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Study of the Factors Affecting the Formation of Copper–Chromium/Aluminum Oxide Compounds with a Spinel Structure

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Abstract—The effect of the Cr^{3+}/Al^{3+} ratio on the crystallization temperature of mixed oxide compounds with a spinel structure and their structural features and morphological characteristics have been studied using a combination of physicochemical methods: thermal analysis, IR spectroscopy, X-ray powder diffraction, and electron microscopy. The role of temperature of synthesis and drying of Cu–Cr/Al hydroxy precursors in the formation of copper-containing spinels $CuCr_xAl_{2-x}O_4$, where $x = 0–2$, has been elucidated. The results are of interest for selection of the optimal composition and conditions of synthesis and formation of copper-containing spinels for their practical use.

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At present, oxide compounds with a spinel structure are widely used owing to their magnetic, electrical, optical, and catalytic properties [1]. They have high thermal and mechanical stability and hydrophobicity and low surface acidity [2].

Copper chromite is a normal spinel [3, 4], while copper aluminate is a partially inverse spinel [5]. Mixed copper-containing oxide compounds that exhibit different redox properties can be of great interest for practical use [6].

Spinel oxide structures can form in the course of heat treatment of mixed hydroxy compounds synthesized through coprecipitation of metal cations or by annealing metal oxides at high temperature. However, annealing metal oxides leads to large particles with a small specific surface area, which is a detrimental factor for using these compounds as catalysts. This disadvantage is absent when samples are prepared by coprecipitation. At the same time, the effect of the heat treatment temperature of hydroxy compounds on the structural characteristics of spinels remains an important issue. Low-temperature structures differ from high-temperature ones in that the anionic framework of the former contains the anions of initial compounds [7].

The aim of this work is to study the effect of temperatures of drying and calcination of copper–chromium/aluminum hydroxy compounds on the formation of mixed oxides $CuCr_xAl_{2-x}O_4$, where $x = 0–2$, and the effect of the Cr^{3+}/Al^{3+} ratio in a mixed oxide on the crystallization temperature of copper-containing spinels and their structural characteristics, as well as the morphological characteristics of spinel particles.

EXPERIMENTAL

Samples of Cu-Cr/Al hydroxy compounds were produced by coprecipitation from aqueous solutions of copper, chromium, and aluminum nitrates with a sodium carbonate solution at constant pH and temperature, using a continuous synthesis method. The pH and temperature of the suspension in the course of synthesis were maintained within 6.6–6.8 and 65–70°C, respectively. Once the coprecipitation was completed, the suspension was aged under synthetic conditions for 1–4 h with the aim to determine the effect of the process on the degree of crystallinity of hydroxycarbonate precursor compounds. Then, the precipitate was washed with distilled water to remove sodium ions to ≤0.01 wt %. Samples dried at room temperature were further dried in air at 110, 150, or 200°C for 2 h.

The cationic composition of samples was determined by atomic emission spectroscopy (AES) on a Perkin Elmer Optima 4300 DV spectrometer.

Table 1. Chemical composition of the samples

Sample	Chemical composition, at %			Experimental Cr^{3+}/Al^{3+} ratio
	Cu	Al	Cr	
$CuAl_2O_4$	34	66	–	–
$CuCr_{0.25}Al_{1.75}O_4$	38	51	11	1/4.6
$CuCr_{0.75}Al_{1.25}O_4$	37	36	27	1/1.3
$CuCrAlO_4$	36	29	35	1.2/1
$CuCr_{1.25}Al_{0.75}O_4$	36	21	43	2/1
$CuCr_{1.75}Al_{0.25}O_4$	34	12	54	4.5/1
$CuCr_2O_4$	30	–	70	–

Thermal analysis was carried out using a Netzsch STA-409 PC Luxx system in the temperature-programmed mode in an Ar flow at a rate of 40 mL/min. The heating rate was 10 K/min. A weighed sample of 10–20 mg was placed into a platinum crucible.

X-ray powder diffraction analysis was performed on a Bruker D-8 diffractometer with CuK_α radiation (graphite monochromator in the reflected beam). Patterns were recorded in scan mode with a step of 0.02°–0.05°; the counting time was 5 s per point. The accuracy of measurement of angles $\Delta\theta$ was 0.01°–0.02°, and that for interplanar spacings (Δd) was 10^{-3} Å. The phases were identified using the International Database ICDD.

