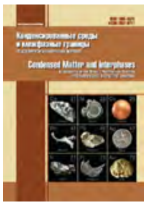

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Review

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Zirconium dioxide. Review

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Abstract

A review of zirconium dioxide or zirconia ZrO_2 is presented. The finding of zirconium compounds in nature, the physical and chemical properties of ZrO_2 are given, the polymorphism of zirconium oxide, and the phase diagrams of systems with its participation are considered. The areas of application of zirconia compounds are highlighted: automotive industry, electronics industry, energy and industrial ecology, equipment manufacturing and mechanical engineering the production of zirconium-based refractories, ceramics, enamels, glass, superhard materials, applications in medicine, nuclear energetics, and many others areas of human activity. Cubic modification of zirconium dioxide, stabilized by oxides of rare earth elements, is a jewelry stone (fianite). Partially stabilized zirconium dioxide is a versatile structural material with very high resistance to crack propagation. Solid solutions of REE oxides, especially scandium, have a high oxygen conductivity, which is used in sensors for measuring the partial pressure of oxygen and in fuel cells. Attention is paid to heat-resistant oxide ceramic materials with low thermal conductivity used in the quality of heat-resistant coatings. Considerable attention was paid to the second most important mineral of zirconia - baddeleyite (ZrO_2). Baddeleyite is widely used in the production of refractory materials. It is mined for the production of metallic zirconium. The achievements of Soviet and Russian scientists in the development of technologies for the production of fianite and artificial baddeleyite are presented.

Keywords: Fianite, Baddeleyite, Zircon, Ceramics, Solid solutions, Oxides of rare earth elements, Phase diagrams, Inert matrix nuclear fuel

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1. Introduction

Zirconia ZrO_2 was first synthesized in 1789. In 1892 in Sri Lanka and in Brazil the mineral baddeleyite was discovered. Since 1900 stabilized zirconia with high ionic conductivity was already widely in use as a glow bar for lighting (“Nernst caps”). Since the 1920s tons of zirconia were used as refractory ceramics [1–7]. Now, materials based on zirconia are widely used as single crystals, structural and functional ceramics, film coatings, microfibres and nanopowders, and composite materials [8–35].

Large transparent crystals of cubic zirconia stabilized by rare earth (REE) oxides dopants are used in jewellery as an imitation diamonds due to their high refractive index and dispersion. In the USSR such crystals were called fianite, abbreviated from the Russian name Physical Institute of the Russian Academy of Sciences of the USSR where they were synthesised using the original cold crucible technique [9]. Partially stabilized two-phase zirconia (PSZ) with a small concentration of stabilizing additive is a material with a very high fracture toughness, as a result of which it is used, for example, for the manufacture of cutting tools [10, 11].

Ceramics based on zirconia (ZrO_2) are versatile construction materials for various purposes (*https://www.ceramtec.ru*), characterized by their refractoriness and high corrosion resistance [8, 12-18]. It should be noted that zirconia ceramics are significantly more expensive than alumina ceramics. Thus, zirconia ceramics are used for the manufacture of critical parts, for example, in the nuclear industry [36], in metallurgy for troughs, crucibles for the continuous casting of steels, crucibles for melting platinum and rare earth elements [19], pipes, in the manufacture of drawing tools for forming wire products, and in the automotive industry for the manufacture of brake discs for high-end cars.

In the aviation and space industry, it is irreplaceable, since due to its properties aircraft and spaceships can withstand very high temperatures [16–17, 20–21, 28–31]. It is also used in medicine, for example, for endoprosthetic as the heads of artificial hip joints. It exhibits its best qualities for dental prostheses in dentistry [22–23].

Solid solutions based on ZrO_2 with a fluorite structure are solid electrolytes. Under heating, they exhibit high oxygen electrical conductivity, which makes these materials a suitable working medium for solid oxide fuel cells (SOFC) [10, 24–26]. They are also used in other electrochemical devices such as oxygen partial pressure sensors. High ionic conductivity correlates with low thermal conductivity [27], and films of solid solutions based on ZrO_2 are used for the production of heat-insulating (thermal barrier) coatings that combine heat resistance, very low thermal conductivity, and high strength [28–31].

A wide range of composite materials of various types with the participation of zirconia is being developed [8, 13, 32–35]. Ceramometal materials are used, for example, for joining ceramic and steel parts.

Recently, interest in heat-resistant fibres for thermal insulation purposes (https://www.ceramtec.ru), [20, 37, 38], as well as zirconia nanopowders, has increased [39–41]. Nanopowders are hydrophilic; their surface is covered with adsorbed water [42]. NanoFormula (Estonia) produces the nanopowders NZirconiumOxide-01 (pure ZrO_2 monoclinic structure, average particle size 20 nm, specific surface area 25 m^2/g) and NZirconiumOxide-02 (tetragonal crystal system, stabilized by 3–8 % Y_2O_3, average particle size 40 nm, specific surface area 40 m^2/g). Their areas of application are extensive: functional ceramics, high-purity pigments, porcelain, glazes, pyro-optical elements, in high-capacity capacitors, optical carriers, in elements that reproduce images, in optical shutters, in glass for stereoscopic television, in memory devices, in abrasive materials, insulators, in fire-retardant materials, in X-ray technology, in high-temperature and corrosion-resistant components, in pipes, in crucibles, in piezoelectric elements, in ion exchange, filters, in transmitting elements, in heating elements, in artificial jewelry, as additives in fuel, in batteries (*nanoformula.tiu.ru*).

This review discusses zirconia, its minerals, occurrence in nature, applications, chemical properties, features of isomorphism, and materials based on it.

2. Distribution in nature

Zirconium compounds are widespread in the lithosphere. According to various Clarke numbers (numbers expressing the average content of chemical elements in the earth's crust, hydrosphere, Earth, cosmic bodies, geochemical or cosmochemical systems, etc., in relation to the total mass of this system), zirconium content ranges from 170 to 250 g/t. Concentration in seawater is $5 \cdot 10^{-5}$ mg/l.

Zirconium is a lithophilic element. In nature, there are only its compounds with oxygen in the form of oxides and silicates. Despite the fact that zirconium is a trace element, there are about 40 zirconium minerals: zircon ($ZrSiO_4$) (67.1 % ZrO_2), baddeleyite (ZrO_2), eudialyte $(Na, Ca)_5(Zr, Fe, Mn)[O, OH, Cl][Si_6O_{17}]$, and etc. In all deposits, zirconium is accompanied by hafnium, which isomorphically substitutes zirconium [43].

