Original articles

Phase diagrams of zirconium dioxide systems with yttrium and scandium oxides

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Abstract

The literature data on the study of phase equilibria in systems zirconia with yttria and scandia are analysed. Possible schemes of low-temperature phase equilibria in ZrO_2-Y_2O_3 and ZrO_2-Sc_2O_3 systems are presented taking into account the third law of thermodynamics.

The coordinates of non-variant transformations in these systems are tabulated. A sign of non-equilibrium states is the observation of non-diffusion processes of ordering of solid solutions. The modified cryoscopy method is used to calculate the distribution coefficients of scandia and yttria during the crystallization of the ZrO_2 melt.

The possibilities for the existence of a set of ordered phases in the ZrO_2-Y_2O_3 system and diffuse phase transition in the cubic modification of zirconia are discussed.

Keywords: Zirconia, Yttria, Scandia, Solid solutions, Ordering, Phase diagrams, Distribution coefficients

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1. Introduction

Phase diagrams are the physical and chemical basis for the synthesis of functional materials. In addition, they allow predicting the behaviour of the material under operating conditions. Solid solutions of oxides of rare earth elements (REE) R_2O_3 in high-temperature cubic modifications of zirconia $Zr_{1-x}R_xO_{2-0.5x}$ are among the most refractory oxides with a melting temperature above 2700°C [1, 2]. Materials based on them are widely used as jewellery crystals (fianites) [3, 4] and refractory and corrosion-resistant ceramics [5–9]. The high anionic conductivity of these solid solutions is combined with a low thermal conductivity [10]. These circumstances determine the use of appropriate materials in electrochemical devices (fuel cells, oxygen sensors) [11–13] and also as thermal barrier coatings [14, 15]. Materials based on zirconia are the basis of nuclear fuel with an inert matrix [16].

A lot of studies were dedicated to the study of phase equilibria in ZrO_2-R_2O_3 systems, but the result of these studies is not satisfactory. These systems have been studied by various groups of researchers. A summary of the data is provided in [17, 18]. The results obtained for different REE do not fit well with each other. Difficulties are associated both with high melting temperatures and with very long time intervals required to achieve equilibrium in the low-temperature region [19-22]. As in previous studies, we will denote regions of phase diagrams where the time required to establish equilibrium exceeds a year as being low-temperature regions. Cubic solid solutions of $Zr_{1-x}R_xO_{2-0.5x}$ are obviously thermodynamically unstable at low temperatures. However, the negligibly small diffusivity of cations [23] prevent the decomposition of solid solutions, which makes the corresponding materials indefinitely stable at ambient temperatures. The insufficiency of the annealing used in a number of studies was demonstrated by researchers from the Tokyo Institute of Technology [24, 25]. In particular, it turned out that the temperature of the eutectoid decomposition of a solid solution based on the medium-temperature tetragonal modification in the ZrO_2-Er_2O_3 system, determined in the study [26], was underestimated by about 500 ºC [24].

The synthesis of samples under hydrothermal conditions sharply accelerates the processes of phase formation in refractory oxide systems [2, 27]. However, additional problems arise in this case, associated, in particular, with the contamination of samples with hydroxyl ions, which distort the pattern of phase equilibria [28]. In addition, the resulting nanocrystals of intermediate phases often "get stuck" in metastable states [29–30].

The purpose of this study is a critical analysis of the available data on the study of phase equilibria in key ZrO_2-Y_2O_3 and ZrO_2-Sc_2O_3 systems and construction of assumed phase diagrams with extrapolation to absolute zero temperature in accordance with the third law of thermodynamics.

2. Analysis methodology

In this study, we applied the methodology that we used earlier in [31–33]. According to the consequence of the third law of thermodynamics, as the temperature tends to absolute zero in quasi-equilibrium processes, all phases of variable composition should disappear through the decomposition or contraction of compositions to stoichiometric ones [20, 34]. In this case, the limiting solubility curves should have vertical tangents as the temperature approaches absolute zero [33]. The second important thermodynamic condition is the so-called Hume-Rothery rule, according to which, when an ordered phase with a narrow homogeneity region appears, the region of existence of a neighbouring disordered phase should sharply narrow [35].

The corresponding approach using the extrapolation of the most reliable experimental data in the study of phase equilibria allows by extrapolating phase fields to the region of low temperatures, to obtain information for those regions of phase diagrams where an experiment aimed at realizing equilibrium states is complicated or simply impossible. Previously, using this approach, we outlined the scheme of phase equilibria in the ZrO_2-Er_2O_3 system [22].

An alternative technique is the thermodynamic computer simulation of phase equilibria. The construction of thermodynamic models of the studied systems is an ideal goal to strive for [36–38]. However, there are problems associated, among other things, with the determination of the thermodynamic properties of phases of variable composition and with the choice of

reliable experimental data for their processing [39–42]. The thermodynamic modelling of phase equilibria in ZrO_2-Y_2O_3 system was performed in [43–46]. The results differ significantly.

3. Results

3.1. ZrO_2-Y_2O_3 system

The ZrO_2-Y_2O_3 system is a classic and model system. It has been studied by various groups of researchers [17, 18, 47]. Solid-liquid equilibria were studied by Rouanet [48], Noguchi et al. [49], Lopato et al. [50]. The most detailed studies of phase equilibria in the solid state were carried out by Pascual and Duran [51] and Stubican et al. [52], with an annealing duration of up to 8 months. These studies provided similar results.

Based on the work data Pascual and Duran, see Fig. 1a. In this study the samples were annealed for 3 hours at 2000°C, 10 hours at 1800°C, and 385 hours at 1450°C, which appears acceptable [22]. However, it is obvious that the 8 months used in this study for annealing at 800°C were completely insufficient. The corrected pattern of phase equilibria is shown in Fig. 1b. At the same time, the designations of the phase composition of the samples annealed and quenched in the study of Pascual and Duran were applied to the figure.

Extensive regions of heterovalent solid solutions based on the high-temperature polymorph of ZrO_2 with fluorite structure (phase F, space group $Fm3m$) and low-temperature cubic modification Y_2O_3 (phase C, bixbyite type, space group $Ia3$) were formed in the system. Although the bixbyite type is derived from the fluorite type with an ordered arrangement of vacancies [53], the presence of a two-phase F+C region in the phase diagram was reliably recorded as early as by Duwes et al. [36].

