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Cryosol Synthesis of $Al_{2-x}Cr_xO_3$ Solid Solutions

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We report for the first time synthesis of $Al_{2-x}Cr_xO_3$ solid solutions by a newly developed cryosol method. The essence of the method is the treatment of an aqueous solution containing chromium and aluminum nitrates by an anion-exchange resin in the OH^- form producing hydroxide sols. The freeze-drying of these sols results in hydroxide precursors, and their further annealing yields finally solid solutions. It is shown that the application of the crysol method enables the synthesis of single-phase ruby powders containing 7 mol % Cr at relatively low annealing temperatures ($T = 950$ °C) and times (2.5 h). Also, we investigated the influence of the organization of the initial colloid system on the properties of final $Al_{2-x}Cr_xO_3$ solid solutions. The data are used for the refinement of the sub-solidus part of the $Al_2O_3-Cr_2O_3$ phase diagram.

Introduction

Chemical methods for ceramic synthesis offer a lower temperature route to ceramic materials compared to the conventional solid-state reaction between oxide powders.[1] One of the techniques yielding high-quality homogeneous precursors is the sol−gel method based on the controlled hydrolysis of either metal−aqua complexes or metal alkoxides. Recently, in refs 2−4 we suggested a novel variant of the sol−gel route, the so-called cryosol technique (Figure 1), which is based on the hydrolysis of purely inorganic reagents.

In the previous papers we showed that the cryosol synthesis of individual oxides leads to the formation of highly dispersed systems with some unusual properties.[5−6] However, application of this technique to binary and multicomponent systems is of special interest because of the major importance of such systems in materials chemistry.

Taking into account the mechanism of anion exchange, one could expect that employment of the cryosol method for the synthesis of binary (and more complex) oxides would result in precursors characterized by an improved homogeneity of the components.

It should be noted that depending on the chemical nature of the components, the systems obtained by the cryosol method could be subdivided into two main groups.

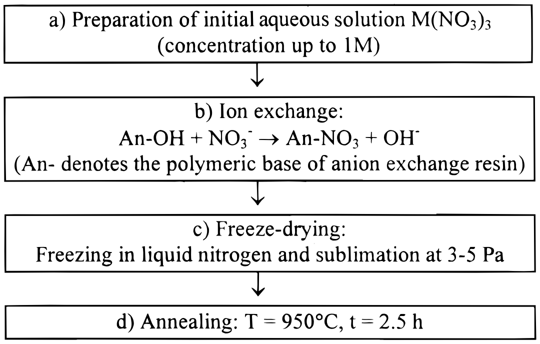

Figure 1. Scheme of the cryosol technique.

The first group comprises systems in which all individual components are able to form stable sols (for instance, $Al_{2-x}Cr_xO_3$ and $Zr_{1-y}Ga_yO_{2-y/2}$). In this case the possible variants of organization are as follows: (1) ion exchange of the initial solution containing all the cations in the form of soluble salts; (2) separate treatment of the single-component solutions with their subsequent mixing.

Systems containing components, some of which do not form stable colloid solutions (e.g., β-alumina, $Zr_{1-y}Y_yO_{2-y/2}$, and $BaTiO_3$) comprise the second group. Such systems can also be organized in two different ways: (1) ion exchange of the initial solution containing all components in the form of soluble salts; (2) addition of the nitrate (chloride) solution of the component(s) that do not form stable sols to the previously synthesized colloid solution containing the other components.

Yet, no systematic investigation of the influence of a system organization on the properties of the final products prepared by the cryosol method has been reported. In the present paper we studied the effect of the system organization on the properties of $Al_{2-x}Cr_xO_3$ solid solutions.

