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THERMAL PROPERTIES OF $La_xBa_{1-x}MnO_3$ COMPOUNDS AT HIGH TEMPERATURES

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Abstract. The thermal properties of the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ were studied in the temperature range 25 °C < T < 950 °C. The studies were carried out using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Although several thermal effects were observed in the study objects, in each of them these transitions occurred through the same mechanism. The effect that occurs at DSC T ~ 100 °C was explained by the splitting of hydroxide groups formed by water crystals present in the samples. At higher temperatures, the main effects were explained by the oxidation of metal atoms free on the surface of the samples. The thermal effects observed in the DSC spectrum were also confirmed in the TGA spectrum.

Keywords: *Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Perovskite, Manganite.*

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1. Introduction

Perovskite (ABO_3) compounds are considered to be the compounds with the most interesting physical properties among the complex oxides. These compounds exhibit semiconductor, ferroelectric, and ferromagnetic properties. It is known that these physical properties vary depending on temperature. Therefore, studying perovskites under the influence of temperature is very important for studying the physical processes occurring in them. On the other hand, perovskite compounds are used as model objects in the study of phase transitions. Therefore, the study of these structures creates new opportunities for obtaining, studying and applying new structures (Jabarov & Aliyev, 2023; Khan *et al.*, 2020; Isohama *et al.*, 2011; Hashimov, 2021).

Among perovskite compounds, manganites occupy a special place. Because these materials exhibit magnetic properties. In the course of research, it was found that the magnetic properties of these compounds are observed mainly at low temperatures.

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Antiferromagnetic properties were observed in $BiMnO_3$ and $BaMnO_3$ compounds at low temperatures. However, there are manganites that exhibit magnetic properties even at room temperature. When studying the $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ compound using neutron diffraction, it was found that this compound has antiferromagnetic properties at room temperature. The value of the specific magnetic moment of Mn(Fe) atoms is $\mu = 0.9\ \mu_B$ (Hanif *et al.*, 2017; Fang *et al.*, 2013; Dang *et al.*, 2018).

It is known that the magnetic properties of materials depend on temperature. As the temperature increases, the magnetic properties weaken. Therefore, it is necessary to study the thermal properties of magnetic materials. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) methods are considered unique methods for studying the thermal properties of solids. Using these methods, it is possible to study the processes of evaporation, melting, decomposition, phase transitions and melting in highly researched materials. By determining thermodynamic functions in functional materials, it is possible to study the system as a whole. Recently, similar studies have been carried out in semiconductor and magnetic materials (Agayev *et al.*, 2020; Mirzayev, 2020; Azimova *et al.*, 2020). Thermal processes in perovskite manganates have not been sufficiently studied. The $La_{1-x}Ba_xMnO_3$ system has been widely studied to study cation-cation interactions in manganite materials. It has been established that the complex oxides $La_{0.97}Ba_{0.03}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.5}Ba_{0.5}MnO_3$ have a cubic crystal structure with space group Pm-3m. As a result of SEM studies, it was established that the crystallite size in $La_xBa_{1-x}MnO_3$ solid solutions is in the range d = 2-10 μm (Nabiyeva *et al.*, 2023). Although the structural properties of these compounds have been studied, their thermal properties have not been well studied. In this work, the thermal properties of the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ were studied by DSC and TGA in the temperature range 25 °C < T < 950 °C.

2. Experiments

2.1. Synthesis

$La_{1-x}Ba_xMnO_3$ polycrystals were synthesized using a standard procedure consisting of several stages. The oxides La_2O_3, Mn_2O_3 and $BaCO_3$ were used as starting materials. First, H_2O and CO_2 molecules were removed from La_2O_3 oxide by heating under normal conditions at 100 °C for 2 hours. The oxides were then mixed and pressed in appropriate quantities. The prepared material was heated at 1000 °C for 5 hours and barium carbonate was decomposed. The sample was then ground again and turned into powder. At the next stage, the sample was placed on a platinum substrate and heated at a temperature of 1550 °C for 10 hours. At the last stage, the sample was cooled at a rate of 80 °C/h.