Dissolution of yttrium oxide in high-temperature ZrO_2 modification stabilizes the fluorite structure, and a maximum occurs on the liquidus curve. The maximum point on the melting curves of the solid solution is non-variant, and the liquidus and solidus curves merge at it in the presence of a common horizontal tangent. When depicting phase equilibria in this region Pascual and Duran made an unfortunate mistake, which is corrected in Fig. 1b. The course of the liquidus curve in this system was determined using a solar furnace in the studies
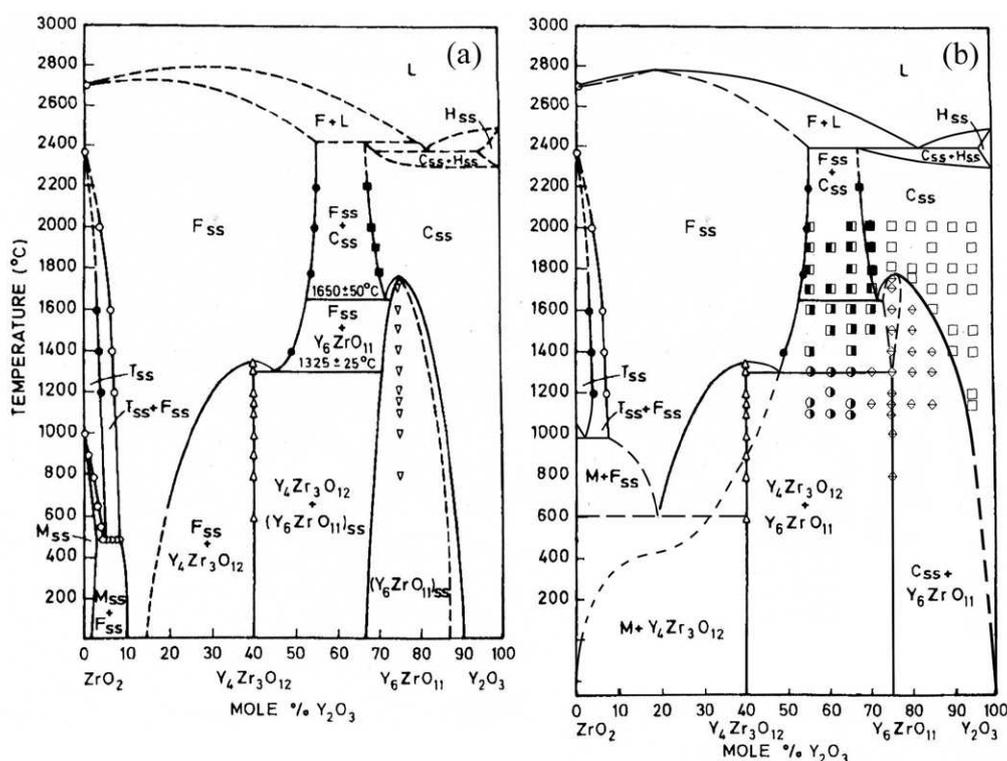

Fig. 1. Phase diagram of the ZrO_2-Y_2O_3 system according to [51] (a) and its correction taking into account the requirements of the third law of thermodynamics (b)

[48–50], see Fig. 2. When constructing Fig. 1b, we used data of Shevchenko et al. [50].

At a high concentration of yttrium oxide, the melt and three solid phases F, C, and H (a solid solution based on the high-temperature modification of Y_2O_3) should provide two three-phase equilibria, displayed as horizontal segments on the phase diagram. Experimentally, the temperatures of these equilibria are not resolved, and computer simulation [43-46] provides a difference in temperatures within 10-25 degrees. Thus, this system at normal pressure is located in the vicinity of the bifurcation point of A_1II type [54] corresponding to the equilibrium of four condensed phases.

As the temperature decreases, the solid solutions based on the F and C phases undergo ordering with the separation of $Y_4Zr_3O_{12}$ and Y_6ZrO_{11} phases (idealized composition), respectively. The data of [51] and [52] studies agree very well (± 10 °C) in terms of the phase transition temperature $F \leftrightarrow Y_4Zr_3O_{12}$. Our correction in the region of high concentrations of yttrium oxide includes a significant decrease in the region of homogeneity of the ordered phase, which, as the temperature is lowered, must shrink to the ideal Y_6ZrO_{11} composition, as well as the position of the decomposition curve of the solid solution based on the cubic modification of yttrium oxide, which should come to the point of the pure component at $T \to 0$ K.

Probably, the observation of a wide region of the ordered phase "Y_6ZrO_{11}" in the absence of a two-phase region with phase C was caused by the fact that the ordering in this system in

an experimental study [51] occurred according to a non-equilibrium non-diffusion mechanism that does not require overcoming the potential barrier to the nucleation of a new phase in the volume of the old one. A similar phenomenon, as shown by the analysis, was observed during low-temperature ordering in the Ni-Pt system [33], as well as in the HfO_2-R_2O_3 systems (fluorite-pyrochlore transitions) [22].

The region of low concentrations of yttrium oxide (the decomposition of the tetragonal phase – a solid solution based on the medium-temperature modification of ZrO_2) was corrected by analogy with the data of Yashima and others [24], which, when studying equilibria in a similar ZrO_2-Er_2O_3 system, annealed samples at 1690 °C for 48 hours and 8 months at 1315 °C. At the same time, the temperature of the eutectoid decomposition of the tetragonal phase was raised by us by several hundred °C in comparison with the variants of the phase diagram presented in [51, 52]).

The dotted line denotes the metastable continuation of the curve of the maximum concentration of this solid solution (the solvus curve of phase F). This curve must pass through the origin of the coordinates and have a vertical tangent at this point. This condition can be fulfilled only if there is a point of inflexion on the solvus curve (in this case, on the metastable part of this curve). It should be noted that the eutectoid corresponding to the decomposition of the fluorite phase should be located above the metastable solvus curve. Accordingly, the temperature of the eutectoid decomposition of the cubic solid solution was presumably targeted at 600 ± 100 °C. This is much higher than is accepted in all studies on phase equilibria in this system, both experimental and calculated.

Thus, the proposed version of the phase diagram of the ZrO_2-Y_2O system (Fig. 1b) is characterized by the following non-variant equilibria, presented in Table 1.

