

## THE REVEALING OF DIMENSION EFFECT IN ELECTRON SUBSYSTEM PROCESSES OF DISPERSED $ZrO_2$ IN SPECTRUMS OF ULTRAVIOLET REFLECTION

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The influence of surface disorder of dispersed  $ZrO_2$  on internal transitions ( $d-d$  transition) of electron subsystems of Zr atom is investigated by the method of ultraviolet reflection. It is shown, that shift of absorption bands in frequency region  $20000 - 21000 \text{ cm}^{-1}$  is caused by the  $d-d$  transitions namely between  $e_g t_{2g}$  sublayers but spectrum band  $15700 \text{ cm}^{-1}$  doesn't shift, has impurity character and is related to  $Fe^{3+}$  ions.

In papers [1-6] it is shown, that surface disorder of grains in dispersed mediums (DM), depending on their dimensions, influences on phase content [1,6-8], processes of formation and electronic excitation [9-13]. The probability of last carrying out is defined by surface specific character [1-4] and depends on density (or distances between defects), charge of structure defect of intrinsic or impurity character and is defined by their donor-acceptor nature, differing by electron configurations and phase content of near-surface layer [1,2,4,6,10]. The formed surface specific character of DM in the comparison with their massive samples changes the relaxation time of localized and intermediate active states or particles as a result of change both of formation time and carrying out mechanism of electron processes in the volume [14-18]. However, the role of granule dimension factor with structure defects of intrinsic and impurity character in change of phase content and its influence on the mechanism of electron process formation and internal transitions in electron subsystems from the dimension effect point of view hasn't been investigated enough [4,5,12,15].

In this connection in the present paper the influence of degree of dispersion and sintering temperature, i.e. phase composition on electron transition in  $ZrO_2$  samples in the region of intrinsic absorptions by the method of ultraviolet reflection has been studied.

The fractional samples of fire-proof dielectric  $ZrO_2$  (fraction dimensions  $d \sim 50, 80, 100, 125, 160$  and  $200 \text{ mcm}$ ) with impurity quantity  $\sim 10^{-3}\%$  are used as DM. The content of having impurities  $Fe^{3+}$ ,  $Mn^{3+}$  and  $Cu^{2+}$  and etc. was defined by electron spectroscopy of chemical analysis (ESCA method). The tablets by thickness  $1 \text{ mm}$  and diameter  $16 \text{ mm}$  at pressure  $500 \text{ kG/cm}^2$  are prepared for each fraction. The tablets were sintered at temperatures  $873$  and  $1723 \text{ K}$  in platinum crucible of hydrogen-muffle furnace [3,4,13]. The changes of structure and phase states in  $ZrO_2$  samples were controlled by X-ray analysis and by infrared method on spectrophotometer SPECORD 71 IR. The spectrums of ultraviolet reflection were taken from spectrophotometer SPECORD UV VIS M-40 in frequency region ( $54000 - 14000$ )  $\text{cm}^{-1}$ .

The spectrums of ultraviolet reflections in the frequency region ( $30000 \div 10000$ )  $\text{cm}^{-1}$  for different fractions of  $ZrO_2$  tablets, annealed at  $873 \text{ K}$ , are presented on the figure 1. It is seen, that the value of reflecting ability in region of intrinsic absorptions for different fractions differs on  $\sim 20\%$  from each other (fig.1, c.1-5) and correspondingly increases with the granule dimensions till frequency  $14000 \text{ cm}^{-1}$  and at the more high frequencies the strong decrease is observed. At this two

absorption bands with frequency  $\nu_1 \sim 20000 \text{ cm}^{-1}$  (with energy  $\varepsilon \sim 2,5 \text{ eV}$ ) and  $\nu_2 \sim 15700 \text{ cm}^{-1}$  ( $\sim 1,95 \text{ eV}$ ) reveal independently on fraction dimension.

