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Vibrational Analysis and Raman Spectra of Tetragonal Zirconia

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The nanocrystalline powders and polycrystalline materials on the basis of stabilized zirconia with tetragonal type of structure have been investigated. The forms of the normal vibrations of the t-ZrO_2 have been built using the theory group methods. The peculiarities of experimentally obtained Raman spectra of studied materials have been explained with the help of analysis of symmetry and the forms of the fundamental vibrations.

Keywords: zirconia, polymorphic modification, lattice dynamics, Raman spectra.

Introduction

Zirconia (ZrO_2) is promising for creation of such materials as piezo- and constructional ceramics, bioceramics, materials for solid electrolytes, optical materials and in some other applications. The significant attention to the materials on the basis of zirconia is caused by their unique combination of properties such as high strength and fracture toughness, resistance to effect of aggressive chemical conditions, low thermal conductivity, and special electro-physical properties. These properties essentially depend on the crystal structure of the mentioned materials.

There are three polymorphic modifications of zirconia: monoclinic (m), tetragonal (t) and cubic (f) of such type as fluorite structure. The phase relationship and the structure-property correlation have been extensively studied by many researchers [1–4]. The systems containing ZrO_2 are characterised by the phase transformation reactions of monoclinic modification into tetragonal and tetragonal modification into cubic (fluorite type), the formation of some intermediate metastable phases during this transformations, the short-range and long-range of dopant ions and oxygen vacancies. The martensitic polymorphic tetragonal→monoclinic transformation, which occurs under cooling of materials below 1000^0C (ZrO_2), balks the practical use of the high-temperature forms of ZrO_2. This transformation often results in destruction of materials. Therefore the significant attention is given to the process of stabilization of the high-temperature forms of zirconia. Yttria is one of the most effective stabilizers of high-temperature polymorphic modifications of ZrO_2. The tetragonal phase can be retained by alloying with oxides

of rare-earth elements. The great attention is given to the various methods of study of structural-sensing properties of ceramics.

The application of Raman spectroscopy considerably expands the possibilities of study of the material crystal structure, the phase transformation peculiarities, the quantum size effect, compositional effects, the material evolution with treatment. For example, it has been shown in [5] that Raman line shape resulted from phonon confinement and spatial correlation effects and yielded information about the material nanostoichiometry level. It should be mentioned that the methodology of comparison of Raman studies of treated or nanoscale zirconia and bulk zirconia makes it possible to conclude the changes of structure and phase composition of these materials [6]. Actually despite a huge volume of the literature dedicated to the Raman spectra of the tetragonal polymorph of ZrO_2 this problem is still not resolved (e.g. see different assignments of bands collected in Tab.1). Therefore it is important to elucidate the lattice dynamics of pure zirconia in order to obtain unambiguous assignment of observed Raman spectra.

I. Experiments

The nanocrystalline powders and polycrystalline materials have been investigated. Nanocrystalline powders and polycrystalline samples were obtained by the method of the high-temperature hydrothermal synthesis which allows obtaining more homogeneous powders with the narrow size particle distribution. The control of phase composition of samples has been carried out by X-ray phase analysis.

Raman spectra were recorded by a double grating

spectrometer DFS-24, with a photomultiplier and a photon counting system. The experiment geometry (a $90°$-geometry and a back-scattering geometry) has been changing depending on the type of the sample. The spectra were excited with an argon ion laser operating at 514.5 nm and 488.0 nm wavelengths. Spectra of each specimen were taken over the range of $50 – 800$ cm^{-1}.

II. Results

Taking into account the above mentioned problems with martensitic polymorphic transformation we have carried out the group theoretical analysis of phonon states of tetragonal (t) phase of zirconia which is characterizing with P4$_2$/n 2$_1$/m 2/c (D_{4h}^{15}) space group. As the frequencies and intensities of vibrations depend on the forms of lattice vibrations we have built the forms of the normal vibrations of the t-ZrO$_2$.