3.2. ZrO_2-Sc_2O_3 system

Phase equilibria in the ZrO_2-Sc_2O_3 system have been studied in numerous papers [55–66]. The approximate phase diagram of ZrO_2-Sc_2O_3 system, plotted in accordance with the data of Spiridonov et al. [57], Shevchenko et al. [60–62] and Fujimori et al. [65, 66] with extrapolation to 0 K is shown in Fig. 3. The coordinates of the non-variant points
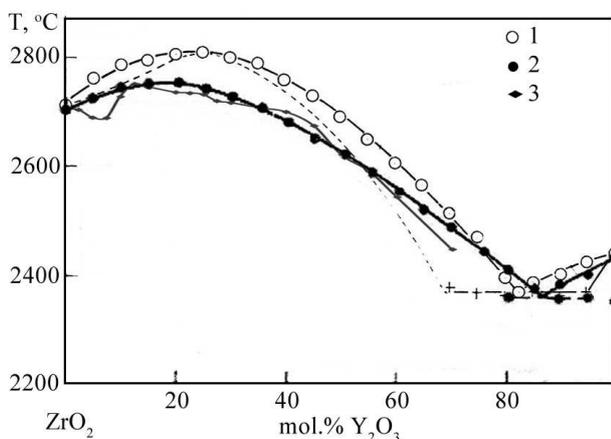

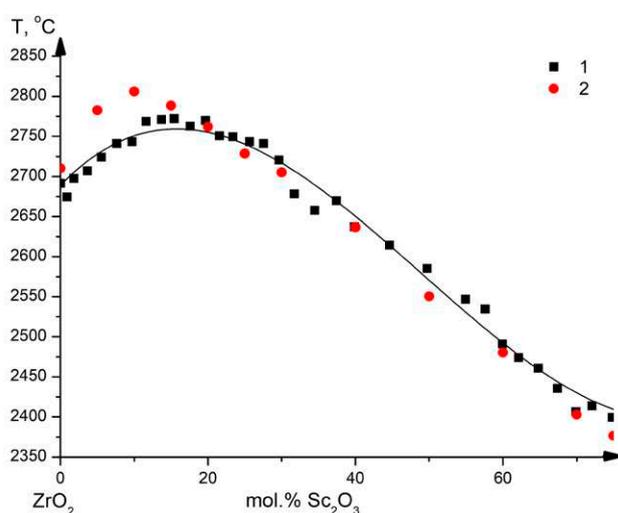**Fig. 2.** Liquidus of the ZrO_2-Y_2O_3 system. *1* – data [48], *2* – data [50], *3* – data [49]

Table 1. Non-variant equilibria in the ZrO_2-Y_2O_3 system

Name	Phase balance	Composition, mol % Y_2O_3	Temperature, ℃	Temperature, K
Dystectics (maximum on the solid solution melting curve)	L ↔ F	20±2	2750±25	3023
A_1II type bifurcation	L+F+C+H	–	2360±50	2633
Distectoid	F ↔ $Y_4Zr_3O_{12}$	40	1380±10	1653
Distectoid	C ↔ Y_6ZrO_{11}	75	1750±50	2023
Eutectoid	T ↔ M + F	3±1	950±25	1223
Eutectoid	F ↔ $Y_4Zr_3O_{12}$+ M	18±3	600±100	873
Eutectoid	F ↔ $Y_4Zr_3O_{12}$+ Y_6ZrO_{11}	45±3	1350±25	1623
Eutectoid	C ↔ Y_6ZrO_{11}+ F	68±2	1650±50	1923
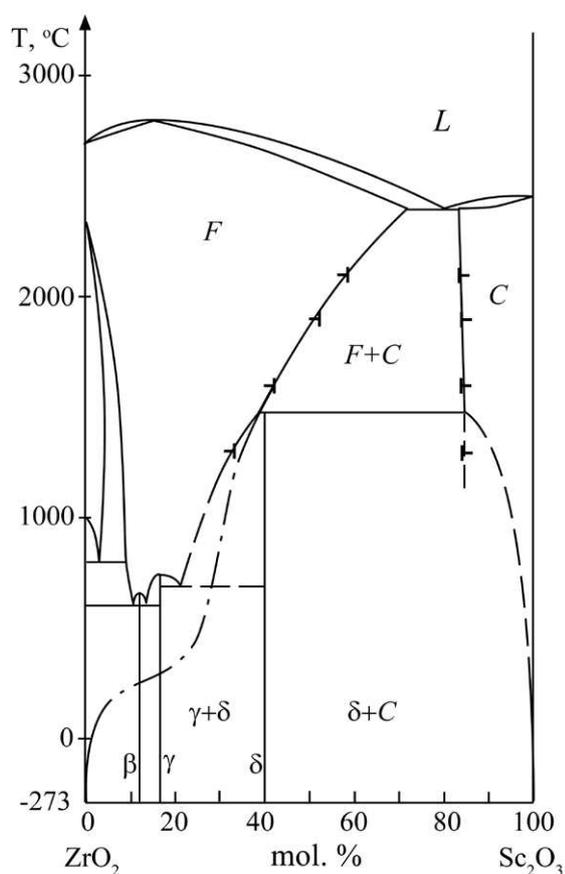
Fig. 3. Summary phase diagram of the ZrO_2-Sc_2O_3 system

Fig. 4. Liquidus of the ZrO_2-Sc_2O_3 system *1* – data [60], *2* – data [58]

are summarized in Table 2. Wide regions of solid solutions based on scandia (bixbyite type, phase C) and cubic high-temperature modification of zirconia (phase F) were formed in the system. A maximum was formed on the melting curves of the fluorite solid solution. A comparison of the liquidus curves obtained in [58, 60] is shown in Fig. 4.

With decreasing temperature, the fluorite solid solution (phase F) undergoes ordering with the release of ordered phases, which were originally assigned the designations β, γ, and δ and $Zr_7Sc_2O_{17}$, $Zr_5Sc_2O_{15}$ and $Zr_3Sc_4O_{12}$ compositions (cubic solid solution, phase F was designated as phase α). The decodering of crystal structures [67–69] allowed refining the composition of the β phase: $Zr_{50}Sc_{12}O_{118}$. Compound $Zr_3Sc_4O_{12}$ was described as a rare mineral found in meteorites [70]. This compound isostructural to the corresponded yttrium phase $Zr_3Y_4O_{12}$ and forms a continuous solid solution with it [63].

