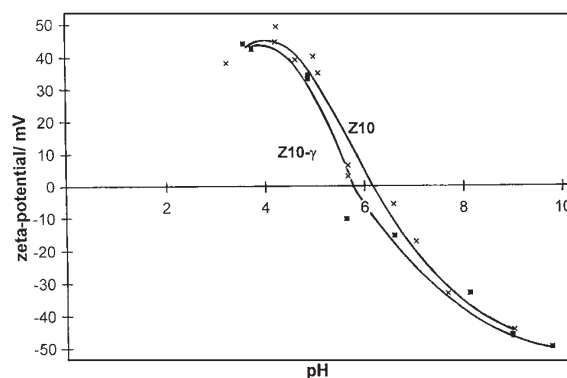


Fig. 1 Zeta-potential measured for samples Z10 and Z10- γ as a function of pH

Figure 1 shows the influence of pH on the zeta-potentials of samples Z10 and Z10- γ . The curves obtained are approximately the same throughout the whole pH region. This result indicates that the γ -irradiation had very little effect on the surface properties of the zirconium hydroxide precipitated at pH 10.4.

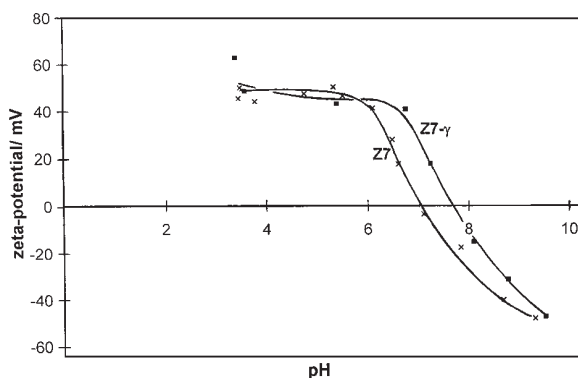


Fig. 2 Zeta-potential measured for samples Z7 and Z7- γ as a function of pH

Figure 2 depicts the influence of pH on the zeta-potentials of samples Z7 and Z7- γ . From the results it could be concluded that the γ -irradiation of zirconium hydroxide precipitated at pH 7 had a slight effect on its electrophoretic mobility at both high and low pH. However, the value of pH_{iep} increased from ~ 7.0 for sample Z7 to ~ 7.7 for sample Z7- γ (Table 1). Structural defects in the vicinity of the surface of the zirconium hydroxide particles, caused by γ -irradiation, changed their acid/base properties, which is in accordance with the literature [32].

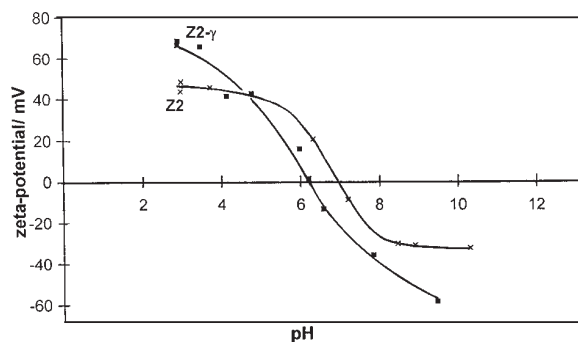


Fig. 3 Zeta-potential measured for samples Z2 and Z2- γ as a function of pH

Figure 3 illustrates the influence of pH on the zeta-potentials of samples Z2 and Z2- γ . The results demonstrate that the γ -irradiation of zirconium hydroxide precipitated at pH 2 caused a decrease in the pH_{iep} from ~ 7.0 (sample Z2) to ~ 6.2 (sample Z2- γ), and also increases in electrophoretic mobility in the high and low pH regions. The observed increases in electrophoretic mobility at both high and low pH indicated that the γ -irradiation affected the surface properties of the zirconium hydroxide precipitated at pH 2 in such a way as to increase its adsorption capacity. The results indicated that zirconium hydroxide precipitated at pH 2 is the most susceptible to the influence of γ -irradiation, which is in agreement with previous results [8].

Thermochemical data obtained from the DSC curves of the irradiated and non-irradiated samples are given in Table 2. The DSC curves of non-irradiated samples Z10, Z7 and Z2 (Fig. 4) contained one endothermic peak resulting from dehydration and one exothermic peak due to crystallization [8, 13]. The DSC curve of sample Z2 displayed another endothermic peak, with maximum at $\sim 350^\circ\text{C}$, due to the elimination of nitrates [14]. The DSC curves of irradiated samples Z10- γ , Z7- γ and Z2- γ were very similar to the DSC curves of the corresponding non-irradiated samples. The intensities of the endothermic peaks of dehydration were lower for the irradiated samples, indicating the loss of water during the γ -irradiation. The intensities and shapes of the exothermic peaks of crystallization, and the temperature of crystallization, remained unchanged after γ -irradiation (Table 2).

