

РЕГІОНАЛЬНА ТА ГЕНЕТИЧНА МІНЕРАЛОГІЯ

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RECHARGING PROCESSES OF POINT DEFECTS
IN ZIRCONIUM DIOXIDE NANOSCALE PARTICLES

Electron paramagnetic resonance and proton magnetic resonance were used in order to study nanoscale particles of ZrO_2 with different contents of impurities. It has been investigated EPR signals of Zr^{3+} (samples without chromium impurities) and Cr^{5+} ions (samples with chromium impurities). Annealing temperatures of appearance of EPR signals from Zr^{3+} and Cr^{5+} ions for different samples are not the same. Annealing curves of EPR signals due to Cr^{5+} ions has an extremum for $T = 500-600$ °C. On contrary, annealing curves for Zr^{3+} ions rising monotonically at increasing of annealing temperature.

INTRODUCTION

In nature zirconium dioxide (ZrO_2) represented as mineral baddeleit. At the same time, zirconium dioxide can be produced due to metamict decomposition of zircon ($ZrSiO_4$) under exposure of autoradiation. During metamictization zircon decomposes into zirconium dioxide (ZrO_2) and silicon dioxide (SiO_2). Although metamict zircon kept its morphological features, crystal structure of mineral transferred into amorphous state. Thus, crystal phase decreased and amorphous phase increased. As result of metamictization processes, zirconium dioxide nanoscale particles can be produced. Study of zircon and its decomposition products is an important task for solution of geochronology problems. To obtain information about properties of zirconium dioxide that formed as result of metamict decomposition, synthetic powders of zirconium dioxide with different impurities were investigated

Due to the heating zirconium dioxide undergoes series of phase transition that make difficult for its using as high temperature material. To stabilize of ZrO_2 crystal lattice it is used different impurities [1-3], which prevent phase transitions and make better characteristics of products that made on the basis of zirconium dioxide. Many investigations dedicated to study structure and properties of ZrO_2 nanoscale particles and influence of impurities on its characteristics [1-3]. Despite of that, many questions concerned about properties of zirconium dioxide remain studied insufficiently. Ions Zr^{3+} and Cr^{5+} are most interesting paramagnetic centers in ZrO_2 . In spite of lot investigations, formation mechanisms of these paramagnetic centers studied insufficiently.

The goals of present work are: to study formation mechanisms of paramagnetic centers which caused by Zr^{3+} and Cr^{5+} ions, to clarify peculiarities of charge state changing under influence of external exposures.

EXPERIMENTAL

Initial (annealed) samples are represented by hydroxides of zirconium and hydroxides of doping elements. During the annealing (due to hydroxylation processes) initial samples transform into zirconium dioxide that can have different type of crystal lattice (monoclinic, tetragonal and cubic phases) and contain different impurities. Impurities can replace zirconium ions, get into interstice or form autonomous phases. Dimension of

particles in initial samples was equal to 3-5 nm. Experiments were carried out with samples of four groups. Their composition is not the same. First group represented by nominally pure ZrO_2 powders, i.e. special injected impurities were absent. For samples of second group mixture composition corresponded to formula ($ZrO_2 + 3$ mol % Y_2O_3), ($ZrO_2 + 8$ mol % Y_2O_3) and ($ZrO_2 + 8$ mol % Sc_2O_3). Mixture composition for samples of third group corresponded to formula ($ZrO_2 + n$ mol % Cr_2O_3), where $n = 0.5; 1.0$ and 2.0 , and for four group corresponded to formula ($ZrO_2 + 3$ mol % $Y_2O_3 + n$ mol % Cr_2O_3), where $n = 0.1; 0.25; 0.5$ and 1.0 .

Samples were annealed in a tubular furnace in air in temperature range 100-900 °C. The annealing was 1h. The EPR spectra were measured using a Radiopan SE/X-2444 (Poland) and RE-1306 (Russia) EPR spectrometers operating in three-centimeter wavelength range. The proton magnetic resonance (PMR) signals were measured at room temperature using an RYa-2301 spectrometer (Russia) operating in a cw mode at a frequency of 16 MHz. The PMR method was applied to study samples annealed in air in the temperature range (100 – 600)°C.