Zircon is the most abundant zirconium mineral. It is found in all types of rocks, but mainly in granites and syenites. The largest zirconium deposits are located in the USA, Australia, Brazil, and India. In Russia, which accounts for 10 % of the world's zirconium reserves (3rd place in the world after Australia and South Africa), the main deposits are Kovdor bedrock baddeleyite-apatite-magnetite in Murmansk oblast, Tugan placer zircon-rutile-ilmenite in Tomsk oblast, Central placer zircon-rutile-ilmenite in Tambov oblast, Lukoyanovskoe placer zircon-rutile-ilmenite in the Nizhny Novgorod oblast, Katuginskoe bedrock zircon-pyrochlore-cryolite in the Chita region and Ulug-Tanzek primary zircon-pyrochlore-columbite deposit. Almost unlimited reserves of zirconium are concentrated in the alkaline syenites of the Khibiny Massif on the Kola Peninsula, where this metal is part of many minerals, in particular eudialyte. In industry, the raw materials for the production of zirconium are zirconium concentrates with a mass content of zirconia of at least 60-65%, obtained by the enrichment of zirconium ores [1–6].

3. Polymorphism

Zirconia (ZrO_2) with a melting point of about 2700 °C is one of the most refractory metal oxides. Its density is 5.68 g/cm^3 at 20 °C. It exists in three crystalline forms: stable under standard conditions monoclinic (*m*) modifications (space group $P2_1/c$, Z = 4), occurring in nature in the form of the mineral baddeleyite [44, 45]; medium temperature tetragonal (*t*) modifications (space group $P4_2/nmc$, Z = 4), metastable under normal conditions, and high-temperature cubic polymorph (*c*) of fluorite type (space group $Fm\overline{3}m$, Z = 4) [46]. The data on the temperatures of phase transitions determined in different studies differ significantly (see the summary in [47]). Intervals of <1170; 1170–2370; 2370–2680 °C can be considered as the regions of thermodynamic stability of the phases [48]. However, the scheme of ZrO_2 polymorphism is still the subject of discussion [49].

Both monoclinic and tetragonal structures are distortions of the cubic structure of the fluorite type with coordination numbers 7, 8, and 8 for these structural types. The transition of the tetragonal phase to the monoclinic phase is reversible athermal (i.e., not characterised by any specific transition temperature) martensitic transformation associated with a large temperature hysteresis (~ 200 °C), a change in volume (~ 7 %), and a large shear deformation (~ 15 %). Upon cooling, the transformation may be explosive [1,50]. This has a very significant negative impact from the point of view of technologies for materials based on zirconia. Both high-temperature cubic and medium-temperature tetragonal modifications are easily stabilized by various impurities.

The regions of stability of various modifications of zirconia substantially depend not only on the purity of the reagents, but also on the partial pressure of oxygen. The reducing atmosphere leads to the formation of a wide range of ZrO_{2-x} solid solution and stabilizes the cubic modification both upward and downward in temperature (maximum on the melting curve at 2800 °C and eutectoid equilibrium at 1460 °C and the composition $ZrO_{1.86}$) [47]. Oxygen-deficient samples are black and have specific intrinsic luminescence [51].

Under high pressure, another cotunnite-type modification of ZrO_2 with the structural type $PbCl_2$ (orthorhombic crystal system, space group *Pnam*, Z = 4) occurs [48].

4. Preparation and chemical properties

Zirconia can be obtained by metal oxidation, oxidation of tetrachloride in an oxygen atmosphere, calcining thermally unstable compounds (oxychloride, nitrate, oxalate, etc.), or the heat treatment of hydroxides. In the latter case, amorphous zirconia is first formed, which is converted into monoclinic phase at 450–480 °C. Moreover, cubic and tetragonal modifications that are metastable under these conditions can form as intermediate phases [4].

The gel $ZrO_2{\cdot}nH_2O$ easily precipitates from aqueous solutions of zirconium salts, for example, zirconyl nitrate $ZrO(NO_3)_2{\cdot}\,nH_2O$ [52]. However, the dehydration of the gel and its purification from adsorbed impurities is not an easy task. In addition to direct heat treatment, it can be achieved by hydrothermal treatment [53] and spray drying methods [54]. Zirconia with superacid properties is obtained by the heat treatment of a mixture of zirconium hydroxide with sulphuric acid. Fibres with a diameter of 100–200 nm were obtained by the electrospinning method from an aqueous solution of a mixture of zirconium oxychloride with polyvinyl alcohol, which, after annealing at temperatures above 800 °C, contained only zirconia [38]. Technology for obtaining ZrO_2 by processing zircon concentrate using ammonium fluorides was developed [55].

Complex compositions with the participation of zirconia were obtained by various methods: fusion in a cold crucible, sintering, co-precipitation [56, 57], hydrothermal synthesis [56, 58], plasma chemistry [25–33, 40], sol-gel method [59–60], chemical combustion [61–63], etc.

Zirconia during heating is not completely reduced by magnesium; it is reduced by calcium hydride to metallic zirconium at 800 °C. Heating with oxides of calcium, strontium, or barium as well as with alkalis or alkali metal carbonates provides metazirconates. It easily dissolves in boiling hydrofluoric acid, forming hexafluorozirconic acid. Zirconia practically is not decomposed by cold and hot hydrochloric and nitric acids. The reaction with hydrochloric acid takes place only if the zirconia is thoroughly ground. It reacts with hot concentrated sulphuric acid. It is partially soluble in 50 % KOH. It does not react with chlorine and bromine even at high temperatures. It does not react with halides of alkali and alkaline earth metals, metallic sodium, oxygen, sulphur, selenium, or tellurium. It does not react with hydrogen even at 2000 °C with a pressure of 150 atm. It does not react with beryllium at 1600 °C. It does not react with fluorine at 100 °C, but at 525 °C it completely fluorinated to zirconium tetrafluoride. Above 300 °C it reacts with either carbon tetrachloride or phosgene to form zirconium tetrachloride. Above 600 °C in the presence of carbon, it reacts with chlorine to form zirconium tetrachloride. Above 1400 °C it reacts with carbon to form zirconium carbide. When heated to 1800 °C it reacts with boron to form zirconium borides and boron oxides. At 550 °C it reacts with anhydrous hydrogen fluoride to form zirconium tetrafluoride. At 1000 °C it reacts with carbon disulphide to form zirconium sulphide. It reacts with silicon to form zirconium silicides in an electric furnace. It does not react with molten aluminium at its melting point (660 °C), but at high temperatures, the reaction proceeds to form aluminium oxide and an intermetallic compound of zirconium and aluminium. During heating with titanium tetrachloride, it forms zirconium tetrachloride. During heating it reacts with hexafluorosilicates, forming hexafluorozirconates [2-7]. The chemical activity of zirconia increases with the transition to the nano state.

