INTRODUCTION

The literature data presents that cuprates, manganites, zincates of the rare-earth elements substituted with oxides of the alkali and alkaline-earth metals have a certain scientific and practical importance for the inorganic materials science because of their promising physico-chemical properties and compounds based on manganese alloys are widely used in metallurgy [1-7].

WAYS OF STUDY

In connection with the above-stated this paper demonstrates the results of calculation of the standard thermodynamic properties of our first synthesized nanostructured quadruple copper-zinc manganites of lanthanum, alkali and alkaline-earth metals of the compositions of LaMeI2CuZnMnO6 and LaMeIIICuZnMnO6 (MeI – Li, Na, K; MeII – Mg, Ca, Sr, Ba). The high-temperature synthesis of the mentioned manganites was performed with the ceramic technology in the interval of 800-1200 °C similar to [5] from La2O3 (“especially pure”), ZnO, CuO, Mn2O3 and carbonates of the alkali and alkaline earth metals (qualification “analytically pure”). The low temperature annealing was performed to obtain the low temperature equilibrium phases at 400 °C. The obtained new phases were ground to the nanostructured particles on the Retsch MM301 vibration mill (Germany) and their sizes were determined on the electron microscope MJRA3, LMU Tescan. The X-ray analysis of the samples was performed on the DRON-2.0. It was determined that all test compounds were crystallized in the cubic syngony.

Referring to the above-mentioned, the objective of this paper is to calculate the standard thermodynamic characteristics of our obtained compounds, which are of interest for processes with their use and for their directed synthesis. The thermodynamic constants of the new compounds are the initial information collection for the fundamental reference books and data banks of the thermodynamic constants. It should be noted that our investigation of the physical and chemical properties of some similar cobalte (nickelite) -cuprate-manganites of lanthanum, the alkali and alkaline earth metals were published in papers of [8, 9].

In order to calculate the values of the standard enthalpies of formation of the test compounds, our developed method was used to calculate the standard enthalpy of formation of the double and triple manganites of the rare earth, alkali and alkaline earth metals of composition of LnMeI3MeII3Mn4O12 (MeI – alkali, MeII – alkaline earth, Ln – rare earth metals) [5, 10, 11].

The calculation method is as follows:

The similarity coefficient $K_f$ was calculated from the ratio of

$$K_f = \frac{\Delta H^o(298,15)\text{Ln(MnO}_3)_3}{\Delta_h H^o(298,15) \text{ Ln(MnO}_3)_3}$$

where $\Delta H^o(298,15)\text{Ln(MnO}_3)_3$ – a standard enthalpy of formation of permanganate of the rare-earth metals from the simple oxides, $\Delta_h H^o(298,15) \text{ Ln(MnO}_3)_3$ – a sum of the enthalpy of formation from simple oxides or the conditionally taken standard enthalpy of formation of permanganate of the rare earth metals from oxides, is equal to

$$\Delta_h H^o(298,15) \text{ Ln(MnO}_3)_3 = 0,5 \Delta H^o(298,15) \text{ Ln}_2O_3 + 1,5 \Delta H^o(298,15) \text{ Mn}_2O_7.$$
\[ K_3 = \frac{\Delta H^\circ(298,15) \text{MeIMnO}_4}{\Delta_{ok} H^\circ(298,15) \text{MeIMnO}_4}, \quad (3) \]

where \( \Delta_{ok} H^\circ(298,15) \text{MeIMnO}_4 \) – a standard enthalpy of formation of permanganate of alkali metal from oxides is equal to
\[
\Delta_{ok} H^\circ(298,15) \text{MeIMnO}_4 = \\
= \Delta H^\circ(298,15) \text{Me}_2 \text{O} + \\
+ 0,5 \Delta H^\circ(298,15) \text{Mn}_2 \text{O}_7. \quad (4) \]