EXPERIMENTAL RESULTS AND DISCUSSION

Dependencies of the mass loss and PMR signals from annealing temperature

Dependencies of mass loss of initial (unannealed) samples are studied for two character samples that have mixture compositions corresponded to formula $ZrO_2 + 0.5$ % Cr_2O_3 (sample 1) and $ZrO_2 + 3$ % $Y_2O_3 + 0.5$ % Cr_2O_3 (sample 2). Dependencies of the mass loss for these samples show that samples 1 and 2 during the heating are losing 30.4 and 32.4 % of mass respectively.

PMR spectra of initial samples 1 and 2 represented by single narrow lines which have peak-to-peak width equal to 0.1 ± 0.01 mT. Although heating of samples for $T = 100$ °C leads to sufficient decreasing of intensities of these lines, their still dominate in PMR spectra of investigated samples. Form of PMR signals sufficiently changes for samples which heated for temperatures ($125 \div 150$) °C. After annealing in this temperature range narrow lines disappearing and PMR spectra contain only broad lines. Width of these lines is equal to $\Delta B = 0.22 \pm 0.02$ mT and their intensity monotonically decreasing during further increasing of annealing temperature. Dependencies of intensity of broad lines from

annealing temperature we assigned as I(OH).

On the basis of data about width of PMR signals and temperature stability of narrow and broad lines we can make next conclusions. Narrow line in the PMR spectra is caused by H₂O water molecules, which adsorbed on particles surface; broad line is caused by hydroxyl groups OH, which localized in crystal structure of investigated samples. It is possible to find out quantity of adsorbed water in samples 1 and 2 by comparison data of mass loss of samples that correspond to disappearance of narrow PMR signal. Based on experimental data we can conclude that initial samples contain 22 и 20 % adsorbed water.

As it was mentioned above, after deletion of adsorbed water the PMR signal disappearing. Further heating leads to mass loss of samples and to the decreasing of broad lines intensities due to deletion of hydroxyl groups that associated with samples crystal lattice. Experimental data show that after deletion of adsorbed water hydroxyl groups approximately make up 10 and 15 % of mass of samples 1 and 2, i.e. sample 2 contains much more hydroxyl groups than sample 1. Hence, we may conclude that yttrium, which contains in sample 2, promote increasing contribution of hydroxyl groups in mass of initial samples. Thus, consider samples before deletion of hydroxyl groups represented by mixture of zirconium hydroxides ZrO(OH)₂ and Zr(OH)₄. Besides, probably studied samples contain amorphous ZrO₂ and hydroxides and oxides of yttrium. It is noteworthy that although basic mass of hydroxyl groups deleting from samples under annealing in the temperature range 150 – 500 °C, nevertheless few amount of hydroxyl groups (1-3 %) has high temperature stability and stay in samples' structure up to $T \sim 1000$ °C. Besides, for sample, which at the same time contains yttrium and chromium impurities, for temperature close to 300 °C there are sufficient anomalous. We supposed that these anomalous are because of presence of different phases in samples. Characteristics of hydroxyl groups of different samples are different.

Influence of annealing on the intensity of signals caused by Zr³⁺ and Cr⁵⁺ ions

For initial (unannealed) samples only very weak EPR signals were observed, whose study was complicated because of low signal-to-noise ratio. Annealing of samples leads to appearance of different EPR signals. Most intensive EPR signals in samples of first and second group (which don't contain chromium impurities) caused by Zr³⁺ ions, and for samples of third and fourth groups (which contain chromium impurities) signals caused by Cr⁵⁺ ions.

There are some differences in form and shape of EPR signals from Zr³⁺ и Cr⁵⁺ ions for samples annealed at different temperatures and for samples with different content of impurities as well. In spite of proximity of spectroscopic characteristics for signals caused by Zr³⁺ и Cr⁵⁺ ions, dependencies of intensities from annealing temperature are different. Corresponding annealing curves for Zr³⁺ and Cr⁵⁺ ions represented in fig. 1 and 2. As we can see in fig. 3, at increasing of annealing temperature signal intensity caused by Zr³⁺ monotonically increasing too. Nevertheless, temperature of arising corresponding EPR signals T (Zr) essentially dependent from content of studied samples. For nominally pure samples ZrO₂ and for samples with impurities (ZrO₂ + 3 mol % Y₂O₃), (ZrO₂ + 8 mol % Y₂O₃), (ZrO₂ + 8 mol % Sc₂O₃) T (Zr) value is approximately

equal to 200, 350, 400 и 500 °C correspondingly. Thus, activation processes energy, which associated with generation of Zr³⁺ ions, essentially depends on content and quantity of impurities in the investigated samples.