5. Crystal structure stabilisation and phase diagrams

If monoclinic zirconia is heated to ~ 1170 °C, then it transforms into a tetragonal form, accompanied by a noticeable decrease in volume. During cooling a reverse transition occurs with great supercooling, and moulded parts such as fibres or ceramic parts are destroyed by thermal cycling. This causes the technical need for the stabilization of the crystal structure in order to exclude phase transitions, namely, for the transformation of the monoclinic lattice into tetragonal or cubic forms, stable over a wide temperature range. The stabilization was carried out by introducing dopants with the formation of solid solutions due to the isomorphic substitutions of cations. Such stabilization can be carried out with isovalent isomorphism, for example, in the ZrO_2–CeO_2 system, see Fig. 1 (cerium dioxide crystallises in the cubic structure of fluorite and is isostructural to the high-temperature modification ZrO_2) [64]. However, heterovalent isomorphic substitutions are most effective [66–88]. In ZrO_2–MO (M = Mg, Ca) and ZrO_2–R_2O_3 (R – rare earth elements) systems, wide regions of cubic solid solutions of $Zr_{1-x}M_xO_{2-x}$ and $Zr_{1-x}R_xO_{2-0.5x}$ are formed based on the high-temperature modification of ZrO_2. The area of their existence is in the zone of low temperatures, in a non-equilibrium state this is up to room temperature. In addition, in a number of systems, the formation of such solid solutions is accompanied by the formation of maxima on the melting curves, i.e., high-temperature stabilization. In phase diagrams, these solid solutions decompose upon cooling according to the eutectoid scheme (Fig. 2), and at low temperatures, they are thermodynamically unstable. However, these transformations (decompositiion) are strongly inhibited. In addition, in ZrO_2–MO and ZrO_2–R_2O_3 systems ordered fluorite-like phases are formed, bounding the regions of fluorite solid solutions, such as $R_4Zr_3O_{12}$ (R is the REE of the yttrium subgroup), $R_2Zr_2O_7$ pyrochlore type (R – REE of the cerium subgroup) $Ca_6Zr_{19}O_{44}$, $CaZr_4O_9$. A number of ordered phases are formed in the ZrO_2–Sc_2O_3 system, the composition of which is the subject of discussion [77, 78, 81]. In the ZrO_2–CaO system a binary compound – calcium zirconate $CaZrO_3$, melting at 2300 °C is also formed [65].

Oxides CaO, MgO, Y_2O_3 are most widely used as stabilisers [13]. Joint industrial alloying with calcium and magnesium is possible using cheap dolomite raw materials [89]. Stabilisation of ZrO_2 at a annealing temperature of 1700–1750 °C is achieved with the addition of 10 mol. % CaO or MgO, or 8 mol. % Y_2O_3. The degree of stabilisation of ZrO_2 depends on the type of stabiliser, its amount, the temperature of the stabilising annealing, the amount of impurities contained in zirconia, and other factors. A decrease in the size of crystallites leads to an expansion of the stability regions. Zirconia stabilised with CaO and Y_2O_3 is less prone to destabilisation than zirconia stabilised with magnesium oxide. In the presence of moisture, destabilisation is accelerated [88, 90].

The interest in zirconia systems with yttria (Fig. 2) and especially scandia is determined by the high anionic conductivity of fluorite solid solutions, which determines the choice of materials based on them as a working body for fuel cells [71–88, 91–93]. The problem of the stability of solid $Zr_{1-x}Sc_xO_{2-0.5x}$ solutions and their relatively rapid degradation (ageing) under operating conditions is important [85, 91–93]. For increased stability of the solid solution, co-doping is used, the introduction of additives, such as Y_2O_3

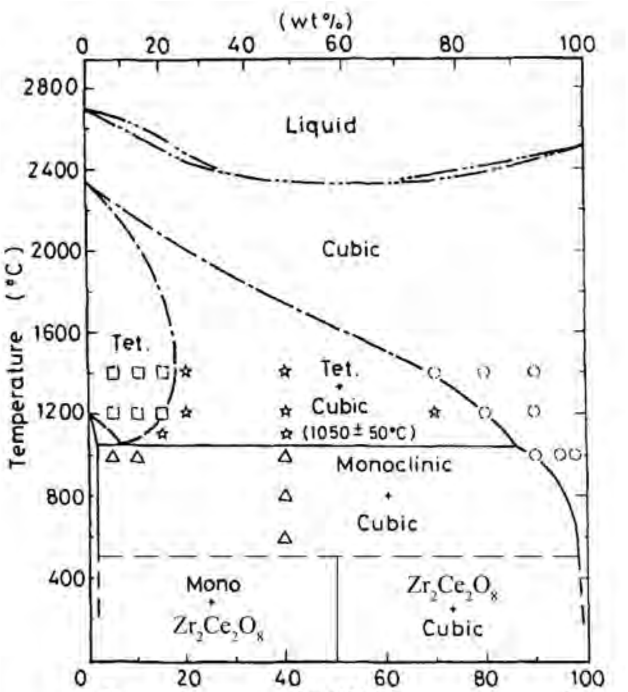


Fig. 1. Phase diagram of ZrO_2–CeO_2 system according to [64, 65]

