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COORDINATION COMPOUNDS

Synthesis of Micro- and Nanosized Manganese Oxides from Hydrated Manganese Oxalates and Products of Their Chemical Modification with Ethylene Glycol

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Abstract—The reactions of ethylene glycol with manganese oxalates $MnC_2O_4 \cdot 2H_2O$ and $MnC_2O_4 \cdot 3H_2O$ on heating in air were studied. At temperature below 100°C, ethylene glycol was found to displace water from oxalates to give a new solvate compound according to the reaction $MnC_2O_4 \cdot nH_2O + HOCH_2CH_2OH = MnC_2O_4(HOCH_2CH_2OH) + nH_2O\uparrow$. The crystals of the solvates retain the morphology of the initial oxalates, which is then inherited by the products of their thermolysis. Thus, thermolysis of $MnC_2O_4 \cdot 3H_2O$ and $MnC_2O_4(HOCH_2CH_2OH)$ having quasi-unidimensional structure gave Mn_3O_4 and Mn_2O_3 nanowhiskers in air and MnO in an inert gas environment. Heating of $MnC_2O_4 \cdot nH_2O$ in ethylene glycol at temperatures above 100°C results in anhydrous manganese oxalate.

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The development and progress of new effective methods for the synthesis of new oxide materials with extended particles (whiskers, rods, fibers, wires, ribbons, tubes) is a key task of the modern preparative nanochemistry. A promising and widely used method for the synthesis of these materials is based on the phenomenon of pseudomorphism, i.e., the ability of the initial compound to convert into oxide upon heat treatment without a considerable change in particle morphology [1]. Previously, we described methods for the synthesis of micro- and nanosized whisker and fiber crystals of complex oxides MCo_2O_4 (M = Zn, Mn) with the spinel structure from solvates $M_{1/3}Co_{2/3}C_2O_4(HOCH_2CH_2OH)$ consisting of 20–50-μm long needle- and fiber-shaped crystals with a cross section of less than 0.5 μm [2, 3]. On heating in air, solvates $M_{1/3}Co_{2/3}C_2O_4(HOCH_2CH_2OH)$ are converted into oxides MCo_2O_4 with a cubic spinel structure, the morphology of the parent extended crystals being inherited by the products of thermolysis. The whisker crystals of MCo_2O_4 formed upon thermolysis have a cross section of ~30–40 nm and a length of not less than 20 μm [3].

Manganese oxides traditionally find use as magnetic materials, sorbents, catalysts, and semiconductor termistors [4, 5]. Manganese(II) oxalate is actively used to produce nanosized manganese oxides in different oxidation states. In this study, micro- and nanocrystal whiskers of manganese oxides were obtained using synthesized manganese oxalate $MnC_2O_4 \cdot 3H_2O$ and the solvate $MnC_2O_4(HOCH_2CH_2OH)$ obtained upon replacement of water in the trihydrate structure by ethylene glycol. This compound was chosen due to the fact that $MnC_2O_4 \cdot 3H_2O$ precipitates from solution as slightly pink-colored needle crystals [6, 7]. The replacement of water by ethylene glycol may result [2, 3] in the formation of thinner crystals of the solvate $MnC_2O_4(HOCH_2CH_2OH)$, which opens up prospects for the formation of manganese oxides as nano-sized whisker crystals upon thermolysis.

EXPERIMENTAL

The synthesis of $MnC_2O_4 \cdot 3H_2O$ was performed by adding a stoichiometric amount of a cooled solution of manganese(II) sulfate to a cooled solution of oxalic acid with continuous stirring. After 20 min, the precipitated $MnC_2O_4 \cdot 3H_2O$ was separated from the mother liquor, washed with ethanol on a vacuum filter, and dried to constant weight in air at ambient temperature. The solid solution $Mg_{0.2}Mn_{0.8}C_2O_4 \cdot 3H_2O$ was synthesized in a similar way by adding a mixture of manganese and magnesium sulfates to oxalic acid. The oxalate $MnC_2O_4 \cdot 2H_2O$ was prepared by the following procedure: a 0.2 M solution of manganese(II) sulfate heated to 70°C was added from a dropping funnel over a period of 30–40 min to a 0.2 M aqueous solution of oxalic acid (taken in a 50% excess) heated to the same temperature. Precipitation was carried out at a temperature of 70°C with continuous stirring for 60 min. After maturing for 24 h, the precipitates were washed with distilled water until the test for SO_4^{2-} was negative, and dried under ambient conditions to a constant weight.

