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RESEARCH ARTICLE

Neutron-diffraction study of the cubic-tetragonal phase structural transition in the single crystals of the solid solutions of zirconium and yttrium oxides

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Abstract

Objectives. *The determination of the phase relations, crystallographic characteristics, microstructure features, and atomic crystal structure of zirconium oxide crystals that are partially and completely stabilized by yttrium oxide additives, and the identification of the crystallographic and crystal-chemical correlations with the physicochemical properties of single crystals.*
Methods. *The neutron structure of the crystals was studied using the neutron time-of-flight and constant wavelength methods using a high-resolution Fourier diffractometer on the IBR-2 pulsed fast reactor and a four-circle neutron diffractometer "Syntex." Single crystals were grown by directed crystallization from the melts of mixtures* $(1 - x)ZrO_2 \cdot xY_2O_3$, $x = 0.03$ *and* $x = 0.12$ *with different growth rates (10 and 40 mm/h).*
Results. *It was observed that when growing single crystals with* $x = 0.03–0.05$, *the crystal was stratified into cubic and tetragonal phases, and the ratio between the phases depended on the growth rate. At a growth rate of 40 mm/h, the content of the cubic phase was insignificant. In the crystals of partially stabilized zirconium dioxide* (ZrO_2) *with the additions of 3 mol %* Y_2O_3, *the coherent coexistence of cubic and tetragonal phases was established, and the twin law for a tetragonal component (rotation of unit cell axis by 90° around the* ***a*** *(****b****) axis) that was observed during the phase transition from high-temperature cubic phase to tetragonal phase was determined. For the fully stabilized zirconium oxide of the cubic symmetry (with 12 mol %* Y_2O_3), *the 0.3 Å displacements of oxygen atoms from their partial structural positions in the directions [100] and [111] were determined. These displacements correlated with the directions of the ion transport.*
Conclusions. *Previous studies have shown that the ratio between the cubic and tetragonal phases of the single crystals of the* $ZrO_2–Y_2O_3$ *system depends on the growth rate of the single crystals. The content of* Y_2O_3 *in the cubic and tetragonal phases of a single crystal was determined using the non-destructive neutronography method on the same volume sample of a solid solution of this system. Moreover, the displacements of oxygen atoms from the main position of the crystal were determined.*

Keywords: *yttrium oxide-stabilized* ZrO_2 *crystals, neutron structure analysis, crystal microstructure, atomic crystal structure*

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НАУЧНАЯ СТАТЬЯ

Нейтронографическое исследование структурного перехода кубическая–тетрагональная фаза в монокристаллах твердых растворов оксида циркония с оксидом иттрия

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Аннотация

Цели. *Определение фазовых соотношений, кристаллографических характеристик, особенностей микроструктуры и атомно-кристаллической структуры кристаллов оксида циркония, частично и полностью стабилизированных добавками оксида иттрия, выявление кристаллографических и кристаллохимических корреляций с физико-химическими свойствами монокристаллов.*
Методы. *Нейтроноструктурные исследования кристаллов проведены методами времени пролета нейтронов и постоянной длины волны с использованием Фурье дифрактометра высокого разрешения на импульсном быстром реакторе ИБР-2 и четырехкружного нейтронного дифрактометра «Синтекс». Монокристаллы были выращены направленной кристаллизацией из расплавов смесей* $(1 - x)ZrO_2{\cdot}xY_2O_3$, $x = 0.03$ *и* 0.12 *с разными скоростями роста (10 и 40 мм/ч).*
Результаты. *Установлено, что при выращивании монокристаллов с* $x = 0.03–0.05$ *происходит расслоение кристалла на кубическую и тетрагональную фазы, соотношение между которыми зависит от скорости выращивания. При скорости роста 40 мм/ч содержание кубической фазы незначительно. В кристаллах частично стабилизированного диоксида циркония* ZrO_2 *(с добавками 3 mol %* Y_2O_3*) установлено когерентное сосуществование кубической и тетрагональной фаз и определен закон двойникования для тетрагональной компоненты (вращение осей элементарной ячейки на 90° вокруг осей* ***a*** *(****b****)), возникающего при фазовом переходе из высокотемпературной кубической фазы в тетрагональную. Для полностью стабилизированного диоксида циркония кубической симметрии (с 12 mol %* Y_2O_3*) определены смещения атомов кислорода на 0.3 Å из их частных структурных позиций в направлениях [100] и [111]. Эти смещения коррелирует с направлениями ионного транспорта.*
Выводы. *Исследования показали, что соотношение между кубической фазой и тетрагональной фазой монокристаллов системы* $ZrO_2–Y_2O_3$ *зависит от скорости выращивания монокристаллов. На одном и том же объемном образце твердого раствора этой системы неразрушающим методом нейтронографии определено содержание* Y_2O_3 *и в кубической, и в тетрагональной фазе монокристалла. Определены смещения атомов кислорода из основной позиции кристалла.*