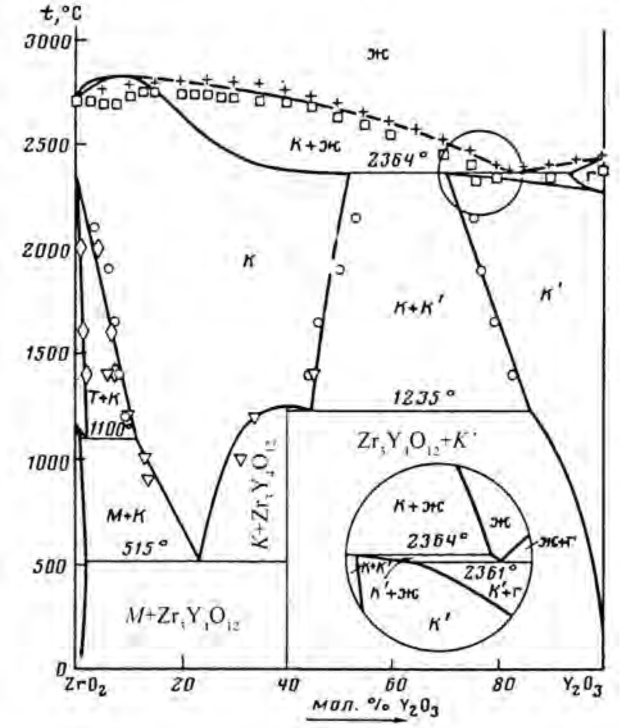


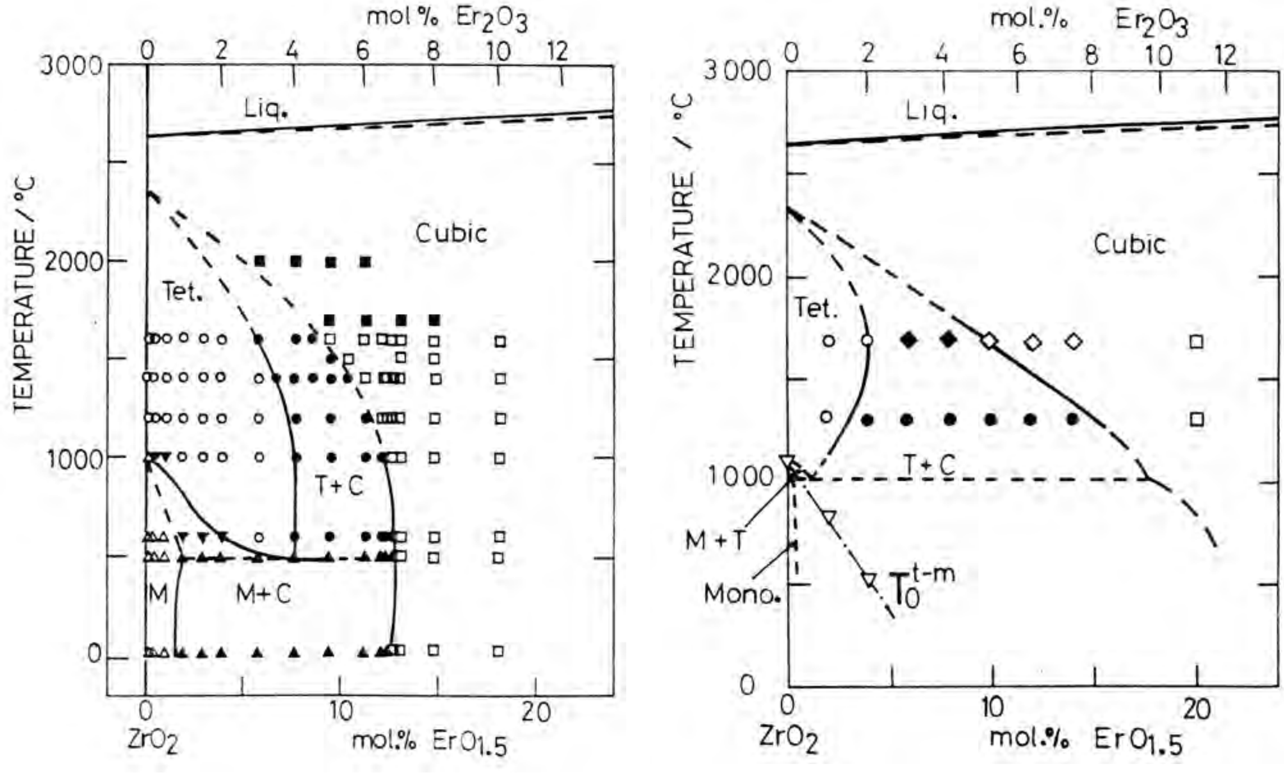
Fig. 2. Phase diagram of ZrO_2–Y_2O_3 system according to [68]

and other oxides together with scandia [72].

The study of phase diagrams with the participation of zirconia encountered great difficulties due to the refractoriness of the studied objects. A major achievement was the development of a method for thermal analysis using solar ovens, which allowed obtaining reliable information on liquidus curves [94, 95]. For plotting phase diagrams in reactive-active systems containing refractory oxides, an original method of melting in a cold crucible was used [36, 96].

In the published versions of the phase diagrams of systems with zirconia, there are serious contradictions, caused primarily by insufficient equilibration time. The activation energy of cationic diffusion in these systems is very high and amounts to about 400 kJ/mol [97, 98]. The fallacy of numerous studies devoted to the study of phase equilibria in the low-temperature region has been demonstrated by Japanese researchers from the Tokyo Institute of Technology [73,100], see fig. 3. On numerous published $(Zr,Hf)O_2 – R_2O_3$ “phase diagrams” at temperatures below 1600 °C frozen states are depicted instead of equilibrium phase regions (see, for example, [76, 99]). In particular, the results of numerous studies of $ZrO_2–Sc_2O_3$ in the low-temperature region are extremely contradictory [71, 77–86]. The use of the liquid phase (hydrothermal synthesis) for acceleration of achieving equilibrium allowed obtaining the most reliable data on $ZrO_2–R_2O_3$ (R = Er, Y, Sc), $ZrO_2–CeO_2$ systems [64, 71, 100].

The actual behaviour of materials in systems based on zirconia upon cooling is determined mainly not by equilibrium phase transformations, but by diffusionless phase transitions. Accordingly, the so-called metastable phase diagrams, in which, instead of two-phase regions, there are martensitic phase transformation lines, are of great importance see Fig. 3b (line $T_0^{\text{t-m}}$). These transitions are accompanied by the mass twinning of the samples. In cooled samples of binary oxides, in addition to the phases *m*, *t*, *c* corresponding to zirconia polymorphs, the second tetragonal *t*’ phase with a low degree of tetragonality (the ratio of the unit cell parameters *c*/2*a* ~ 1.005) is also systematically present, as well as the phase *t*’’ for which the cubic lattice metric is preserved



a *b*

Fig. 3. Incorrect (a) and correct (b) versions of the phase diagram of $ZrO_2–Er_2O_3$ system according to [99] and [100], respectively

($c/2a$ = 1.000) [71]. Tetragonal distortions corresponding to space group $P4_2/nmc$, is caused by displacements in the anionic sublattice and, apparently, do not affect the cationic motif. These phases appear during quenching of a high-temperature cubic solid solution. Differences between the *t′*, *t″* and *c* phases are clearly detected by the Raman scattering method [71, 73].

