Phase Transformations in Mechanically Activated Gadolinium Manganites

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Abstract - Nanostructured powders of $GdMnO_{3+\delta}$ were obtained by mechanical processing in a high-energy ball mill. Structural phase transitions in gadolinium manganite were studied using thermogravimetry, thermal analysis, mass spectrometry and high-temperature X-ray diffraction. Appreciable increase in the intensity of the interaction between mechanically activated samples and air gas phase and the activation of structural phase transformations were established. Mechanically activated $GdMnO_{3+\delta}$ samples were found to adsorb CO_2 to a large extent at temperatures 400-450°C. Effect of mechanical activation was also manifested in a slight shift of the Jahn-Teller structural phase transition temperature to lower values.

Keywords - *Nanostructured materials, Rare-Earth Manganites, Mechanochemical processing, Phase Transformations, X-ray Diffraction, Thermal analysis*

I. INTRODUCTION

Multiferroic ternary oxides, $RMnO_3$ with R=Sc, Y, La–Lu, is a class of oxide materials of great scientific and technological interest. Rare earth manganites exhibit a rich variety of crystallographic, electronic and magnetic phases [1]. They are promising materials in terms of their use in spintronics, optoelectronics, magnetic storage devices, magnetic field sensors, high temperature solid oxide fuel cells and other areas due to their unique properties. Among rare earth manganites, the doped $LaMnO_3$ compounds are the most extensively investigated. $GdMnO_3$ is one of the multiferroic rare–earth manganites where magnetic and ferroelectric orders coexist. It shows fascinating physical properties as functions of temperature, magnetic field and external pressure. Studies of the structural, optical, electrical and, mainly, the magnetic properties of $GdMnO_3$ are presented in literature [e.g. 2-6]. The diversity of magnetic order forms in gadolinium manganite is noticed. But there is a lot of contradictory information regarding magnetoelectric effects in this oxide. Ceramic polycrystalline samples [7-9] and single crystals of $GdMnO_3$ [10, 11] are mainly the object of study. Among the nanostructured $GdMnO_3$ samples, nanoparticles produced by sol-gel method [12] and thin films [13] are considered. Stabilization of ferromagnetic ordering has been found in nanostructured $GdMnO_3$ samples. The emerging of a ferromagnetic response in the thin films [13] has been explained as a consequence of the structural strain induced by matching both film and substrate during the growth process, which alters the balance between competitive antiferromagnetic and ferromagnetic interactions. Any research on mechanically activated $GdMnO_3$ oxides is absent in the literature to date. Meanwhile, it has been shown [14] that mechanically activated powders of $SmMnO_3$ have significantly different magnetic characteristics (transition temperatures, coercive forces, remanent magnetizations) in comparison with initial microcrystalline samarium manganite. It was established that the magnetic properties of the samples were strongly dependent on the mode of mechanical activation and their structural features.

One more important aspect of research on mechanically activated $GdMnO_3$ oxides is catalysis. Rare-earth manganites have a great potential for environmental application as catalysts [15]. The following factors are considered to determine the catalytic activity: morphology (including microstructure, crystalline phase and specific surface area), redox properties, surface chemical species. Mechanical activation is one of the most effective tools to increase catalytic activity of materials (including oxides) [16]. In this regard, the study of structural peculiarities of mechanically activated $GdMnO_3$ oxides, their stability, and features of the interaction with air gas phase is topical.

In the present work, the structural properties and specificity of phase transformations in mechanically activated $GdMnO_{3+\delta}$ manganites have been investigated. These transformations include both redox processes and structural phase transitions which are not accompanied by a significant change of the oxidation degree. The presence of such transformations always affects the functional properties of the material and limits its application.

II. EXPERIMENT

The synthesis of the oxide $GdMnO_{3+\delta}$ was carried out by ceramic technology in air from oxides Gd_2O_3 and Mn_2O_3 ("special pure" grade) at 1400°C for 90 hours followed by cooling in the furnace.

X-ray diffraction (XRD) analysis of the samples was performed on SHIMADZU diffractometer XRD-7000 using CuK_α-radiation with a monochromator. Shooting was realized in regime of stepwise scanning in the angle range of 10-72° with a step size $\Delta(2\theta)=0.02°$ and step scan of 2 s.