Ключевые слова: *стабилизированные оксидом иттрия кристаллы* ZrO_2, *нейтроноструктурный анализ, микроструктура кристаллов, атомно-кристаллическая структура*

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INTRODUCTION

The first practical application of a solid electrolyte based on the ceramics comprising yttrium-stabilized zirconium oxide was described in the patent of the famous German physicochemist, Walter Nernst, in the autumn of 1897 [1]. The patent was concerned with the description of the design of an incandescent lamp, where an oxygen-containing solid electrolyte was first used as an incandescent element. This was the so-called Nernst lamp, which worked in open air without vacuuming the bulb. Materials based on stabilized zirconium oxide are now widely used in applications such as to create oxide fuel cells, solids, and chemically resistant electrolytes for the sensors of oxygen content in liquid and gaseous media in high-temperature ranges. An important advantage for the design development is the presence of high mechanical and strength properties, which are possessed by materials based on stabilized zirconium oxide.

However, ceramic materials based on zirconium oxide still have certain mechanical drawbacks, such as low cracking resistance, poor antifrictionality, and brittleness. Therefore, a fundamentally new step in the materials science of the composite materials based on zirconium oxide was the development of a method for producing zirconium oxide single crystals by the directional crystallization of the melt in a “cold container.” This was performed at the Institute of General Physics of the Russian Academy of Sciences using direct high-frequency heating, and fully stabilized zirconium dioxide was produced using this method with high ionic conductivity. Further, a relatively new material, i.e., partially stabilized zirconium dioxide (PSZD), which has high mechanical and tribological characteristics, was afforded [2].

CRYSTALLOGRAPHY OF THE PHASES OF ZIRCONIUM OXIDE

Pure zirconium dioxide has three polymorphic phases [3]: cubic (*Fm*–3*m*) at $T > 2640$ K, tetragonal ($P4_2/nmc$) at $T = 1440$–2640 K, and monoclinic ($P2_1/c$) at $T < 1440$ K. The monoclinic and tetragonal phases are the distorted modifications of the cubic structure of the fluorite type. The phases with a cubic structure can be obtained at room temperature by adding stabilizing oxides, such as MgO, CaO, CeO_2, and Y_2O_3, to ZrO_2. The phase diagram of the ZrO_2–Y_2O_3 system is shown in Fig. 1. In the ZrO_2–Y_2O_3 system, the areas of the phase diagram are of interest wherein a tetragonal phase (~3 mol % Y_2O_3) and a cubic phase (>8 mol % Y_2O_3) are present. In the 3 mol % region, the phase transition with a decrease in temperature was performed through the region of coexistence of the cubic and tetragonal phases. The resulting tetragonal phase is commonly referred to as the metastable *t*-phase. It is believed that the resulting compressive stresses improve the mechanical properties of tetragonal zirconium dioxide compared to fully stabilized (cubic) zirconium dioxide. In the literature on the study of systems based on zirconium oxide, two tetragonal phases *t*′ and *t*″ have been considered [4–6].

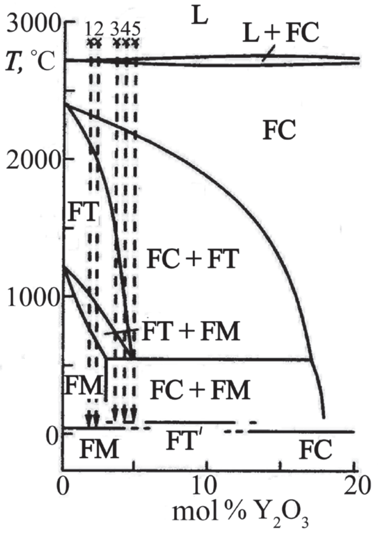


Fig. 1. Phase diagram of the ZrO_2–Y_2O_3 system in the region rich in zirconium dioxide; dotted lines are the cooling lines of the initial compositions: $(1-x)ZrO_2{:}xY_2O_3$ with $x = 0.0086$ (1), 0.0100 (2), 0.0178 (3), 0.0200 (4), and 0.0234 (5) [3] (L – liquid phase, FC, FT, and FM – fluorite cubic, tetragonal, and monoclinic phases, respectively).

In the mechanical properties of single crystals compared to that of ceramics, some features are present that are not solely associated with the absence of grain boundaries inherent in ceramics. The fundamental fact is that the tetragonal phase forms a domain microstructure in a single crystal [7].

