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On the Phase Relations and the Electrical Conductivity in the System ZrO_2–Sc_2O_3†

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Phase relations in the ZrO_2–Sc_2O_3 system have been investigated by the methods of high-temperature X-ray analysis, dilatometry, differential thermal analysis, and electrical conductivity measurements in the composition range 3–40 mol % Sc_2O_3 and the temperature range 20–2000°C. The phase diagram has been constructed in its subsolidus regions.

Existence regions have been refined for three known compounds, $Sc_2Zr_7O_{17}$, $Sc_2Zr_5O_{13}$, and $Sc_4Zr_3O_{12}$, and the region corresponding to high-temperature, cubic, fluorite-type solid solutions has been established.

The character of the thermal dependence of the electrical conductivity for the compositions studied agrees with the phase transformations. The maximum value of the electrical conductivity at 1200°C was observed for the composition 7.5–9 mol % Sc_2O_3. With increasing temperature, in the field of the high-temperature solid solutions, there occurs a broadening of this maximum and a lateral displacement to higher content of scandium oxide.

Information in the literature on the system ZrO_2 is rather limited. References (*1–8, 14*) are dedicated to the study of the interaction between ZrO_2 and Sc_2O_3. Investigation into the conductivity of several compositions of the system is carried out in Refs. (*9–14*).

Lefevre (*4, 5*) discovered the existence of three new phases β, γ, δ and constructed a rough section of the state diagram of the system (Fig. 1). It was he who showed that the structure of these phases is derived from a cell of the fluorite type.

It was further established that phases β, γ, and δ are the specific chemical compounds: $Sc_2Zr_7O_{17}$ (*6*), $Sc_2Zr_5O_{13}$ (*15, 16*), and $Sc_4Zr_3O_{12}$ (*7, 17*), respectively. The aforementioned compounds exist in various intervals of concentration, i.e., their composition can depart from the stoichiometric (Table I).

Determination of the crystalline structure of the compounds $Sc_2Zr_5O_{13}$ and $Sc_4Zr_3O_{12}$ according to the data from powder diffractometry (*15*) also emphasized their genetic relation to a cell of the fluorite type and indicated that the rhombohedral distortion of the latter is exclusively a consequence of the presence of oxygen vacancies. The compound $Sc_2Zr_7O_{17}$ undergoes the transformation, rhombohedral ⇄ cubic phase, near 600°C (*4, 6*). The remaining compounds are stable to 2000°C. (*4*).

In measuring the electrical conductivity polytherms a departure from the Arrhenius equation was noticed for several compositions (*9, 10*). In the opinion of (*11*) this is tied to the phase transitions of the "ordered–disordered" type, which, however, were not corroborated by radiographs. The high conductivity in the system ZrO_2–Sc_2O_3 (*11–14*) raises great interest in connection with the possibility of using these materials for solid electrolytes.

The curves of the dependence of conductivity on temperature obtained by the authors of the present work had a complex character and couldn't be completely explained on the basis of published data. Therefore, the study of the phase relations in the system ZrO_2–Sc_2O_3 was carried out on specimens

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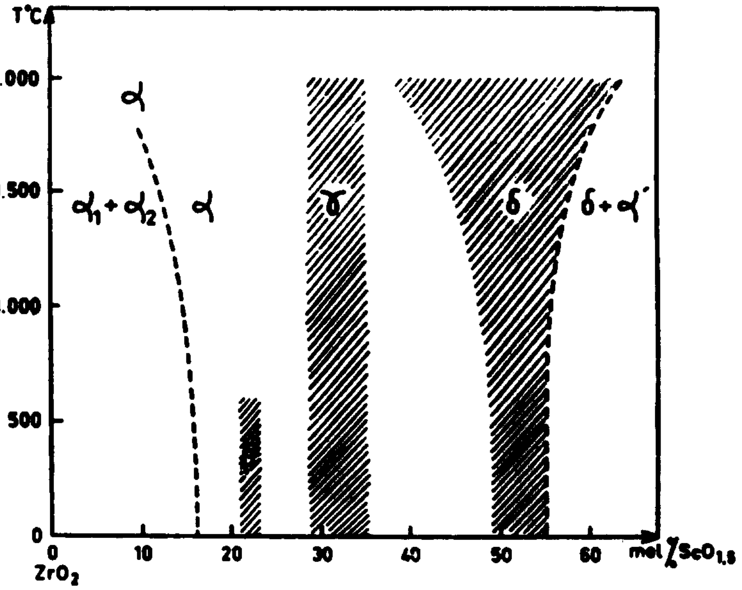

FIG. 1. Phase diagram for the system ZrO_2–Sc_2O_3 by Lefevre (*4*).

with a content of from 3 to 40 mol% of Sc_2O_3 and at a temperature interval of 20–2000°C.