The low-temperature phases β, γ, and δ are characterized by the trigonal distortion of the fluorite lattice due to the ordered arrangement of anion vacancies [61]. The differentiation of cations over crystallographic positions practically does not occur due to frozen diffusion [55], although it is energetically favourable [69].

Table 2. Non-variant equilibria in the ZrO_2-Sc_2O_3 system

Name	Phase balance	Composition, mol % Sc_2O_3	Temperature, °C	Temperature, K
Distectics (maximum on the solid solution melting curve)	L ↔ F	15±5	2800±50	3073
Eutectic	L ↔ F+ C	78±2	2400±50	2673
Distectoid	F ↔ β		650±50	923
Distectoid	F ↔ γ		750±50	1023
Peritectoid	F + C ↔ δ	40±2	1550±100	1733
Eutectoid	T ↔ M + F	3±1	800±100	1073
Eutectoid	F ↔ M + β	11±1	600±50	873
Eutectoid	F ↔ β + γ	13±1	600±50	873
Eutectoid	F ↔ β + δ	21±2	700±50	973

The transition temperature of the phase β to a disordered state (phase F) is close according to the data of [57, 60–62, 65–66], and is 650±50 ºC. Phase disorder temperatures γ and δ indicated in the literature are very different. This may be due to the non-quenchability of the high-temperature disordered cubic phase upon cooling [57]. Data of Zyrin et al. were preferential for the construction of Fig. 4 [61]. In particular, for the transition α↔γ, Spiridonov et al. [57] and Ruh et al. [59] reported a temperature of ~1100 ºC. The same group of researchers reported a γ phase disorder temperature equal to 1480°C [61] and 1650°C [62]. This region of the phase diagram of ZrO_2-Sc_2O_3 system requires further research.

It should be noted that the continuation of the line of the maximal concentration of the cubic solid solution (solvus curve of the phase F) to zero coordinates (ZrO_2) subject to the presence of a vertical asymptote is impossible without the assumption of the presence of an inflection point on the metastable continuation of this curve.

3.3. Distribution coefficients

Accurate measurement of the liquidus curve of solid solutions allow calculating the distribution coefficients of the impurity component during the crystallization of the matrix from the melt using the modified cryoscopy method. Previously, such calculations were carried out for a number of ZrO_2–R_2O_3 systems [71]. The basis of the modified cryoscopy method is the Van't Hoff limit equation:

$$m = [RT_0^2/\Delta H](k\text{-}1), \qquad (1)$$

where ΔH and T_0 [K] are enthalpy of melting and melting temperatures of the matrix, R is the universal gas constant, k is the impurity distribution coefficient, m is the liquidus slope. This equation is valid for infinite dilution.

In the modified cryoscopy method, the value m is not determined based on precision measurements of small values of temperature depression with the introduction of low impurity concentrations, but by approximating liquidus curves in a wide range of concentrations, followed by differentiation of analytical expressions [72, 73].

Previously, this method was used to process the data of [48, 49] using the liquidus curve of the F phase in the ZrO_2–Y_2O_3 system and study [60] for the ZrO_2–Sc_2O_3 system. In this study, the data of Shevchenko et al. [50] for the ZrO_2–Y_2O_3 system and data of Sekiya et al. [58] for the ZrO_2–Sc_2O_3 system were processed using this method. The points of the liquidus curves in a wide concentration range were processed using the least squares method in the form of a 3rd order polynomial. In this case, the melting point of ZrO_2 (2710 °C) was fixed by the provision of a tenfold weight to this point. Primary data were obtained by digitizing the graph provided in [58].

Data for ZrO_2-Y_2O_3 [50] and ZrO_2-Sc_2O_3 [58] systems are well described by third-order polynomials with correlation coefficients of 0.999 and 0.980, respectively. By differentiating the obtained equations for $x = 0$, the values of the liquidus slope (depression) were obtained for an infinitesimal impurity content $m = (\partial T/\partial x)_{x=0}$, namely 594 and 1005 deg/mol, respectively. Hence, according to equation (1) using the enthalpy of ZrO_2 melting, ΔH = 16.40 kcal/mol [74], we obtain the distribution coefficients of Y_2O_3 and Sc_2O_3 during crystallization of the ZrO_2 melt. The obtained value k_Y = 1.55 agrees well with

the calculated value obtained from the data of Noguchi et al. [49], but diverges from the value obtained from the data of Rouanet [48], see [22]. The calculated value $k_{Sc} = 1.93$ significantly differs from the value $k_{Sc} = 2.87$ calculated according to Shevchenko et al. [22]. The discrepancies are determined by the complexity of conducting experiments at temperatures above 2700 °C, see Figs. 2 and 4.

4. Discussion

The wide regions of solid solutions formed in ZrO_2-R_2O_3 systems are striking examples of the so-called grossly nonstoichiometry [55]. The maxima on the melting curves of these solid solutions are a characteristic feature of heterovalent isomorphism with a variable number of atoms in the unit cell and correlate with high ionic conductivity and low thermal conductivity [9, 75, 76].

The formation of such solid solutions is characterized by the accumulation of defects associated with charge compensation and the formation of ordered phases with decreasing temperature. This effect that is observed in the studied systems and in this case it is weakened and smeared out due to low cationic diffusion. The absence of pronounced differentiation of cations over crystallographic positions during the formation of ordered fluorite-like phases sharply distinguishes oxide systems from analogous fluoride systems. It can be assumed that the complete cationic ordering will change the thermodynamic stability of the corresponding phases and, thus, it will shift the temperature limits of their existence in the phase diagrams of ZrO_2-R_2O_3. Probably, the observed pattern of ordering (the formation of only two fluorite-like phases $Y_4Zr_3O_{12}$ and Y_6ZrO_{11} in the ZrO_2–Y_2O_3 system and three ordered phases in the ZrO_2–Sc_2O_3 system) is not complete. For comparison, we can refer to the CeO_2-Ce_2O_3 model system, where the set of ordered phases is much richer [77]. In particular, it can be expected that in the yttrium system the same ordered phases as in the scandium system are formed , and the absence of phases of the β and γ types in the ZrO_2–Y_2O_3 system associated only with kinetic difficulties [62]. In addition, the existence of the phase $Y_5Zr_2O_{11.5}$, which is isostructural to the erbium analogue can be expected [78].