The formation of the microstructure of single crystals depends on the type and concentration of the stabilizing oxides as well as on the residual temperature stresses that occur during the growth and cooling of the single crystal. However, the main studies on the materials based on zirconium dioxide have been conducted on polycrystalline samples. To the best of our knowledge, no extensive study has been conducted on the microstructure of the single crystals of tetragonal zirconium dioxide from the crystallographic point of view. Several questions remain unclear. For example, how do the cubic and tetragonal phases relate to each other in terms of symmetry in the region of their coexistence after the phase transition; what is the law of symmetry among the domains in the tetragonal phase. This study was undertaken to obtain additional information about the microstructure of the tetragonal phase based on zirconium dioxide. The use of neutron diffraction, on the one hand, was due to the comparable scattering power of the elements that make up the crystal, and consequently, the structural parameters of oxygen atoms were accurately determined. On the other hand, the large penetrating power of neutrons allowed us to study relatively large samples with linear dimensions up to several millimeters.

OBJECTIVES OF THE STUDY

1. To determine phase relations and crystallographic characteristics for the microstructure of single crystals grown by directed crystallization from the melts of mixtures $97ZrO_2 \cdot 3Y_2O_3$ and $88ZrO_2 \cdot 12Y_2O_3$ with different growth rates (10 and 40 mm/h).
2. To determine the oxygen content in samples with 3 mol % Y_2O_3 and samples grown from the region with 12 mol % Y_2O_3, depending on the unit cell parameters of the concentration.
3. To identify the crystallographic and crystal-chemical correlations with the physicochemical properties of single crystals.

EXPERIMENTAL

Growth of oxide single crystals by directed crystallization using direct high-frequency melting in a cold container

The crystals of partially and fully stabilized ZrO_2 (3 and 12 mol % Y_2O_3) were grown by directed melt crystallization in a cold container through direct high-frequency heating using the Kristall-407 apparatus (Physical Institute of the Russian Academy of Sciences, Moscow, Russia) [2]. The growth rates varied from 10 to 40 mm/h. Moreover, the obtained crystals were 5–20 mm in cross section and 40 mm in height. When the melt was crystallized, the single crystals of ZrO_2 PSZD (3 mol % Y_2O_3) at high temperature had a cubic structure of the fluorite type, and as the temperature decreased, they experienced polymorphic transformations according to the phase diagram (Fig. 1). Furthermore, the external shape of the crystal was preserved, similar to the shape of a single crystal of a single-phase cubic solid solution based on zirconium dioxide; however, unlike that of the latter, which are optically transparent, the crystals of the PSZD were opaque.

The composition of the crystals of the present work was determined by the composition of the initial charge. The variable parameter for single crystals with 3 mol % Y_2O_3 was the growth rate, which was 10 and 40 mm/h. For the structural study, crystals with a diameter of 5 mm were cut from large columnar crystals.

Neutron-diffraction installations

In the present work, using a high-resolution neutron-diffraction setup for the interplanar distance was necessary. This was caused by the need for the precise measurement of the lattice parameters, a confident separation of the phases formed in the system after the phase transition during the growth of crystals according to the measured parameters of the unit cell, and the determination of the change in their ratio with varying growth rates. Conversely, the knowledge of the unit cell parameters with high accuracy enables the use of their known dependence on the concentration to determine the concentrations of the elements in the system and, first of all, oxygen.

For high-resolution experiments, a high-resolution Fourier diffractometer (HRFD) was used at the IBR-2 pulsed reactor in Dubna (Russia), and accordingly, the neutron time-of-flight method [8, 9]. Previously, the main axis was derived for the crystals on the neutron-diffraction spectrometer, NPMS (neutron pulsed magnetic spectrometer, Joint Institute for Nuclear Research, Dubna, Russia) [10]. For the diffraction studies of single crystals, a three-circle goniometer was placed on the central table of the spectrometer, which comprised a χ-ring with a Euler saddle and the axes φ and ω. Thus, the crystal could be freely moved to any reflecting position. The software enabled to search on a crystal with an unknown crystallographic direction at a given interplanar distance d [11]. The samples were further processed on the goniometer of the HRFD installation.

The distribution of atoms in the unit cell and the distances among them are significantly important characteristics that are associated with the basic properties of the crystal. This problem was solved using the constant wavelength method, and the experiment was conducted on a neutronography unit for the study of single crystals at the stationary water–water nuclear reactor VVR-c in Obninsk (Russia) [12].

Microstructure, unit cell parameters, and phase composition of the single crystals of the zirconium oxide–yttrium oxide system

To understand the “crystallographic” state of the crystals and microstructure (the phase ratio and the model of crystal twinning after the phase transition), the inverse lattice of the single crystals was initially studied emplyoing a copper-based photomethod on an X-ray Weissenberg installation (Fig. 2), and then, to achieve a better resolution, on the neutron photomethod installation (neutron Weissenberg installation, Hahn and Meitner Institute, Berlin, Germany), and on the “flat cone (E2)” installation (Hahn and Meitner Institute, Berlin, Germany) on the constant power reactor at the Berlin Neutron Center [13]. The geometry of the diffraction reflection arrangement and the lattice parameters determined from the rotation neutronogram as well as the “0” layer scan for a crystal with 12 mol % Y_2O_3 allowed us to establish that the studied crystals had cubic symmetry, the lattice parameter a = 5.15 Å, and the reflection extinction law corresponded to the $Fm{-}3m$ space group. The rotation neutronogram and the “0” layer scan (Fig. 3a and 3b) showed diffuse scattering, which was caused by the defect structure of the crystal.