- The similarity coefficient \( K_3 \) was calculated from the ratio of
\[
K_3 = \frac{\Delta H^\circ(298,15) \text{MeII(MnO}_4)_2}{\Delta_{ok} H^\circ(298,15) \text{MeII(MnO}_4)_2}, \quad (5) \]

where \( \Delta_{ok} H^\circ(298,15) \text{MeII(MnO}_4)_2 \) – a standard enthalpy of formation of permanganate of the alkaline earth metal from oxides is equal to
\[
\Delta_{ok} H^\circ(298,15) \text{MeII(MnO}_4)_2 = \\
= \Delta H^\circ(298,15) \text{Me}_2 \text{O} + \\
+ \Delta H^\circ(298,15) \text{Mn}_2 \text{O}_7. \quad (6) \]

- The average similarity coefficient \( \overline{K} \) was calculated from:
\[
\overline{K} = \frac{(K_1+K_2+K_3)/3}{(7)} \]

- \( \Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12} \) was calculated from:
\[
\Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12} = \\
= 0,5 \Delta H^\circ(298,15) \text{Ln}_2 \text{O}_3 + \\
+ 1,5 \Delta H^\circ(298,15) \text{Me}_2 \text{O}_3 + \\
+ 3 \Delta H^\circ(298,15) \text{MeO} + \\
+ 2 \Delta H^\circ(298,15) \text{Mn}_2 \text{O}_3. \quad (8) \]

- Similar to equations of (1, 3, 5), the ratio can be described as:

\[
\overline{K} = \frac{\Delta H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}}{\Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}}, \quad (9)
\]

where it can be calculated as
\[
\overline{K} = \frac{\Delta H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}}{\Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}} = \overline{K}. \quad (10)
\]

In connection with the absence of the reference date on \( \Delta H^\circ(298,15) \) manganites, the first approximate values \( \overline{K} \) were calculated from data on \( \Delta H^\circ(298,15) \) permanganates, which used to calculate \( \Delta H^\circ(298,15) \) of the test compounds. Thus it was taken into account that the values \( \overline{K} \) of manganites do not differ much from permanganates \( \overline{K} \).

Based on the above-said and taken the ratios of (11, 12) for the copper-zinc manganites of lanthanum, the alkali and alkaline earth metals, the following ratios can be demonstrated as:

\[
\frac{\Delta H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}}{\Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}} = \overline{K} \quad (11)
\]

\[
\frac{\Delta H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}}{\Delta_{ok} H^\circ(298,15) \text{LnMe}_3\text{MeII}_3\text{Mn}_4\text{O}_{12}} = \overline{K} \quad (12)
\]

Table 1 shows the initial data to calculate the standard enthalpies of formation of the copper-zinc manganites of lanthanum, the alkali and alkaline earth metals [5, 11-17].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \Delta_{ok} H^\circ(298,15) ) / kJ / mol</th>
<th>( \overline{K} )</th>
<th>( \Delta_{ok} H^\circ(298,15) ) / kJ / mol</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaLi(_2)Mg(_2)Mn(<em>4)O(</em>{12})</td>
<td>5 514,4</td>
<td>1,2375</td>
<td>6 824,1</td>
<td>[5, 11]</td>
</tr>
<tr>
<td>LaNa(_2)Ca(_2)Mn(<em>4)O(</em>{12})</td>
<td>5 340,5</td>
<td>1,3084</td>
<td>6 987,5</td>
<td>-/-</td>
</tr>
<tr>
<td>LaK(_2)Sr(_2)Mn(<em>4)O(</em>{12})</td>
<td>5 127,3</td>
<td>1,3545</td>
<td>6 944,8</td>
<td>-/-</td>
</tr>
<tr>
<td>LaRb(_2)Ba(_2)Mn(<em>4)O(</em>{12})</td>
<td>4 965,6</td>
<td>1,3703</td>
<td>6 804,3</td>
<td>-/-</td>
</tr>
<tr>
<td>Li(_2)O</td>
<td>-</td>
<td>593,94</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>-</td>
<td>414,84</td>
<td>-</td>
<td>[12]</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>-</td>
<td>362,33</td>
<td>-</td>
<td>[13]</td>
</tr>
<tr>
<td>Mg(_2)O</td>
<td>-</td>
<td>601,49</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>Ca(_2)O</td>
<td>-</td>
<td>635,09</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>Sr(_2)O</td>
<td>-</td>
<td>590,53</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>Ba(_2)O</td>
<td>-</td>
<td>548,10</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>La(_2)O (_3)</td>
<td>-</td>
<td>1 794,94</td>
<td>-</td>
<td>[15]</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>-</td>
<td>162,11</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>Zn(_2)O</td>
<td>-</td>
<td>350,86</td>
<td>-</td>
<td>[16]</td>
</tr>
<tr>
<td>Mn(_2)O (_3)</td>
<td>-</td>
<td>957,72</td>
<td>-</td>
<td>[17]</td>
</tr>
</tbody>
</table>
Table 2 The standard thermodynamic characteristics of the copper-zinc manganites of lanthanum, the alkali and alkaline-earth metals