Experimental Part

As starting materials we used 99.8% purity ZrO_2 and 99.8% Sc_2O_3. Mixtures of specified molar ratio were prepared by precipitating scandium hydroxide from hydrochloric acid solution with ammonia at pH = 8–9 in a highly dispersed suspension of ZrO_2 (average particle size $< 1\mu$). The carefully stirred mixtures were dehydrated, ground, pressed into 8–16 mm diameter pellets under a pressure of 400–500 kg/cm^2 and held at temperatures of 1200, 1400, 1700, and 2000°C for a period of 400, 125, 10, and 2 hr, respectively, with subsequent quenching. The samples which had been equilibrated at the previously mentioned degrees of heat treatment were then subjected to heating. Up to 1700°C, the treatment was carried out in air; at 2000°C, in a vacuum furnace with tungsten heating elements.

To establish the boundaries of the phases and of the phase transformations, a combination of several physico-chemical methods was used: X-ray, differential thermal analysis (DTA), polythermal measurements of dilatometry and conductivity, determina-

TABLE I

CHARACTERISTICS OF INTERMEDIATE COMPOUNDS IN THE SYSTEM ZrO_2–Sc_2O_3

	Area where it exists			Cell parameters Å		
Compound	Mol % Sc_2O_3	°C	Structure	a_H	c_H	References
$Sc_2Zr_7O_{17}$	11.7–13	20–580 20–610	Rhombohedral[a]	a = 5.085[a]	α = 88° 48'[a]	(*4*, *5*) (*6*)
$Sc_2Zr_5O_{13}$	17–21.2	20–2000	Rhombohedral	9.508	17.46	(*4*, *5*)
	18–25	20–2000	Rhombohedral			(*17*)
			Rhombohedral	9.53	17.44	(*15*)
$Sc_4Zr_3O_{12}$	25–48	20–2000	Rhombohedral	9.405	17.42	(*5*)
			Rhombohedral	9.37	8.71	(*15*)

[a] Subcell.

tion of microstructure. The X-ray analysis was carried out by the powder method on specimens quenched from the respective temperatures, using a (DRON-1) diffractometer and a Guinier–de Wolff (Holland) focusing-cell monochromator with the high-temperature cell of Guinier–Lenne (Holland) and photographic registration at 1200°C after one hour of being held at temperature for filming.

The DTA was carried out on Kurnakov's photo-registering pyrometer NTR-63 at a cooling and heating rate of 5°C/min. The accuracy of the temperature registration was ± 10°C. The specimens annealed at 1200°C were examined.

The dilatometry curves were obtained on a graphite dilatometer located in the furnace with tungsten heating elements at a temperature–change rate of 5°C/min. Changes in the length of the specimens were determined by an indicator with 0.001 mm subdivision on the basis of which the average coefficient of volume expansion α was calculated in the corresponding temperature interval.

The measurement of conductivity was carried out in air to a temperature of 1500°C by the double-probe method with an alternating current at a frequency of 1000 Hz. The rate of temperature change was 6–7°C/min. The dilatometer tests and measurements of conductivity were executed on pellets of 10–15-mm height and diameter which had been heated at 1700°C for 10 hr and which had