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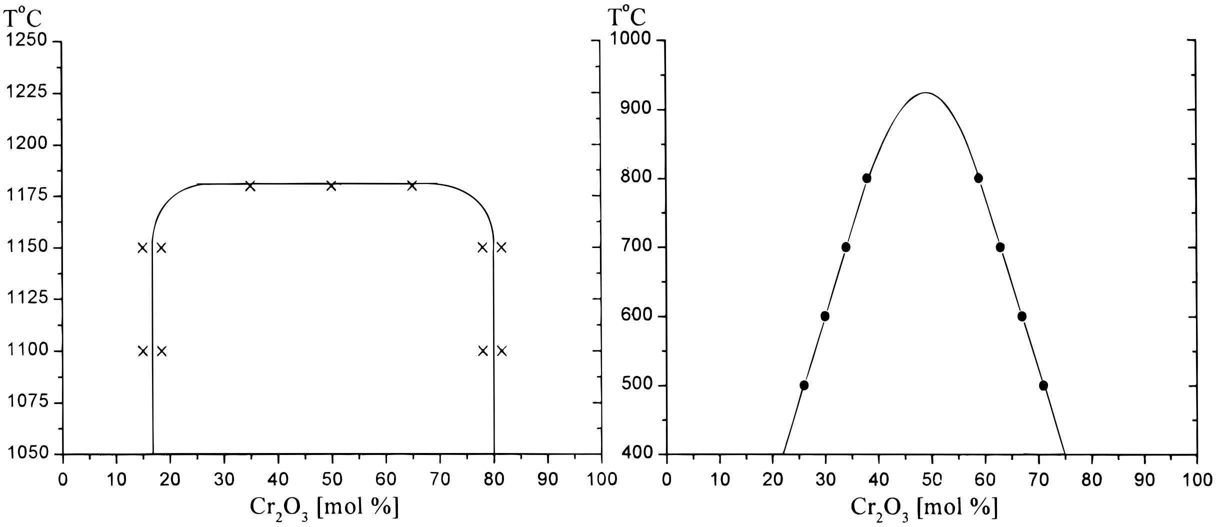

a) b)

Figure 2. Two types of irreversible segregation diagrams for $Al_{2-x}Cr_xO_3$ solid solutions cited in the literature: (a) Type I diagrams; (b) type II diagrams. See the text for explanations.

Ruby powder is one of the materials widely used in fiber optics, namely in linear amplifiers in long-distance connections. The traditional way for the preparation of ruby powders is annealing of an Al_2O_3 and Cr_2O_3 solid mixture at $T = 1500$ °C. Temperature and time of the synthesis may be substantially lowered by the use of coprecipitated aluminum and chromium hydroxides from an aqueous solution,[7,8] decomposition of aluminum and chromium nitrates,[7] hydrothermal method,[9,10] or method of a "nascent reagent".[11] It should be noted that the homogeneous distribution of the components and low temperature of the synthesis is crucial for ruby powders to be used in fiber optics.[12] Thus, application of the cryosol method may result in the products with improved characteristics.

Another potential outcome of the application of the cryosol method for the preparation of $Al_{2-x}Cr_xO_3$ solid solutions is the possibility to refine the phase diagram of the system. Currently, there exists a considerable discrepancy between the segregation diagrams of $Al_{2-x}Cr_xO_3$ solid solutions cited in the literature. These diagrams can be subdivided into two main types shown in Figure 2 (parts a and b). Type I diagrams[7,13] are characterized by a maximum at approximately 1300 °C, while type II diagrams[10,13,14] possess a maximum at 900−950 °C. Such a difference is due to the fact that equilibrium in the solid-state system under consideration establishes very slowly[7] as discussed in more detail in the section on solid solutions and segregation. Therefore, all segregation diagrams mentioned in the literature are nonequilibrium. Since the kinetics of formation of the solid solutions is diffusion-limited, one can expect that the use of more homogeneous precursors will enable one to obtain improved segregation diagrams.

Experimental Section

Synthesis of Colloid Solutions. First, aqueous solutions of aluminum and chromium nitrates were prepared by dissolving the calculated amounts of $Al(NO_3)_3{\cdot}9H_2O$ and/or $Cr(NO_3)_3{\cdot}9H_2O$ (reagent grade) in distilled water. The following aqueous solutions were prepared: (1) Sample Al: 0.5 M $Al(NO_3)_3$. (2) sample Cr: 0.5 M $Cr(NO_3)_3$. (3) sample AlCr-1: joint solution $Al(NO_3)_3 + Cr(NO_3)_3$ containing 50 mol % Cr (total concentration of the components = 0.5 M). (4) sample AlCr-2: joint solution $Al(NO_3)_3 + Cr(NO_3)_3$ containing 7 mol % Cr (total concentration of the components = 0.5 M).