The t-ZrO$_2$ contains two formula units per unit cell. The lattice constants are $a = 3.64$ Å and $c = 5.27$ Å [2]. The atom positions in primitive cell (fig. 1) were chosen according to the following set of coordinates in crystallographic coordinate system:
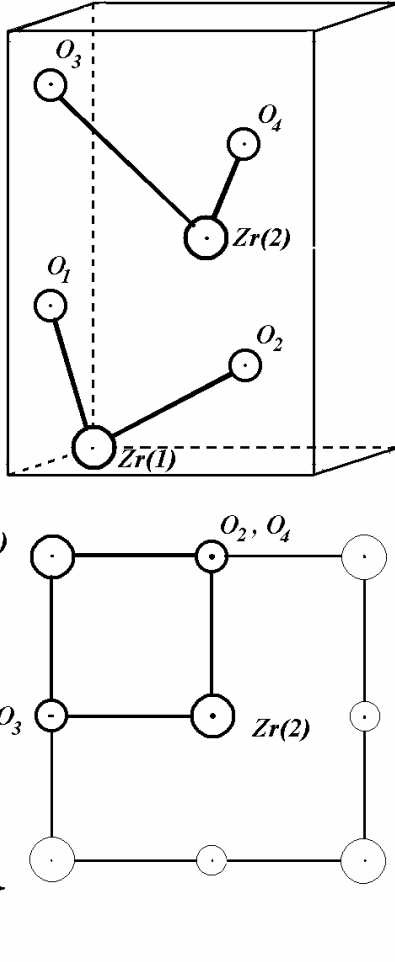

Fig. 1. The unit cell of tetragonal ZrO$_2$.

$$Zr_1 (X, Y, Z), \ Zr_2 (X + \frac{1}{2}, Y + \frac{1}{2}, Z + \frac{1}{2});$$

$$X = 0, Y = 0, Z = 0;$$

$$O_1 (0, \frac{1}{2}, z_O), \ O_2 (\frac{1}{2}, 0, \overline{z}_O), \ O_3 (0, \frac{1}{2}, \frac{1}{2} + z_O),$$

$$O_4 (\frac{1}{2}, 0, \frac{1}{2} - z_O)$$

with $z_O = 0.185$ c.

The group theory predicts 18 phonon branches for tetragonal zirconia. Near the centre of the Brillouin zone the fundamental vibration modes are classified according to irreducible representations of point group D_{4h} in such a way:

$$\Gamma_{dis.} = A_1^+ + 2 A_2^- + 2 e_1^+ + e_2^- + 3 Г^+ + 3 Г^-$$

$$\Gamma_{ac.} = A_2^- + Г^-$$

$$\Gamma_{opt.} = A_1^+ + A_2^- + 2 e_1^+ + e_2^- + 3 Г^+ + 2 Г^-$$

15 optical vibrational modes are divided into 9 Raman active modes ($A_1^+ + 2 e_1^+ + 3 Г^+$), 5 infrared active modes ($A_2^- + 2 Г^-$) and e_2^- mode which is inactive («silent» mode).

We have constructed the normal vibration forms for hypothetic (i.e. without influence of atoms of stabilising dopants) t-ZrO$_2$ structure from symmetrized displacements S_i^μ, where μ – type of irreducible representation, i – index number of symmetrized displacement, using the well-known method of projective operator technique [11]. The normal vibrations for all symmetry types are to be the orthogonal linear combination of the symmetrized displacements of definite symmetry type for definite form of irreducible representations:

$$A_1^+: \ \varphi^{A_1^+} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 - z_2) + \frac{1}{\sqrt{2}}(z_3 - z_4) \right]$$

$$2 A_2^-: \varphi_1^{A_2^-} = \frac{1}{\sqrt{2}}(Z_1 + Z_2) +$$

$$+ \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 + z_2) + \frac{1}{\sqrt{2}}(z_3 + z_4) \right]$$

$$\varphi_2^{A_2^-} = \frac{1}{\sqrt{2}}(Z_1 + Z_2) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 + z_2) + \frac{1}{\sqrt{2}}(z_3 + z_4) \right]$$