Table 2 Thermochemical data obtained from DSC curves and results of laser Raman phase analysis of the samples heated to 600°C inside DSC. The volume fractions of $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$ were estimated following the procedure proposed by Clarke and Adar [26]

| Sample | DSC analysis | | | | Phase composition (volume fraction) |
|---------------|---------------------------------|---------------------------------|-------------------------|-------------------------|---|
| | $\Delta H_d/\text{kJ mol}^{-1}$ | $\Delta H_c/\text{kJ mol}^{-1}$ | $t_{c1}/^\circ\text{C}$ | $t_{c2}/^\circ\text{C}$ | |
| Z10 | 69 | -21 | 467 | - | $m\text{-ZrO}_2(0.80)+t\text{-ZrO}_2(0.20)$ |
| Z10- γ | 48 | -21 | 468 | - | $m\text{-ZrO}_2(0.80)+t\text{-ZrO}_2(0.20)$ |
| Z7 | 58 | -21 | 458 | - | $t\text{-ZrO}_2(0.84)+m\text{-ZrO}_2(0.16)$ |
| Z7- γ | 47 | -21 | 459 | - | $t\text{-ZrO}_2(0.84)+m\text{-ZrO}_2(0.16)$ |
| Z2 | 52 | -10 | 458 | 467 | $t\text{-ZrO}_2$ |
| Z2- γ | 43 | -10 | 457 | 466 | $t\text{-ZrO}_2$ |

Descriptions: ΔH_d – enthalpy of dehydration, ΔH_c – enthalpy of crystallization, t_{c1} – temperature of first maximum in exothermic peak of crystallization, t_{c2} – temperature of second maximum in exothermic peak of crystallization

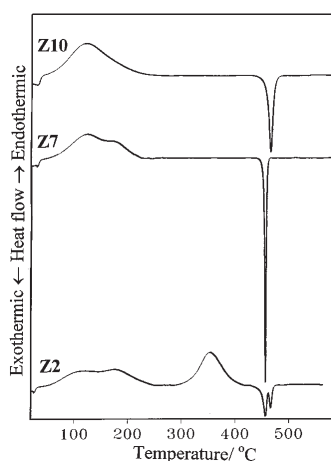


Fig. 4 DSC curves of non-irradiated zirconium hydroxide samples Z10, Z7 and Z2

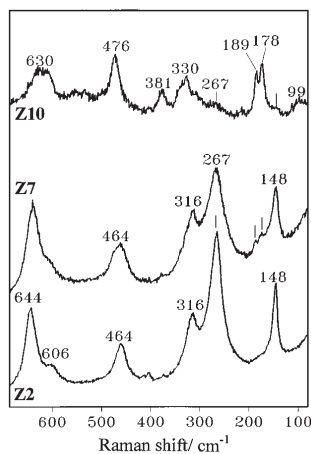


Fig. 5 Laser Raman spectra of non-irradiation samples Z10, Z7 and Z2, heated up to 600°C inside DSC instrument

The laser Raman spectra of the samples heated up to 600°C inside the DSC instrument indicated that, regardless of the pH of precipitation, γ -irradiation had no influence on the thermal behaviour of hydrous zirconia. Although the phase compositions of the products of calcination differ, depending on the pH (Fig. 5), there is no difference in phase composition between irradiated and non-irradiated samples precipitated at the same pH (Table 2). The Raman spectra of the heated samples precipitated at pH 10.4 contained both bands typical of *m*-ZrO₂ and *t*-ZrO₂ [8, 9], but the intensity of the *m*-ZrO₂ bands was much stronger. The Raman spectra of the heated samples precipitated at pH 7 contained not only the *t*-ZrO₂ bands, but also two very small bands at 189 and 178 cm⁻¹, indicating the presence of a minor fraction of *m*-ZrO₂ [8, 9]. The Raman spectra of the heated samples precipitated at pH 2 contained only bands typical of *t*-ZrO₂.

Conclusions

The present study indicated that the natures of zirconium hydroxide particles obtained at different pH-s are not identical, although all these particles were amorphous on XRD. The susceptibility of the resulting zirconium hydroxide particles to the influence of γ -irradiation proved to be pH-dependent. In contrast with mechanical treatment, which influences the thermal behaviour or zirconium hydroxide [8], the γ -irradiation of zirconium hydroxide particles had very little (if any) influence on its thermal behaviour or on the phase composition of the ZrO₂ products obtained. However, the results of microelectrophoretic measurements on the γ -irradiated samples demonstrated, in agreement with the results of DSC analysis of ball-milled samples [8], that the susceptibility of zirconium hydroxide particles increased with decrease of the pH of precipitation. In both cases, zirconium hydroxide precipitated at pH 2 proved to be the most susceptible to γ -irradiation or ball-milling, while zirconium hydroxide precipitated at pH 10.5 was the most stable.