The neutron diagram of the rotation and the zero layer of the 3 mol % Y_2O_3 crystal around the axis [110] are shown in Fig. 3b and 3d. The calculation showed that the period along this direction is doubled with respect to the cubic cell. Also, the period along the direction of the “***a***” axis on the zero-layer scan was doubled for the cubic crystal when rotating along the axis [110]. The observed geometry of the location of reflexes in the back of the grid was suggested to be due to a possible twinning in the expected tetragonal phase after the phase transition from the cubic phase, and the proposed twinning law is the rotation of the axis of the direct lattice of a crystal by 90° around the axis “***a***” and/or the axis “***b***.” The twinning scheme is shown in Fig. 4.

No reflexes that could belong to the monoclinic phase were observed. Based on the twinning law, we expect a characteristic splitting of the reflexes along the direction [h00]. Notably, the splitting of reflexes can only be observed on the high-resolution neutron-diffraction patterns.

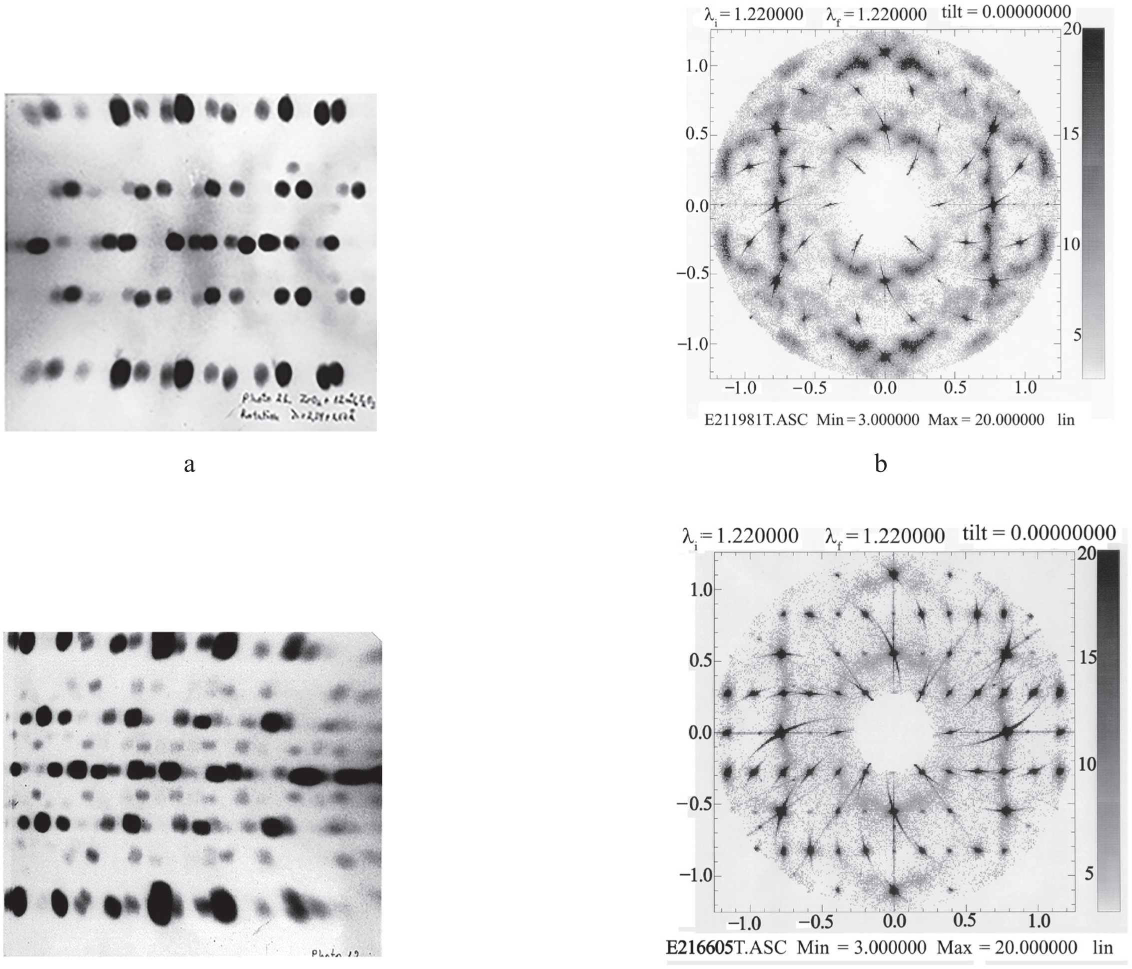
For this purpose, the diffraction spectra of (h00) and (hh0) reflections from the single crystals with a 3% Y_2O_3 content grown at a growth rate of 10 and 40 mm/h, as well as from a single crystal with a 12% Y_2O_3 content, were measured on the HRFD neutronography unit.