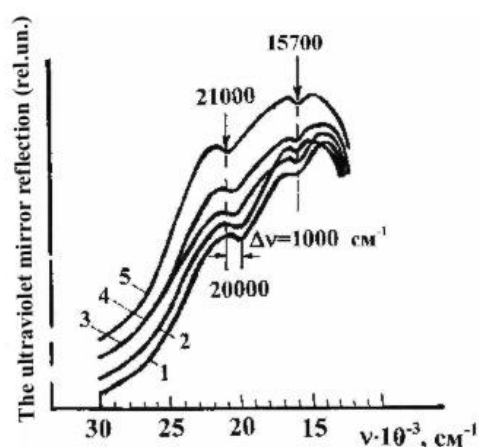


Fig.1. The ultraviolet mirror reflections of  $ZrO_2$  tablets with fraction dimensions  $d=50(1), 100(2), 125(3), 160(4)$  and  $200(5)$ , treated at temperature:  $T=873 \text{ K}$ .

At increase of fraction dimensions from  $50$  till  $200 \text{ mcm}$  the band position of  $\nu_2 \sim 15700 \text{ cm}^{-1}$  doesn't change (fig.1, c.2-5) has the impurity character, is related to  $Fe^{3+}$  ions, that is agreed with investigations results [19-21]. The position constancy of frequencies  $\nu_2 \sim 15700 \text{ cm}^{-1}$  with change of fraction dimension proves about bond strength of replaced free-charged iron cations ( $Fe^{3+}$ ) by four-charged zirconium cations ( $Zr^{4+}$ ) in  $ZrO_2$  lattice [3,7,20], that doesn't cause any change in crystal modification (deformation or slip) both cubic and monoclinic ones.

However, the band absorption with frequency  $\nu_1$  correspondingly with increase of granule dimension shifts to the side in short-wave region of spectrum and shift difference is  $\Delta\nu = (21000 \div 20000) \text{ cm}^{-1}$  and corresponding to [13, 19, 20] is caused by  $d-d$  transition, i.e. between sublayers  $e_g t_{2g}$  [11, 15, 19, 22]. The shift of absorption band  $\nu_1$  on  $\Delta\nu = 1000 \text{ cm}^{-1}$  probably is connected with influence of surface field of localized states, forming as a result of ionization of surface defects in near-surface layer of  $ZrO_2$  granules [5,6,10,12]. The presence of surface field and its influence on shift of absorption band  $\nu_1$  (fig.1) is confirmed by results of EPR-investigations of formation regularities and decay of localized charges, i.e. paramagnetic centers (PMC), carried out for extreme dimensions  $d \sim 50$  and  $200 \text{ mcm}$  [9,12,13]. On the

basis of mechanism of PMC thermal decay it is established, that activation energy for these extreme dimensions differs and is equal to 0,18 and 0,23eV, correspondingly. The results of both independent methods are self-coordinated.

The initial region of reflection spectrum independently on granule-fraction dimensions of differs by value of reflection ability, that is caused by energy change of optic ionization of volume F- and F<sup>+</sup>-centers, depending on phase content and existing in cubic (ionization energy ~3,8 and 2,81 eV [8,15,16,21,23]), monoclinic (~3,07 and 1,95 eV [19,20,23]) modifications. The difference of values of reflection ability probably connects with influence of surface charge states [1-16,12,14] on volume ionization processes of localization anion centers. The sustaining factor of this is coincidence and slip of reflection spectrums independently on fraction dimensions in ZrO<sub>2</sub> tablets, treated at temperature 1773K (fig.2).

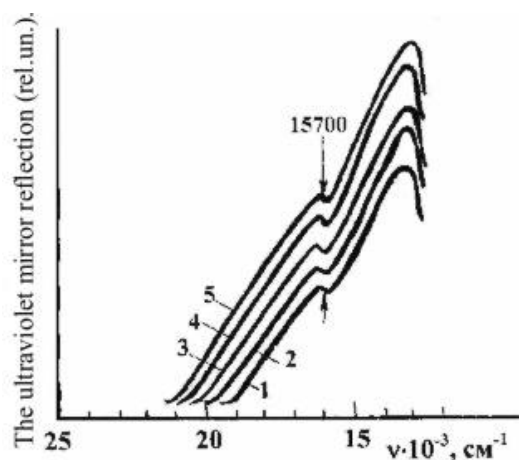


Fig.2. The ultraviolet mirror reflections of ZrO<sub>2</sub> tablets with fraction dimensions  $d=50(1)$ ,  $100(2)$ ,  $164(3)$  and  $200(5)$ , treated at temperature:  $T=1673K$ .