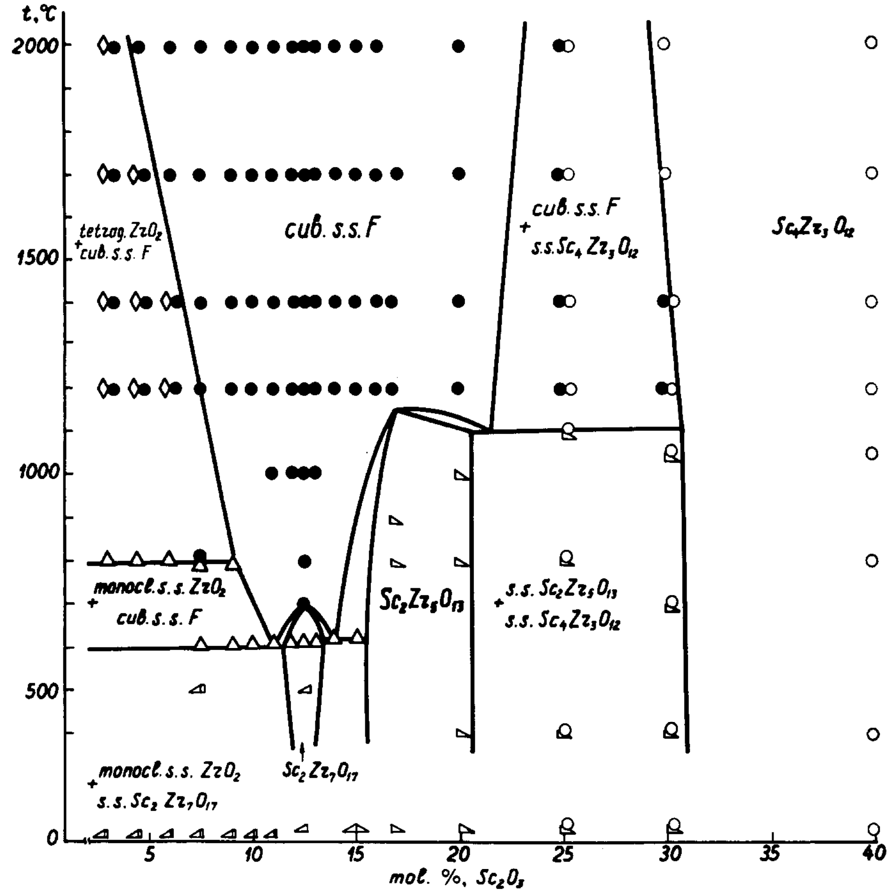

FIG. 2. Phase diagram for the system ZrO_2–Sc_2O_3.

●—cubical solid solution, fluorite type structure;
□—monoclinic solid solution ZrO_2;
◇—tetragonal solid solution ZrO_2;
◿—rhombohedral compound $Sc_2Zr_7O_{17}$;
◺—rhombohedral compound $Sc_2Zr_5O_{13}$;
○—rhombohedral compound $Sc_4Zr_3O_{12}$;
△—DTA data.

detectable porosity in the limits of 0.1–1% and a relative density of 0.90–0.96.

Discussion of the Results

The aspect of the phase relations in the system is entirely different at high and at low temperatures (Fig. 2).

At low temperatures (below 600 ~ 1100°C) all three compounds described in the literature are present: $Sc_2Zr_7O_{17}$, $Sc_2Zr_5O_{13}$, and $Sc_4Zr_3O_{12}$. Their stoichiometric compositions correspond to an Sc_2O_3 content of 12.5, 16.7, and 40 mol%, respectively. Their lattices are derived from a cubic cell of the fluorite type with insignificant rhombohedral distortion in $Sc_2Zr_7O_{17}$ and $Sc_2Zr_5O_{13}$. The rhombohedral compound $Sc_4Zr_3O_{12}$ has a cubic subcell.

With a rise in temperature, however, the splitting of the intense reflections in the powder photos of the compounds $Sc_2Zr_7O_{17}$ and $Sc_2Zr_5O_{13}$ disappears and they return to cubic solid solutions of the fluorite type near 600 and 1100°C, respectively. Above 1200°C only $Sc_4Zr_3O_{12}$ remains stable.

Region with a Small Content of Sc_2O_3 (3–11 mol %)

The complexity of the diagram in this section (Fig. 2) is caused by the presence of several phase transformations. Below 600°C lies the heterogeneous area: the monoclinic solid solution ZrO_2 and the rhombohedral solid solution $Sc_2Zr_7O_{17}$ (β).

On the thermograms of these specimens (Table II) there are near 600–620°C small thermal effects caused by the transition of the rhombohedral phase (β) into the cubic phase (F) of the fluorite type. These phenomena are also manifest in the measurements of conductivity (Fig. 3). Between 600 and 800°C there is the second mixed area: the monoclinic phase + the cubic phase (F).