Mixtures of synthesized manganese oxalates and ethylene glycol were heat treated in heat-resistant glass beakers at various temperatures. The initial oxalate powders were mixed with a fivefold excess of $HOCH_2CH_2OH$ until a uniform blend formed and stirred for 18 h at 80 and 150°C. The solid reaction products were separated from the liquid phase by vacuum filtration, washed with acetone, dried in air at 40°C, and placed in tightly closed sample bottles for storage. The sample with the composition $Mg_{0.2}Mn_{0.8}C_2O_4 \cdot 3H_2O$ was treated only at lower temperature.

Phase analysis was performed using a DRON UM-1 X-ray diffractometer (CuK_α radiation) and a POLAM C-112 polarization microscope in the transmitted light. Thermogravimetric analysis was carried out on a Q-1500D derivatograph in air with heating from 20 to 1000°C at a rate of 10 K/min. IR spectra were measured on a Spectrum-One spectrophotometer in the 400–4000 cm^{-1} range. Morphological studies were carried out for the initial oxalates, products of their treatment with ethylene glycol, and the products of thermolysis in air and in a helium atmosphere at 150–600°C. The shape and size of the particles formed upon thermal decomposition were determined by scanning electron microscopy (SEM) on a Tesla BS-301 instrument. Elemental analysis for Mn and Mg was carried out by atomic absorption spectroscopy in an acetylene–air flame on a Perkin-Elmer instrument and by inductively coupled plasma atomic emission spectroscopy on a JY 48 spectral analyzer.

RESULTS AND DISCUSSION

According to powder X-ray diffraction, microscopic examination, IR spectroscopy, thermogravimetric analysis, and elemental analysis, the oxalate samples prepared by the above-described procedure were single phases. Powdered $MnC_2O_4 \cdot 2H_2O$ is white-colored and looks under a microscope as plate crystals with high birefringence. The refractive indices are $Ng = 1.558$ and $Np = 1.501$. The $MnC_2O_4 \cdot 3H_2O$ powder is slightly pink-colored and looks under a microscope as needle crystals with a size of $\sim 1 \times 50$ μm; the refractive indices are $Ng = 1.546$ and $Np = 1.470$. Similar crystals are formed by the complex oxalate $Mg_{0.2}Mn_{0.8}C_2O_4 \cdot 3H_2O$. $MnC_2O_4 \cdot 3H_2O$ is a metastable compound because on storage in air it is gradually converted into the more stable $MnC_2O_4 \cdot 2H_2O$. The needle morphology of the trihydrate is not retained in this process. This feature of the $MnC_2O_4 \cdot 3H_2O$ phase was noted in the literature; the formula $\{[Mn(\mu\text{-ox})(H_2O)_2] \cdot H_2O\}$ was proposed to emphasize the nonequivalent positions of H_2O molecules with respect to the chains of structural polyhedra $M–C_2O_4–M–C_2O_4–$ [7]. The introduction of magnesium (to a maximum content of 2.4 wt %) into the $MnC_2O_4 \cdot 3H_2O$ structure stabilizes the needle-shaped phase based on the oxalate trihydrate. According to our data, $Mg_{0.2}Mn_{0.8}C_2O_4 \cdot 3H_2O$ stored in a sample bottle for more than 2 years did not undergo morphological or structural degradation, whereas $MnC_2O_4 \cdot 3H_2O$ partly converted into $MnC_2O_4 \cdot 2H_2O$ within one month after the synthesis.