The solutions were repeatedly treated by small (∼1 g) portions of anion-exchange resin IRA-410 (Amberlite) for 15 min. The anion exchanger was preliminary transferred into the OH-form by 2 M KOH and washed to pH = 7 by distilled water. After each cycle of the treatment, the anion-exchange resin was filtered out, and the solutions were aged for 30−60 min to achieve the hydrolytic equilibrium.

The composition of the hydroxide sols obtained as a result of ion-exchange treatment was controlled by pH and pNO_3 measurements. pH measurements were carried out on the ChemCadet (Cole-Parmer) instrument with a combined Cole-Parmer 60648 electrode. pNO_3 measurements were performed on a Ecotest-01 (NPO Izmeritelnaya Technika) device with a NO_3-selective electrode EM-020604. The total cation concentration of the sols was determined by gravimetric analysis.

Freeze-Drying. The obtained solutions were frozen in liquid nitrogen (block freezing) and dried in a serial sublimator SMH 15 (USIFROID) under pressure of 3−5 Pa. The temperature of the heating plates was gradually changed from −65 to +50 °C for 24 h. The final products were very friable ($\rho \approx 0.03{-}0.1$ g/cm^3) nonhygroscopic powders of amorphous hydrated oxides. The solid solutions $Al_{2-x}Cr_xO_3$ were synthesized by annealing the freeze-dried precursors at temperatures between 600 and 1300 °C.

Characterization. The products of the freeze-drying were characterized by thermal analysis with Ulvac thermobalances (Sinku-Riko).

The hydroxide precursors and samples after annealing were studied by means of scanning electron microscopy (JEOL JEM-2000FXII) and X-ray diffraction analysis. The latter was carried out in Guinier camera (Cu Kα radiation) using Ge as

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Table 1. Results of Guinier Studies for Samples SS1, SS2, and SS3

		phase I			phase II		
sample	annealing T/°C	lattice parameters		Cr_2O_3 (mol %)	lattice parameters		Cr_2O_3 (mol %)
		a	*c*		*a*	*c*	
SS1	600	4.8001 ± 0.0014	13.1176 ± 0.0012	21.2	4.8985 ± 0.0014	13.4132 ± 0.0018	70.4
	700	4.8021 ± 0.0009	13.1237 ± 0.0012	22.3	4.8965 ± 0.0003	13.4072 ± 0.0018	69.2
	800	4.8041 ± 0.0013	13.1297 ± 0.0018	22.8	4.8945 ± 0.0017	13.4011 ± 0.0011	68.5
	900	4.8102 ± 0.0012	13.1478 ± 0.0016	25.7	4.8884 ± 0.0006	13.3830 ± 0.0018	64.6
	1000	4.8182 ± 0.0014	13.1719 ± 0.0012	30.3	4.8804 ± 0.0017	13.3589 ± 0.0015	61.2
	1100	4.8292 ± 0.0018	13.2051 ± 0.0015	35.2	4.8694 ± 0.0020	13.3257 ± 0.0007	55.4
	1200	4.8486 ± 0.0017	13.2647 ± 0.0013	45.4			
SS1[a]	600	4.8071 ± 0.0014	13.1387 ± 0.0019	24.5	4.8915 ± 0.0014	13.3921 ± 0.0014	66.8
	700	4.8081 ± 0.0013	13.1418 ± 0.0018	25.3	4.8905 ± 0.0014	13.3891 ± 0.0013	65.9
	800	4.8102 ± 0.0011	13.1478 ± 0.0014	26.2	4.8884 ± 0.0019	13.3830 ± 0.0019	65
	900	4.8142 ± 0.0010	13.1599 ± 0.0013	28.4	4.8844 ± 0.0009	13.3710 ± 0.0009	63.2
	1000	4.8242 ± 0.0014	13.1900 ± 0.0012	33.1	4.8744 ± 0.0014	13.3408 ± 0.0004	57.7
	1100	4.8312 ± 0.0019	13.2111 ± 0.0013	36.2	4.8674 ± 0.0012	13.3197 ± 0.0018	54.1
	1200	4.8493 ± 0.0009	13.2654 ± 0.0025	45.5			
SS2	600	4.8108 ± 0.0018	13.1496 ± 0.0015	26.3	4.9280 ± 0.0002	13.5019 ± 0.0011	84.7
	700	4.8114 ± 0.0015	13.1514 ± 0.0015	26.6	4.9274 ± 0.0010	13.5001 ± 0.0014	84.4
	800	4.812 ± 0.0011	13.1532 ± 0.0008	26.9	4.9268 ± 0.0012	13.4982 ± 0.0009	84.1
	900	4.8126 ± 0.0007	13.1550 ± 0.0007	27.2	4.9262 ± 0.0003	13.4964 ± 0.0011	83.8
	1000	4.8132 ± 0.0019	13.1568 ± 0.0013	27.5	4.9256 ± 0.0013	13.4946 ± 0.0018	83.5
	1100	4.8138 ± 0.0018	13.1586 ± 0.0014	27.8	4.9250 ± 0.0019	13.4928 ± 0.0011	83.2
	1200	4.8583 ± 0.0015	13.2926 ± 0.0013	50.0			
SS2[a]	600	4.8168 ± 0.0011	13.1677 ± 0.0021	29.3	4.9240 ± 0.0014	13.4898 ± 0.0015	82.7
	700	4.8174 ± 0.0019	13.1695 ± 0.0013	29.6	4.9234 ± 0.0008	13.4880 ± 0.0013	82.4
	800	4.8180 ± 0.0018	13.1713 ± 0.0011	29.9	4.9228 ± 0.0011	13.4862 ± 0.0009	82.1
	900	4.8186 ± 0.0013	13.1731 ± 0.0009	30.2	4.9222 ± 0.0013	13.4844 ± 0.0013	81.8
	1000	4.8192 ± 0.0019	13.1749 ± 0.0008	30.5	4.9216 ± 0.0012	13.4826 ± 0.0013	81.5
	1100	4.8198 ± 0.0016	13.1767 ± 0.0009	30.8	4.9210 ± 0.0013	13.4808 ± 0.0007	81.2
	1200	4.8591 ± 0.0022	13.2944 ± 0.0015	50.3			
SS3	950	4.7785 ± 0.0017	12.9200 ± 0.0020	7.04			