Electron microscopic studies were carried out on a JEOL JEM-2010 transmission electron microscope (resolution 0.14 nm, accelerating voltage 200 kV). Elemental analysis was performed on a Phoenix Edax energy dispersive X-ray spectrometer. Samples were deposited on a molybdenum grid after ultrasonication in ethanol.

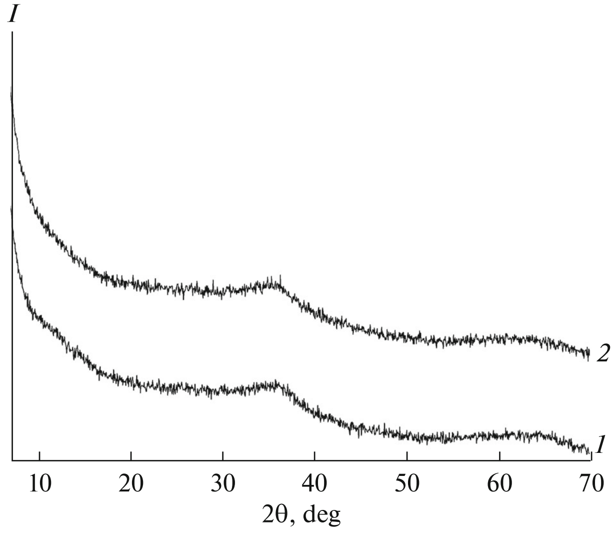

Fig. 1. X-ray powder diffraction patterns of $CuAl_2O_4$ samples dried in air and having different suspension aging times at 70°C: (*1*) 1 and (*2*) 4 h.

IR absorption spectra were recorded on two spectrophotometers. The spectra in the range 400–2500 cm^{-1} were recorded on a Shimadzu FTIR 8300 spectrophotometer with a resolution of 4 cm^{-1} (acquisition of 100 scans), and spectra in the range 50–600 cm^{-1} were recorded on a Bruker spectrophotometer. The resulting spectra were combined into a single spectrum, using the wavenumber 400 cm^{-1}. Samples were prepared in a KBr matrix.

RESULTS AND DISCUSSION

The cationic composition of synthesized Cu–Cr/Al samples is presented in Table 1.

All the synthesized samples are X-ray amorphous hydroxy compounds. Figure 1 shows, as an example, the X-ray powder diffraction patterns of copper aluminate at the aging time of the working suspension of 1 and 4 h. Both patterns show two halos at 2θ angles ~35° and 65° characterizing a nanodispersed two-layer hexagonal packing of anions with disordered distribution of cations inside a two-layer package and in the interlayer space [4]. Increasing the duration of synthesis of Cu–Cr/Al hydroxy compounds by increasing the suspension aging time from 1 to 4 h at 70°C almost does not improve the degree of crystallinity of the samples.

According to transmission electron microscopy (TEM) data, the dry samples contain amorphous mesoporous aggregates. The dark field image of a fragment of such a sample reveals structural homogeneity and the absolute lack of crystallites in aggregates (Fig. 2).

The heat treatment of hydroxy compounds is accompanied by endothermic and exothermic events accompanied by weight change. Figure 3 shows, as an example, the thermoanalytical curves for the copper–aluminum and copper–chromium/aluminum sam-

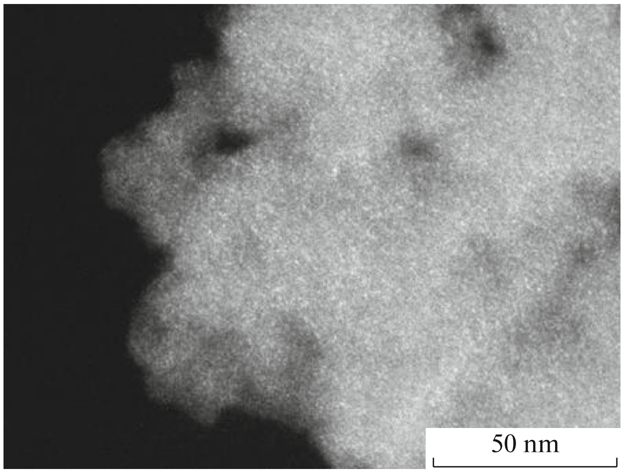

Fig. 2. Dark field TEM image of the $CuCrAlO_4$ dried in air at room temperature.