2.2. Thermal analysis

The thermal properties of $La_{1-x}Ba_xMnO_3$ polycrystals were studied by DSC and TGA in the temperature range 25 °C < T < 950 °C. The studies were carried out on a DSC3 STARe device manufactured by Mettler Toledo, temperature control was carried out using Multistar sensors. The measurements were carried out in an argon (Ar) atmosphere at a heating rate of 20 ml/min, 5 °/min. The cooling process was carried out using the cooling system of the Sofrigerated Liquid Nitrogen Un 1977 analyzer.

3. Discussion of results

To study the thermal properties of $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ perovskites, DSC and TGA studies were carried out at high temperatures. In Fig. 1 shows spectra characterizing the change in mass (TGA) and heat flow (DSC) of the $La_{0.5}Ba_{0.5}MnO_3$ compound in the temperature range $25°C \leq T \leq 950°C$.

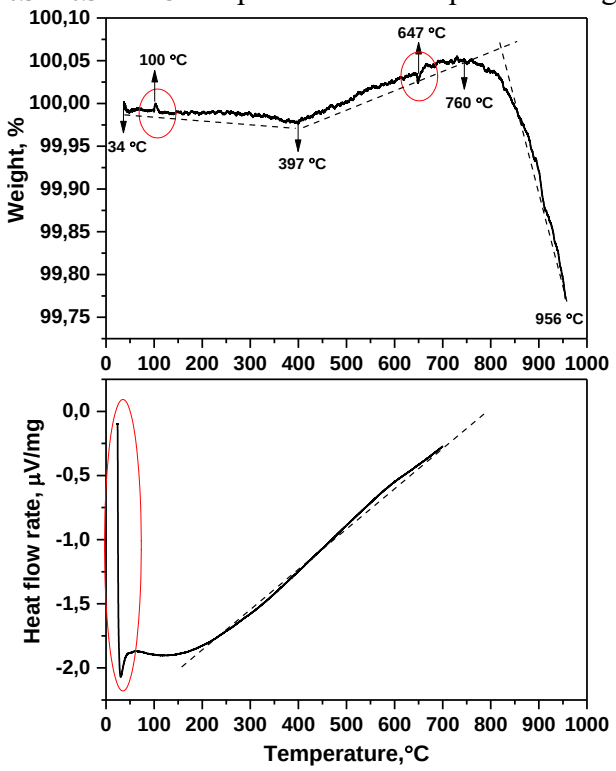

Fig. 1. TGA and DSC spectra of the $La_{0.5}Ba_{0.5}MnO_3$ compound at high temperatures

As can be seen from Fig. 1, a deep endo-effect was observed in the mass spectrum in the temperature range 25 °C < T < 110 °C. The central peak, corresponding to the temperature T = 100 °C, is due to the endo-effect the dissociation of water molecules adsorbed by the surfactant. The splitting of water molecules during the endo-effect is a sign of the occurrence of a single mechanism of a chemical reaction. In this case, the crystalline bonds of the OH groups are weak or are included in chemical bonds in very small quantities. The mass spectrum represents a stable region up to temperature T = 397 °C, and the interval 397 °C < T < 760 °C is a region of mass increase or oxidation. During this oxidation reaction, free La, Ba and Mn atoms and oxygen atoms form new covalent chemical bonds, which leads to an increase of 0.05% in the total mass. The temperature range 760 °C < T < 956 °C is called the breakthrough decomposition region. This region ends with a change in the chemical composition of the compound and the formation of a new phase. All changes in the mass spectrum are parallel to the kinetics of the heat flow spectrum. It has been established that the value of the enthalpy of decomposition of adsorbed water in the temperature range 25 °C < T < 100 °C is 0.17 J/g, 2.18 J/g for the oxidation region 97 °C < T < 760 °C and the region 760 °C ≤ T ≤ 956 °C of discontinuous decomposition and is 6.57 J/g. The heat flux value was set at 2.0 mW/mg for the entire process.

In order to study the effect of La → Ba substitutions on the thermal properties of the $LaMnO_3$ compound, the thermal properties of the $La_{0.73}Ba_{0.27}MnO_3$ compound were also studied. In Fig. 2 shows spectra characterizing the change in mass (TGA) and heat flow (DSC) of the $La_{0.73}Ba_{0.27}MnO_3$ compound in the temperature range 25 °C ≤ T ≤ 950 °C.