$$2 B_1^+: \varphi_1^{B_1^+} = \frac{1}{\sqrt{2}}(Z_1 - Z_2) +$$

$$+ \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 - z_2) - \frac{1}{\sqrt{2}}(z_3 - z_4) \right]$$

$$\varphi_2^{B_1^+} = \frac{1}{\sqrt{2}}(Z_1 - Z_2) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 - z_2) - \frac{1}{\sqrt{2}}(z_3 - z_4) \right]$$

$$B_2^-: \ \varphi_1^{B_2^-} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(z_1 + z_2) - \frac{1}{\sqrt{2}}(z_3 + z_4) \right]$$

$$3 E^+: \varphi_{1\alpha}^{E^+} = \frac{1}{\sqrt{2}}(Y_1 - Y_2) +$$

$$+ \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(y_1 - y_2) + \frac{1}{\sqrt{2}}(y_3 - y_4) \right]$$
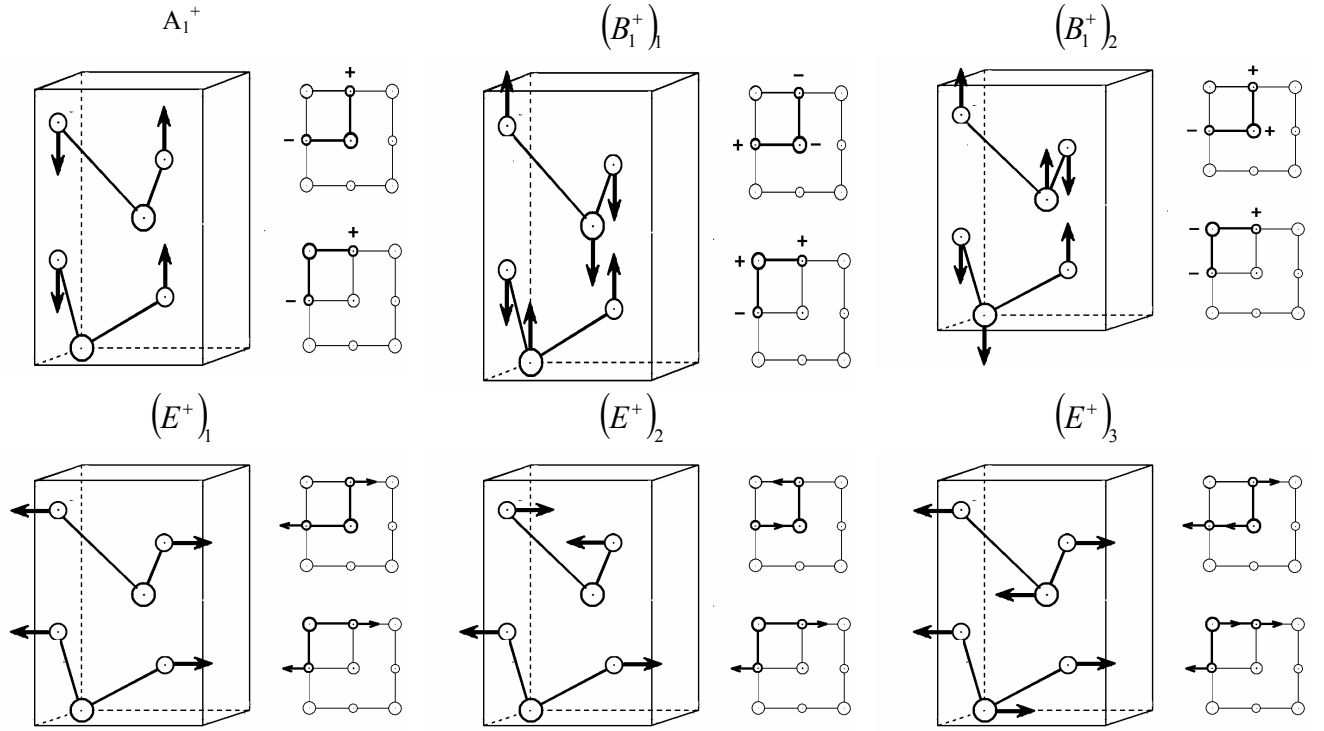
Fig. 2. Normal vibrations of crystal lattice of t-ZrO$_2$ (Raman-active modes).