It should be noted that all thermodynamic models for the ZrO_2–Y_2O_3 system provide for the presence of only one ordered phase $Y_4Zr_3O_{12}$, which significantly limits their reliability. In this case, 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 [43–46], and in [46] it falls below absolute zero, which contradicts the third law of thermodynamics. The diagram constructed by us (Fig. 1b) is closest to the thermodynamic model of Degtyarev and Voronin [43].

The inflection points on the extrapolated solvus curves of the F phases deserve special attention. Such points are characteristic of all binary systems with heterovalent solid solutions based on compounds with the fluorite structure [79], which is associated with diffuse phase transitions in fluorite matrices [80, 81]. In particular, such a behaviour of the solvus line takes place in the system UO_2–UO_3 [82], and the presence of a diffuse phase transition in uranium dioxide is discussed [80, 83–85]. Thus, the results of low-temperature extrapolation of the solvus curves both in the analysed systems and the corresponding curves in other systems with the participation of zirconia and hafnium oxides [22] suggest the presence of a diffuse phase transition in the cubic ZrO_2 and HfO_2 polymorphs. For zirconium and hafnium oxides, we do not know any indications of its existence.

Conditional estimation of approximate temperature of this transition (since this is diffuse transition, and it is not a phase transition in the thermodynamic sense) based on $T \sim (0.7-0.8)T_{melt}$ [K] ratio provides a value of 1680–2100 °C, i.e. below the temperature of polymorphic transformation between the cubic and tetragonal modifications of ZrO_2 (2170 °C [2]). Thus, probably, all solid solutions of the fluorite structure formed in systems with the participation of zirconia are solid solutions in the disordered initial ZrO_2 form. This creates additional difficulties for constructing the corresponding thermodynamic models.

On numerous published "phase diagrams" of $(Zr,Hf)O_2$-R_2O_3 systems at temperatures below 1300 °C frozen states are shown instead of equilibrium phase regions. The actual behaviour of materials in these systems upon cooling is

determined mainly not by equilibrium phase transformations, but by non-diffusion phase transitions. Accordingly, on phase diagrams, in some cases, two-phase regions degenerate, and instead of them lines of phase transformations of the martensitic type are present.

A scandium solid solution of optimal concentration is thermodynamically stable at temperatures above 700 °C, i.e., the corresponding products are stable in terms of phase composition for an indefinitely long period of time if they are operated at this temperature without lowering it.

5. Conclusions

Phase equilibria at low temperatures in systems involving zirconia and hafnia are among the unresolved fundamental issues. Since the time of achieving equilibrium controlled by cationic diffusion increases exponentially with decreasing temperature, the study of low-temperature equilibria is a very complicated and often unsolvable problem.

It should be noted that ordering processes in systems with zirconia and hafnium oxides have been very poorly studied. Significant discoveries can be expected here.

Other methods for the investigation of low-temperature phase formation in the discussed systems are required. It can be expected that the use of salt melts will allow progress to be made in solving this problem. It should be noted that salt melts, in contrast to hydrothermal synthesis, contribute to the formation of micron rather than nanoscale powders, which probably less prone to the formation of metastable equilibria.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflicts of interest

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

References

1. Sabbarao E. C. Zirconia - an overview. *In: Proc. First Int Conf.: Science and Technology of Zirconia*. Cleveland, Ohio; 1981. p. 1–24.

2. Fedorov P. P., Yarotskaya, E. G. Zirconium dioxide. Review. *Condensed Matter and Interphases*. 2021;23(2): 169–187. https://doi.org/10.17308/kcmf.2021.23/3427

3. Kuzminov Yu. S., Osiko V. V. *Fianites**. Moscow: Nauka Publ.; 2001. 280 p. (In Russ.)

4. Osiko V. V., Borik M. A., Lomonova E. E. Synthesis of refractory materials by skull melting. In: *Springer Handbook of Crystal Growth*. N.Y.: Springer; 2010. pp. 433–477. https://doi.org/10.1007/978-3-540-74761-1_14

5. Zhigachev A. O., Golovin Yu. I., Umrikhin A. V., … Dyachek T. A. *Ceramic materials based on zirconium dioxide**. Golovin Yu. I. (ed.). Moscow: Tekhnosfera Publ.; 2018. 357 p. (In Russ.)

6. Kablov E. N. Strategical areas of developing materials and their processing technologies for the period to 2030. *Aviation Materials and Technologies*. 2012;S: 7–17. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=18084815

7. Kelly J. R., Denry I. Stabilized zirconia as a structural ceramics: An overview. *Dental Materials*. 2008;24(3): 289–298. https://doi.org/10.1016/j.dental.2007.05.005

8. Daou E. E. The zirconia ceramic: strengths and weaknesses. *The Open Dentistry Journal*. 2014;8(1): 33–42. https://doi.org/10.2174/1874210601408010033

9. Fedorov P. P., Popov P. A. Principle of equivalency of the disorder sources and heat conductivity of solid. *Nanosystems: Physics, Chemistry, Mathematics*. 2013;4(1): 148–159. (In Russ., abstract in Eng.). Available at: https://www.elibrary.ru/item.asp?id=18964066

10. Haering C., Roosen A., Schichl H., Schnoller M. Degradation of the electrical conductivity in stabilized zirconia system. Part. II: Scandia-stabilized zirconia. *Solid State Ionics*. 2005;176(3-4): 261–268. https://doi.org/10.1016/j.ssi.2004.07.039

11. Fergus J. F. Electrolytes for solid oxide fuel cells. *Journal of Power Sources*. 2006;162: 30–40. https://doi.org/10.1016/j.jpowsour.2006.06.062

12. Mahato N., Banerjee A., Gupta A., Omar S., Balani K. Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science*. 2015;72: 141–337. https://doi.org/10.1016/j.pmatsci.2015.01.001

13. Borik M. A., Bredikhin S. I., Kulebyakin A. V., … Tabachkova N. Yu. Melt growth, structure and properties of $(ZrO_2)_{1-x}(Sc_2O_3)_x$ solid solution crystals. *Journal of Crystal Growth*. 2016;443: 54–61. https://doi.org/10.1016/j.jcrysgro.2016.03.004

14. Clarke D. R., Phillpot S. R. Thermal barrier coatings. *Materials Today*. 2005;8(6): 22–29. https://doi.org/10.1016/S1369-7021(05)70934-2

15. Zhang H., Liu Zh., Yang X., Xie H. Interface failure behavior of YSZ thermal barrier coatings during thermal shock. *Journal of Alloys and Compounds*. 2019;779: 686–697. https://doi.org/10.1016/j.jallcom.2018.11.311

16. Degueldre C. Zirconia inert matrix for plutonium utilisation and minor actinides disposition in reactors. *Journal of Alloys and Compounds*. 2007;444-445: 36–41. https://doi.org/10.1016/j.jallcom.2006.11.203

17. Andrievskaya E. R. Phase equilibria in the refractory oxide systems of zirconia, hafnia and yttria with rare-earth oxides. *Journal of the European Ceramic Society*. 2008;28(12): 2363–2388. https://doi.org/10.1016/j.jeurceramsoc.2008.01.009

18. Andrievskaya E. R. *Phase equilibrium in systems of hafnium, zirconium, yttrium oxides with oxides of rare earth elements*[*]. Kyiv: Naukova Dumka Publ.; 2010. (In Russ.)