The products of reaction of $MnC_2O_4 \cdot nH_2O$ with ethylene glycol at low temperatures are individual chemical compounds. They are formed upon replacement of two or three water molecules in the oxalate structure by one ethylene glycol molecule according to the reaction

$$\begin{aligned} & MnC_2O_4 \cdot nH_2O + HOCH_2CH_2OH \\ & \longleftrightarrow MnC_2O_4(HOCH_2CH_2OH) + nH_2O\uparrow. \end{aligned} \quad (1)$$

After low-temperature heat treatment, a mixture of $MnC_2O_4 \cdot 2H_2O$ plate crystals with ethylene glycol gives the solvates $MnC_2O_4(HOCH_2CH_2OH)$ as very small flattened crystals with a square cross section. The replacement of water by ethylene glycol in $MnC_2O_4 \cdot 3H_2O$ gives rise to thinner needles and fibers of $MnC_2O_4(HOCH_2CH_2OH)$. Reaction (1) was found to be reversible as $MnC_2O_4(HOCH_2CH_2OH)$ is hydrolyzed upon contact with water or water vapor at room temperature. The $HOCH_2CH_2OH$ molecule is displaced from the solvate by two water molecules to give $MnC_2O_4 \cdot 2H_2O$. The X-ray diffraction patterns of $MnC_2O_4 \cdot 2H_2O$ formed upon hydrolysis of $MC_2O_4(HOCH_2CH_2OH)$ show broad lines, indicating a low degree of crystallinity.

Under a microscope, the precipitates obtained by high-temperature treatment of manganese oxalate di- and trihydrates mixed with ethylene glycol are small platelike crystals shaped like rectangles and squares with low birefringence. The refractive indices are $Ng = 1.579$, $Np = 1.564$.

The thermal decomposition in air of $MnC_2O_4(HOCH_2CH_2OH)$ fibers prepared from $MnC_2O_4 \cdot 3H_2O$ occurs in two stages (Fig. 1a). The first exotherm corresponds to the removal of ethylene glycol ($t \sim 200$–290°C), and the second one observed in the temperature range of 290–420°C with a maximum at 310°C corresponds to the decomposition of magnesium oxalate. The decomposition of the $MnC_2O_4(HOCH_2CH_2OH)$ sample prepared from $MnC_2O_4 \cdot 2H_2O$ also occurs in two stages (Fig. 1b), the removal of 1 mole of ethylene glycol and onset of manganese oxalate decomposition being reflected by an inflection in the TG curve at ~220°C. Thermal decomposition of manganese oxalate