At higher temperature (~ 800°C) an inversion of ZrO_2 from the monoclinic to tetragonal takes place. The conversion is noted on the dilatometry curves (Fig. 4). Above 800°C, there is the third heterogeneous area, consisting of tetragonal (the solid solution ZrO_2) and cubic (the solid solution F) phases. Its range (mol % of Sc_2O_3) is limited significantly by a rising temperature 3–11 at 800°C, 3–6 at 1400°C, and 3–4.5 at 2000°C.

The Rhombohedral Compounds $Sc_2Zr_7O_{17}$ ($Sc_2O_3 \cdot 7ZrO_2$)

The compound $Sc_2Zr_7O_{17}$ has a very narrow range of existence both in concentration (11–13 mol% Sc_2O_3) and in temperature (from room temperature to 620°C). At a higher temperature, it is converted into a cubic solid solution of the fluorite type [Table III, Fig. 5(a)]. Although at both low and high temperatures the states of this specimen appear single phased, there is no uninterrupted transition between them. At 500°C, there are on the powder diagram, along with the lines of the compound

TABLE II

DIFFERENTIAL—THERMAL ANALYSIS OF SPECIMENS IN THE SYSTEM ZrO_2–Sc_2O_3

	Temperature of phase transitions, °C			
	$Sc_2Zr_7O_{17} \rightleftarrows$ cubic phase		Monoclinic $ZrO_2 \rightleftarrows$ tetragonal ZrO_2	
Composition, mol% of Sc_2O_3	Heating	Cooling	Heating	Cooling
3.0	No effect	No effect	800–814	780–775
4.5	—	—	800	780
6.0	—	—	766–795	761
7.5	601–615	—	805	760
9.0	619	601	800	762
10.0	611–620	601–596	No effect	No effect
11.0	626–637	624–606	—	—
12.0	627	—	—	—
12.5	622–635	616–601	—	—
13.0	620–636	620–606	—	—
14.0	642	611	—	—
15.0	650	643	—	—