19. Fedorov P. P. Determination of the annealing duration in the study of phase equilibrium in the solid state of binary systems[*]. *Russian Journal of Inorganic Chemistry*. 1992;37(8): 1891–1894. (In Russ.)

20. Fedorov P. P. Third law of thermodynamics as applied to phase diagrams. *Russian Journal of Inorganic Chemistry*. 2010;55: 1722–1739. https://doi.org/10.1134/S0036023610110100

21. Fedorov P. P., Alexandrov A. A., Voronov V. V., Mayakova M. N., Baranchikov A. E., Ivanov V. K. Low-temperature phase formation in the SrF_2–LaF_3 system. *Journal of the American Ceramic Society*. 2021;104(6): 2836–2848. https://doi.org/10.1111/jace.17666

22. Fedorov, P. P., Chernova, E. V. The conditions for the solid state synthesis of solid solutions in zirconia and hafnia systems with the oxides of rare earth elements. *Condensed Matter and Interphases*. 2022;24(4): 537–544. https://doi.org/10.17308/kcmf.2022.24/10558

23. Sakka Y., Oishi Y., Ando K. Zr-Hf interdiffusion in polycrystalline Y_2O_3–$(Zr+Hf)O_2$. *Journal of Materials Science*. 1982;17: 3101–3105. https://doi.org/10.1007/bf01203471

24. Yashima M., Ishizawa N., Nama T., Yoshimura M. Stable and metastable phase relationships in the system ZrO_2-$ErO_{1.5}$. *Journal of the American Ceramic Society*. 1991;74(3): 510–513. https://doi.org/10.1111/j.1151-2916.1991.tb04052.x

25. Yashima M., Kakihana M., Yoshimura M. Metastable-stable phase diagrams in the zirconia-containing systems utilized in solid-oxide fuel cell application. *Solid State Ionics*. 1996;86: 1131–1149. https://doi.org/10.1016/0167-2738(96)00386-4

26. Duran P. The system erbia – zirconia. *Journal of the American Ceramic Society*. 1977;60: 510–513. https://doi.org/10.1111/j.1151-2916.1977.tb14095.x

27. Roy R. Aids in hydrothermal experimentation: II, Method of making mixtures for both "dry" and "wet" phase equilibrium studies. *Journal of the American Ceramic Society*. 1956;39(4): 145–146. https://doi.org/10.1111/j.1151-2916.1956.tb14180.x

28. Fedorov P. P., Nazarkin M. V., Zakalyukin R. M. On polymorphism and morphotropism of rare-earth sesquioxides. *Crystallography Reports*. 2002;47(2): 281–286. https://doi.org/10.1134/1.1466504

29. Almjasheva O. V., Smirnov A. V., Fedorov B. A., Tomkovich M. V., Gusarov V. V. Structural features of ZrO_2-Y_2O_3 and ZrO_2-Gd_2O_3 nanoparticles formed under hydrothermal conditions. *Russian Journal of General Chemistry*. 2014;84(5): 804–809. https://doi.org/10.1134/S1070363214050028

30. Shuklina A. I., Smirnov A. V., Fedorov B. A., Kirillova S. A., Almjasheva O. V. Structure of nanoparticles in the ZrO_2-Y_2O_3 system, as obtained under hydrothermal conditions. *Nanosystems: Physics, Chemistry, Mathematics*. 2020;11(6): 729. https://doi.org/10.17586/2220-8054-2020-11-6-729-738

31. Fedorov P. P., Volkov S. N. Au–Cu Phase Diagram. *Russian Journal of Inorganic Chemistry*. 2016;61: 772–775. https://doi.org/10.1134/S0036023616060061

32. Fedorov, P.P., Shubin, Y.V. & Chernova, E.V. Copper–Palladium Phase Diagram. *Russian Journal of Inorganic Chemistry*. 2021;66: 891–893. https://doi.org/10.1134/S0036023621050053

33. Fedorov P. P., Popov A. A., Shubin Yu. V., Chernova E. V. Phase diagram of the nickel-platinum system[*]. *Russian Journal of Inorganic Chemistry*. 2022;67(12): 1805–1809. (In Russ.). https://doi.org/10.31857/S0044457X22600748

34. Abriata J. P., Laughlin D. E. The third law of thermodynamics and low temperature phase stability. *Progress in Materials Science*. 2004;49: 367–387. https://doi.org/10.1016/s0079-6425(03)00030-6

35. Hume-Rothery W., Raynor G. V. *The structure of metals and alloys*. London: The Inst. of metals; 1956.

36. Gusarov V. V., Semin E. G., Suvorov S. A. Calculation of thermodynamic parameters of solid solutions based on metal oxides. *Russian Journal of Applied Chemistry*. 1980;53(8): 1911–1914. (In Russ.)

37. Voronin G. F. New possibilities for thermodynamic calculation and phase diagram construction of heterogeneous systems. *Russian Journal of Physical Chemistry A*. 2003:77(10): 1685–1694. Available at: https://www.elibrary.ru/item.asp?id=13425953

38. Suvorov S. A., Semin E. G., Gusarov V. V. *Phase diagrams and thermodynamics of oxide solid solutions*. Leningrad: Leningrad University Publ.; 1986. 140 p.