In the diffractograms for the tetragonal samples (Fig. 5a and 5b), a splitting of the reflexes occurred. However, the most intense peak (400) showed splitting, not into the expected two, but three peaks. The data on the interplanar distances calculated from the diffraction spectrum along the direction [h00] and the corresponding unit cell parameters are shown in Table 1. Based on the phase diagram and the measured values of the parameters, we propose a model for the coexistence of the tetragonal and cubic phases in the sample under study. It is advisable to compare the diffraction spectra for two samples with 3 mol % Y_2O_3 (tetragonal + cubic phase) and samples with 12 mol % Y_2O_3. Notably, according to the values of the structural factors, a pure cubic sample with 12 mol % Y_2O_3 lacked reflex 600. In the tetragonal samples with 3 mol % Y_2O_3 with an admixture of the cubic phase, only reflexes 600 and 006 belonging to the tetragonal phase were present, and no reflex 600 from the cubic phase was present. Further, in a tetragonal sample with an admixture of the cubic phase, the diffraction spectrum in the reflection region 400 comprised three reflexes, of which two extreme reflexes corresponded to the tetragonal reflexes 400 and 004, and one reflex in the center corresponded to the position of the reflex 400 of the cubic phase.

a

b

Fig. 2. Weissenberg film of the layers (0hl) of the $(1-x)ZrO_2{\cdot}xY_2O_3$ crystal: (a) x = 0.12, cubic phase; (b) x = 0.03, tetragonal phase.



a b

c d

Fig. 3. Reciprocal lattice of $(1-x)ZrO_2{\cdot}xY_2O_3$ single crystals:
(a, c) the neutronograms of the rotation of crystals with $x = 0.12$ (a) and 0.03 (c).
The axis of rotation [110]. Weisenberg neutron installation.
(b, d) scan "0" layer with $x = 0.12$ (b) and 0.03 (d). The axis of rotation [110].
The installation of E2. Flat cone neutron diffractometer.

The diffraction spectra showed that the content of the cubic phase in the PSZD crystals with 3 mol % Y_2O_3, with the simultaneous presence of the tetragonal and cubic phases, is noticeably high in crystals having the growth rate of 10 mm/h. Notably, a special material science study has shown that the growth rate of 10 mm/h is optimal for obtaining PSZD crystals that have the necessary functional and operational characteristics, which should be, for example, a structural material for an electrosurgical instrument [14].

According to the parameters of the unit cell obtained in the present work (Table 1) using the ratio $a_{cub} = 5.1063 + 0.200x$, Å, where x is the content of Y_2O_3 according to the formula $(1-x)ZrO_2{\cdot}xYO_{1.5}$ [15], the concentration of yttrium oxide for the cubic phase was determined. To determine the content of yttrium oxide in the tetragonal phase $(1-x)ZrO_2{\cdot}xY_2O_3$, the following relations were proposed in [16]: $a_{tetr} = 5.060 + 0.6980x$, Å; $c_{tetr} = 5.195 - 0.6180x$, Å. According to Table 1, calculations based on these ratios afforded ~3 mol % Y_2O_3 for the cubic phase, and ~4 mol % Y_2O_3 for the tetragonal phase. Given the approximate nature of the formulas, the contents of Y_2O_3 in the two phases of the samples under study were similar.

In general, during cooling, in the region of 3–5 mol % Y_2O_3, the crystal was stratified into cubic and tetragonal phases with almost the same content of yttrium oxide, ~3 mol % Y_2O_3. No traces of the monoclinic phase were observed. Thus, the data of this study are consistent with the data of [17], according to which the monoclinic phase in the single crystals grown from the melt appears only when the Y_2O_3 content is below 2.5 mol %. Further, as the present study shows, the cubic and tetragonal phases are strictly crystallographically oriented and coherently connected by the planes of the {100} type.

