

PARAMAGNETIC CENTERS FORMATION
IN ZrO₂-GeO₂ PREPARED BY THE
SOL-GEL TECHNIQUE

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The study of ZrO₂ has attracted considerable attention because of the variety of its important applications. The electron spin resonance (ESR) characteristics of ZrO₂ are strongly related to its reactivity with oxygen, water and CO [1]. These reactions significantly influence the electronic and catalytic properties of zirconia. However, to the best of our knowledge, there have been no reports regarding the ESR investigation of ZrO₂-GeO₂, which was prepared by the sol-gel technique. It is well known that aliovalent dopants, such as Y, Sc, Ca, and Mg, can stabilize the high-temperature polymorphs of zirconia. Oxygen vacancies created by these dopants for charge compensation have been shown to play an important role in stabilizing the cubic and tetragonal structures [2]. Tetravalent dopants do not create anion vacancies, yet they still stabilize tetragonal zirconia against monoclinic distortion [3]. The origin of this stability is not completely understood.

In the present work, we examined samples of thermally treated ZrO₂-GeO₂ coprecipitates, which were prepared by ammonia-promoted hydrolysis of the diluted aqueous solutions of ZrO(NO₃)₂ and GeO₂ (hex) followed by drying and gradual calcinations in air. Samples with different Zr:Ge molar ratio were characterized with XRD, DTA, IR, ESR, and PL. The ESR measurements (Fig. 1, 2, Table, for typical data) of the samples calcined at different temperatures in air revealed that all of them possess paramagnetic signals. The respective intensities were depended upon the following parameters: Zr:Ge molar ratio, preparation method and heat treatment temperature. The above signals were assigned to: Zr³⁺ (paramagnetic 4d¹ ions), O₂⁻ (surface adsorbed oxygen), O⁻ (non-bridging oxygen), E⁻ (single charged oxygen vacancy) centers. Depending on the calcinations temperature and preparation method, concentration of the paramagnetic centers (PC) reached the maximum after the calcinations at 500-600°C.

Experimental results under investigation indicate that the Zr:Ge ratio exerts a strong effect on the coprecipitated samples phase composition, mostly by dramatically increasing the PC concentration.

Oxygen in dioxides occupies the basic volume and, at this point, any changes in anionic lattice will lead to changes in the dioxides properties, thereby modifying properties of the respective material. In addition, the IR and XRD studies indicate the formation of more thermally stable tetragonal ZrO₂ with higher PC concentration in the samples. Therefore, it is quite possible that specific oxygen defects may play an important role in the stabilization of tetragonal zirconia against monoclinic distortion.

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[2] A.N. Kharlanov e.a. *Russ. J. Phys. Chem.* **71** (1997) 872.

[3] E. Tani e.a. *J. Am. Ceram. Soc.* **66** (1983) 506.

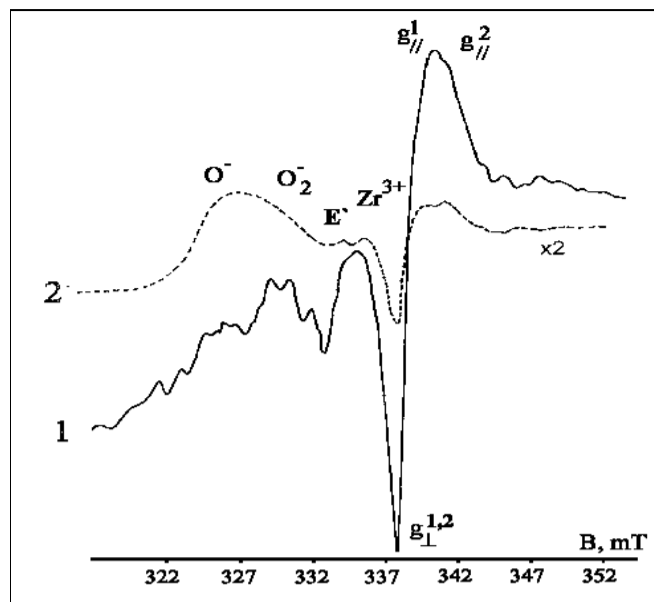


Fig.1. Comparison of ESR-spectra (300K) of xerogels calcined at 500°C in air: 1 – ZrO₂, 2 - ZrO₂-GeO₂ (Zr:Ge = 90:10)

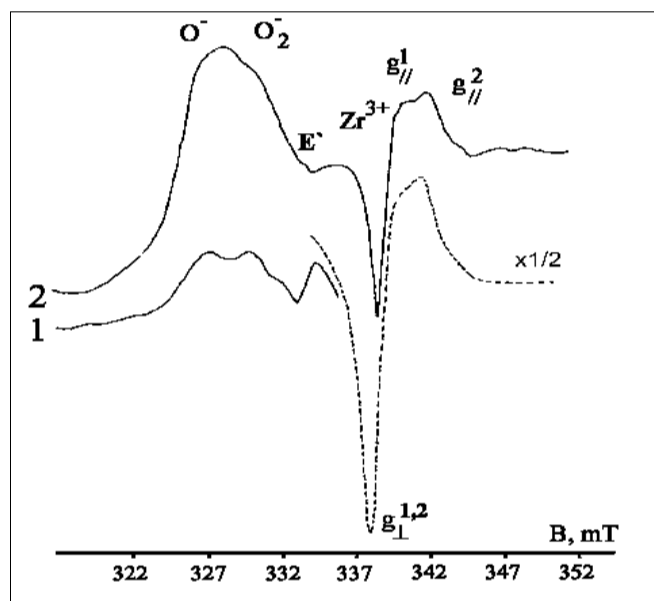


Fig.2. Comparison of ESR-spectra (300K) of precipitates calcined at 500°C in air: 1-ZrO₂, 2-ZrO₂-GeO₂(Zr:Ge=90:10)

Characterization of samples	g-factor of Zr ³⁺	C _{Zr³⁺} g ₋₁ ¹⁷ x 10 ¹⁷	g-factor of O ⁻	C _{O⁻} g ₋₁ ¹⁷ x 10 ¹⁷
ZrO ₂ xerogel, 500°C	g _⊥ = 1.977 g _∥ = 1.961	7	2.045	1
ZrO ₂ :GeO ₂ xerogel, 500°C	g _⊥ = 1.977 g _∥ = 1.959	6.5	2.040	10
ZrO ₂ :GeO ₂ xerogel, 600°C	g _⊥ ^{1,2} = 1.978 g _∥ ¹ = 1.965 g _∥ ² = 1.953	0.3	2.040	1
ZrO ₂ precip., 500°C	g _⊥ = 1.978 g _∥ = 1.958	6	2.040	0.4
ZrO ₂ :GeO ₂ precip., 500°C	g _⊥ = 1.979 g _∥ = 1.962	9.5	2.040	1.5
ZrO ₂ :GeO ₂ precip., 600°C	g _⊥ = 1.979 g _∥ = 1.958	0.4	2.040	20

Table. Comparison of ESR data of ZrO₂ and ZrO₂-GeO₂ (molar ratio of Zr:Ge = 90:10) samples