39. Degtyarev S. A., Voronin G. F. Solution of ill-posed problems in thermodynamics of phase equilibria. The ZrO_2-Y_2O_3 system. *Calphad*. 1988;12(1): 73–82. https://doi.org/10.1016/0364-5916(88)90031-4

40. Degterev S. A., Voronin G. F. Solution of ill-posed problems of thermodynamics of phase equilibria. I System ZrO_2-Y_2O_3[*]. *Zhurnal Fizicheskoi Khimii*. 1987;61(3): 611–616. (In Russ.)

41. Zaitseva I. A., Skolis Yu. Ya. Partial thermodynamic functions of yttrium-oxide in css-solutions of the ZrO_2-Y_2O_3 system*. *Zhurnal Fizicheskoi Khimii.* 1990;64(1): 251–253. (In Russ.)

42. Zaitseva I. A., Dobrokhotova Zh. V. Thermodynamic functions of zirconium oxide in fluorite-like solutions of the ZrO_2-Y_2O_3 system*. *Inorganic Materials*. 1994;30(7): 955–958. (In Russ.)

43. Degtyarev S. A., Voronin G. F. Calculation of the phase diagram in the ZrO_2-Y_2O_3 system*. *Zhurnal Fizicheskoi Khimii.* 1987;61(3): 617–622. (In Russ.)

44. Du Y., Jin Z., Huang P. Thermodynamic assessment of the ZrO_2-$YO_{1.5}$ system. *Journal of the American Ceramic Society.* 1991;74: 1569–1577. https://doi.org/10.1111/j.1151-2916.1991.tb07142.x

45. Jacobson N. S., Liu Z.-K., Kaufman L., Zhang F. Thermodynamic modeling of $YO_{1.5}$-ZrO_2 system. *Journal of the American Ceramic Society.* 2004;87: 1559–1566. https://doi.org/10.1111/j.1551-2916.2004.01559.x

46. Chen M., Hallstedt B., Gauckler L. J. Thermodynamic modeling of the ZrO_2-$YO_{1.5}$ system. *Solid State Ionics*. 2004;170: 255–274. https://doi.org/10.1016/j.ssi.2004.02.017

47. Duwez P., Brown F. H., Odell F. The zirconia-yttria system. *Journal of the Electrochemical Society.* 1951;98(9): 356–362. https://doi.org/10.1149/1.2778219

48. Rouanet A. Contribution a l'etude des systems zircon-oxydes des lanthanides au voisinage fe la fusion. *Revue Internationale Des Hautes Temperatures et Des Refractaires*. 1971;8: 161–180.

49. Noguchi T., Mizuno M., Yamada T. The liquidus curve of the ZrO_2-Y_2O_3 system as measured by a solar furnace. *Bulletin of the Chemical Society of Japan.* 1970;43: 2614–2616. https://doi.org/10.1246/bcsj.43.2614

50. Shevchenko A. V., Tkachenko V. D., Lopato L. M., Ruban A. K., Pasichnyi V. V. A method of determining phase-transition temperatures using solar heating. *Soviet Powder Metallurgy and Metal Ceramics*. 1986;25(1): 79–82. https://doi.org/10.1007/bf00843028

51. Pascual C., Duran P. Subsolidus Phase Equilibria and ordering in the system ZrO_2-Y_2O_3. *Journal of the American Ceramic Society.* 1983;66: 23–28. https://doi.org/10.1111/j.1151-2916.1983.tb09961.x

52. Stubican V. S., Corman G. S., Hellmann J. R., Sent G. Phase relationships in some ZrO_2 system. In: *Advanced in Ceramics*. N. Clausen, A. Ruhle, A. Heuer (eds.). Columbus: American Ceramic Soc Inc; 1984;12: 96–106.

53. Gaboriaud R. J., Paumier F., Lacroix B. Disorder-order phase transformation ia a fluorite-related oxide film: in situ diffraction and modeling of the residual stress effects. *Thin Solid Films*. 2016;601: 84–88. https://doi.org/10.1016/j.tsf.2015.08.030

54. Fedorov P. P. *T-x* phase diagrams of binary systems in the condensed state: I. Equilibrium of four phases. *Russian Journal of Physical Chemistry.* 1999;73(9): 1381-1386.

55. Thornber M. R., Bevan D. J. M., Graham J. Mixed oxides of the type MO_2 fluorite-M_2O_3. III crystal structures of the intermediate phases $Zr_5Sc_2O_{15}$ and $Zr_3Sc_4O_{12}$. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*. 1968;24(9): 1183–1190. https://doi.org/10.1107/s0567740868003948

56. Thornber M. R., Bevan D. J. M., Summerville E. Mixed oxides of the type MO_2 Fluorite-M_2O_3. V. Phase studies in the systems ZrO_2-M_2O_3 (M = Sc, Yb, Er, Dy). *Journal of Solid State Chemistry.* 1970;1: 545–553. https://doi.org/10.1016/0022-4596(70)90140-4

57. Spiridonov F. M., Popova L. N., Popil'skii R. Ya. On the phase relations and electrical conductivity in the system ZrO_2-Sc_2O_3. *Journal of Solid State Chemistry.* 1970;2(3): 430–438. https://doi.org/10.1016/0022-4596(70)90102-7

58. Sekiya T., Yamada T., Hayashi H., Noguchi T. High temperature phase in the ZrO_2-Sc_2O_3 system. *Nippon Kagaku Kaishi.* 1974;9: 1629–1636 (in Japan). https://doi.org/10.1246/nikkashi.1974.1629

59. Ruh R., Garrrett H. J., Domagala R. F., Patel V. A. The system zirconia-scandia. *Journal of the American Ceramic Society.* 1977;60(9-10): 399–403. https://doi.org/10.1111/j.1151-2916.1977.tb15521.x

60. Shevchenko A. V., Maister I. M., Lopato L. M. Interaction in the HfO_2-Sc_2O_3 and ZrO_2-Sc_2O_3 systems at high temperatures. *Izvestiya Akademii Nauk SSSR. Neorganicheskie Materialy.* 19867;23(8): 1320–1324.

61. Zyrin A. V., Red'ko V. P., Lopato L. M., Shevchenko A. V. Ordered phases in the $ZrO2$–Sc_2O_3 and HfO_2–Sc_2O_3 systems. *Izvestiya Akademii Nauk SSSR. Neorganicheskie Materialy.* 1987:23(8): 1326–1329.