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\Delta H^\circ$ (298.15) / kJ mol⁻¹</th>
<th>$C^\circ_V$ (298.15) / J (mol⁻¹K⁻¹)</th>
<th>$S^\circ$ (298.15) / J (mol⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaLi₂CuZnMnO₆</td>
<td>3 072.2</td>
<td>246.4</td>
<td>245.0</td>
</tr>
<tr>
<td>LaNa₂CuZnMnO₆</td>
<td>3 013.9</td>
<td>258.6</td>
<td>285.2</td>
</tr>
<tr>
<td>LaK₂CuZnMnO₆</td>
<td>3 048.5</td>
<td>261.0</td>
<td>310.4</td>
</tr>
<tr>
<td>LaMgCuZnMnO₆</td>
<td>3 073.2</td>
<td>227.2</td>
<td>232.5</td>
</tr>
<tr>
<td>LaCaCuZnMnO₆</td>
<td>3 293.6</td>
<td>232.3</td>
<td>248.0</td>
</tr>
<tr>
<td>LaSrCuZnMnO₆</td>
<td>3 349.5</td>
<td>234.3</td>
<td>259.0</td>
</tr>
<tr>
<td>LaBaCuZnMnO₆</td>
<td>3 330.9</td>
<td>233.4</td>
<td>269.6</td>
</tr>
</tbody>
</table>

The calculation of the standard heat capacities and standard entropies of the test compounds was received with a method of the ionic entropy increments [18]. In order to calculate $C^\circ_V$ (298.15) of the copper-zinc manganites, the following values of the ionic increments (C_i) of heat capacity [J (mol⁻¹K⁻¹)] were used: Li⁺ – 20.7; Na⁺ – 26.8; K⁺ – 28.0; Mg²⁺ – 22.2; Ca²⁺ – 27.3; Sr²⁺ – 29.3; Ba²⁺ – 28.4; La³⁺ – 29.3; Cu²⁺ – 25.0; Zn²⁺ – 25.5; Mn³⁺ – 25; O²⁻ – 16.7; and the values of the ionic entropy increments (S_i) [J (mol⁻¹K⁻¹)] were used to calculate $S^\circ (298,15)$ of compounds: Li⁺ – 34.7; Na⁺ – 25.5; O²⁻ – 28,4; Mn³⁺ – 28.0; Mg²⁺ – 22,2; Ca²⁺ – 27,3; Sr²⁺ – 29,3; Ba²⁺ – 28,4; La³⁺ – 29,3; Cu²⁺ – 25,0; Zn²⁺ – 25,5; Mn³⁺ – 25; O²⁻ – 16,7.

When the initial information collection for the fundamental reference books and databases of the thermodynamic values.

CONCLUSION

The standard enthalpies of formation of the copper-zinc manganites, the alkali and alkaline-earth metals of compositions of LaMeCuZnMnO₆ and LaMeCuZnMnO₆ (Me¹ – Li, Na, K; Me² – Mg, Ca, Sr, Ba) were first calculated with our developed method.

In order to calculate $C^\circ_V$ (298.15) of the copper-zinc manganites. The accuracy of calculation referring to [18] was ± 3.0 %.

Acknowledgements

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REFERENCES

[2] R. M. Yeremina, K. R. Sharipov, L. V. Mingaleiva et al., Investigation of properties of ceramics of La₄MnO₉, Sr₂MnO₄, Zn₂MnO₄ (x = 0.075, 0.095, 0.115), Solid state physics 54 (2012) 6, 1090-1095.

Note: The responsible translator for English language is Issakova Yelena Pavlovna, Karaganda, Kazakhstan