[a] Sample was subjected to preliminary annealing at $T = 1300$ °C.

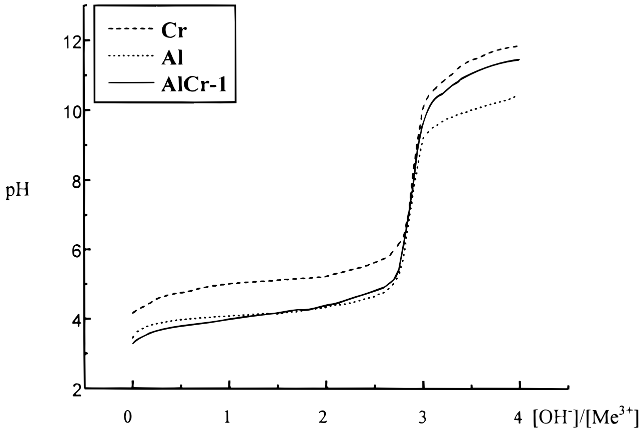

Figure 3. Titration of the initial samples Al, Cr, and AlCr-1 with 0.5 M KOH.

an internal standard. The composition, *x*, of the $Al_{2-x}Cr_xO_3$ solid solutions synthesized at different annealing temperatures was determined from the linear dependence of the *a* and *c* lattice parameters upon chromium content experimentlly determined in refs 8 and 14. The results of the Guinier study are presented in Table 1 (see the Sol Preparation section for explanation of the sample notations). It should be noted that the deviation from the linear relationship between the lattice constants *a* and *c* and chromium content was reported in ref 15. Such a positive deviation from Vegard's law may be associated with partial microsegregation in the samples.[10]

Results and Discussion

Sol Preparation. To study hydrolytic equilibrium in the system $Al^{3+}-Cr^{3+}-H_2O$, the titration of the initial samples Al, Cr, and AlCr-1 was carried out with 0.5 M KOH. The results of the titration shown in Figure 3 suggest the formation of joint aluminum−chromium polynuclear hydroxocomplexes in the latter case since isopotential points are similar for all three samples. As one can see from Figure 3, the composition of the joint hydroxocomplexes is similar to that of the individual aluminum hydroxocomplexes. This hypothesis is in agreement with the results of ref 16 based on the ^{27}Al NMR studies of coprecipitated aluminum and chromium hydroxides. Thus, one can expect that the anion exchange of a solution containing both aluminum and chromium cations results in a highly homogeneous distribution of the components.