$$\varphi_{2\alpha}^{E^+} = \frac{1}{\sqrt{2}}\left(Y_1 - Y_2\right) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(y_1 - y_2\right) + \frac{1}{\sqrt{2}}\left(y_3 - y_4\right)\right]$$

$$\varphi_{3\alpha}^{E^+} = \frac{1}{\sqrt{2}}\left(Y_1 - Y_2\right) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(y_1 - y_2\right) - \frac{1}{\sqrt{2}}\left(y_3 - y_4\right)\right]$$

$$\varphi_{1\beta}^{E^+} = \frac{1}{\sqrt{2}}\left(X_1 - X_2\right) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 - x_2\right) + \frac{1}{\sqrt{2}}\left(x_3 - x_4\right)\right]$$

$$\varphi_{2\beta}^{E^+} = \frac{1}{\sqrt{2}}\left(X_1 - X_2\right) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 - x_2\right) + \frac{1}{\sqrt{2}}\left(x_3 - x_4\right)\right]$$

$$\varphi_{3\beta}^{E^+} = \frac{1}{\sqrt{2}}\left(X_1 - X_2\right) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 - x_2\right) - \frac{1}{\sqrt{2}}\left(x_3 - x_4\right)\right]$$

$$3\,E^-:\ \varphi_{1\alpha}^{E^-} = \frac{1}{\sqrt{2}}\left(X_1 + X_2\right) +$$

$$+ \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 + x_2\right) + \frac{1}{\sqrt{2}}\left(x_3 + x_4\right)\right]$$

$$\varphi_{2\alpha}^{E^-} = \frac{1}{\sqrt{2}}\left(X_1 + X_2\right) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 + x_2\right) + \frac{1}{\sqrt{2}}\left(x_3 + x_4\right)\right]$$

$$\varphi_{3\alpha}^{E^-} = \frac{1}{\sqrt{2}}\left(X_1 + X_2\right) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(x_1 + x_2\right) - \frac{1}{\sqrt{2}}\left(x_3 + x_4\right)\right]$$

$$\varphi_{1\beta}^{E^-} = \frac{1}{\sqrt{2}}\left(Y_1 + Y_2\right) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(y_1 + y_2\right) + \frac{1}{\sqrt{2}}\left(y_3 + y_4\right)\right]$$

$$\varphi_{2\beta}^{E^-} = \frac{1}{\sqrt{2}}\left(Y_1 + Y_2\right) - \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(y_1 + y_2\right) + \frac{1}{\sqrt{2}}\left(y_3 + y_4\right)\right]$$

$$\varphi_{3\beta}^{E^-} = \frac{1}{\sqrt{2}}\left(Y_1 + Y_2\right) + \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(y_1 + y_2\right) - \frac{1}{\sqrt{2}}\left(y_3 + y_4\right)\right]$$

These forms for Raman-active modes are represented graphically in the fig. 2. The symmetries and forms of the normal vibrations for this structure also have been obtained for correct correspondence of spectral lines and fundamental modes.

Observed Raman spectra contain six fundamental optical modes, as predicted by the group theoretical analysis, both for powders and polycrystalline pressed pellets of the same composition (Fig. 3). The band intensity relationship depends on the type of sample. Raman spectra of powders have all main peculiarities of the spectra of ceramics based on corresponding systems, but all bands broaden and shift towards higher wavenumbers. Moreover there are additional three bands in the middle part of frequency range (around 400 cm^{-1}). The intensity and halfwidths of these lines increase as the dopant content increases, which is the evidence of some structure disorder due to substituting dopants.