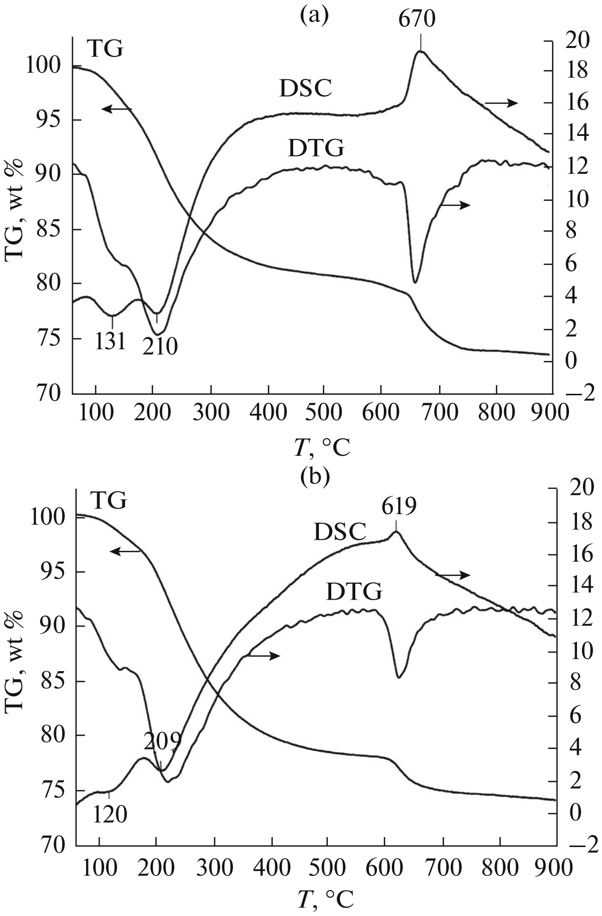

Fig. 3. Thermoanalytical curves obtained in an argon flow at a heating rate of 10 K/min. The samples were preliminarily dried in air at 150°C for 2 h: (a) $CuAl_2O_4$ and (b) $CuCrAlO_4$.

ples, and Table 2 summarizes the data of thermal analysis for all the samples.

As follows from Fig. 3, and Table 2, hydroxy compounds decompose in three steps. In the first step at temperatures ~120–130°C, adsorbed and weakly bound water is removed, which is accompanied by a small endotherm with a weight loss of 3–5%. The second step of decomposition, presumably involving removal of hydroxy and carbonate groups from the interlayer space of two-layer packages, is observed at 205–240°C and accompanied by a weight loss of ~17–22%. X-ray powder diffraction (Fig. 4) demonstrates that, above 200°C, there are formed anion-modified oxides with a nanodispersed spinel structure characterized by diffuse diffraction maxima at 2θ of ~25°, 35°, and 63°. The IR spectra of copper–chromium/aluminum samples at 200°C (Fig. 5) show absorption bands at 530 cm^{-1} due to Al–O and Cr–O stretching vibrations; absorption bands at 1093 and 1402 cm^{-1} related to symmetric and antisymmetric stretching vibrations of CO_3^{2-} anions; absorption bands at 833, 933, 1365, 1505, and 1600 cm^{-1} arising from C–O stretching vibrations of mono- and biden-

Table 2. Thermal analysis data (heating rate 10 K/min, Ar, preliminary drying in air at 150°C for 2 h)

Sample	First effect		Second effect		Third effect	
	endotherm, °C	weight loss, %	endotherm, °C	weight loss, %	exotherm, °C	weight loss, %
$CuAl_2O_4$	131	4.6	210	16.5	670	6.2
$CuCr_{0.25}Al_{1.75}O_4$	130	3.5	210	18.8	659	2.8
$CuCr_{0.75}Al_{1.25}O_4$	126	3.6	205	19.5	640	2.0
$CuCrAlO_4$	120	2.9	209	19.1	619	4.0
$CuCr_{1.25}Al_{0.75}O_4$	120	3.1	210	20.4	620	2.4
$CuCr_{1.75}Al_{0.25}O_4$	122	2.7	220	20.6	618	2.4
$CuCr_2O_4$	130	2.6	240	22.0	620	3.0