The composition of the hydroxide sols as obtained by pH and pNO_3 measurements and by gravimetric analysis is summarized in Table 2. It should be noted that the sol consisting of pure chromium hydroxide contains more nitrate ions than the other samples. However, attempts to remove these by additional anion-exchange treatment resulted in spontaneous precipitation of chromium hydroxide. At the same time, it is well seen that in all cases NO_3^- content is very low. Thus, the anion-exchange step enables the synthesis of stable hydroxide sols with low content of impurities.

On going from the sols to final products, we attempted to compare the two possible ways of organization of initial colloid systems mentioned above. The colloid solutions for freeze-drying were prepared as follows: (1) from sample AlCr-1 (sample SS1, joint ion-exchange treatment) and (2) by mixing equal volumes of sols Al and Cr (sample SS2, separate treatment). Finally, ruby itself was synthesized from sample AlCr-2, containing 7 mol % Cr (sample SS3, joint treatment). In the latter case, the chromium content of 7 mol % was chosen because of the following reason. As it was shown above, aluminum and chromium ions are likely to form joint

Table 2. Properties of the Hydroxide Sols Obtained as a Result of the Anion-Exchange Treatment

sample	Cr_2O_3 content (mol %)	pH	pNO_3	formulas	gravimetric data: total concentration [Al] + [Cr] (mol L^{-1})
Al	0	6.00	3.07	$Al(OH)_{2.998}(NO_3)_{0.002}$	0.490
Cr	100	5.57	1.38	$Cr(OH)_{2.92}(NO_3)_{0.08}$	0.483
AlCr-1	50	5.21	2.46	$Al_{0.5}Cr_{0.5}(OH)_{2.993}(NO_3)_{0.007}$	0.491
AlCr-2	7	6.5	5.47	$\approx Al_{0.93}Cr_{0.07}(OH)_3$	0.498

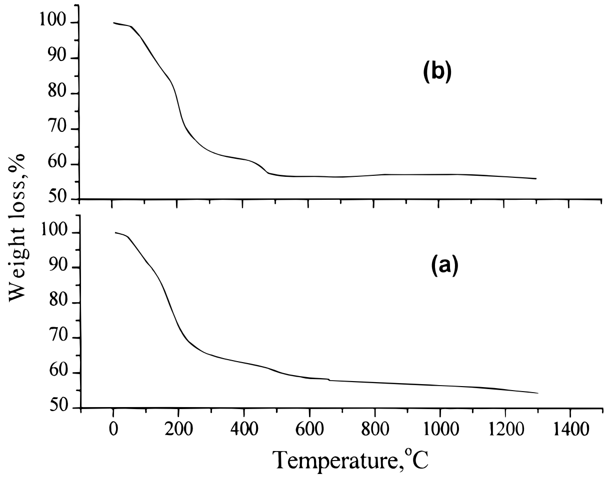

Figure 4. Thermogravimetric analysis of the samples: (a) SS1 and (b) SS2.

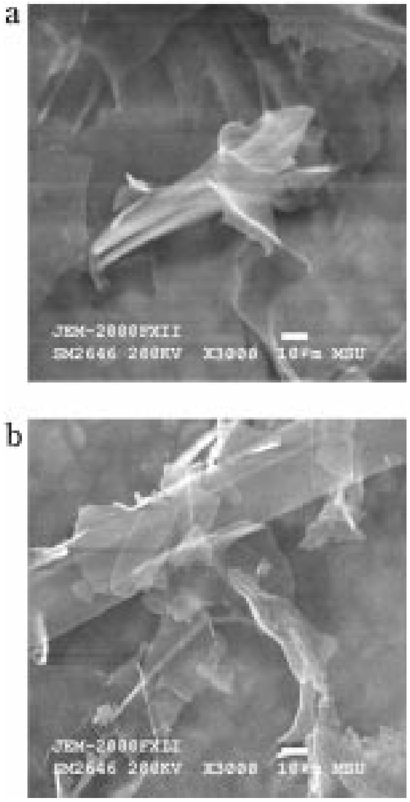

Figure 5. SEM micrographs of the as-prepared samples: (a) SS1 and (b) SS2.