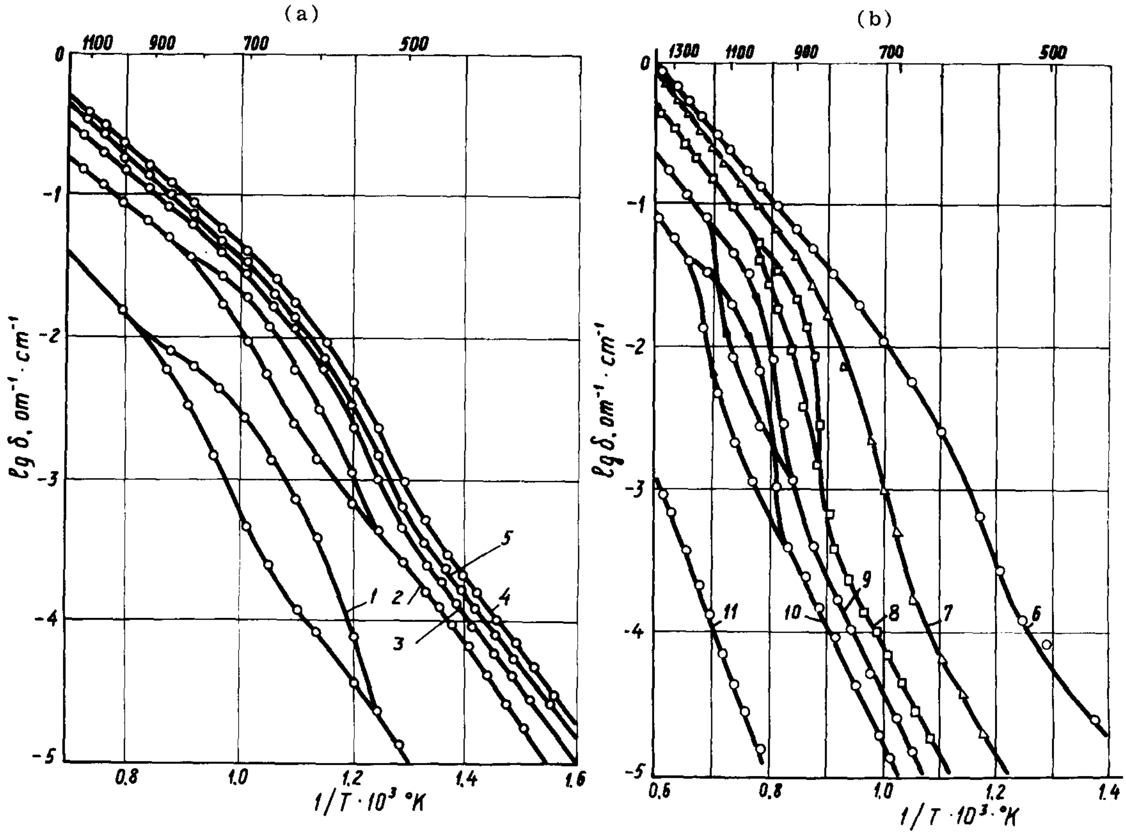

FIG. 3. Electrical conductivity polytherms in the system ZrO_2–Sc_2O_3. (a) Curve 1, 3.0 mol % Sc_2O_3: Curve 2, 4.5; Curve 3, 6.0; Curve 4, 7.5; Curve 5, 9.0.

(b) Curve 6, 12.5 mol % Sc_2O_3: Curve 7, 15.0; Curve 8, 16.7; Curve 9, 20.0; Curve 10, 30.0; Curve 11, 40.0.

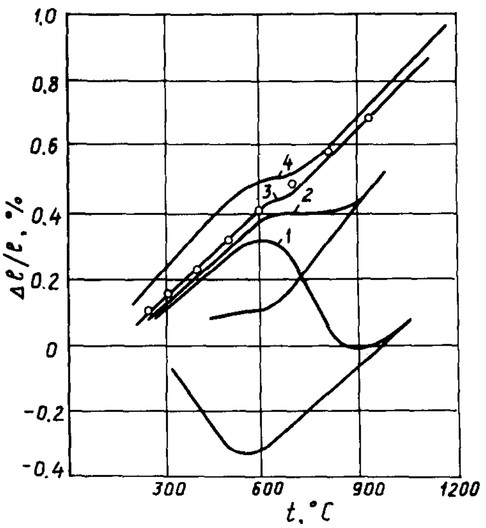

FIG. 4. Dilatometric curves for the ZrO_2–Sc_2O_3 system samples: Curve 1, 3.0 mol % Sc_2O_3; Curve 2, 4.5; Curve 3, 7.5; Curve 4, 12.5.

$Sc_2Zr_7O_{17}$, the intense reflections of phase F [Fig. 5(a)]. This apparently is the reason for the bend noticed at 530°C in the polytherm of the conductivity at this composition (Fig. 3). However, on the DTA curves the effect caused by the conversion $\beta \rightleftarrows F$ is observed only at 620°C.

Because of the near-identity of the crystal structures of $Sc_2Zr_7O_{17}$ (rhombohedrally distorted fluorite) and phase F (true fluorite) the conversion $\beta \rightleftarrows F$ is evidently accompanied by only an insignificant restructuring of the crystal lattice, which is also indicated by the small size of the thermal effect on the DTA curve. Therefore, one must suggest that this conversion is a first order phase change and, in all probability, is connected with the change in the second coordination sphere (*18*).

The powder photographs of the specimens with higher Sc_2O_3 content, 13–15 mol% Sc_2O_3, fix the existence of a mixed area between the solid solutions of the two compounds: $Sc_2Zr_7O_{17}$ and $Sc_2Zr_5O_{13}$ (γ), both of which have been examined above.

TABLE III

RADIOGRAPHIC DATA FOR THE COMPOUND $Sc_2Zr_7O_{17}$

	Subcell parameters			Coefficient of thermal Expansion $\alpha_v \times 10^5$	
Temperature	a_0, Å	α_0	V_0, Å^3	X-ray	Dilatometry
20	5.086	88°48′	131.4		
500	5.102	88°55′	132.8	2.22 (20–500°)	2.40 (20–500°)
800	5.112	90°00′	133.6	2.15 (20–800°)	2.16 (20–800°)
1000	5.118	90°00′	134.1	2.10 (20–1000°)	2.04 (20–1000°)

Rhombohedral Compounds $Sc_2Zr_5O_{13}$ ($Sc_2O_3 \cdot 5ZrO_2$)

The compound $Sc_2Zr_5O_{13}$ exists in a wider interval of concentration of Sc_2O_3 compared to $Sc_2Zr_7O_{17}$: 16 ~ 21 mol%, which is in satisfactory agreement with (*4*).