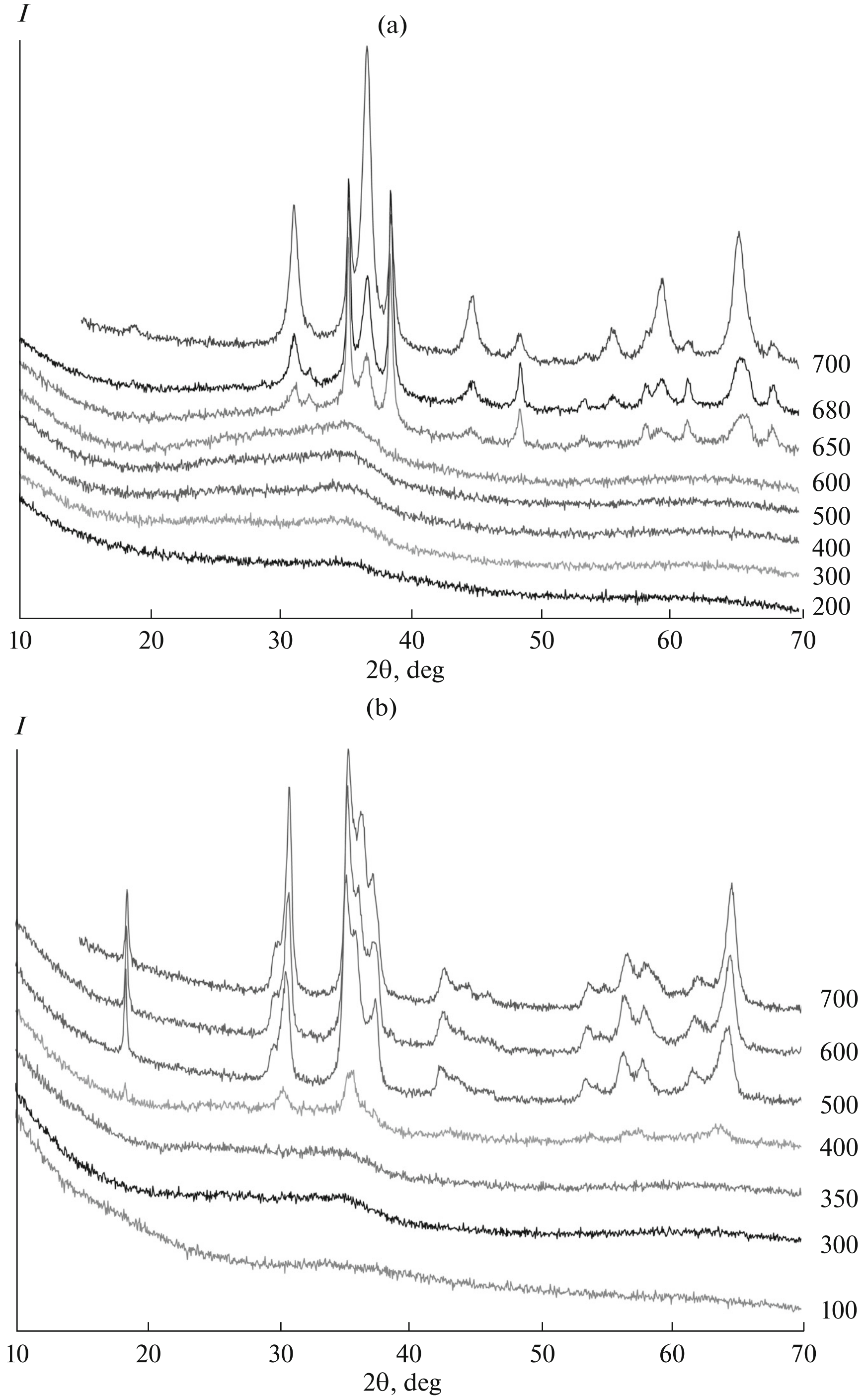

Fig. 4. Structural characteristics of samples as a function of calcination temperature. Calcination time at a given temperature is 4 h, air: (a) $CuAl_2O_4$ and (b) $CuCrAlO_4$.

tate carbonates bound to copper cations. On heating the samples to 350°C, some carbonates, predominantly monodentate (absorption bands at 1505 cm^{-1}), decompose, and a portion of CO_2 is encapsulated in sample pores, which follows from the presence of a narrow band at 2340 cm^{-1} in the spectra.