As it is seen from the fig.2 the absorption band of frequency  $\nu_1 \sim 20000 \text{cm}^{-1}$  disappears independently on fraction dimension, whereas the position of absorption band  $\nu_2 \sim 15700 \text{cm}^{-1}$  doesn't change (c.1-5). The curves of

reflection spectrums shift to the side of short-wave region of spectrum with increase of granule dimensions of fractions  $d \sim 50 \div 200 \text{mcm}$ , and their form doesn't change. However, the boundary of reflection spectrum shifts with respect to fraction dimensions: into low-frequency region at  $d < 125 \text{mcm}$  that indicates about bias of monoclinic modification and into short-wave region at  $d > 125 \text{mcm}$  that is the result of the increase of cubic modification part in near-surface layer of ZrO<sub>2</sub> samples. This is connected with reconstruction of crystal cubic modification because of decrease of density of surface defects both cationic and anionic vacancies [3-6,8-10], that causes the decrease of value of surface field of localized charges [1,2,9,12]. That's why the shift in initial part of spectrum into short-wave region (fig.1 and 2) is observed for ZrO<sub>2</sub> samples, thermo-treated at  $T=873$  and  $1773K$  in spectrums of ultraviolet reflection. The coincidence of spectrum boundaries takes place at comparison with the samples, annealed at  $873K$  [15,16,19]. The shift of initial boundary of absorption spectrum with decrease of granule dimensions connects with formation of crystal phase, the volume part of cubic modification remains but it decreases in near-surface layer. At that the increase of part of monoclinic modification increases in near-surface layer. The dimension dependence of change of modification part is proved by investigation results of lattice dynamic by infrared method and X-ray analysis. It is established, that part of crystal phase both in volume and on surface increase with decrease of granule dimensions, i.e. two phases dominate: cubic and monoclinic ones. However, part of crystal phase for samples, treated at  $873K$  at granule dimensions  $50 < d < 125 \text{mcm}$  tops one in comparison with samples of granule dimensions  $125 < d < 200 \text{mcm}$  because of influence of surface field, causing the increase of degree of order of volume content [1-8, 21].

Thus, the behavior of absorption bands  $\nu_1$  and  $\nu_2$  in ultraviolet reflection spectrums in the dependence on grain dimensions and temperature of preliminary thermotreatment indicates about the fact, that first of them is caused by  $d$ - $d$  transition, and second one is connected with presence of impurity centers of Fe<sup>3+</sup>, which replace of Zr atoms of regular lattice ZrO<sub>2</sub>.

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**UB GÜZGÜ ƏKSOLUNMA SPEKTRLƏRİNDƏ DISPERS ZrO<sub>2</sub>-NİN ELEKTRON ALTSİSTEMLƏRİNDƏ ÖLÇÜ EFFEKTİNİN YARANMASI**

UB-güzgü əksolunma metodu ilə dispers ZrO<sub>2</sub>-də səth nizamlılığının Zr atomunun elektron altsistemlərinin daxili keçidlərində (*d-d* keçidi) rolu tədqiq olunmuşdur. Ölçü asılılığı əsasında göstərilmişdir ki 20000-21000 sm<sup>-1</sup> tezlik oblastında udulma zolağının yerini dəyişməsi *d-d*, daha doğrusu *e<sub>g</sub>t<sub>2g</sub>* altsaviyələri arasındakı keçidlər ilə əlaqədardır, 15700 sm<sup>-1</sup> zolaq isə yerini dəyişmir, aşqar xarakteri daşıyır və Fe<sup>3+</sup> ionuna aiddir.

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**ПРОЯВЛЕНИЕ РАЗМЕРНОГО ЭФФЕКТА В ЭЛЕКТРОННЫХ ПОДСИСТЕМНЫХ ПРОЦЕССАХ ДИСПЕРСНОГО ZrO<sub>2</sub> В СПЕКТРАХ УФ-ОТРАЖЕНИЯ**

Методом УФ-зеркального отражения исследована роль поверхностной разупорядоченности дисперсного ZrO<sub>2</sub> на внутренние переходы (*d-d* переход) электронных подсистем атома Zr. На основе размерной зависимости показано, что смещение полос поглощения в области частот 20000-21000 см<sup>-1</sup> обусловлена *d-d* переходами, точнее переходами между подуровнями *e<sub>g</sub>t<sub>2g</sub>*, а полоса 15700 см<sup>-1</sup> не смещается, имеет примесный характер и отнесена к ионам Fe<sup>3+</sup>.

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