6. Fianites

The introduction of bivalent and trivalent cations into the fluorite lattice during the formation of wide regions of solid solutions based on the cubic high-temperature modification of ZrO_2 is accompanied by the formation of anionic vacancies, which are structural defects. With an increase in the concentration of solid solutions, there is an accumulation of vacancies associated with impurity cations with a lower charge. The short-range order transforms into the long-range one upon the formation of ordered fluorite-like phases. Features of structural changes can be traced by X-ray diffraction [73], Raman scattering [71, 73, 101–103], by the luminescent label methods [87], high-temperature neutron diffraction [75], EXAFS [75], transmission electron microscopy, and electron diffraction [72, 77]. Raman scattering is more sensitive to structural changes in the lattice of solid solutions than the X-ray diffraction method [104].

The high content of vacancies in doped samples leads to a sharp increase in the anionic conductivity of the corresponding solid solutions. Concentration dependences of electrical conductivity pass through a maximum at a content of about 10 mol. % R_2O_3 reaching values of 5.10^{-2} $Ohm^{-1}cm^{-}1$ at 800 °C [71]. The highest electrical conductivity is realised in the ZrO_2–Sc_2O_3 system. Many options for a qualitative explanation of such dependences have been proposed, but there are no quantitative models. It should be noted that monocrystalline samples of solid solutions based on ZrO_2 have a higher ionic conductivity than ceramics of the same composition. This is true even for ceramics with negligible porosity, and this is an unexpected circumstance, since the surface conductivity is usually higher than the bulk conductivity due to the facilitated movement of ions through grain boundaries. This effect is associated with the pushing back to the boundaries of ceramic grains impurities (in particular, silicon) with the formation of phases with low electrical conductivity [72].

The accumulation of both cationic substitutional defects and anionic vacancies in the structure causes the effective scattering of phonons in crystals. It leads to a dramatic drop in the thermal conductivity of solid solutions with an increase in the concentration of REE oxides. In this case, the temperature dependences of thermal conductivity acquire the form characteristic of glass, with a monotonic decrease with decreasing temperature, in contrast to the crystals, characterised by the presence of a maximum of thermal conductivity at low temperatures [103, 105–106]. High ionic conductivity correlates with low thermal conductivity [27]. Assessment of the thermal conductivity of samples is the simplest way to distinguish artificial fianites from diamonds, which have very high thermal conductivity.

Stabilisation of the high-temperature cubic modification of zirconia with a face-centred cell of the fluorite type by forming wide regions of solid solutions that do not undergo phase transformations down to low temperatures allows growing single crystals of the corresponding composition from the melt. The maxima on the melting curves of these solid solutions facilitate the preparation of single crystals of high optical quality. The old name for artificial cubic ZrO_2 stabilised by various impurities is arkelite [3].

In 1970–1972, at the Lebedev Physical Institute of the Academy of Sciences of the USSR (FIAN), a breakthrough in the synthesis of crystalline materials based on ZrO_2 and HfO_2, which were called fianites, was made [9]. The breakthrough was achieved by a new technology for obtaining high-temperature dielectric crystals by Direct Radio Frequency Heating Technique using a cold container (skull melting) [9, 107].

In the working area of the crystal growth apparatus a “cold” container is located. This container is a water-cooled cylindrical crucible, consisting of several copper hollow segments (Fig. 4). A mixture of ZrO_2 and an oxide of the stabilising element is loaded into the crucible. For the initial melting, a small amount of metal (20–50 g) that will not contaminate the melt

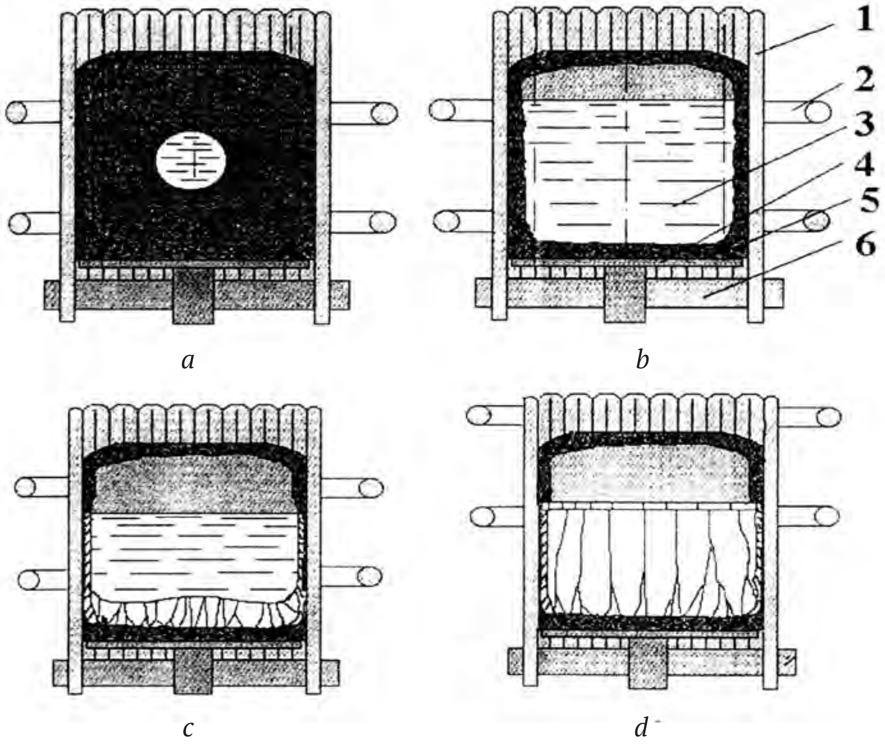


Fig. 4. Stages of crystal synthesis by directed crystallisation of the melt in a cold container using direct radio frequency heating technique. a – starting melting; b – homogenisation of the melt; c – crystal growth process; d – complete crystallisation of the volume of the melt. *1* – walls of the cold container; *2* – inductor; *3* – melt; *4* – cooled bottom; *5* – garnissage; *6* – insulating ring

is placed in the central part of the crucible, for example, Zr or Y. When the process is started, the metal heats up and melts with the formation of an electrically conductive liquid phase that initiates the melting of the batch mixture. In this case, the entire batch mixture is melted, except for the garnissage – a layer 3–5 mm thick near the walls and at the bottom of the water-cooled crucible. If necessary, a batch mixture is added to the melt using a special device. In order to stabilise the melt-garnissage boundary, the melt is usually kept for 0.1–1 hour before the onset of crystallisation. Then, the pulling mechanism is turned on, and the crucible with the melt is vertically lowered from the influential section of the electromagnetic field at a speed of 2–30 mm/h with such a simultaneous decrease in the generator power that the temperature of the residual melt remains within the specified limits. As a result of the synthesis, an ingot of crystals is formed, covered on the outside with a layer of unmelted batch mixture and on top with a glassy crust of the residual melt. Under mechanical action, the ingot is easily split, with the formation of columnar-shaped fianite crystals. The quality and yield of colourless fianite largely depends on the purity of the batch mixture components. Out of the harmful impurities, SiO_2 should be mentioned. Sometimes in colourless fianite, a slight yellowish tint is observed, which can be removed by annealing the crystals in air at temperatures above 800 °C. Coloured crystals can be synthesised using substandard colourless fianite previously ground into powder, as a component of the batch mixture. This technique is especially effective when obtaining densely coloured crystals and allows reducing the cost of production.