At ~620–670°C, the thermal curves (Table 2) show exotherms accompanied by small weight changes (~2–6%), presumably reflecting removal of residual anions and crystallization of spinel oxides. Table 2 also shows that the crystallization temperature of oxides depends on the Cr^{3+}/Al^{3+} ratio. The highest crystalli-

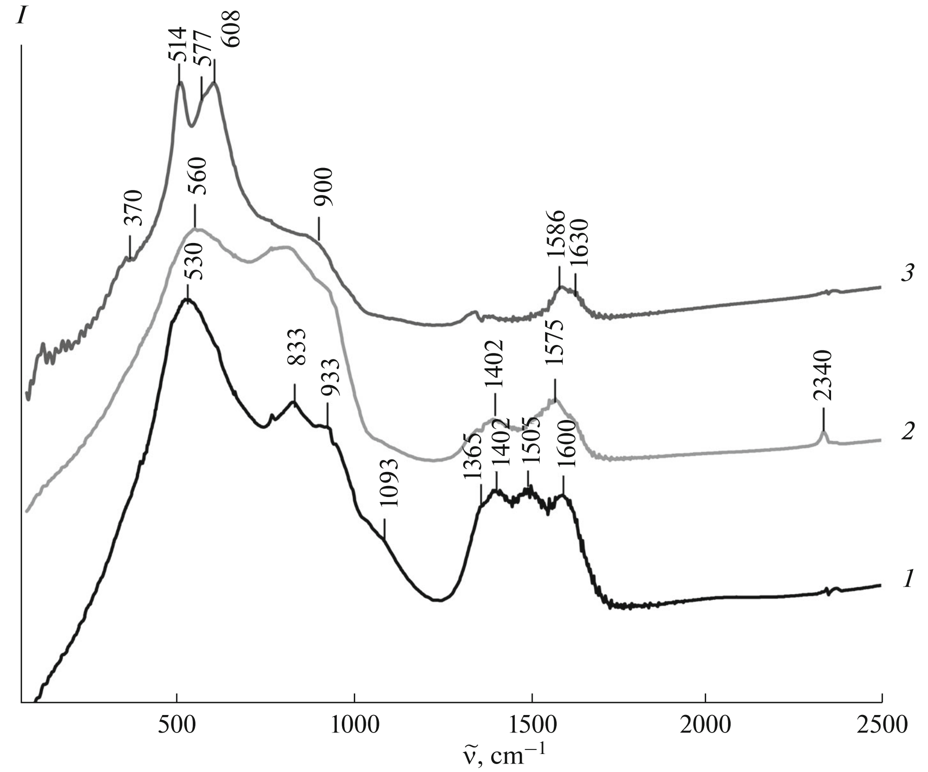

Fig. 5. IR spectra of the $CuCrAlO_4$ sample calcination in air at (*1*) 200, (*2*) 350, and (*3*) 500°C.

zation temperature (670°C) is observed for $CuAl_2O_4$. The introduction of chromium cations leads to a decrease in crystallization temperature.

According to X-ray powder diffraction (Fig. 4) and IR spectroscopy (Fig. 5), calcination the Cu–Cr/Al samples at $T \geq 500$°C leads to the formation of a phase with a spinel structure. The IR spectra (Fig. 5, curve *3*) show a set of new narrow absorption bands at 514, 577, and 608 cm^{-1}, related to a spinel phase. The band at ~900 cm^{-1} can be assigned to the alumina phase, and the band at 370 cm^{-1} is presumably caused by the presence of CuO. The formation of the spinel crystalline

Table 3. Phase composition of and lattice parameters of Cu-containing spinels (calcination in air at 650 and 900°C for 4 h)

Sample	650°C		900°C	
	phase composition	parameter, Å	phase composition	parameter, Å
$CuAl_2O_4$	Cubic spinel + CuO (30%)	$a = 8.071$	Cubic spinel + CuO (1%)	$a = 8.077$
$CuCr_{0.25}Al_{1.75}O_4$	Cubic spinel + CuO (11%)	$a = 8.105$	Cubic spinel	$a = 8.112$
$CuCr_{0.75}Al_{1.25}O_4$	Tetragonal (40%) + cubic (55%) spinels + CuO (5%)	$a = 5.964$ $c = 7.880$ $a = 8.155$	Cubic spinel + tetragonal spinel (traces)	$a = 8.154$
$CuCrAlO_4$	Tetragonal (76%) + cubic (24%) spinel + CuO (traces)	$a = 5.975$ $c = 7.880$ $a = 8.184$	Tetragonal spinel + cubic spinel (traces)	$a = 5.940$ $c = 7.880$
$CuCr_{1.25}Al_{0.75}O_4$	Tetragonal spinel	$a = 5.981$ $c = 7.879$	Tetragonal spinel	$a = 5.940$ $c = 7.841$
$CuCr_{1.75}Al_{0.25}O_4$	Tetragonal spinel + Cr_2O_3 (12%)	$a = 6.012$ $c = 7.873$	Tetragonal spinel + Cr_2O_3 (6%)	$a = 6.014$ $c = 7.820$
$CuCr_2O_4$	Tetragonal spinel	$a = 6.032$ $c = 7.788$	Tetragonal spinel	$a = 6.032$ $c = 7.788$