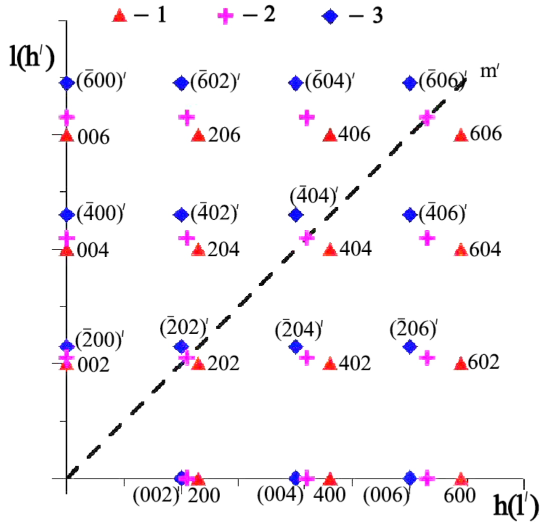


Fig. 4. Reciprocal lattice of the $(1-x)ZrO_2{\cdot}xY_2O_3$ single crystal with $x = 0.03$. Section $h0l$. Coherent coexistence of tetragonal and cubic phases. The twinning law in the tetragonal phase: rotation around the axis ***a*** (=***b***) by 90°. Equivalent to the plane of symmetry $m' = (110)$ in the cubic phase. (1) The first component of the twin of the tetragonal phase; (2) the cubic phase; and (3) the second component of the twin of the tetragonal phase.

Displacements of oxygen atoms from the main position in the cubic phase

For a detailed study on the structural features of the solid solution of the zirconium oxide–yttrium oxide system in the cubic phase, a neutron-structural study of a single crystal with 12 mol % Y_2O_3 was carried out. The experiment was conducted on a stationary reactor at the branch of the L.Y. Karpov Research Institute of Physics and Chemistry in Obninsk, Russia. A set of integral intensities of Bragg reflexes was obtained using a four-circle neutron diffractometer "Syntex" from *Syntex*, USA. The monochromatic wavelength was $\lambda = 1.167$ Å. After the refinement of the positional and thermal parameters of the structure by the least-squares method, the Fourier difference syntheses of the nuclear density were performed. In the Fourier difference syntheses of the nuclear density (Fig. 6a and 6b) from a single crystal of the cubic phase in the region of the main position of the oxygen atom O1, additional peaks are noted with the coordinates given in Tables 2a and 2b. That is, for oxygen, not only a vacancy is present in its main position *8c* but also embedded oxygen atoms O2, which were displaced from the main position and located statistically at position *48g* and O3 at position *32f*. A general view of the structure with basic and displaced atoms is shown in Fig. 7a. The 0.3 Å displacements of O3 oxygen atoms from the main position in the tetragonal phase along the direction [100] (Fig. 7b and Table 3) were also observed in the studies on polycrystals [18].

In [19], in addition to the displacement of oxygen atoms, the displacement of zirconium atoms from their main positions was also noted, and the short-range order with displaced atoms in the averaged unit cell was interpreted by the authors [19] as a solid solution crystal memory of the equilibrium configuration of the initial zirconium and yttrium oxides. The presence of the statistical positions of oxygen atoms along the direction [100] and [111] can be considered as the domain structure of the anionic sublattice, which is usually associated with the lighter direction of ion transport. In this case, these displacements, established in the present work, assume a two-dimensional grid of the movement of oxygen ions from position *8c* in the direction of position *48g*

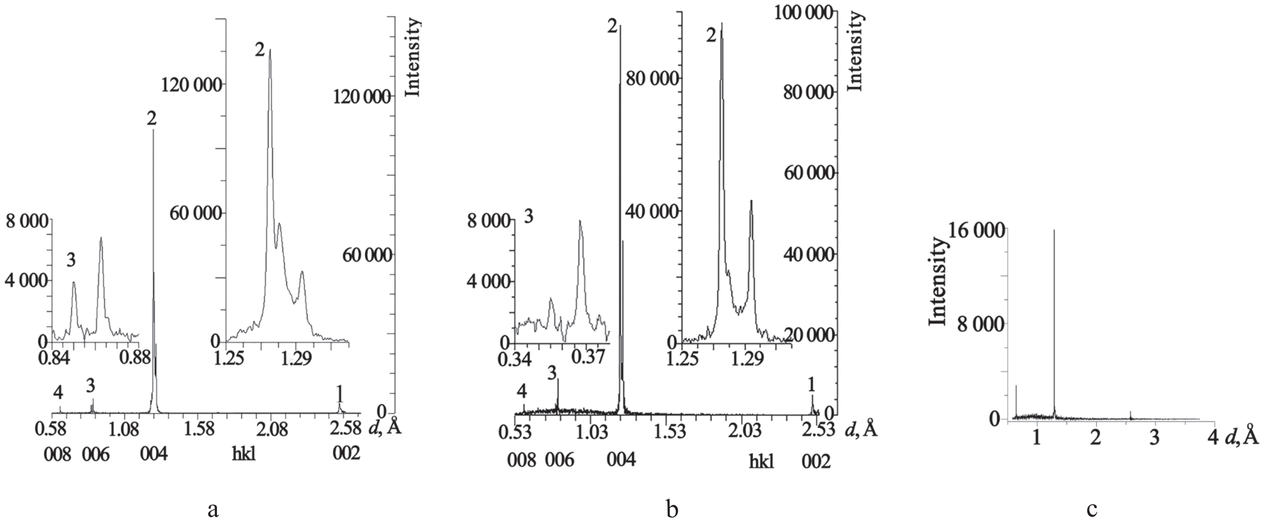


Fig. 5. High-resolution diffraction spectra in the direction of [h00] for the $(1-x)ZrO_2{\cdot}xY_2O_3$ single crystals: (a) $x = 0.03$, 10 mm/h; (b) $x = 0.03$, 40 mm/h; and (c) $x = 0.12$ mol.