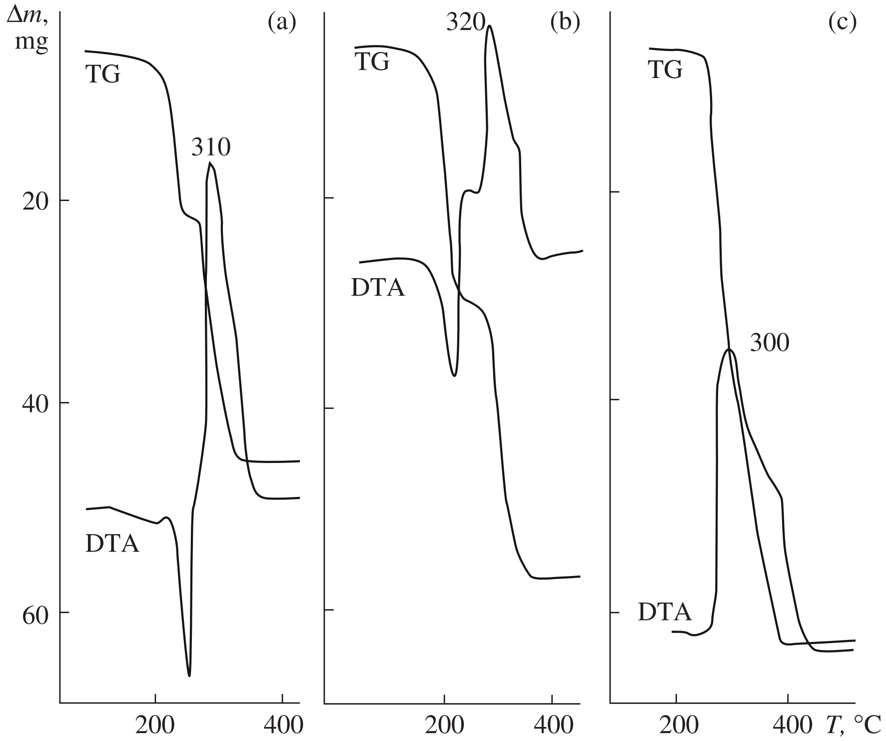

Fig. 1. TG and DTA curves of (a) fibrous $MnC_2O_4(HOCH_2CH_2OH)$, (b) finely crystalline $MnC_2O_4(HOCH_2CH_2OH)$, and (c) anhydrous MnC_2O_4.

glycolated at 150°C is exothermic and occurs in one stage with a maximum at 300°C (Fig. 1c). The final product of themolysis is Mn_2O_3.

The X-ray diffraction patterns of the initial $MnC_2O_4 \cdot 3H_2O$, oxalates subjected to heat treatment under various conditions, and thermolysis products obtained in air and in an inert gas environment are presented in Fig. 2. Analysis of the X-ray spectra leads to the conclusion that the solvate $MnC_2O_4(HOCH_2CH_2OH)$ is an individual compound. According to powder X-ray diffraction (Fig. 2a) and DTA (Fig. 1c), treatment of a mixture of manganese oxalate di- and trihydrate with ethylene glycol at 150°C gives MnC_2O_4 as the final product. The formation of anhydrous manganese oxalate occurs in two stages to give intermediately $MnC_2O_4(HOCH_2CH_2OH)$, which decomposes upon temperature rise according to the following equation:

$$MnC_2O_4(HOCH_2CH_2OH) \longrightarrow MnC_2O_4 + HOCH_2CH_2OH. \quad (2)$$

Reaction (2) describes an irreversible process, because it had been shown that anhydrous oxalates do not react with ethylene glycol [2, 3].

According to powder X-ray diffraction, thermolysis of $MnC_2O_4(HOCH_2CH_2OH)$ fibers in air at temperatures up to 500°C yields Mn_2O_3 (Fig. 2b, pattern *1*). During annealing under these conditions, finely crystalline $MnC_2O_4(HOCH_2CH_2OH)$ decomposes to give Mn_3O_4 (Fig. 2a, pattern *2*). Analogous dependences were found for thermal decomposition of the di- and trihydrate of manganese oxalate [6]. The annealing of $MnC_2O_4 \cdot 2H_2O$ at $t \leq 450°C$ gives Mn_2O_3, while the trihydrate forms Mn_3O_4 in the same temperature range. In a helium atmosphere at $T \geq 350°C$, thermolysis of $MnC_2O_4(HOCH_2CH_2OH)$ gives MnO (Fig. 2b, pattern *3*). Heating of $Mg_{0.2}Mn_{0.8}C_2O_4(HOCH_2CH_2OH)$ to 600°C induces the formation of the complex $Mg_{0.4}Mn_{1.6}O_3$ having the structure of α-Mn_2O_3.

According to SEM and optical microscopy, thermal decomposition of $MnC_2O_4 \cdot 3H_2O$ and $MnC_2O_4(HOCH_2CH_2OH)$ in air or in an inert gas environment completely conserves the crystal shape of the initial compound. An increase in temperature to 700°C does not result in a substantial change in the particle shape or size. Figure 3 shows the SEM images of $MnC_2O_4 \cdot 3H_2O$, $MnC_2O_4(HOCH_2CH_2OH)$, and the products of thermolysis of the solvate in air and in the