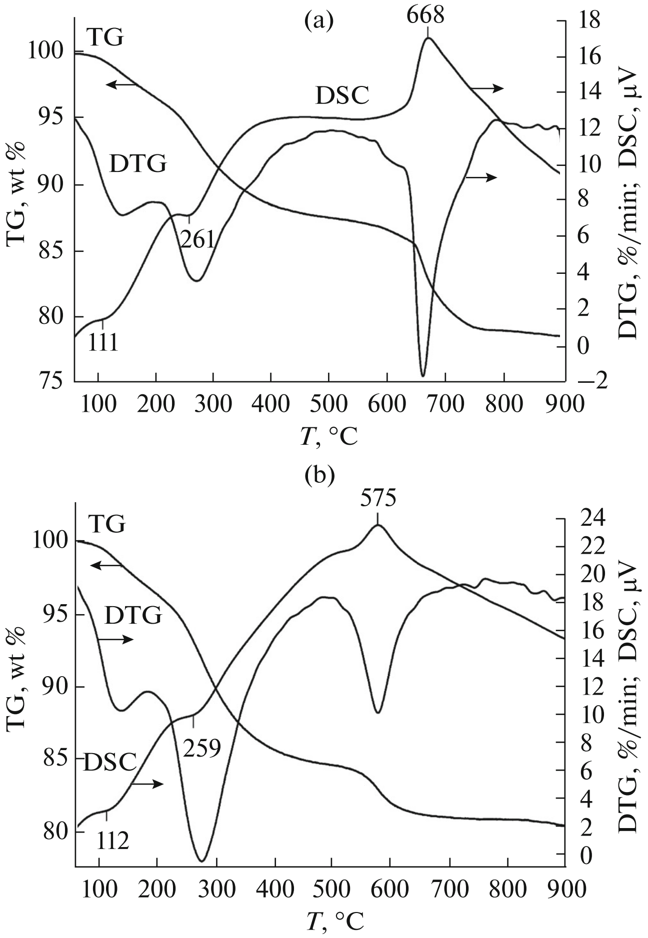

Fig. 6. Thermoanalytical curves obtained in an argon flow at a heating rate of 10 K/min. The hydroxyl precursors of the samples were preliminarily dried in air at 200°C for 2 h: (a) $CuAl_2O_4$ and (b) $CuCrAlO_4$.

phase is accompanied by the decomposition of carbonates and simultaneous removal of encapsulated CO_2 [8].

An increase in the drying temperature of hydroxyl precursors from 150 to 200°C leads to a decrease in the crystallization temperature of the oxide phase (Fig. 6). Comparison of the thermal curves of the samples Figs. 3, 6) shows that the largest decrease in crystallization temperature (by up to ~40–50°C) of the three-component copper–chromium/aluminum samples as compared with the two-component samples.

Table 4. Elemental composition of $CuCrAlO_4$ calcined in air at 700°C for 4 h

Segment in Fig. 8	Composition, at %		
	Al*K*	Cr*K*	Cu*K*
1	8.46	32.40	59.15
2	28.89	5.45	65.65
3	3.82	6.32	89.87
4	13.81	23.93	62.27

Thus, according to thermal analysis data, the oxide phase crystallization temperature depends on the Cr^{3+}/Al^{3+} ratio in copper-containing samples, as well as on the preliminary drying temperature of hydroxy precursors.

The thermal analysis data are consistent well with X-ray diffraction data. It follows from Fig. 4 (it shows the patterns for two samples as an example) that the oxide phase with a spinel structure forms at ~500–650°C, which is close to the temperature at which the exotherm caused by crystallization is observed; the degree of crystallinity of the oxide phase increases with calcination temperature.

Figure 7 show the X-ray powder diffraction patterns of copper–chromium/aluminum samples annealed at 650 and 900°C, and Table 3 summarizes X-ray diffraction data for all the samples.