However, in contrast to the results of Lefevre (*4, 5*) who showed that this compound (the γ phase) is stable to 2000°C, in the present work it has been established with the aid of high-temperature radiography that it also undergoes a transformation between rhombohedral and cubic around 1100°C [Table IV, Fig. 5(b)].

In the curves of the temperature dependence of conductivity (Fig. 3, curves 6–8) there are not only breaks but hysteresis loops. Thus, based on the character of their high-temperature conversions, the compounds $Sc_2Zr_7O_{17}$ and $Sc_2Zr_5O_{13}$ are different from each other, which is explained by the different degree of ordering in their crystal lattices.

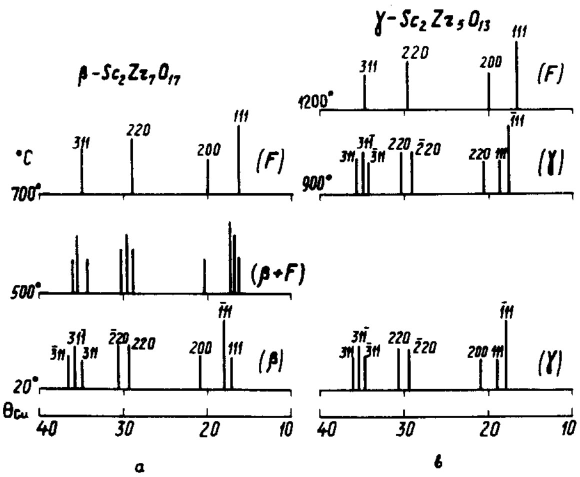

FIG. 5. High-temperature polymorph transformation. (a) $Sc_2Zr_7O_{17}$; (b) $Sc_2Zr_5O_{13}$.

Between the areas of the compounds $Sc_2Zr_5O_{13}$ and $Sc_4Zr_3O_{12}$ (δ) there is situated a rather broad mixed area (~ 21 ~ 30 mol% of Sc_2O_3).

The Rhombohedral Compounds $Sc_4Zr_3O_{12}$ ($2Sc_2O_3 \cdot 3ZrO_2$)

The compound $Sc_4Zr_3O_{12}$ occupies the widest area of homogeneity compared to both compounds examined above: 30–40 mol% of Sc_2O_3 (the maximum limit of Sc_2O_3 content in this work). On rise of temperature, this area broadens slightly.

The polytherm of the conductivity of this compound is linear at all temperature intervals which is characteristic only of the composition under discussion and which confirms the lack of any phase transformation in it, at least up to 1500°C. The results of (*11*) support this, but it contradicts the data of (*7*).

Several characteristics of the compound $Sc_4Zr_3O_{12}$ are presented in Table V.

In Table V for axis *c* the cells were given values near 17.5 Å, while in Bevan's work (*15*) a value twice smaller was found (Table II). As was shown earlier (*19*), the unit cells of the interstitial compounds in the system M_2O_3–$ZrO_2(HfO_2)$, except for compounds of the pyrochlore-type $M_2Zr_2O_7$, formed by groupings of M_7O_x from seven atoms of 3- and 4-valent metals in varying coordination (M_7O_{11}–$M_7O_{11.5}$–M_7O_{12}–M_7O_{13}) and are uniformly derived from a cell with a fluorite structure. The transformation from a cell of the fluorite type (a_0, α_0) to the hexagonal unit cells of the interstitial compounds is accomplished by the formulas (*20*):

$$a_H = (a_0)(\sqrt{7}/\sqrt{2})\sqrt{1-\cos\alpha_0},$$
$$c_H = (a_0)(2\sqrt{3})\sqrt{1+2\cos\alpha_0}.$$

From this, we get a value of ~ 17.5 Å for the *c* axis of the cell of $Sc_4Zr_3O_{12}$ (M_7O_{12}).