Dependencies of EPR signals from annealing temperature for Cr⁵⁺ ions (fig. 2) are essentially different from corresponding dependences for Zr³⁺ ions. Annealing curves for Cr⁵⁺ ions represented by curves with extremum. At the same time, for samples of third group annealing temperature corresponded to extremum of annealing curves T_{max} is in 500-600 °C temperature range and it is moving to region of more higher temperatures at increasing of Cr₂O₃ in composition mixture of investigated samples. Annealing temperature T (Cr) of arising EPR signals from Cr⁵⁺ ions for samples (ZrO₂ + 0.5 mol % Cr₂O₃), (ZrO₂ + 1 mol % Cr₂O₃) and (ZrO₂ + 2 mol % Cr₂O₃) is approximately equal to 200, 250 и 300 °C correspondingly. Besides, according to fig. 2 for annealing temperatures $T > T_{max}$, rate of decreasing the intensity of EPR signals from Cr⁵⁺ ions is increasing with enlargement of content Cr₂O₃ in mixture composition.

Annealing curves for EPR signals from Cr⁵⁺ ions for samples of fourth group are similar to that one for samples of third group. Regularity of impurities influence

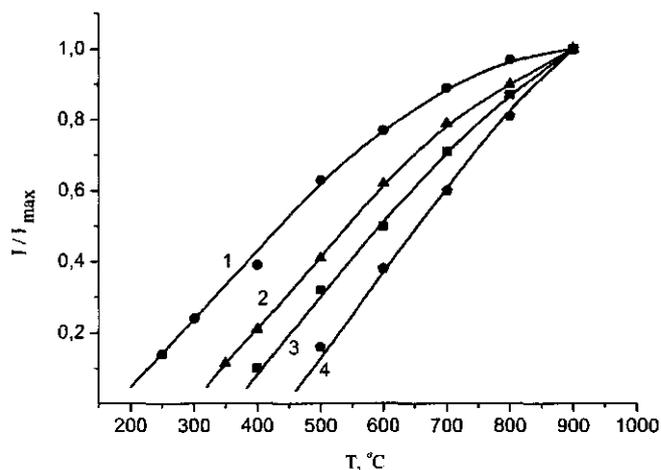


Fig. 1. Dependences of relative EPR signals intensities caused by Zr³⁺ ions from annealing temperature (samples of first and second groups).

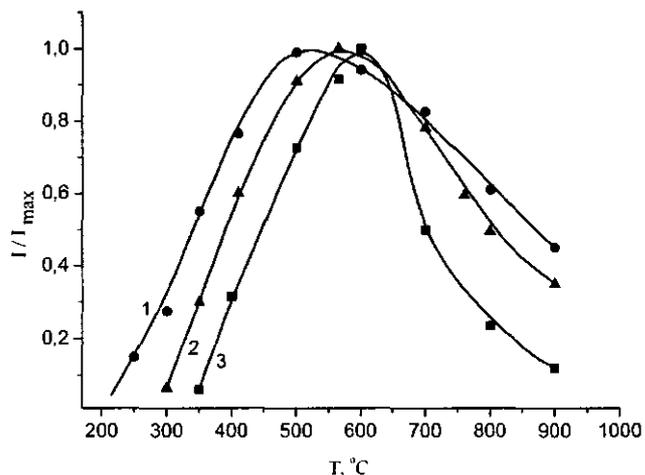


Fig. 2. Dependences of relative intensities of EPR signals caused by Cr⁵⁺ ions from annealing temperature (samples of third group).

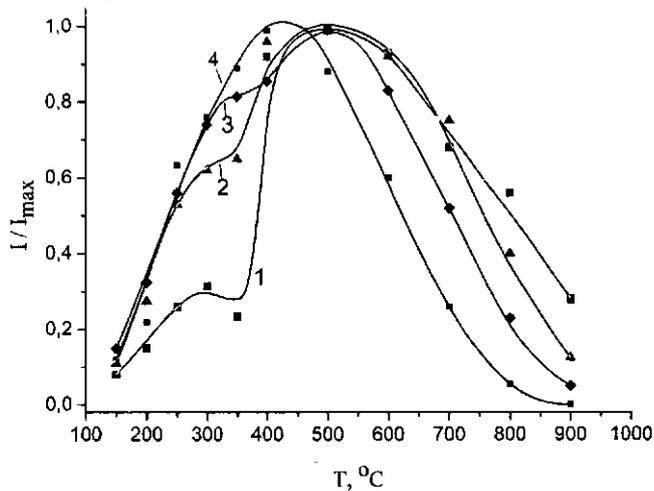


Fig. 3. Dependences of EPR signals intensities caused by Cr^{5+} ions from annealing temperature (samples of fourth group).