It follows from Table 3 that the *a* parameter of the cubic spinel $CuAl_2O_4$ gradually increases as chromium cations are introduced in the sample composition. At calcination temperature of 650°C, the presence of both structural modifications of spinel—cubic and tetragonal—is clearly seen in the $CuCr_{0.75}Al_{1.25}$ sample. Tetragonal spinel phases are observed in the $CuCr_{1.25}Al_{0.75}$ and $CuCr_{1.75}Al_{0.25}$ samples. The character and degree of distortion of the Cu–Cr/Al spinels depend on the Cr^{3+}/Al^{3+} ratio. With an increase in the chromium content of the samples, the *a* parameter of cubic spinel increases, and the cubic phase gradually transforms, through the formation of cubic and tetragonal phases, to the tetragonal modification of the $CuCr_2O_4$ structure.

According to TEM, copper–chromium/aluminum samples calcined at 700°C contain a polycrystalline phase composed of block crystals up to ~100 nm in size and aggregated highly dispersed particles (Fig. 8). The elemental analysis data for the spots shown in Fig. 8 are presented in Table 4.

As follows from Fig. 8 and Table 4, the cationic composition of the crystals corresponds to spinel (spots 1 and 4); this composition is nearly the same, and some difference is caused by the fact that the electron probe "covers" a small fraction of "foreign" tiny particles. However, the highly dispersed mass (spot 2) is inhomogeneous in composition and contains separate particles among which copper and aluminum oxides predominate and chromium oxide traces are present. Copper cations in the dispersed mass (spot 3) are incorporated in separate copper oxide particles, which are plate-like and about 30 nm in size. After calcination at 900°C for 4 h (Fig. 9), the composition of the samples becomes more homogeneous in morphology and particle size, and the content of the highly dis-