hydroxocomplexes resembling that of pure aluminum ions. Thus, one can expect that the structure of these complexes at the late stages of hydrolysis is close to that of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ (Al_{13}), which is believed to be the main structural unit of colloidal particles in hydroxide sols.[17−19] A composition of 7 mol % Cr gives the ratio Al:Cr ≈ 12:1, and thus corresponds to the substitution of one octahedrally coordinated aluminum atom in Al_{13} by a chromium atom. Therefore, in this case one can expect the most homogeneous distribution of chromium in the system.

The annealing behavior of the freeze-dried samples was studied by thermal analysis (Figure 4). Scanning electron microscopy (Figure 5) showed that the samples after freeze-drying were composed of two-dimensional platelets characteristic for species prepared by the cryosol technique.[4] The microstructure of the samples SS1 and SS2 annealed at 1000 °C is shown on Figure 6. It should be noted that the thermal behavior of the samples SS1 and SS2 is quite similar (Figure 4), as well as their microstructure at different temperatures (Figures 5 and 6). However, in the next section we shall see that the organization of the initial sol strongly affects the process of the formation of solid solutions.

Solid Solutions and Segregation. It is well-known that the formation of solid solutions in the $Al_2O_3-Cr_2O_3$ system is a very slow process. According to ref 13, it takes about 1000 h at 1500 °C to obtain a solid solution of equilibrium composition from a solid oxide mixture. The reason for the difference between the diagrams shown in Figure 2 (parts a and b) arises because of different synthesis routes applied for the preparation of precursors. Type I diagrams[7,13] are obtained by heating a precursor *up* to a certain temperature and the resulting nonequilibrium curve lies *above* the equilibrium one because of the low rate of formation of the solid solution. At the same time, type II diagrams cited in many reference books and textbooks[10,13,14] are obtained for the initially single-phase samples cooled *down* to a certain temperature. In this case segregation of the solid solutions existing at higher temperatures occurs only partially and a sub-solidus curve lies *below* the “ideal” equilibrium one. One consequence of the low segregation rate is the deviation from the linear relationship between the lattice constants *a* and *c* and chromium content reported in ref 15. Such a positive deviation from Vegard’s law is characteristic for the systems with segregation on the micro level.[10]

It is clear from the above discussion that the equilibrium segregation line is placed somewhere between type I and type II diagrams. Previously, we have shown[11] that the position of the equilibrium line may be defined more exactly if a precursor with highly homogeneous distribution of the components is used for the preparation of solid solutions.

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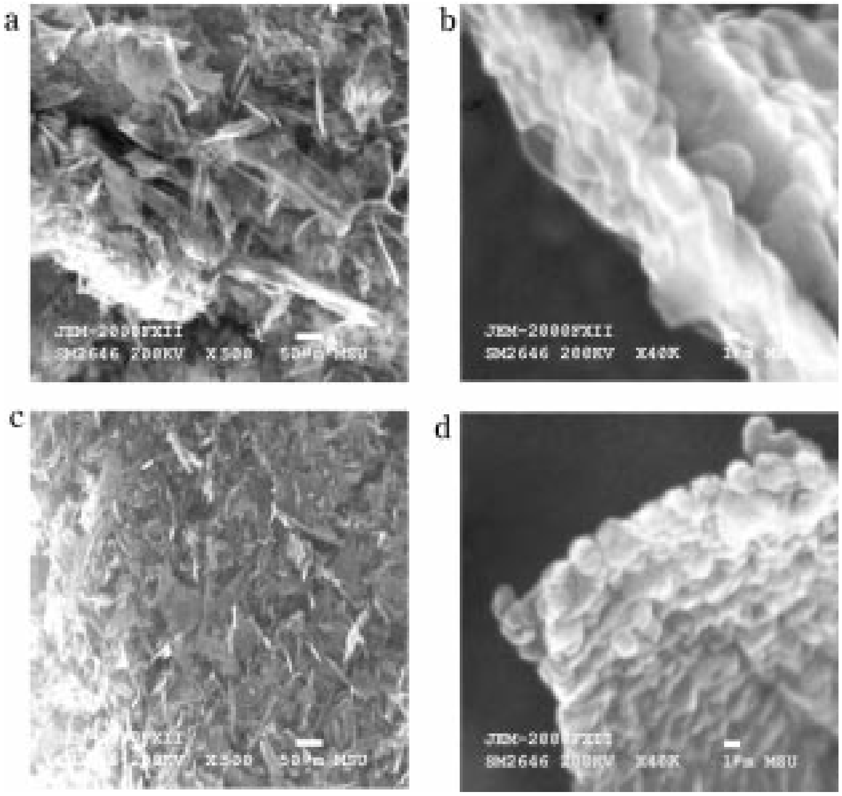