Fianites of various compositions have high refractoriness and chemical resistance. The melting point of fianites is 2600 - 2750 °C. They do not oxidise or evaporate at temperatures above 2500 °C. Fianite is an insulator up to 300 °C, at temperatures above 300 °C it acquires noticeable ionic conductivity. Hardness according to the Mohs hardness scale is 8, microhardness is 14,000–

20,000 MN/m^2, density 5.5–6 g/cm^3, refractive index dispersion 0.059–0.065 [107, 108]. The colour of fianites and their density are determined by the chemical composition. A black colour, close to the colour of morion, is obtained by annealing fianites in a vacuum or by processing with γ-radiation.

Optical lenses, providing a high degree of magnification are made from fianites. This material is promising in the chemical industry for the manufacture of high-temperature heaters operating in oxidising environments. The traditional use of fianites as a raw material for making jewellery is based on their high optical properties, hardness, and various colours of stones (Table 1). Fianite is processed in certain crystallographic directions, when faceted to enhance the "play" of the stone, the upper platform is made large, and the lower part of the stone is increased in height.

The industrial production of fianites for jewellery purposes was started in the USSR in 1972 [9]. A crystalline material similar to fianite, imitating precious stones, is produced abroad under the name cubic zirconia (CZ). The names "diamonesque" (USA), "djevalit" (Switzerland), "zirconia" (Austria) are outdated. The jewellery name "zircon", which is used in Russia, is not correct. A large amount of fianite-like material is produced in the countries of south-east Asia (China, Burma, Thailand, Hong Kong). Crystalline materials of emerald green and sapphire blue colour based on ZrO_2 are known on the world market under the trade name "siox".

At VNIISIMS (the now closed All-Russian Institute for the Synthesis of Mineral Raw Materials) [109], technologies for the synthesis of fianites of various colours, including polychrome crystals, with differently coloured zones within a single crystal were developed. The melting of batch mixtures of various compositions was carried out sequentially in one container, and before the melting of each subsequent composition of the batch mixture, partial crystallisation of the melt of the batch mixture of the previous composition occurred.

7. Partially Stabilised Zirconia

A separate class of materials based on ZrO_2 is the so-called group of partially stabilised zirconia (PSZ) [10, 11]. When an amount of stabiliser, insufficient for the formation of the cubic phase, is introduced into zirconia, a material is formed containing a tetragonal phase, usually, together with a monoclinic or cubic phase. In the ZrO_2–Y_2O_3 system, partially stabilised zirconia is formed from the melt at a content of 2–5 mol. % of yttria [110].

Table 1. The colour range of coloured phianites depending on the introduced chromophore [109]

Chromophore	Content, %	Colour	Imitation of natural stone
Y^{3+}	14–44	Colourless	Diamond
Pr^{3+}	2–20	Dark cherry	Ruby
Ce^{4+}	2–20	Red-burgundy	Ruby
Ce^{3+}	0.1–2	Yellow-orange	Padparadscha
Er^{3+}	fifteen	Pink	Vorobyevite
Tb^{3+}	0.01–5	Yellow	Heliodor
Pr^{3+}	0.1–2	Amber	Amber
Cu^{2+}	0.5–2	Dark yellow	Citrine
Ti^{4+}	0.1–2	Yellow brown	Hyacinth
Ni^{2+}	0.1–2	Light brown	Topaz
Ho^{3+}	0.1–5	Green yellow	Demantoid
Fe^{3+}	0.01–0.8	Yellow green	Chrysolite
Tm^{3+}	1–5	Pale green	Beryl
Nd^{3+}	0.1–1	Gray green	Grossular
Dy^{3+}	3–5	Salad green	Chrysoprase
Cr^{3+}	0.1–1	Olive	Olivine
Cu^{2+}	0.1 –0.5	Light blue	Aquamarine
Co^{3+}	0.01–0.5	Red-violet	Amethyst
Mn^{4+}	0.1–1	Brown violet	Sapphire

King and Yavorsky [111] were the first to note that during heating (cooling) in a two-phase sample stabilised with magnesium oxide a reversible $t \rightarrow m$ phase transition occurs, which is accompanied by a change in the stress pattern in grains or around grains and affects the microhardness. Garvey, Hannink, and Pascoe [10] proposed a stress-relief phase transition model, increasing the strength of such materials. Mechanical stresses at the tip of a growing microcrack initiate a phase transition, accompanied by a local increase in volume, and, accordingly, pressures of compressive stresses weaken tensile stresses at the tip of a microcrack, which stabilises the crack, slowing its growth.

The PSZ samples have a thin twinned domain structure, are opaque, characterized by high microhardness (13.5–15.0 GPa) and crack resistance (about 6–13 MPa $m^{0.5}$). The materials may contain other phases, for example, a mixture of phases *t* and *t*' with varying degree of tetragonality (*c*/2*a*), which is 1.014–1.015 and 1.004–1.005 for *t*-and *t*′-phases, respectively, in the $ZrO_2–Sc_2O_3–Y_2O_3$ system [112]. Phase *t* transforms under load.

By varying the amount of the added stabiliser, it is possible to achieve optical effects that mimic those of natural opal. In particular, opalescent translucent and opaque crystals were synthesised in the $ZrO_2–Y_2O_3–Gd_2O_3–Sm_2O_3$ system [109]. A similar effect was obtained by E. Polyanskii using the introduction of carbon microimpurities into the melt [109]. These stones are usually polished as cabochons. Opalescent crystals of the corresponding colours can be synthesised by the introduction of different luminophores into ZrO_2. It is possible to obtain banded opalescent stones, in which there is an alternation of transparent and opalescent layers, as in natural agates and onyx. The formation of such bands is associated with the formation of structurally different layers in the melt.