γ -Irradiation of zirconium hydroxide precipitated at pH 2 caused an increase in its ion-exchange capacity, which can lead to a catalysis effect.

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References

- 1 R. Stevens, Zirconia and Zirconia Ceramics, Magnesium Electron Publication No. 113, Published by Magnesium Electron Ltd., July 1986, Twickenham, U.K.
- 2 T. Yamaguchi and J. W. Hightower, *J. Am. Chem. Soc.*, 99 (1977) 4201.
- 3 Y. Nakano, T. Izuka, H. Hattori and K. Tanabe, *J. Catal.*, 57 (1979) 1.
- 4 M. A. Aramendia, V. Borau, C. Jimenez, J. M. Marinas, A. Porras and F. J. Urbano, *J. Chem. Soc. Faraday Trans.*, 93 (1997) 1431.
- 5 B. H. Davis, *J. Am. Ceram. Soc.*, 67 (1984) C-168.
- 6 R. Srinivasan, M. B. Harris, S. F. Simpson, R. J. DeAngelis and B. H. Davis, *J. Mater. Res.*, 3 (1988) 787.
- 7 R. Srinivasan and B. H. Davis, *Catal. Lett.*, 14 (1992) 165.
- 8 G. Štefanić, S. Musić and A. Sekulić, *Thermochim. Acta*, 273 (1996) 119.
- 9 G. Štefanić, S. Musić, S. Popović and A. Sekulić, *J. Molec. Struct.*, 408/409 (1997) 391.
- 10 K. Tanabe, *Mater. Chem. Phys.*, 13 (1985) 347.
- 11 R. Srinivasan, T. R. Watkins, C. R. Hubbard and B. H. Davis, *Chem. Mater.*, 7 (1995) 725.
- 12 R. Srinivasan, R. A. Keogh, D. R. Milburn and B. H. Davis, *J. Catal.*, 153 (1995) 123.
- 13 G. Štefanić, S. Musić and S. Popović, *Thermochim. Acta*, 259 (1995) 225.
- 14 G. Štefanić, S. Popović and S. Musić, *Thermochim. Acta*, 303 (1997) 31.
- 15 IUPAC Commission on Colloid and Surface Chemistry Including Catalysis, *J. Pure Appl. Chem.*, 63 (1991) 895.
- 16 M. Schultz, St. Grimm and W. Burckhardt, *Solid State Ion.*, 63–65 (1993) 18.
- 17 J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry* (3rd ed.), Wiley, 1990.
- 18 W. H. Cropper, *Science*, 137 (1962) 955.
- 19 A. A. Davranov, S. I. Kuzina, M. R. Muidinov and I. M. Barkalov, *Khim. Vys. Energ.*, 24 (1990) 326.
- 20 D. D. Eley and M. A. Zammit, *J. Catal.*, 21 (1971) 366.
- 21 T. K. Kang, I. H. Kuk, Y. Katano, N. Igawa and H. Ohno, *J. Nucl. Mater.*, 209 (1994) 321.
- 22 A. Baufeld, D. Baither, U. Messerschmidt, M. Bartsch and I. Merkl, *J. Am. Ceram. Soc.*, 76 (1993) 3163.
- 23 S. W. Wang, J. K. Guo, X. X. Huang and B. S. Li, *Mater. Lett.*, 25 (1995) 151.
- 24 S. V. Phadnis and M. K. Asundi, *Indian J. Eng. Mater. Sci.*, 2 (1995) 172.
- 25 R. J. Hunter, *Zeta Potential in Colloid Science*, Academic Press London, 1981.
- 26 D. R. Clarke and F. Adar, *J. Am. Ceram. Soc.*, 65 (1982) 284.
- 27 E. Henly and E. Johnson, *The Chemistry and Physics of High Energy Reactions* (Russian Translation), Moscow Atomizdat, 1974.
- 28 A. I. Swallow, *Radiation Chemistry, An Introduction* (Russian Translation), Moscow Atomizdat, 1976.

- 29 V. V. Orlov, T. P. Vasina, V. I. Ermakov and P. A. Zagorec, *Khim. Vys. Energ.*, 9 (1975) 379.
- 30 K. C. Ray and S. Khan, *Ind. J. Chem.*, 13 (1975) 577.
- 31 M. A. Blesa, A. J. G. Maroto, S. I. Passaggio, N. E. Figliolia and G. Rigotti, *J. Mater Sci.*, 20 (1985) 4601.
- 32 G. A. Parks, *Chem. Rev.*, 65 (1965) 177.