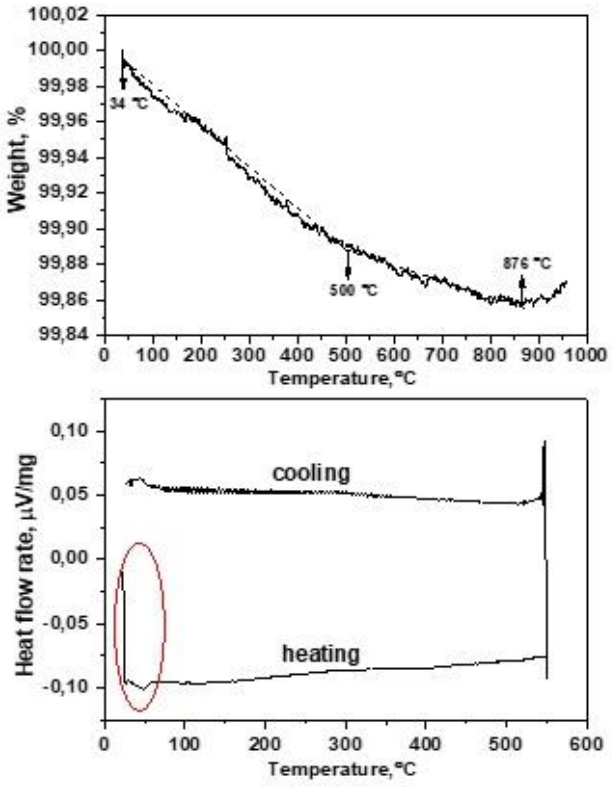

Fig. 2. TGA and DSC spectra of the $La_{0.73}Ba_{0.27}MnO_3$ compound at high temperatures

In contrast to the $La_{0.5}Ba_{0.5}MnO_3$ compound, the endo-effect was observed in the mass spectrum in the range 25 °C ≤ T ≤ 110 °C. This is due to the fact that the number of absorbed water molecules and weak chemical bonds on the active surface of the sample is very small. In the mass spectrum, a region of a sharp decrease to a temperature T < 500 °C was observed, and a stable mass region of 500 °C < T < 876 °C was observed. It has been established that a change in the ratio of the concentrations of La and Ba atoms in the composition of the compound causes a change in the spectrum of mass and heat flow. It is clear from the spectra that no oxidation reaction occurs during the process and no crystallization is observed during the cooling process. In the $La_{0.73}Ba_{0.27}MnO_3$ compound, as well as in the $La_{0.5}Ba_{0.5}MnO_3$ compound, no phase transition was observed.

To further study the thermal properties of the $La_{1-x}Ba_xMnO_3$ system, the thermal properties of the $La_{0.97}Ba_{0.03}MnO_3$ compound were also studied. In Fig. 3 shows spectra characterizing the change in mass (TG) and heat flow (DSF) of the $La_{0.97}Ba_{0.03}MnO_3$ compound in the temperature range 25 °C ≤ T ≤ 950 °C.

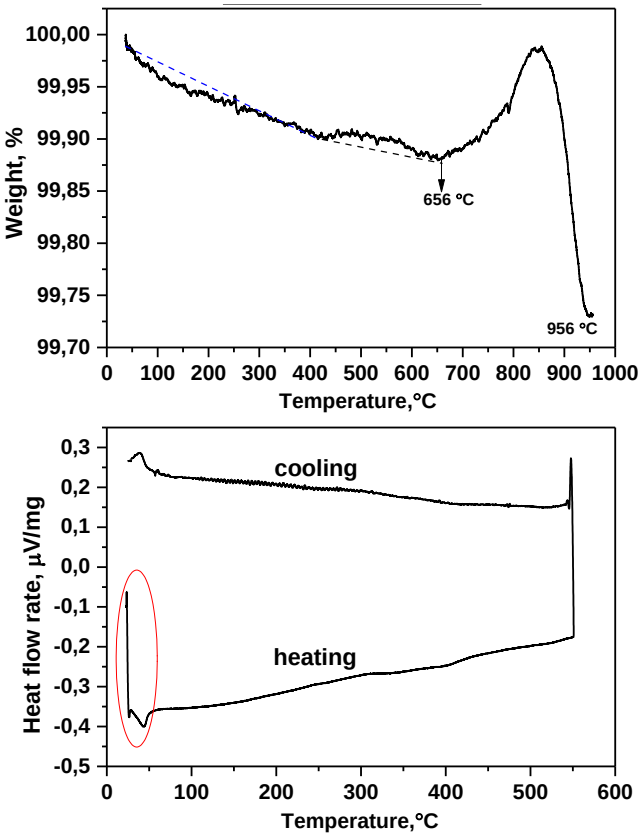

Fig. 3. TGA and DSC spectra of the $La_{0.97}Ba_{0.03}MnO_3$ compound at high temperatures