Mechanically activated samples were obtained by intensive mechanical processing of initially synthesized $GdMnO_{3+\delta}$ using a high-energy planetary mill AGO-2 [17] with water cooled drums (V=150 ml) at its most intense mode with a centrifugal factor of 60g. The balls load was 203 g, the material loading - 5 g. The dry milling of powders was performed after preliminary mill lining. The duration of continuous grinding ranged from 30 seconds to 5 minutes.

High temperature X-ray studies were carried out on a sample heating attachment HA-1001 (Shimadzu) in the following mode: heating in the temperature range 500-1300°C at the rate of 10°C/min., holding for 10 minutes after every 50-100°C, surveying in the angle range of 20-60° on 2Θ scale with a step of 0.03° and 4 seconds exposure.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were carried out in an air atmosphere using a synchronous thermoanalyserSTA 449F3 Jupiter (NETZSCH) and a thermal analyzerNetzsct STA 449C Jupiter (Germany), combined with a mass spectrometer Netzsct QMS 403C Aëolos (Germany) for evolved gas analysis. The rates of heating and cooling of samples were 10 K/min.

III. RESULTS AND DISCUSSION

The synthesized samples of $GdMnO_3$ had perovskite-type orthorhombic structure (Pbnm space group) with the following unit cell parameters at room temperature: a=0.5312(3), b=0.5818(4), c=0.7431(4) nm.

Table 1 presents the structural characteristics of the samples $GdMnO_3$, subjected to mechanical activation in high-energy ball mill AGO-2. One can see the lattice parameters vary insignificantly after mechanical activation. The relationship $\left(\frac{c}{a\sqrt{2}}-1\right)$ which characterizes the Jahn-Teller distortion does not change sign. The suppression of the Jahn-Teller effect in the gadolinium manganite after mechanical activation has not been found.

The change in the lattice parameters (see table 1) does not exclude the formation of superstoichiometric oxygen during mechanical activation. The generic formula for the studied manganite is $GdMnO_{3\pm\delta}$. Decrease in the unit cell volume with increasing duration of mechanical activation can be due to the difference in the ionic radii: Mn^{3+} has an ionic radius of 0.72Å and Mn^{4+} - 0.68Å, with each having a coordination number of 6 (22). There are solitary published works which report experimentally determined values of oxygen nonstoichiometry in $GdMnO_{3\pm\delta}$ [18-20]. Most authors write stoichiometric composition $GdMnO_3$, not to mention the real oxygen content. And there are discrepancies in the cell parameters measured in studies conducted on samples prepared by identical methods. The values of the unit cell volume of gadolinium manganite obtained by solid-phase synthesis as in this work range from 0.2296 to 0.2313 nm. Unfortunately, the oxygen non-stoichiometry content, δ, in mechanically activated samples has not been determined experimentally in this work. According to [20], $GdMnO_3$ has a nonstoihiometric composition region δ from -0.03 to +0.05 within the range of $\log P_{O_2}$ from -9.47 to 0, correspondingly. Since our samples were prepared in the air, they probably contain excess oxygen in an amount not more than 0.05.

The degree of fineness changing with increasing milling duration is shown in Fig. 1. An abrupt decrease (about 20 times) in the mean size of coherent scattering regions (*D*) occurs in the first 30 seconds of grinding. Further mechanical treatment results in a gradual reduction of the grain size to 20 nm. Microstrain increases monotonically with increasing milling duration, reaching the value of 0.77% at 5 minutes of mechanical activation.