Table 1. Data on interplanar distances *d* and I_{max} intensity maxima on diffraction reflexes, which were obtained from the time-of-flight diffraction spectrum from the $(1-x)ZrO_2{\cdot}xY_2O_3$ single crystal with $x = 0.03$. HRFD. The direction of the ‹*h*00›. *hkl* indexes are given for the tetragonal setting

hkl	***d*, Å**	I_{max}	***a*, Å**
200	2.5498	3.385	5.0996
300	1.7134	0.500	5.1402
400	1.2934	19.439	5.1736
	1.2795	31.287	5.1180
	1.2745	75.891	5.0980
600	0.8623	2.650	5.1738
	0.8499	1.442	5.0994
800	0.6375	3.565	5.1000
020	2.5491	2.858	5.0982
040	1.2927	33.530	5.1708
	1.2799	32.471	5.1196
	1.2745	74.292	5.0980
060	0.8619	10.074	5.1714
	0.8496	3.759	5.0976
080	0.6375	5.601	5.1000
002	2.5475	1.335	5.0950
004	1.2919	28.905	5.1676
	1.2792	25.943	5.1168
	1.2738	60.040	5.0952
006	0.8619	6.993	5.1714
	0.8492	2.181	5.0952
008	0.6371	6.118	5.0968

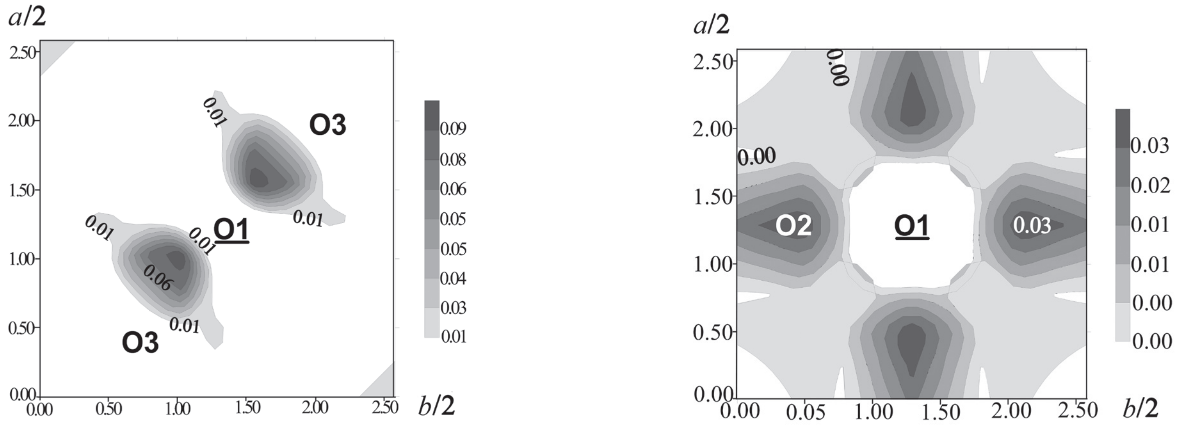
Table 2a. The coordinates *x*/*a*, *y*/*b*, and *z*/*c* of the atoms in the crystal structure of the $(1-x)ZrO_2{\cdot}xY_2O_3$ crystal, $x = 0.12$

Atom	***x*/*a***	***y*/*b***	***z*/*c***	***B*(is/eq), Å²**	***q***	***N***
Zr1	0	0	0	0.80(9)	0.8(14) Zr/0,2(13) (Y)	*4a*
O1	1/4	1/4	1/4	2.72(7)	0.80(2) (O)	*8c*
O2	0.122(24)	1/4	1/4	2.50(4)	0.008 (O)	*48g*
O3	0.298(13)	$-x + 1/2$	$-x + 1/2$	2.52(4)	0.01 (O)	*32f*

Note: *B*(is/eq) is the factor of the isotropic thermal vibrations of the atom, *q* is the population of the position of the atom, and *N* is the designation and multiplicity of the position of the atom according to international tables.