62. Lopato L. M., Red'ko V. P., Gerasimyuk G. I., Shevchenko A. V. Synthesis of some REE zirconates (hafnates). *Soviet Powder Metallurgy and Metal Ceramics*. 1990;29(4): 318–320. https://doi.org/10.1007/bf00797236

63. Maister I. M., Lopato L. M, Zaitseva Z. A., Shevchenko A. V. Interaction in the ZrO_2–Y_2O_3–Sc_2O_3 system at 1300–1900 °C. *Izvestiya Akademii Nauk SSSR. Neorganicheskie Materialy.* 1991;27(11): 2337–2340.

64. Sheu T.-S., Xu J., Tien T.-Y. Phase relationships in the ZrO_2-Sc_2O_3 and ZrO_2-In_2O_3 systems. *Journal of the American Ceramic Society.* 1993;76(8): 2027–2032. https://doi.org/10.1111/j.1151-2916.1993.tb08328.x

65. Fujimori H., Yashima M., Kakihana M., Yoshimura M. Structural changes of scandia-doped zirconia solid solutions: Rietveld analysis and Raman scattering. *Journal of the American Ceramic Society.* 2005;81(11): 2885–2893. https://doi.org/10.1111/j.1151-2916.1998.tb02710.x

66. Fujimori H., Yashima M., Kakihana M., Yoshimura M. β-cubic phase transition of scandia-

doped zirconia solid solution: Calorimetry, X-ray diffraction, and Raman scattering. *Journal of Applied Physics*. 2002;91: 6493–6498. https://doi.org/10.1063/1.1471576

67. Rossell H. J. Crystal structure of some fluorite-related M_7O_{12} compounds. *Journal of Solid State Chemistry*. 1976;19(2): 103–111. https://doi.org/10.1016/0022-4596(76)90156-0

68. Wurst K., Schweda E., Bevan D. J. M., Mohyla J., Wallwork K. S., Hofmann M. Single-crystal structure determination of $Zr_{50}Sc_{12}O_{118}$. *Solid State Sciences*. 2003;5: 1491–1497. https://doi.org/10.1016/j.solidstatesciences.2003.09.008

69. Meyer S., Schweda E., Meta N. J. M., Boysen H., Hoelzel M., Bredow T. Neutron powder diffraction study and DFT calculatuins of the structure of $Zr_{10}Sc_4O_{26}$. *Zeitschrift für Kristallographie*. 2009;224: 539–543. https://doi.org/10.1524/zkri.2009.1218

70. Ma C., Beckett J. R., Rossman G. R. Allendeite ($Sc_4Zr_3O_{12}$) and hexamolybdenum (Mo, Ru, Fe), two new minerals from an ultrarefractory inclusion from the Allende meteorite. *American Mineralogist*. 2014;99(4): 654–666. https://doi.org/10.2138/am.2014.4667

71. Fedorov P. P., Chernova E. V. Distribution coefficients of rare-earth oxides in zirconium dioxide melt crystallization. *Inorganic Materials*. 2021;57(9): 901–905. https://doi.org/10.1134/s0020168521090089

72. Fedorov P. P., Turkina T. M., Lyamina O. I., Tarasova E. V., Zibrov I. P., Sobolev B. P. Calculation of impurity distribution coefficients from liquidus curves of binary systems MF_2-RF_3^*. *Vysokochistye veshchestva*. 1990;6: 67–72. (In Russ.)

73. Ivanov S. P., Buchinskaya I. I., Fedorov P. P. Distribution coefficients of impurities in cadmium fluoride. *Inorganic Materials*. 2000;36(4): 392–396. https://doi.org/10.1007/BF02758088

74. Chase M. W., Davies C. A., Downey J. R., McDonald R. A., Syverud A. N., Valenzuela E. A. JANAF thermochemical tables. *Journal of Physical and Chemical Reference Data*. 1982;11(3): 695–940. https://doi.org/10.1063/1.555666

75. Fedorov P. P., Sobolev B. P. Conditions for the formation of maxima on the fusion curves of solid solutions in salt systems. *Russian Journal of Inorganic Chemistry*. 1979;24(4): 572–575.

76. Fedorov P. P. Heterovalent isomorphism and solid solutions with a variable number of ions in the unit cell. *Russian Journal of Inorganic Chemistry*. 2000;45: S268–S291.

77. Zinkevich M., Djurovic D., Aldinger F. Thermodynamic modeling of the cerium-oxygen system. *Solid State Ionics*. 2006;177: 989–1001. https://doi.org/10.1016/j.ssi.2006.02.044

78. Pascual C., Duran P. Phase equilibria and ordering in the erbia-zirconia system. *Journal of Materials Science*. 1981;16: 3067–3076. https://doi.org/10.1007/bf00540314

79. Fedorov P. P., Alexandrov A. A., Voronov V. V., Mayakova M. N., Baranchikov A. E., Ivanov V. K. Low-temperature phase formation in the SrF_2-LaF_3 system. *Journal of the American Ceramic Society*. 2021;104(6): 2836–2848. https://doi.org/10.1111/jace.17666

80. Bredig M. A. The order-disorder (λ) transition in UO_2 and other solids of the fluorite type of structure. *Colloq. Inter. CNRS*. 1972;205: 183–197.

81. Fossati P. C. M., Chartier A., Boulle A. Structural aspects of the superionic transition in AX_2 compounds with the fluorite structure. *Frontiers in Chemistry*. 2021;9: N723507. http://doi.org/10.3389/fchem.2021.723507

82. Hoekstra H. R., Siegel S., Gallagher X. The uranium-oxygen system at high pressure. *Journal of Inorganic and Nuclear Chemistry*. 1970;32: 3237–3248. https://doi.org/10.1016/0022-1902(70)80206-8

83. Cooper M. W. D., Murphy S. T., Rushton M. J. D., Grimes R. W. Thermophysical properties and oxygen transport in the $(U_xPu_{1-x})O_2$ lattice. *Journal of Nuclear Materials*. 2015;461: 206–214. https://doi.org/10.1016/j.jnucmat.2015.03.024

84. Annamareddy A., Eapen J. Disordering and dynamic self-organization in stoichiometric UO_2 at high temperatures. *Journal of Nuclear Materials*. 2017;463: 132–141. https://doi.org/10.1016/j.jnucmat.2016.10.042

85. Annamareddy A., Eapen J. Low dimensional string-like relaxation underpins superionic conduction in fluorites and related structures. *Scientific Reports*. 2017; 7:44149. https://doi.org/10.1038/srep44149

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