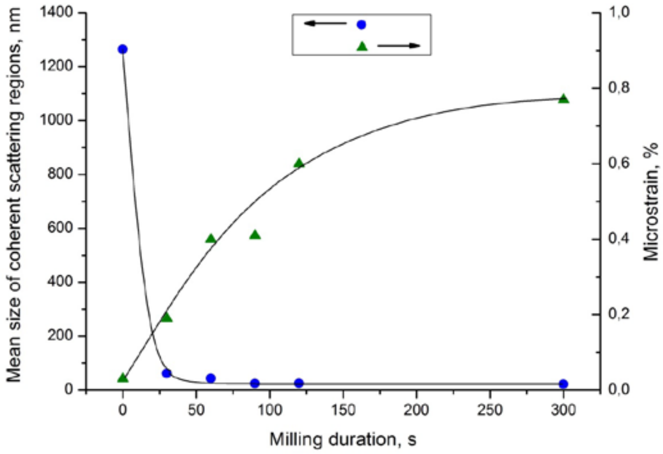

Fig. 1. Change of the mean size of X-ray coherent scattering regions and the mean microstrain value in $GdMnO_3$ under mechanical activation in an AGO-2 mill.

TABLE I. Structural characteristics of $GdMnO_{3+\delta}$ samples milled in AGO-2

Milling duration, s	**Crystal lattice parameters**			**Unit-cell volume V, nm^3**	***D*, nm**	**Microstrain ε, %**
	***a*, nm**	***b*, nm**	**$\frac{c}{\sqrt{2}}$, nm**			
0	0.5312(3)	0.5818(4)	0.5255(4)	0.2296	1265.0	0.03
30	0.5312(4)	0.5822(5)	0.5260(5)	0.2298	61.5	0.19
60	0.5314(4)	0.5813(4)	0.5257(4)	0.2297	44.0	0.43
90	0.5312(4)	0.5806(4)	0.5261(5)	0.2295	25.0	0.37
120	0.5322(4)	0.5786(4)	0.5260(4)	0.2291	25.5	0.60
300	0.5322(4)	0.5767(4)	0.5270(4)	0.2287	22.5	0.77

In order to determine the influence of mechanical activation on the structural phase transitions due to the cooperative Jahn-Teller effect, high temperature diffraction studies were carried out on the original microcrystalline $GdMnO_{3+\delta}$ sample and samples treated in AGO-2 mill.

At room temperature, all samples have the unit cell parameters corresponding to the orbitally ordered (O') phase satisfying the relation: $\frac{c}{\sqrt{2}} < a < b$ (see Table 1). The crystal lattice parameters change with increasing temperature. In the case of the original $GdMnO_3$ sample, parameter *b* decreases gradually starting from the temperature of 700°C, whereas the parameters *a* and *c* continue to grow due to thermal expansion. $GdMnO_3$ undergoes a structural phase transition from orthorhombic O'-type to orthorhombic O-type upon increasing the temperature up to 1000°C. The orbitally disorderd (O) phase also has an orthorhombic structure (s.g. Pbnm) but with a ratio of lattice parameters: $a < \frac{c}{\sqrt{2}} < b$. In mechanically activated samples, the Jahn-Teller transition temperature is shifted to lower values (900-940°C). The vertical dashed lines in Fig. 2 indicate the temperatures corresponding to the completion of the structural transition $O' \rightarrow O$ (T_1 - for the original, T_2 - for mechanically activated samples). The reduced transition temperature in mechanically activated samples indicates the presence of some amount of Mn^{4+} in their structure.

The processes which take place in the original and mechanically activated $GdMnO_{3+\delta}$ samples during heating were investigated by DSC–TGA method using a synchronous thermoanalyser STA 449F3 Jupiter (NETZSCH). The original micropowder oxide $GdMnO_{3+\delta}$ in this respect exhibits thermal stability; there are no visible changes on the mass curve related to this sample (curve 1 in Fig.3). Slight endothermic effect on the DSC-curve in the temperature range 950-1000°C corresponds to cooperative Jahn-Teller phase transition (see Fig. 2 and curve № 1 in Fig. 4).

Mechanically activated samples exhibit a decrease in the mass at the initial stage of heating (up to 300°C), that can be explained by physical desorption of gases from the sample surface. The value of the sample mass loss at this stage shows the amount of adsorbed gases during mechanical activation. According to X-ray diffraction data, the powder particle size decreases with increasing milling duration, thus the total surface area and, correspondingly, the amount of gas adsorbed by the surface increase. However, the sample №6 milled for 5 minutes falls out of this regularity (see the curve №6 in Fig. 3). To explain this fact, one should take into account the phenomenon of aggregation of the powder nanoparticles and difference in the properties of the inner and outer surfaces of the aggregates.