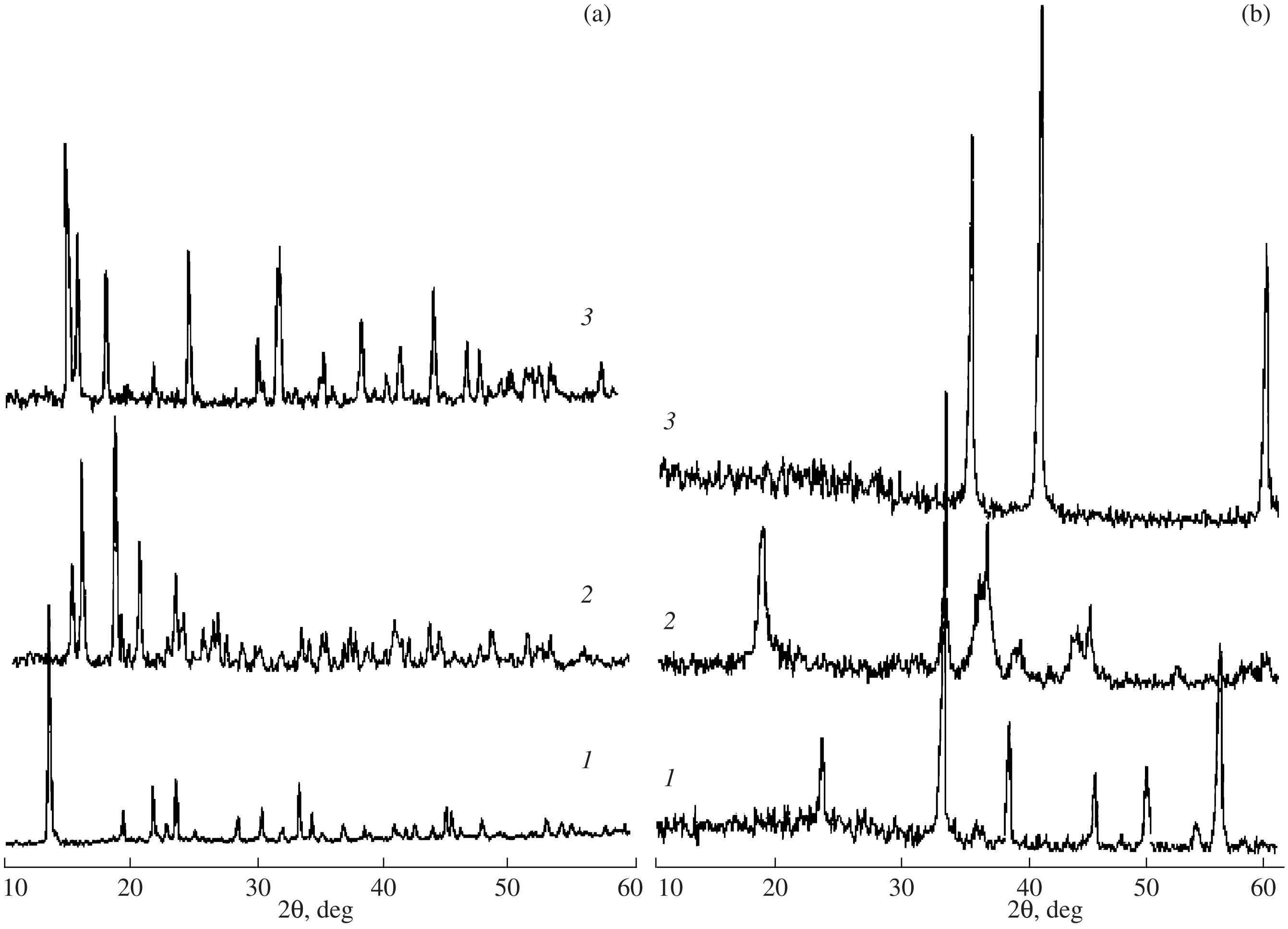

Fig. 2. X-ray diffraction patterns of a: (*1*) $MnC_2O_4 \cdot 3H_2O$, (*2*) $MnC_2O_4(OHCH_2CH_2OH)$, (*3*) MnC_2O_4; b: products of thermolysis of the solvates $MnC_2O_4(OHCH_2CH_2OH)$ in air at 450°C: (*1*) based on $MnC_2O_4 \cdot 3H_2O$ (Mn_2O_3), (*2*) based on $MnC_2O_4 \cdot 2H_2O$ (Mn_3O_4), and (*3*) in an inert gas atmosphere at 600°C (MnO).