8. Baddeleyite

The second important mineral of zirconia is baddeleyite (ZrO_2). It was first discovered in 1892 in Sri Lanka and Brazil. It is named after Joseph Baddeley, who described the mineral in Sri Lanka. Baddeleyite is an accessory mineral in carbonatite deposits, where it occurs near the contact between basic alkaline rocks with limestone. It is characteristic of carbonatites of the Kola Peninsula and Karelia.

It is an ore of zirconium. Also it is used as a raw material for the ceramic industry and in the production of refractories. In Russia it is mined in the Kovdor deposit in Murmansk oblast and it is also mined in Brazil and in South Africa where the largest baddeleyite deposits are located in Phalaborwa. Common impurities are HfO_2 – up to 3 %, Fe_2O_3 – up to 2 %, Sc_2O_3 – up to 1 %.

The baddeleyite crystal system is monoclinic: C_{2h}^5 — $P2_1/c$; lattice parameters: a = 5.169, b = 5.341, c = 5.341 Å; β = 99°15′. Crystals are usually twinned and have a lamellar habitus. The crystal structure represents the distorted structure of CaF_2. Zr is in sevenfold coordination with respect to oxygen atoms, Zr–O distances varie from 2.04 to 2.26 Å. Parallel (100) layers of O atoms, located on the tops of slightly distorted square motifs, alternate with layers in which O atoms form a motif of squares and triangles; in this case, the Zr atoms are located in seven vertex polyhedra formed by the superposition of oxygen layers of both types. The arrangement of the O atoms is almost square in one of the layers is so insignificantly distorted that when rotated by 180° their relative position is almost the same; this explains the frequent twinning of baddeleyite crystals according to (100) [44]. Complex twins are often observed.

The baddeleyite forms oriented intergrowth with pyrochlore, crystals of which grow epitaxically on baddeleyite crystals. It is found in the form of aggregates. Crystals are partly radially fibrous. Baddeleyite has a different colour, it ranges from colourless to iron black. In thin fragments it is translucent. The hardness of baddeleyite is 6.5. Cleavage according to (001) is perfect, according to (010) and (110) it is imperfect.

When heated to 1100–1200 °C, it reversibly transforms into a tetragonal modification (ruffite); the reverse transition occurs at 950-850 °C; the tetragonal modification transition temperature increases in the presence of SnO_2 impurity. At 800 °C it can dissolve up to 10% SnO_2.

For research purposes, single crystals of baddeleyite can be obtained at temperatures up to 1100 °C by various methods, including hydrothermal crystallisation [113]. When grown from a solution in a melt, lead fluoride, $Na_2B_4O_7$, $Li_2Mo_2O_7$ [114], or mixtures of alkali metal fluorides with vanadium or boron oxides can be used as flux [109]. Crystals are recovered by dissolving the flux in acid.

ZrO_2 crystallises at a temperature of about 450 °C from an amorphous gel precipitated as a result of treatment of $ZrOCl_2 \cdot 8H_2O$ with ammonia. The exothermic effect of crystallisation corresponds to almost complete dehydration. However, in this case, a metastable tetragonal modification is formed, stabilised by residual water. The transformation into the monoclinic modification is associated with complete dehydration and occurs above 950 °C [115–116]. VNIISIMS [109] developed practically important methods for the synthesis of baddeleyite by the one-stage annealing of amorphous ZrO_2 with the addition of a mineraliser in the air. Depending on the amount of the mineraliser (fluorides of elements of groups II–III of the periodic system), end products with different amounts of impurities are obtained. An admixture of corundum is formed when aluminium fluoride is used as a mineraliser. Powdered baddeleyite is used as a filler in special-purpose rubbers and fluoroplastics for the manufacture of dielectric film materials.

Until recently, technological ceramics were obtained only from synthetic zirconia, and natural baddeleyite was considered unsuitable even for producing refractories due to the structural polymorphism of zirconia. Meanwhile, it is important for Russia to expand the range of products that can be made from baddeleyite. Golovin, Zhigachev et al. (Tambov State University) [8, 117–118] investigated the possibility of neutralising silicon inclusions in baddeleyite and showed the fundamental possibility of synthesising high-quality structural ceramics from the domestic natural zirconia – baddeleyite.

As a result of ultrafine grinding of the purified baddeleyite of the Kovdor mining and processing plant using planetary mill, powders with a characteristic crystallite size less than 20 nm were obtained. Ground baddeleyite contained up to 80 % tetragonal and cubic phases. Thus, the possibility of obtaining zirconia containing metastable tetragonal and cubic phases based on unconventional raw materials was demonstrated. It is characteristic that the fine grinding of synthetic zirconia led to partial amorphisation of the monoclinic phase, but did not change the phase composition of the powder [119].

The effect of the addition of multilayer carbon nanotubes on the strength and plasticity of ceramics based on baddeleyite, partially stabilized by calcium oxide with the formation of a tetragonal phase, was investigated. It was shown that along with the transformation hardening in the synthesised composites, additional mechanisms of crack deceleration were effectively triggered due to the reinforcing effect of carbon nanotubes. Samples of baddeleyite ceramics modified with carbon nanotubes with high performance characteristics corresponding to the requirements for high-quality ceramics were obtained, synthesised from the traditional imported raw material, synthetic zirconia.

Baddeleyite ceramics are actively used for lining of a glass melting bath due to their chemical and fire resistance properties.

9. Nuclear energetics

Another area for the potential application of materials based on zirconia is inert matrix nuclear fuel (IMF), which is a ceramic nuclear fuel evenly distributed in an inert matrix [120-126]. The benefits of IMF over traditional uranium fuel include the possibility of a more complete use of plutonium, an increase in uranium burn up, the ability to transmute “minor” actinides (Np, Am, Cm), reducing the amount of highly toxic radioactive waste to be buried, and the possibility of burying waste without processing it.

Studies on the creation of IMF were started in the 50-60s in the USA on the basis of ZrO_2–UO_2 and ZrO_2–CaO–UO_2 systems. Subsequently, the phase composition of the IMF was adjusted taking into account the requirements imposed on the material of the inert matrix, namely: low neutron capture cross section; high melting temperature (2500–2800 °C); high thermal conductivity; compatibility with a fissile fuel composition and fuel cladding materials; absence of phase transformations and amorphisation in the range of operating temperatures of a nuclear installation; high radiation resistance; high mechanical strength, sufficient elasticity and hardness; low solubility in hot water or other heat transfer fluids; stability under disposal conditions; acceptable cost.