When the temperature increases above 350°C, the mass of mechanoactivated samples increases and reaches a maximum at 600°C.

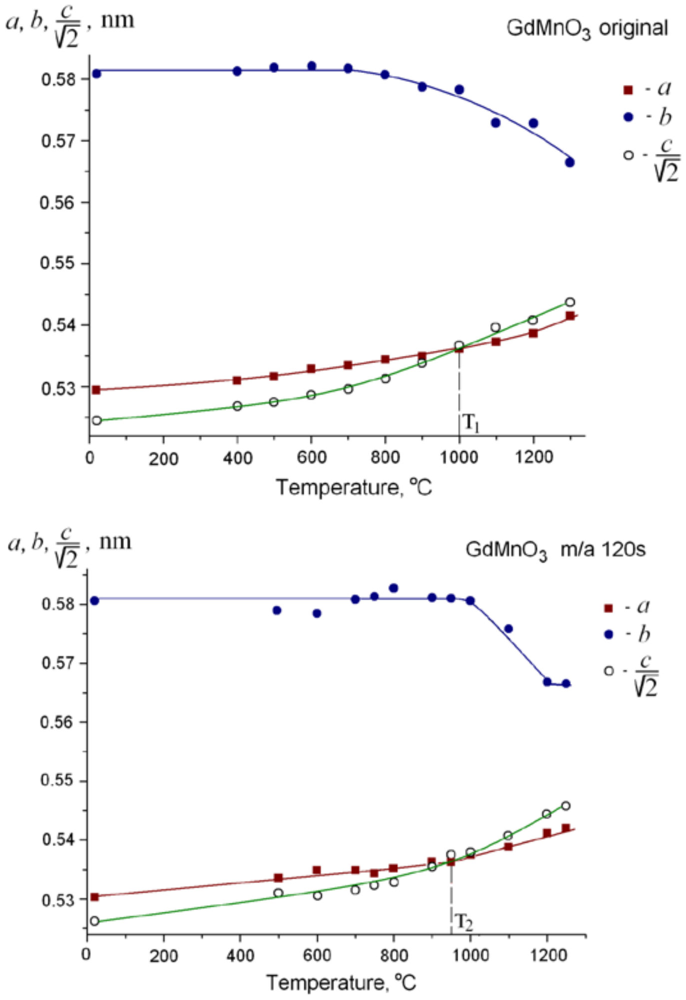

Fig. 2. Temperature dependence of the crystal lattice parameters of $GdMnO_{3+\delta}$. Top: the original sample; bottom: sample mechanically activated for 120s.

Further increase in the temperature of mechanically activated $GdMnO_{3+\delta}$ samples leads to a reaction accompanied by a decrease in mass. In the temperature range 700-750°C, this process attains the highest rate and is accompanied by a clear exothermic peak in the DSC-curves (Fig. 4). The duration of mechanical activation does not affect the temperature of this transformation, but affects its degree. One can assume that the absorption of oxygen from the gas phase and oxidation of $GdMnO_{3+\delta}$ within the region of homogeneity proceed in the temperature interval 300-600°C, and then the reverse reduction process occurs at temperatures of 600-720°C. But the existence of an exothermic peak at 700-750°C contradicts this view.

Above 900°C, the next stage of the mass gain of mechanically activated samples is observed on TG curves (Fig. 3). According to X-ray diffraction data, the two processes - enlargement of particle size and the formation of the second phase - gadolinium oxide Gd_2O_3 simultaneously run in the temperature range 900-

1140°C. At 1140-1160°C, a sharp decrease in weight of samples is observed on TG curves, it is accompanied by endothermic effect in DSC curves (Fig. 4). Endpoint weight loss in samples correlates with the mechanical activation duration: the longer mechanical processing, the greater the weight loss in the sample.