inert gas environment. Manganese oxalate trihydrate tends to form needles about 1 μm in diameter (Fig. 3a). The solvate $MnC_2O_4(HOCH_2CH_2OH)$ crystallizes as thinner needles and fibers that tend to longitudinally intergrow (Fig, 3b). As can be seen from Fig. 3c, heating of $MnC_2O_4(HOCH_2CH_2OH)$ in air and in an inert gas environment results in separation of the initial crystals into thinner extended aggregates of Mn_2O_3 and MnO, respectively.

Analysis of the IR spectra of $MnC_2O_4 \cdot 3H_2O$, MnC_2O_4, and $MnC_2O_4(HOCH_2CH_2OH)$ presented in Fig. 4 and in the table indicates that the denticity of the $C_2O_4^{2-}$ ion in the compounds is retained. According to X-ray diffraction data [7], the crystal structure of $MnC_2O_4 \cdot 3H_2O$ is formed by infinite $–M–C_2O_4–M–C_2O_4–$ chains connected to one another by hydrogen-bonded bridging water molecules. Since the water molecules in $MnC_2O_4 \cdot 3H_2O$ are nonequivalent, its IR spectrum exhibits, in the $\nu(H_2O)$ stretching region, an intense broad band with maxima at 3417, 3317, and 3144 cm^{-1}. The intense broad band with absorption maxima at 1689 and 1606 cm^{-1} corresponds to asymmetric stretching vibrations (ν_{as}) of the O–C–O groups of the oxalate ion. Usually the bending vibrations $C_2O_4^{2-}$ occur in the same region but due to the superimposition of more intense bands of the $C_2O_4^{2-}$ ion, it is impossible to distinguish them in Fig. 4. The symmetrical $\delta(H_2O)$ vibrations are responsible for two narrow intense lines at 1374 and 1318 cm^{-1}. In the region of bending δ(OCO) modes and libration modes ρ(OCO) of coordinated