The analysis of the built normal vibration forms shows that the vibrations of A$_1^+$ and ($\acute{\Gamma}^+$)$_{1\alpha,\beta}$ types of symmetry should have the highest frequencies because only the atoms of oxygen take part in this type of vibrations. Among the E-type vibrations the (E$^+$)$_3$ mode is characterized with the lowest frequency. The frequency of (E$^+$)$_2$ mode seems to be lower than
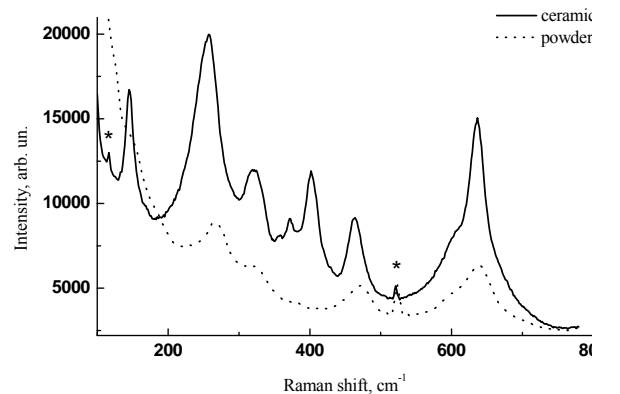

Fig. 3. Raman spectra of stabilized *t*-ZrO$_2$.

frequencies of vibrations of B-symmetry, in which the Zr atoms are involved. The $(B_1^+)_1$ mode should have the lower frequency than $(B_1^+)_2$ one. Therefore we propose such band assignment of observed Raman spectrum: 152 cm^{-1} ($E^+_{3\alpha}$), 265 cm^{-1} ($E^+_{2\alpha}$), 321 cm^{-1} (($B_1^+)_1$), 468 cm^{-1} (($B_1^+)_2$), 610 cm^{-1} ($E^+_{1\alpha}$), 646 cm^{-1} (A_1^+).

Conclusions

The nanocrystalline powders and polycrystalline materials on the basis of stabilized zirconia with tetragonal type of structure have been investigated. The forms of the normal vibrations of the t-ZrO$_2$ have been built using the theory group methods. The full interpretation of Raman spectra of materials under study have been done using of the obtained forms of the fundamental vibrations.

Because of the absence of the pure single crystals of stabilized t-ZrO$_2$, the disorder in the doped samples, the objective impossibility of fulfillment of precise polarized measurements, it seems to be useful further studying of the forms of lattice vibrations for other polymorphic modifications of zirconia and their correlation consideration.

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Table 1

Experimental Raman frequencies of t-ZrO$_2$ and associated symmetries

[7]	[8]	[9]	[4]	[10]	[10], T=1473K
146	155 (B$_{1g}$)	145 (E$_g$)	148 (E$_g$)	155 (B$_{1g}$)	138 (B$_{1g}$)
260	257 (E$_g$)	264 (A$_{1g}$)	265 (A$_{1g}$)	266 (E$_g$)	240 (E$_g$)
317	305 (B$_{1g}$)	320 (B$_{1g}$)	322 (B$_{1g}$)	326 (E$_{1g}$)	290 (B$_{1g}$)
	410 (E$_g$)				
462	465 (E$_g$)	460 (E$_g$)	466 (E$_g$)	474 (E$_g$)	415 (E$_g$)
607	595 (B$_g$)*	606 (B$_{1g}$)	609 (B$_{1g}$)	616 (A$_{1g}$)	550 (A$_{1g}$)
640	630 (A$_{1g}$)	641 (E$_g$)	642 (E$_g$)	645 (E$_g$)	615 (E$_g$)

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Аналіз коливань ґратки та комбінаційне розсіяння світла в тетрагональному діоксиді цирконію

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Досліджені нанокристалічні порошки та полікристалічні матеріали на основі стабілізованого ZrO_2 в тетрагональній фазі. Із залученням теоретико-групових методів побудовані форми нормальних коливань кристалічної ґратки t-ZrO_2. На основі аналізу симетрії та форм основних фундаментальних коливань запропонована інтерпретація експериментально одержаних спектрів комбінаційного розсіяння світла у досліджених матеріалах.