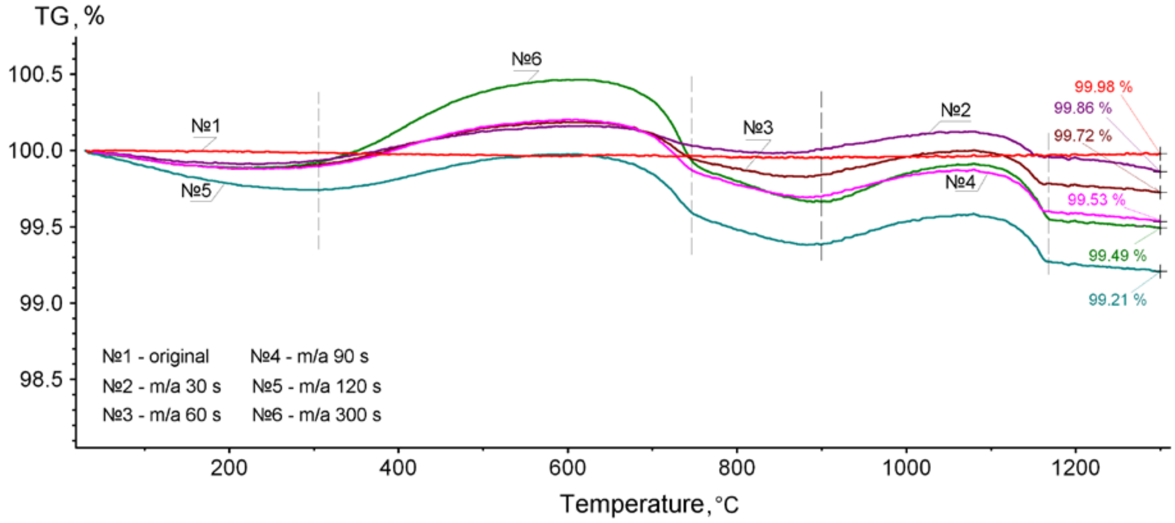

Fig. 3. Thermogravimetric data on $GdMnO_{3+\delta}$ samples at the heating rate of 10°C/min: 1 –original, 2-6 – samples mechanically activated for 30, 60, 90, 120 и 300 seconds, respectively.

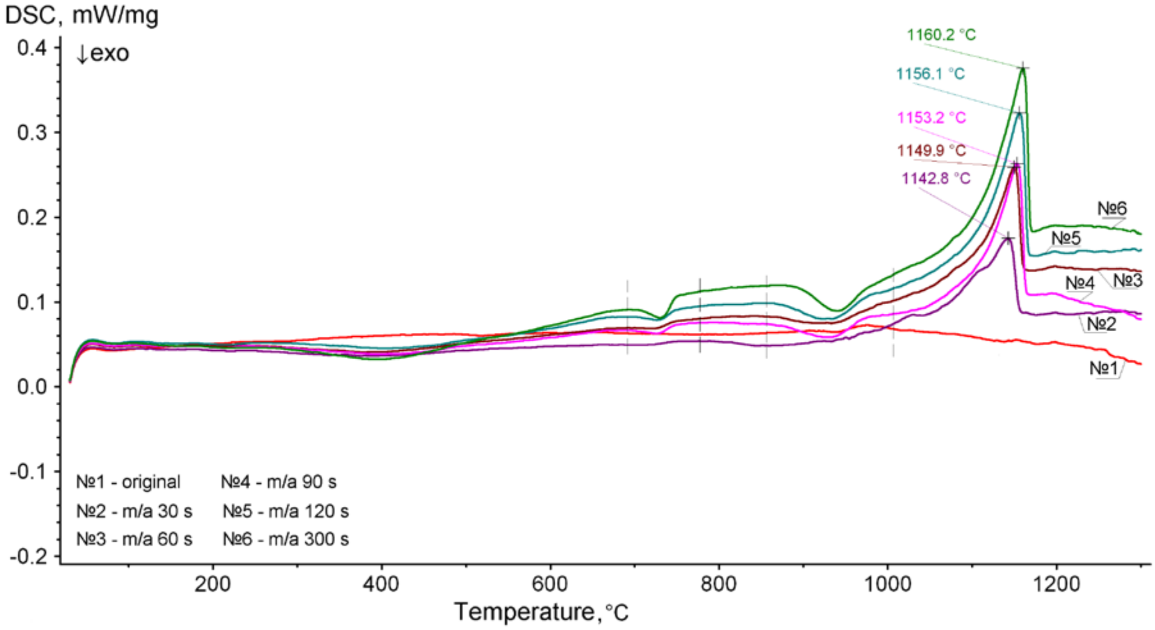

Fig. 4. Calorimetry data on the original and mechanically activated $GdMnO_{3+\delta}$ samples (sample designations as in Fig. 3).