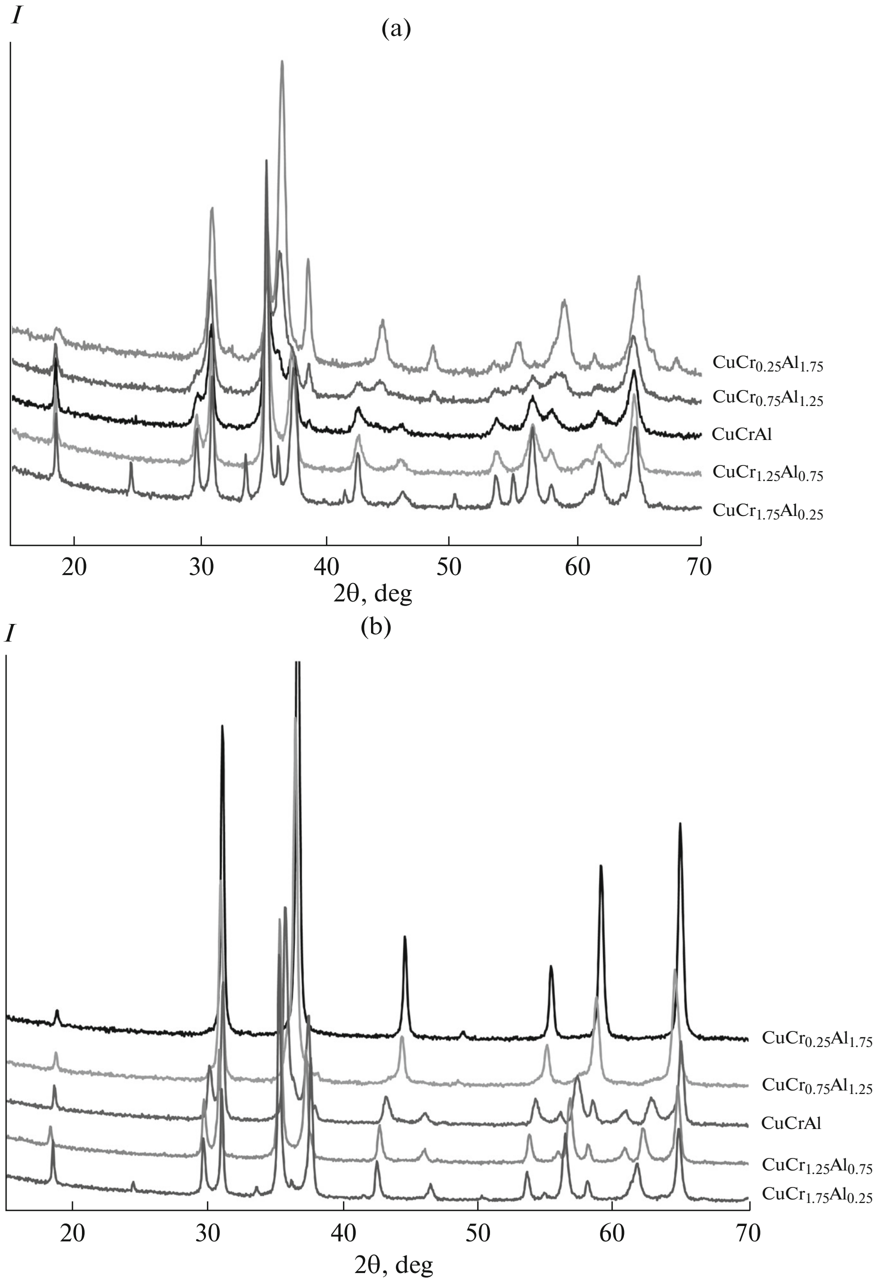

Fig. 7. X-ray powder diffraction patterns of Cu–Cr/Al samples calcined in air for 4 h at (*1*) 650 and (*2*) 900°C.

persed phase decreases. The spinel phase is represented by block crystals about 100 nm in size; the average size and composition of the particles of the highly dispersed mass change only slightly as compared with the samples annealed at 700°C.

Thus, our study has demonstrated that the crystallization temperature of the copper-containing oxide phase with a spinel structure depends on the preliminary drying temperature of hydroxy-compound precursors. Variation of the suspension aging duration (from 1 to 4 h at 70°C) in synthesis of copper–chromium/aluminum hydroxy-compounds does not lead to the increase in the degree of crystallinity of the samples. The Cr^{3+}/Al^{3+} ratio in three-component samples has an effect on the formation of the copper-containing spinel structure. As the chromium content in the compounds increases, the character and degree of distortion of the $CuCr_xAl_{2-x}O_4$ ($x = 0$–2) spinels change. The $CuAl_2O_4$ structure gradually transforms (through the formation of cubic and tetragonal phases) to the tetragonal modification of the $CuCr_2O_4$ spinel. The results of this study can be taken into account when selecting the optimal composition and conditions of

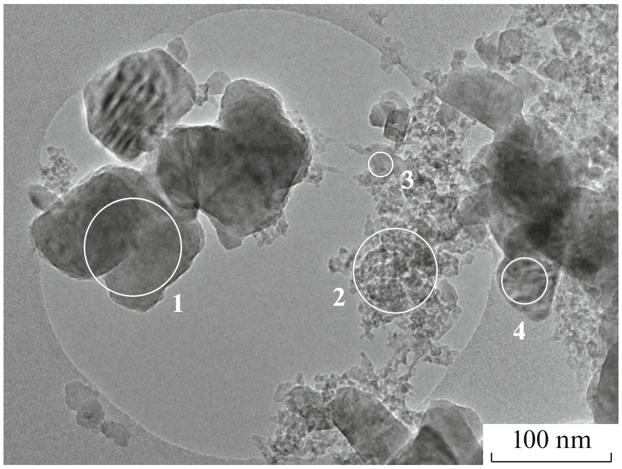

Fig. 8. TEM image of $CuCrAlO_4$, calcined in air at 700°C for 4 h.

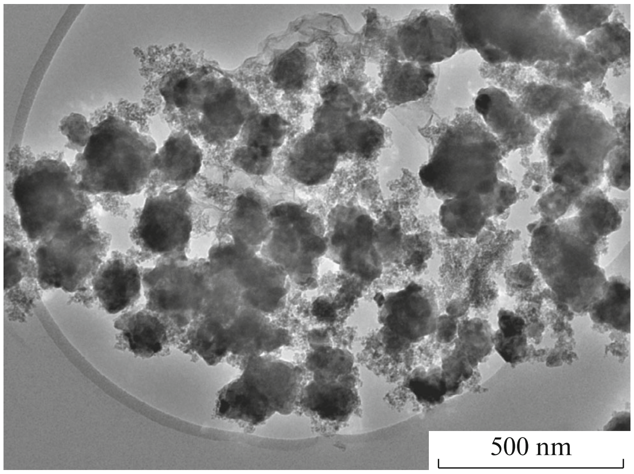

Fig. 9. TEM image of $CuCrAlO_4$, calcined in air at 900°C for 4 h.

synthesis and formation of copper-containing spinels for their practical use.

ACKNOWLEDGMENTS

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