TABLE IV

RADIOGRAPHIC DATA FOR THE COMPOUND $Sc_2Zr_5O_{13}$ AND ITS SOLID SOLUTIONS

Composition, mol % Sc_2O_3	Temperature °C	Lattice parameters a, Å	c, Å	V, Å^3	Coefficient of thermal expansion $\alpha_v \times 10^5$ (X-ray data)
16.7	20	9.474	17.39	1351.5	
	700	9.530	17.48	1374.9	2.55 (20–700°)
	900	9.542	17.51	1380.6	2.45 (20–900°)
	1200	9.556[a]	17.69[a]	1399.1[a]	2.98 (20–1200°)
20.0	20	9.458	17.36	1345.1	
	400	9.490	17.41	1358.0	2.52 (20–400°)
	700	9.512	17.46	1368.1	2.51 (20–700°)
	1000	9.529	17.53	1378.2	2.51 (20–1000°)
	1200	9.535[a]	17.65[a]	1390.0[a]	2.83 (20–1200°)
25.0[b]	20	9.440	17.35	1339.4	
	400	9.486	17.44	1359.0	3.85 (20–400°)
	800	9.521	17.55	1377.7	3.67 (20–800°)
	1100	9.542	17.61	1388.4	3.39 (20–1100°)
	1200	9.546[a]	17.67[a]	1394.4[a]	3.48 (20–1200°)

[a] Calculated from the parameters of the cubic phase.

[b] Two-phase region.

High-Temperature Cubic Solid Solutions (F)

At high temperatures the cubic solid solutions with the fluorite structure (Fig. 2) occupy a broad range. Within the area of homogeneity (~ 7.5 ~ 22 mol% of Sc_2O_3 at 1200°C) there is a linear dependence of lattice parameter on composition (Table VI). With an increase in the content of scandium oxide the parameters and cell size diminish.

It is interesting to note that in the solid solutions, corresponding to 4.5–13 mol% of Sc_2O_3, i.e., formed from the compound $Sc_2Zr_7O_{17}$, the rate and extent of transition depend on the temperature of the preceding heat treatment. Thus, with tempering below 1200°C the transition is fully realized and is detected by the DTA. But if the heat treatment is carried out at higher temperatures, the transition is slowed down extraordinarily or even does not take place at all. Analogous behavior is observed in

TABLE V

RADIOGRAPHIC CHARACTERISTICS OF THE COMPOUND $Sc_4Zr_3O_{12}$ AND ITS SOLID SOLUTIONS

Composition, mol % Sc_2O_3	Temperature °C	Lattice parameters a, Å	c, Å	V, Å^3	Coefficient of thermal expansion $\alpha_v \times 10^5$ (X-ray data)
30.0[a]	20	9.395	17.39	1329.6	
	400	9.420	17.44	1340.4	2.14 (20–400°)
	700	9.430	17.46	1344.5	1.65 (20–700°)
	1050	9.452	17.50	1354.0	1.78 (20–1050°)
	1200	9.471	17.53	1362.1	2.07 (20–1200°)
40.0	800	9.432	17.46	1345.3	
	1050	9.451	17.50	1353.5	2.44 (800–1050°)
	1200	9.460	17.51	1357.3	2.23 (800–1200°)

[a] Two-phase region.

TABLE VI

LATTICE PARAMETERS OF THE CUBIC SOLID SOLUTIONS AT 1200°C

Composition, mol % Sc_2O_3	Cell parameters, Å
7.5	5.135
12.5	5.12[a]
16.7	5.108
20.0	5.097
25.0	5.102[b]
30.0	5.099[b]
40.0	5.056[c]

[a] Calculated from the cell parameters at 1000°C (Table III).

[b] Two-phase region.

[c] Cubic subcell of the compound $Sc_4Zr_3O_{12}$.

the compound $Sc_2Hf_7O_{17}$, quenched from ~ 2550°C. The reason for this is probably tied to the fact that the higher temperatures of tempering gradually eliminate the microdisorders of the lattice that aid formation of crystalline seeds of the low-temperature compounds.

The persistence of "super cooled" metastable solid solutions in the specimens may be the source of the discrepancies in equilibrium studies in the system ZrO_2–Sc_2O_3 (*10*, *14*).

The high-temperature solid solutions formed from the compound $Sc_2Zr_5O_{13}$ do not quench to room temperature.

The energy of activation for conductivity in the solid solutions is less than that in the corresponding low-temperature compounds (Table VII).

Electrical Conductivity

The portion of the phase diagram which has been constructed allows us to explain the complex character of the conductivity in the compositions investigated. The magnitude of the conductivity turned out to be extremely sensitive to structural changes taking place in the specimens. On the curves of the temperature dependence of conductivity one can distinguish three sections (Fig. 3):

1. The low-temperature linear sections which correspond to the regions where the compounds $Sc_2Zr_7O_{17}$ and $Sc_2Zr_5O_{13}$ exist.
2. The intermediate nonlinear sections conditioned by the restructuring of the lattice of the low-temperature phases during their polymorphous transformations.
3. The high-temperature linear sections, corresponding to the conductivity of the cubic solid solutions.