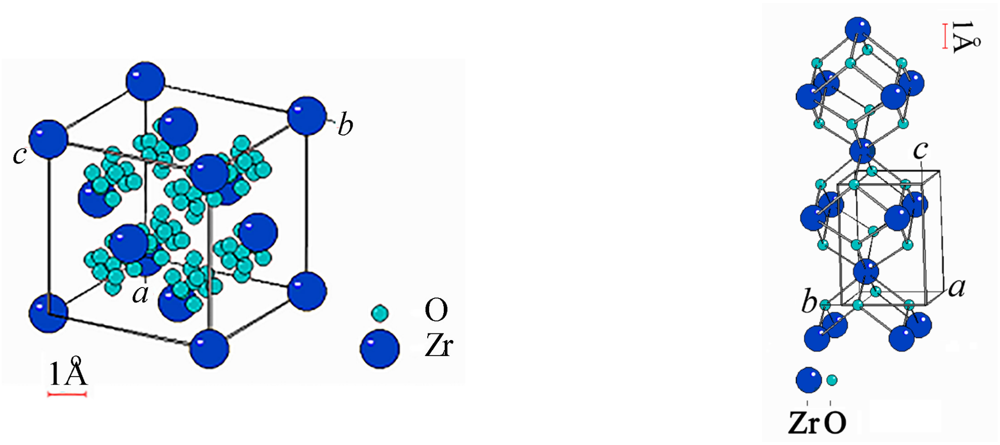
Table 2b. The distance between the atoms in the crystal structure of $(1 - x)ZrO_2{\cdot}xY_2O_3$, $x = 0.12$, Å

Atom	O1	O2	O3
Zr(Y)	2.14; 2.23; 2.30	1.93; 2.67	2.13; 2.66



a b

Fig. 6. Crystal $(1 - x)ZrO_2{\cdot}xY_2O_3$ with $x = 0.12$: (a) the difference Fourier synthesis of the nuclear density. The cross section of the unit cell $z/c = 0.20$; (b) the difference Fourier synthesis of the nuclear density. The cross section of the unit cell $z/c = 0.25$.



a b

Fig. 7. (a) Crystal structure of the $(1 - x)ZrO_2{\cdot}xY_2O_3$ with $x = 0.12$. Averaged unit cell (space group *Fm*–3*m*, *a* = 5.143 Å). Disordering in the oxygen subcell: the main positions and embedded oxygen atoms are shown (the scale of the size of oxygen atoms is especially reduced to show disordering in the oxygen subcell).
(b) Crystal structure of $(1 - x)ZrO_2{\cdot}xY_2O_3$ с $x = 0.03$. ($P4_2/nmc$, *a* = 5.09, *c* = 5.17 Å). Averaged unit cell. The main positions and embedded oxygen atoms are shown (the scale of the size of oxygen atoms is especially reduced to show the atoms in the oxygen subcell).

Table 3. The coordinates *x*/*a*, *y*/*b*, and *z*/*c* of the atoms in the crystal structure of the $(1 - x)ZrO_2{\cdot}xY_2O_3$ crystal, $x = 0.03$. Space group $P4_2/nmc$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(is/eq), Å^2	*N*
Zr1	3/4	1/4	3/4	0.52(9)	2
O1	1/4	1/4	0.4731(13)	2.2(2)	4

Note: *B*(is/eq) is the factor of the isotropic thermal vibrations of the atom; *N* is the designation and multiplicity of the position of the atom according to international tables.

and position *32f*. However, this reasoning applies only to single atoms; for example, to one of the 8 basic oxygen atoms in the independent part of the unit cell, or one of the 48 or 32 embedded oxygen atoms. As shown in the structure of the unit cell shown in Fig. 6, all possible directions of the general type ‹100› and ‹111› should be considered.

MAIN RESULTS AND CONCLUSIONS

1. It was observed that when growing the single crystals of the ZrO_2–Y_2O_3 system from the region of the phase diagram with 3–5 mol % Y_2O_3 at a growth rate of 10 and 40 mm/h, the crystal stratified into cubic and tetragonal phases. The ratio between the cubic and tetragonal phases depends on the growth rate of single crystals. At a growth rate of 40 mm/h, the content of the cubic phase was insignificant.

2. It was observed that the microstructure of the samples was characterized by the presence of a composite structure comprising a micro-double structure of tetragonal phases and coherently connected to it along the planes of {100} cubic phases. The law of the twinning of the tetragonal phase was the rotation of the axis of the unit cell by 90° around the axis ***a*** (***b***).

3. According to the precision measured parameters of the unit cell, it was found that the content of Y_2O_3 in the cubic and tetragonal phases of the single crystal was 3–4 mol %. This determination was performed on the same bulk sample using the non-destructive neutronography method.

4. In the unit cell of a cubic crystal, the 0.3 Å displacement of oxygen atoms from the main position of the crystal was determined. Moreover, the displacement of oxygen atoms in the directions [100] and [111] correlated with the directions of ion transport.

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Authors' contribution

V.A. Sarin – conducting X-ray and neutron structural experiments, processing results, and writing the text of the article;

A.A. Bush – conducting X-ray structural experiments, processing experimental results, and writing the text of the article.

The authors declare no conflicts of interest.

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