Figure 6. SEM micrographs of the samples annealed at 1000 °C: (a) and (b), sample SS1; (c) and (d), sample SS2.

Formation of the solid solutions is a diffusion-limited process.[7,20] Thus, the homogeneity of the components in a precursor and uniformity of the grain size may affect the overall process kinetics. The more homogeneous the distribution of the components is, the closer should be an experimental nonequilibrium diagram to the equilibrium one.

To obtain the nonequilibrium diagrams of segregation, we used the approach described in ref 11. The method is based on determining low- and high-temperature borders restricting the position of the equilibrium $T-x$ diagram.

The first step for obtaining the low-temperature border is the preparation of the samples that are known to be single-phase. The single-phase samples are synthesized by annealing a precursor at the temperature $T = 1300$ °C that is known to be higher than the maximum segregation temperature for the system $Al_2O_3-Cr_2O_3$.[14,21] The samples are then quenched to room temperature. The following firing of the single-phase samples at different temperatures (from 600 up to 1200 °C/3 h) results in partial segregation. However, this segregation does not achieve equilibrium because of kinetic reasons: the annealing time (3 h) is much less than the time necessary for the formation of equilibrium solid solutions ($\approx$1000 h according to ref 13). Thus, trying to plot the $T-x$ diagram, one obtains a curve lying *below* the equilibrium line.

The similar looking curve can be obtained from an as-prepared precursor that was fired at different temperatures (600−1200 °C) *without* preliminary annealing at 1300 °C. In this case, the system also does not achieve the equilibrium, but now because of the low rate of the *formation* of solid solutions. Thus, the obtained nonequilibrium $T-x$ diagram should lie *above* the equilibrium line.

The higher the homogeneity of the distribution of the components in an initial precursor, the lower should be the distance between these two experimental nonequilibrium curves. Figure 7 shows $T-x$ segregation diagrams for the sample SS1. The composition, x, for the solid solutions obtained at different annealing temperatures was determined by XRD analysis from the correlation between the lattice parameters and x.[8] Curve 1 presents the composition of the samples subjected to preliminary annealing at 1300 °C, while curve 2 is plotted for the samples treated without preliminary annealing. The equilibrium line lies between curves 1 and 2. One can see that the application of the cryosol method results in the refinement of the sub-solidus part of the phase diagram.

Comparison of this diagram with the data obtained previously for $Al_{2-x}Cr_xO_3$ solid solutions prepared by various methods[11] evidences that the cryosol technique yields the precursors with the highest level of homogeneity (Figure 7a,b).

The data led us to suppose that the use of the cryosol method may result in a considerable decrease of the temperature necessary for the preparation of ruby. Indeed, a red single-phase solid solution containing 7 mol % Cr_2O_3 was successfully synthesized from the sample SS3 by annealing at 950 °C for 2.5 h. At the same time, application of the most widespread method based on coprecipitation of chromium and aluminum hydroxides requires annealing at 1200 °C for 5 h, while the use of the more advanced "nascent reagent" tech-