In the low-temperature region the maximum value for the conductivity was obtained for specimens containing 7.5 mol% of Sc_2O_3. This composition is located at the low concentration limits of the cubic solid solutions and is characterized by a fine crystalline texture (Table VII). The lowering of conductivity when the content of Sc_2O_3 is larger than 7.5 mol% is connected above all with the formation of the compounds examined above,

TABLE VII

ELECTRICAL CONDUCTIVITY IN THE SYSTEM ZrO_2–Sc_2O_3

Composition mol % Sc_2O_3	Predominant grain size, μ	Energy of activation Q and the preexponential factor σ_0, Ω^{-1} cm^{-1}			
		Low-temperature section		High-temperature section	
		Q, eV	$\sigma_0 \times 10^{-3}$	Q, eV	$\sigma_0 \times 10^{-3}$
6.0	8–10	1.03 ± 0.02	5.37	—	—
7.5	12–15	1.00 ± 0.02	7.60	0.82 ± 0.03	0.43
9.0	~ 20	1.00 ± 0.03	5.90	0.94 ± 0.05	0.68
12.5	25–30	1.15 ± 0.01	7.41	0.97 ± 0.05	1.51
15.0	~ 50	1.29 ± 0.03	3.59	1.01 ± 0.04	3.20
20.0	~ 40	1.65 ± 0.03	5.62	—	—
25.0	15–20	—	—	—	—
30.0	5	1.69 ± 0.08	2.00	—	—
40.0	1–3	1.83 ± 0.05	0.02	1.83 ± 0.05	0.02

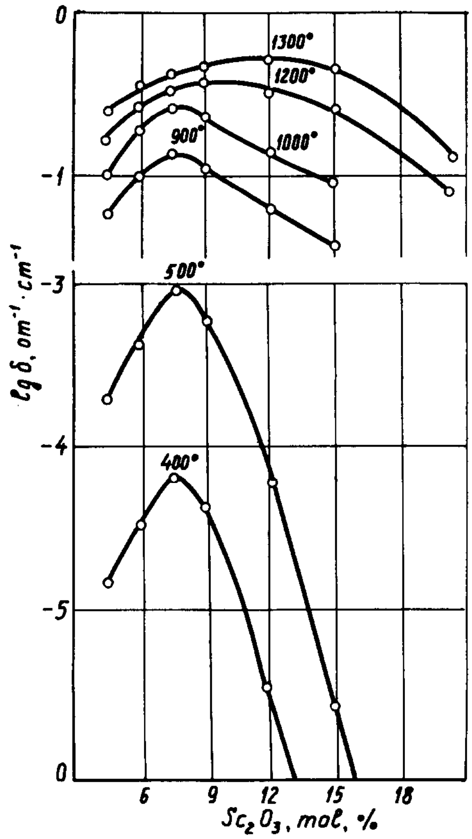

FIG. 6. Electrical conductivity isotherms in the system ZrO_2–Sc_2O_3.

i.e., with a decrease in the number of statistically distributed oxygen vacancies.

When the temperature is raised, the character of the conductivity isotherms gradually changes. Thus, at 900 and 1000°C there is still evident the pronounced maximum for the specimens with 7.5 mol % of Sc_2O_3 (Fig. 6). However, at temperatures $\geqslant$ 1200°C a widening of the maximum is observed as is an evening out of the amount of conductivity in the region where the cubic solid solutions exist: from 7.5 to 20 mol % of Sc_2O_3.

Of the compositions found in this interval, the specimens with 7.5 mol % of Sc_2O_3 have the smallest grain size (Table VII). In agreement with (*21*), the conductivity of the polycrystalline materials based on ZrO_2 is found to depend on the grain size and to decrease with increase in size. A difference in size evidently contributes to the position of the maximum indicated at 900–1000°C. With increase in temperature, the influence of this factor diminishes because of equalization of the movement of oxygen anions on the grain boundaries and in the bulk.

The dependence of the conductivity of the cubic solid solutions of ZrO_2–Sc_2O_3 on microstructure has been confirmed by the authors on specimens prepared by a hot pressure method (to be published).

The different form of the conductivity curves in the intermediate sections indicates the varying character of the polymorphous transformations of the low temperature phases.

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