To clarify the nature of transformations occurring during heating of mechanically activated $GdMnO_{3+\delta}$ samples, an additional experiment was carried out. The sample №5 (milled for 120 s) was annealed in air at 450°C for 3.5 hours. Then, TG – DSC – mass spectrometric study on this sample was conducted using a thermal analyser Netzsct STA 449C Jupiter with a mass spectrometer Netzsct QMS 403C Aëolosin the following mode: heating at 50°C/min from room temperature to 720°C, holding at this temperature for 30 minutes and heating to 1180°C at the rate of 50°C/min. Figure 5 presents the results of this study.

The figure shows that the mass spectrum has no peaks corresponding to oxygen; that testifies against reduction of the manganite with super-stoichiometric oxygen. Four peaks of ionic current corresponding to the carbon dioxide at 300, 720, 900 and 1180°C and two significant peaks associated with the evolution of water at 380 and 720°C are observed. A small H_2O peak at around 100°C is due to removal of unbound water adsorbed by the surface during cooling of the sample from 450°C and storage in air.

Obviously, the adsorption of carbon dioxide from the gas phase proceeds during isothermal holding at 450°C. Intensive adsorption of CO_2 by mechanically activated samples was detected by us earlier on the system $YBa_2Cu_3O_{6+\delta}$ [21]. Carbon dioxide is accumulated on the surface of mechanically activated samples $GdMnO_3$ forming a film. In the surface layer, the formation of oxalates, crystal hydrates and carbonates is possible. These products must decompose upon subsequent heating. Judging by the correlated evolutions of CO_2 and H_2O in two temperature intervals about 300 and 720°C (Fig. 5), some hydrated forms of gadolinium and/or manganese oxide are produced.

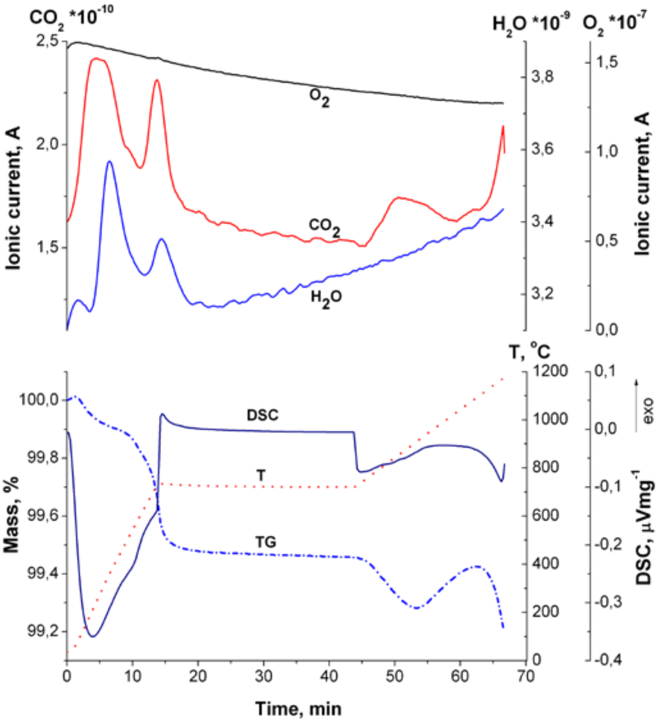

Fig. 5. Thermal analysis results and mass spectrometry data for $GdMnO_3$ sample milled for 120s.