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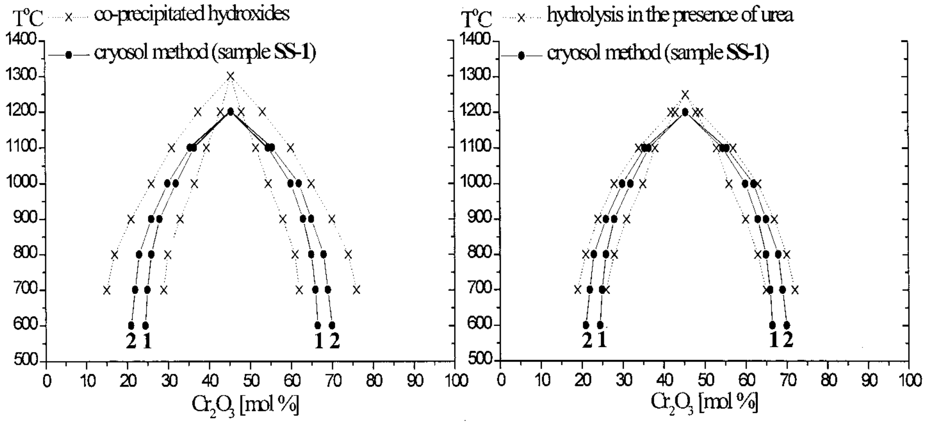
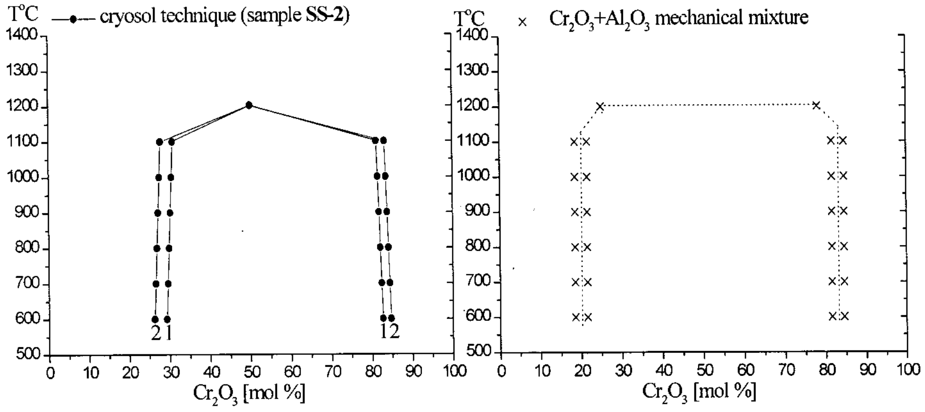


a) b)

Figure 7. Comparison of the phase diagram obtained for sample SS1 with those for $Al_{2-x}Cr_xO_3$ solid solutions prepared by other methods in ref 11: (a) traditional coprecipitation of $Cr(OH)_3$ and $Al(OH)_3$; (b) hydrolysis of $Al(NO_3)_3$ and $Cr(NO_3)_3$ in the presence of urea at 90 °C. See the text for explanations.



a) b)

Figure 8. Irreversible phase diagram for sample SS2 (a), as compared to the diagram obtained in ref 13 for $Al_{2-x}Cr_xO_3$ solid solutions prepared from the mechanical mixture of the corresponding oxides (b).

nique (hydrolysis of $Al(NO_3)_3$ and $Cr(NO_3)_3$ in the presence of urea at 90 °C) demands annealing at no less than 1050 °C for 3 h.[11]

This situation changes dramatically for the sample SS2. It is easy to see that in this case the nonequilibrium segregation diagram (Figure 8a) looks very much like that obtained for $Al_{2-x}Cr_xO_3$ solid solutions synthesized by the conventional ceramic method from the mixture of individual oxides (Figure 2a).[13] Thus, the precursor obtained by a separate ion-exchange treatment is characterized by very poor homogeneity of the distribution of the components.

The difference in the phase diagrams can be ascribed to the different distribution of the components in the precursor. The application of the first route gives rise to the formation of joint polynuclear hydroxocomplexes of Al(III) and Cr(III) and the system is homogeneous on the molecular level. That the curves 1 and 2 for this sample lie closer to each other than that for coprecipitated hydroxides is evidence that the components are distributed more uniformly. Contrarily, the separate treatment of individual aluminum and chromium nitrates results in individual hydroxopolymers, thus leading to a drastic decrease of the homogeneity in the system. In this case the phase diagram resembles that for the mechanical mixture of oxides.

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