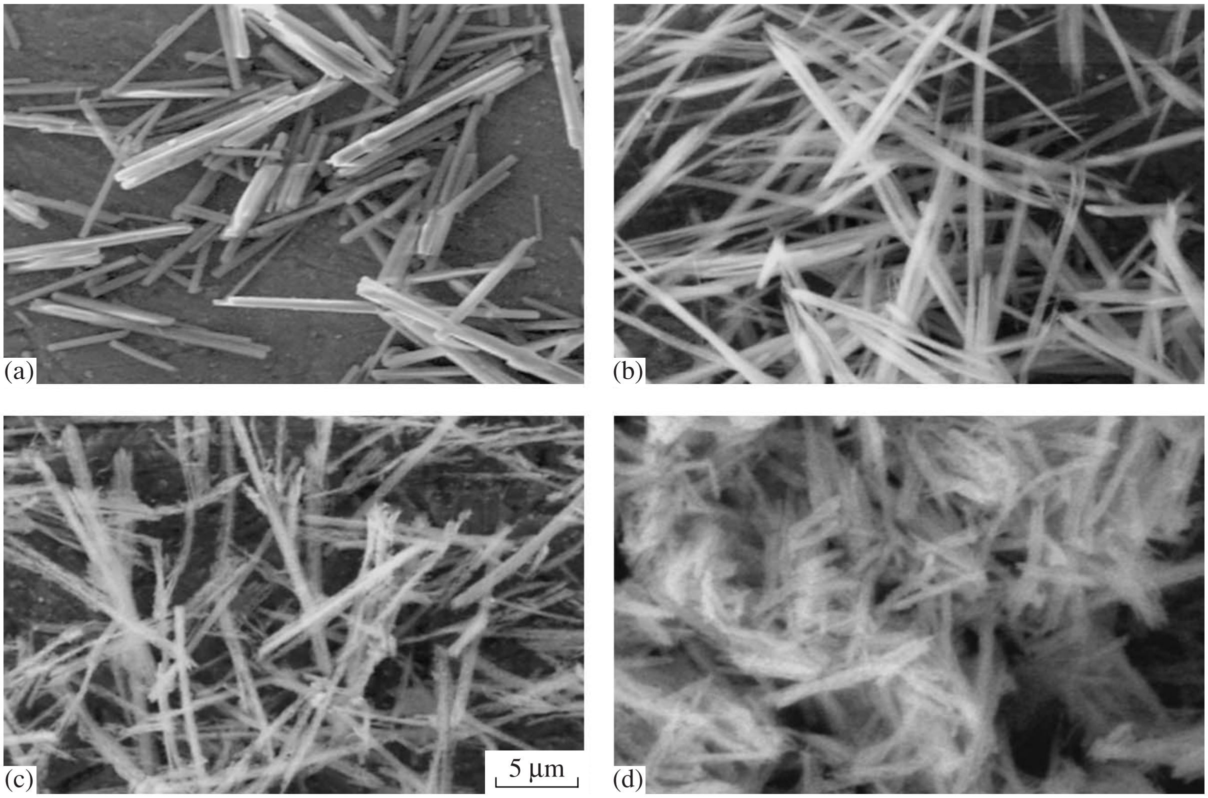

Fig. 3. SEM images (×2500) of (a) $MnC_2O_4 \cdot 3H_2O$, (b) $MnC_2O_4(HOCH_2CH_2OH)$, (c) product of thermolysis of the solvate in air at 450°C, (d) product of thermolysis in a helium atmosphere at 600°C.

water molecules, the spectrum contains three bands at 809, 759, and 617 cm^{-1}. The weak bands with maxima at 496 and 410 cm^{-1} can be assigned to Mn–O stretching vibrations in the MnO_6 octahedra.

The IR spectrum of $MnC_2O_4(HOCH_2CH_2OH)$ is a superposition of absorption bands of the tetradentate $C_2O_4^{2-}$ ion and manganese-coordinated ethylene glycol molecules [8, 9]. As a result of ethylene glycol substitution for water in the structure $MnC_2O_4 \cdot 3H_2O$, the asymmetric stretching bands ν_{as}(OCO) in the IR spectra of the solvates $MnC_2O_4(HOCH_2CH_2OH)$ are split into three components (1699, 1685, and 1619 cm^{-1}). Simultaneously, the band ν(OH) shifts to lower frequency (3190 cm^{-1}) by approximately 180 cm^{-1} with respect to its position in the IR spectrum of liquid ethylene glycol (3368 cm^{-1} [9]) (table). The C–O stretching bands (1087, 1043 cm^{-1}) and CH_2 libration bands (883, 864 cm^{-1}) in ethylene glycol [9] also shift to lower (1069, 1029 cm^{-1}) and to higher (891, 878 cm^{-1}) frequency, respectively, in the solvate spectrum. The band shifts noted in the IR spectrum of $MnC_2O_4(HOCH_2CH_2OH)$, together with