Ceramics based on stabilised zirconia satisfies most requirements and allows obtaining products with a high density (more than 95 % of theoretical). However, it is characterised by low thermal conductivity. In addition, thermodynamically unstable cubic solid solutions are subjected to phase decomposition under severe operating conditions. A promising option is the use of $Zr_2R_2O_7$phases with the pyrochlore structure, where R – rare earth elements of the cerium subgroup (see Fig. 5).

10. Conclusion

The manifestation of the main materials science triad: composition – structure – properties with subsequent application, and the important informational role of phase diagrams is revealed can be seen based on the example of ZrO_2. The phases based on zirconia have such a combination of physicochemical characteristics that make them, in the full sense of the word, polyfunctional materials. The reversible transformation of deformation energy into phase transition energy in a partially stabilised ZrO_2, providing the amazing fracture resistance characteristic of this material is unique. The nano-sized domains penetrating these materials and facilitating the implementation of the stress-induced phase transition suggests the role of nanotechnology in materials science. From the point of view of methodology, this indicates the need to supplement the materials science triad with one more variable – dispersity, which was actually proposed by I. V. Tananaev [127].

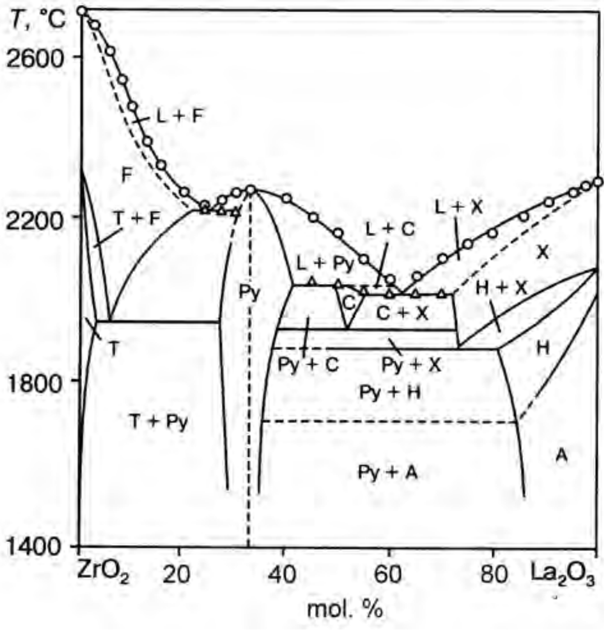


Fig. 5. Phase diagram of ZrO_2–La_2O_3 system according to [94]. F and C are cubic phases with a fluorite structure, Py is a phase with a pyrochlore structure with an idealised composition $Zr_2La_2O_7$, T – solid solution based on the tetragonal modification of ZrO_2, A, H, X – solid solutions based on various modifications of La_2O_3

Heterovalent fluorite solid solutions based on ZrO_2 with a variable number of ions in the unit cell fully combine the features of phases with grossly non-stoichiometry [128], such as the formation of maxima on the melting curves [129], high ionic conductivity combined with low thermal conductivity [27], and the formation of ordered low-temperature phases. By these properties they are similar to fluoride solid solutions formed in MF_2-RF_3 systems [130].

The stabilisation method of high-temperature modifications by heterovalent isomorphic substitutions, which led to the creation of fianites, was used by us for the stabilisation of α-GdF_3 [131] and α-Na_2SO_4 [132] with the growth of laser single crystals.

Phase equilibria at low temperatures in systems with ZrO_2 are among the unsolved fundamental issues. Since the time of achieving equilibrium, controlled by cationic diffusion, increases exponentially with decreasing temperature [133], the study of low-temperature equilibria is a very difficult and often insoluble problem. Regions for which the time for establishing equilibrium by means of dry sintering is about 1 year can be considered as being low-temperature regions. For systems based on zirconium and hafnium oxides, this is about 1600 °C.

The use of solvents, in particular, the method of hydrothermal synthesis, allowed significantly advance towards the low-temperature region in ZrO_2–R_2O_3 and ZrO_2–CeO_2 systems [64, 65, 71]. However, in the ZrO_2–CaO system such experiments [66] were not enough for the accurate determination of the temperature of the eutectoid [89, 134–135]. Thermodynamic modelling is not always reliable. In particular, the temperature of the eutectoid decomposition of the cubic phase in the ZrO_2–Y_2O_3 system differs according to the data of different models by hundreds of degrees [68, 69, 136], and in [47] it was below absolute zero, which contradicts the third law of thermodynamics. It can be expected that the use of salt melts will allow making progress in this matter.

It can be stated that we have a very poor idea of the formation of ordered phases in systems with ZrO_2, their compositions, structures, regions of stability, and their relationships with disordered solid solutions. This is clearly seen in the example of the results of studies of ZrO_2–CaO, ZrO_2–Sc_2O_3 systems. As Bevan rightly emphasised in 1970 [77], we do not know the true structure and compositions of the ordered phases, since the cation lattice in the studied samples shows no signs of ordering. While the anionic sublattice is in the process of ordering, the cationic sublattice is delayed due to the extremely slow cationic diffusion. Despite the active research and accumulated results over the past 50 years, this statement remains true. It can be assumed that the precursors of low-temperature orderly phases are non-equilibrium phases *t′* and *t″*, systematically appearing in PSZ samples. It should be noted that in Ce_2O_3-CeO_2 system, where ordering is determined only by anionic diffusion, a whole homologous series of ordered phases has been revealed [137]. Similar phenomena should be looked for in ZrO_2–R_2O_3 systems. The ZrO_2–In_2O_3 system is of interest from the point of view of searching for ordered phases [138–139], since indium oxide is a crystallochemical low-melting analogue of scandia.

The nature of phase transformations in low-temperature regions of systems with ZrO_2 is traditionally interpreted through the concept of metastable equilibria [71]. However, it is quite possible that the corresponding samples are not in a metastable state, but in a labile state, the escape from which is extremely slow. The practical possibility of using materials in a labile state violates one of the postulates of chemical thermodynamics [140].

According to the third law of thermodynamics, a decrease in temperature leads to a decrease in entropy, a decrease in the concentration of defects, and decomposition of solid solutions, thus the low-temperature region can be a source of new ordered phases, stoichiometric or close to them compositions, which can become the basis for new functional materials.

Author contributions

The authors made an equal contribution to the preparation of the review.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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