Oxalates, carbonates of rare earth elements and their decomposition were the subjects of many studies [22, 23]. A variety of forms of REE oxalate and carbonate (including hydrated forms) was found: $Gd_2(C_2O_4)_3 \cdot 10H_2O$,$Gd_2(C_2O_4)_3$[24], $Gd_2(C_2O_4)_3 \cdot nH_2O$ (n=2, 3) [25], $Gd(OH)CO_3$ [26], $Gd(HCO_3)_3$ [27], $Gd_2(CO_3)_3$[28, 29], $Ln_2O_2CO_3$ [30, 31], $Ln_2(CO_3)_3 \cdot 8H_2O$, $Ln_2O_3 \cdot 2CO_2 \cdot 2H_2O$, $Ln_2O_3 \cdot 2.5CO_2 \cdot 3.5H_2O$ [32]. The decomposition of oxalates and carbonates of rare earth elements was noticed to be multistage. At the first stage, dehydration occurs (which in turn can progress in several steps); at the next stages, the decomposition of anhydrous oxalates and carbonates proceed. One of many possible sequences of reactions in lanthanide carbonates is the following [33]:

$$Ln_2(CO_3)_3 \cdot xH_2O \rightarrow Ln_2(CO_3)_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3 \cdot yCO_2 \rightarrow Ln_2O_3$$

Some authors [e.g. 22] suppose that dioxide-mono-carbonate $Ln_2O_2CO_3$ is the most stable intermediate product in decomposition of oxalates and various forms of carbonates.

As seen from Fig. 5, the dehydration of gadolinium oxide (carbonate or oxalate) proceeds in two stages; that may be due to differences in activation energy for removal of water molecules linked by hydrogen bonds and coordination bonds [23]. However, the correlated mass spectrometric peaks of CO_2 and H_2O leads to the conclusion that almost simultaneous evolution of carbon dioxide together with water is associated with decomposition of different types of hydrated carbonates and/or oxalates. The peaks of H_2O and CO_2 in the temperature range about 300°C are possibly due to decomposition of manganese hydrogen carbonate and/or oxalate. According to [34], the temperature for such reactions under equilibrium conditions is 180-200°C. In the conditions of our experiment (sufficiently rapid heating), the decomposition temperature may be shifted. One can see the noted CO_2 peak is sufficiently broad and complex. That means the degradation of several crystalline hydrates proceeds in the temperature range of 100-500°C.

The second correlated peak at 720°C is probably associated with decomposition of gadolinium carbonates (e.g. $Gd_2(CO_3)_3 \cdot nH_2O$). Authors [22, 23] indicate the temperature of such process equal to 710°C which is close to our experimental data.

A broad peak ion current corresponding to CO_2 in temperatures about of 900°C is probably a continuation of the previous peak interrupted by isothermal holding at 720°C. This peak is broad and, therefore, may be associated with several processes. Probably, the decomposition of gadolinium carbonate continues under the scheme:

$$Gd_2O_2CO_3 \rightarrow Gd_2O_3 \cdot yCO_2 \rightarrow Gd_2O_3.$$

We con not also exclude from consideration the degradation of pre-dehydrated oxalate:

$$Gd_2(C_2O_4)_3 \rightarrow Gd_2O_3 + CO + 3CO_2.$$

Both of these reactions lead to the formation of oxide Gd_2O_3 which was detected by us using X-ray diffraction.

The final stage of transformations during heating is characterized by loss of the sample weight accompanied by the endothermic effect at 1150-1180°C (see Fig. 4 and 5) and the ionic current peak in the mass spectrum corresponding to CO_2. The decomposition of the carbonate $Gd_2(CO_3)_3$ possibly occurs at this stage.

IV. CONCLUSION

Thus, the effect of mechanical activation was studied on the oxide $GdMnO_{3+\delta}$ by thermogravimetry, thermal analysis, mass spectrometry and high-temperature X-ray diffraction methods. Thermal stability of microcrystalline gadolinium manganite in air was shown. Mechanical activation resulted in nanostructural stressed state of the material and led to significant increase in the intensity of the interaction of gadolinium manganite with air gas phase and activation of structural phase transformations. Mechanically activated samples of $GdMnO_{3+\delta}$ were found to largely adsorb carbon dioxide at temperatures 400-450°C.

Insignificant shift of the temperature of the Jahn-Teller structural phase transition from orbital ordering to orbital disordering was revealed in nanostructured mechanically activated $GdMnO_{3+\delta}$ samples to lower values by comparison with the origin micropowder sample.

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