on these curves similar too. This is concern to temperatures $T(\text{Cr})$ and T_{max} , and rate of signals decreasing for annealing temperatures $T > T_{\text{max}}$. At the same time, in contrast to samples of third group, when Y_2O_3 и Cr_2O_3 simultaneously present in samples mixture composition then annealing curves of EPR signals caused by Cr^{5+} ions have additional weak extremum in the range of $T \sim 250\text{-}300$ °C (fig. 3). Presence of this extremum correlate with fact of existing anomalous which associated with loosing of hydroxyl groups in samples contained simultaneously Y_2O_3 и Cr_2O_3 impurities.

CONCLUSION

Regularity of influence of external effects on spectroscopic characteristics for nano and mycro (microns and more) particles are not the same. Impurities properties in nanoscale and large-scale particles are different. That is because scale and surface state of nanoparticles strongly effect on charge state and other characteristics of impurities in nanoscale particles. Due to deletion of hydroxyl groups the internal structure of samples changing. Study of internal structure changes may be useful to control materials based on zirconium dioxide.

REFERENCES

1. Belous A.G., Pashkova E.V., Makarenko A.N. Influence of synthesis conditions on formation process, phase content and degradation of nanocrystal particles

of zirconium dioxide stabilized by yttrium oxide. // Sbornik Nanosistemy, nanomaterialy, nanotekhnologii. - Kiev: Akadempriodika, 2003. - V. 1, No 1. - P. 85-107 (in Russian).

2. Konstantionva T.E., Danilenko I.A., Gorokh A.V., Volkova G.K. Formation of structure of ceramics ZrO_2 - 3 mol % Y_2O_3 during the sintering process and its destruction peculiarities. // Ogneupory i tekhnicheskaya keramika. - 2001. - No 3. - P. 12-16 (in Russian).

3. Konstantionva T.E., Danilenko I.A., Tokij V.V., Volkova G.K., Glazunova V.A., Tokij N.V., N.P. Pilipenko, Doroshkevich A.S. Nanopowders on the basis of zirconium dioxide: obtaining, investigation, application. // Sbornik Nanosistemy, nanomaterialy, nanotekhnologii. - Kiev: Akadempriodika, 2004. - 2, No 2. - P. 609-632 (in Russian).

РЕЗЮМЕ

С помощью методов электронного парамагнитного и протонного магнитного резонансов исследованы наноразмерные частицы ZrO_2 с разным содержанием примесей. Исследованы сигналы ЭПР от ионов Zr^{3+} (образцы без примесей хрома) и ионов Cr^{5+} (образцы с примесью хрома). Температура отжига, при которой появляются сигналы ЭПР от ионов Zr^{3+} и ионов Cr^{5+} , для образцов с разным составом примесей является неодинаковой. Кривые отжига сигналов ЭПР, обусловленных ионами Cr^{5+} , имеют экстремум при $T = 500\text{-}600$ °C, тогда как кривые отжига сигналов ЭПР от ионов Zr^{3+} экстремума не имеют.

РЕЗЮМЕ

За допомогою методів електронного парамагнітного і протонного магнітного резонансу досліджено нанорозмірні частинки ZrO_2 з різним вмістом домішок. Досліджено сигнали ЕПР від іонів Zr^{3+} (зразки без домішок хрому) та іонів Cr^{5+} (зразки з домішкою хрому). Температура відпалу, за якої з'являються сигнали ЕПР від іонів Zr^{3+} та іонів Cr^{5+} , для зразків з різним складом домішок є неоднаковою. Криві відпалу сигналів ЕПР, які обумовлені іонами Cr^{5+} , мають екстремум за $T = 500\text{-}600$ °C, тоді як криві відпалу сигналів ЕПР від іонів Zr^{3+} екстремуму не мають.

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