In the temperature range 25 °C < T < 110 °C, the deep endo-effect observed in the thermal spectrum of the $La_{0.97}Ba_{0.03}MnO_3$ compound was also observed in the thermal spectrum of the $La_{0.5}Ba_{0.5}MnO_3$ compound. In the TGA spectrum, starting from temperature T = 656 °C and ending at T = 850 °C, the amount of oxygen captured by the compound during the oxidation reaction is greater than that of the $La_{0.5}Ba_{0.5}MnO_3$ compound.

It has been established that among the compounds obtained with different concentrations of La and Ba atoms, the compound $La_{0.73}Ba_{0.27}MnO_3$ can be recognized as a temperature-dependent mass- or oxidation-resistant material. Also, the magnitude of the heat flux depends linearly on the concentration of La and Ba. The thermally stable part in $La_{0.97}Ba_{0.03}MnO_3$ compound is 397 °C, 500 °C and 656 °C for $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ compounds respectively. In the temperature range 25 °C < T < 656 °C in the $La_{0.73}Ba_{0.27}MnO_3$ sample, no decomposition of the $La_{0.5}Ba_{0.5}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$ compounds by a binary mechanism was observed. In all samples, it is possible to determine the change in adsorbed water vapor in a differentiated form of the mass spectrum. The oxidation of oxide compounds at high temperatures is a very weak heterophysical process, and experimental results once again confirm this (Li & Qiu, 2007; Popescu, 1996; Mirzayev *et al.*, 2020). In the kinetics of oxidation reactions, the kinetics of the process was determined by the value of the k-diffusion rate. The kinetics of oxidation in the temperature range 397 °C ≤ T ≤ 850°C was calculated using the Jander equation (Mirzayev, 2021; Mirzayev *et al.*, 2019).

$$\left[1-\left(1-\alpha\right)^{\frac{1}{3}}\right]^2 = kt$$

where α is the degree of oxidation, t is the duration of the oxidation reaction. The oxide layer formed on the surface depends on the concentration and molar mass of La and Ba in the sample, as well as on the chemical transformation and molar mass of the resulting oxide compounds, as well as on the specific surface area of the sample. particle and particle size. The depth of oxide formation on the surface can be calculated if we take into account the chemical transitions that occur in the active centers in the oxidation reaction. The kinetics of the oxidation process forms a heterogeneous oxide layer at a certain depth on the surface due to reaction with the oxygen atoms of the active centers. The smallest size of the oxide layer turned out to be 15 nm in the $La_{0.73}Ba_{0.27}MnO_3$ compound. The thickness of the oxide layer for the $La_{0.97}Ba_{0.03}MnO_3$ compound is 32 nm, and the thickness of the heterooxide layer formed on the surface of the $La_{0.97}Ba_{0.03}MnO_3$ compound is 22 nm.

4. Conclusions

The thermal properties of the $La_{1-x}Ba_xMnO_3$ system at high temperatures were studied. It has been established that at high temperatures no phase transition occurs in these compounds. However, the $La_{0.73}Ba_{0.27}MnO_3$ combination has more stable structural properties. Based on the change in mass depending on temperature, the thickness of the oxide layer formed on the surface of the samples was calculated. It has been established that the higher the thermal stability of the samples, the smaller the thickness of the oxide layer formed on the surface. For each of the compounds $La_{0.5}Ba_{0.5}MnO_3$, $La_{0.73}Ba_{0.27}MnO_3$ and $La_{0.97}Ba_{0.03}MnO_3$, thermal regions in the temperature range 25 °C < T < 950 °C were determined and the physicochemical properties of these regions were determined.

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