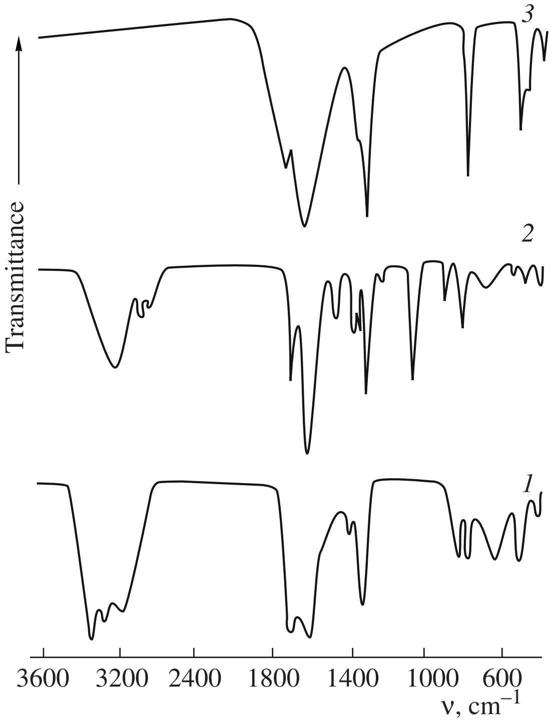

Fig. 4. IR spectra of (*1*) $MnC_2O_4 \cdot 3H_2O$, (*2*) $MnC_2O_4(HOCH_2CH_2OH)$, and (*3*) MnC_2O_4.

IR absorption maxima (cm^{-1}) of (1) $MnC_2O_4 \cdot 3H_2O$ and (2) MnC_2O_4, (3) assignment of bands according to [6], (4) $MnC_2O_4(HOCH_2CH_2OH)$, and (5) $HOCH_2CH_2OH$ (liquid)

1	2	3	4	5
3417 (vs)		$\nu(H_2O)$	3190 (sh)	3368 (vs)
3317 (vs)				
3141 (vs)				
1689 (vs)	1716 (vs)	$\nu_{as}(OCO)$	2960 (w)	2943 (vs)
1607 (vs)	1642	$\delta(H_2O)$		
1373 (m)	1354 (m)	$\nu_s(OCO)$	2852 (w)	2878 (s)
1318 (s)	1317 (s)	$\nu(CO)$	2738 (w)	
			2633 (w)	
809 (m)	791 (m)	$\delta_{as}(OCO)$	1699 (s)	
			1684 (s)	
759 (m)		$\rho(H_2O)$	1618 (vs)	1458 (c)
618 (m)			1460 (m)	1408 (s)
496 (w)	514 (m)	$\nu(MO)(C_2O_4)$	1362 (m)	1332 (w)
410 (w)	496 (m)	$\delta_s(OCO)$	1316 (s)	1255 (w)
	410 (s)	$\nu(MO)$	1228 (w)	1204 (w)
			1069 (s)	1087 (vs)
			1029 (m)	1043 (vs)
			909 (w)	
			891 (m)	883 (s)
			877 (m)	864 (s)
			808 (s)	
			697 (m)	615 (w)
			546(w)	520 (w)
			495(w)	
			417(w)	

Note: $\rho(H_2O)$ are rocking and wagging vibrations of water molecules [6]; vs is very strong, s is strong, m is medium, w is weak, sh is shoulder.

the change in the band intensity, attest to a pronounced interaction of ethylene glycol molecules with the manganese cations. The IR spectrum of anhydrous manganese oxalate obtained by heating of the trihydrate in ethylene glycol, the asymmetric stretching vibrations $\nu_{as}(OCO)$ are manifested as a very broad intense band at 1642 cm^{-1}, the symmetric vibrations $\nu_s(OCO)$ are responsible for two narrow lines at 1354 and 1317 cm^{-1}. In the regions of $\delta(OCO)$ bending mode and Mn–O stretching mode, the spectrum has a very narrow intense band at 792 cm^{-1} and a narrow medium-intensity band at 514 cm^{-1}, respectively.

Thus, moderate heating (to about 50–100°C) of manganese oxalate di- or trihydrate with ethylene glycol results in the displacement of water molecules from the oxalate structure and their replacement by one ethylene glycol molecule, the shape of crystals of the initial compound being retained. When needle $MnC_2O_4 \cdot 3H_2O$ is used as the precursor, the solvates $MnC_2O_4(HOCH_2CH_2OH)$ are formed as extended micro- and nano-sized crystals. As the temperature of the reaction mixture increases, the solvate is destroyed to give MnC_2O_4. It was shown that intercalation of $MnC_2O_4 \cdot 3H_2O$ with magnesium markedly increases the stability of the initial compound and the solvates. In all cases, thermolysis of the solvates in air and in an inert environment gave simple or complex oxides with retention of the shape of particles of the initial compounds.

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