

1 | **Revision 1**

2 | **Natural sepiolite: enthalpies of dehydration, dehydroxylation and formation derived**
3 | **from thermochemical studies**

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11 | **Abstract**

12 | Sepiolite is widely used in various fields due to its unique colloidal-rheological and
13 | physicochemical properties. The first experimental thermochemical study of natural sepiolite
14 | $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \times n\text{H}_2\text{O}$ from Akkermanovskoe field (Southern Ural, Russia) was
15 | performed utilizing the high-temperature heat-flux Tian-Calvet microcalorimeter. X-ray
16 | powder diffraction, thermal analysis, and FTIR spectroscopy methods were used to
17 | characterize sepiolite. Processes of dehydration, dehydroxylation, and various water types'
18 | removal enthalpies were studied using thermochemical methods. The values of
19 | $\Delta_{\text{dehydration}}H^0(298.15 \text{ K})$ of adsorbed, zeolitic, and bound water calculated per 1 mol of released
20 | H_2O , were as follows: 15 ± 4 , 28 ± 8 , $39 \pm 15 \text{ kJ}\cdot\text{mol}^{-1}$ respectively. The enthalpy of
21 | dehydroxylation of sepiolite was found as $145 \pm 14 \text{ kJ}\cdot(\text{mol H}_2\text{O})^{-1}$. Obtained data point at
22 | different binding strengths of water in the structure of sepiolite. The enthalpies of formation
23 | from the elements $\Delta H_f^0(298.15 \text{ K})$ were derived by melt solution calorimetry for sepiolite
24 | with various content of different water types: $-18773 \pm 28 \text{ kJ}\cdot\text{mol}^{-1}$ for
25 | $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \times 4\text{H}_2\text{O}$ and $-16426 \pm 21 \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4$.

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27

28 | **Keywords:** Sepiolite, thermochemistry, microcalorimetry, enthalpy of dehydration, enthalpy
29 | of dehydroxylation, enthalpy of formation

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Introduction

32 Sepiolite is a natural nano-structural hydrous magnesium phyllosilicate with theoretical
33 chemical formula $Mg_8[Si_{12}O_{30}](OH)_4(H_2O)_4 \times 8H_2O$. Minerals of the palygorskite-sepiolite
34 group can be typically found in ancient and modern sediments, deep-sea deposits, soils and
35 crust of weathering of rocks rich in magnesium, however, they do not form large
36 aggregations. They are so-called “special clays” or chain-structure clays. Sepiolite belongs to
37 the mineral group of phyllosilicates, because it contains continuous two-dimensional Si-O
38 tetrahedral sheets. At the same time it differs from other layer silicates since it lacks
39 continuous octahedral sheets. The sepiolite structure can be described as ribbons consisting of
40 2:1 phyllosilicate structure, one ribbon being linked to the next by inversion of SiO_4 tetrahedra
41 along a set of Si-O-Si bonds (Jones and Galan 1988). The important feature of the sepiolite’s
42 structure is the presence of four water types in different crystallographic forms: adsorbed
43 water, zeolitic water, bound water, and constitutional water as hydroxyl groups. Unique
44 structural and physicochemical properties of sepiolite (colloidal-rheological, sorptive, and
45 catalytic), explain its being widely used as as catalyst, filler in polymeric and silicate nano-
46 composites, environmental adsorbent, drilling mud additive, molecular sieves, etc. Therefore,
47 there is a need to determine the chemical and mineralogical composition of sepiolite clays as
48 well as their physicochemical and thermodynamic parameters. The processes of dehydration
49 and dehydroxylation of sepiolite have been studied previously using different methods of
50 thermal analysis (Nagata et al. 1974; Kiyohiro and Otsuka 1989; Frost and Ding 2003;
51 Giustetto et al. 2011), but their quantitative heat characteristics are not provided in the
52 corresponding literature. Experimental data on the thermodynamic properties of sepiolite are
53 also not available. Results of calorimetric study of the thermodynamic properties of some

54 other layered minerals (saponite, nontronite, and vermiculite) were published recently
55 (Gailhanou et al. 2013). The values of the Gibbs energy of sepiolites of various compositions
56 were estimated using different methods (Tardy and Garrels 1974; Birsoy 2002), thus, it is
57 difficult to compare them.

58 The objectives of this work were to study natural sepiolite, and the processes of its
59 dehydration and dehydroxylation; to measure the enthalpies of removal of various water
60 types; and to determine the enthalpy of formation of the studied sepiolite using different
61 methods of high-temperature Calvet microcalorimetry.

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Characteristics of sample and methods

64 Clay Sample

65 The sepiolite sample from the Akkermanovskoe field (Southern Ural, Russia) for our study
66 was taken from the E.A. Fersman Mineralogical Museum of Russian Academy of Sciences (I.
67 I. Ginzburg's collection). The sample was described as a fibrous dense substance of white
68 color. It had, according to the "wet" chemistry analysis data, the following composition
69 (wt%): 53.59 SiO₂, 0.11 Al₂O₃, 0.26 Fe₂O₃, 0.16 FeO, 0.13 CaO, 23.88 MgO, 0.16 NiO,
70 21.44 H₂O (Ginzburg and Rukavishnikova 1951). The water content was determined by
71 calcination of the sample at 850°C for 1 h. The chemical formula calculated on 64 charges has
72 the form $\text{Mg}_{7.93}\text{Ca}_{0.03}\text{Fe}^{2+}_{0.03}\text{Ni}_{0.03}\text{Al}_{0.03}\text{Fe}^{3+}_{0.04}\text{Si}_{11.94}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \times 9.9\text{H}_2\text{O}$ and it is close
73 to ideal $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \times n\text{H}_2\text{O}$. The calculations of the thermodynamic properties of
74 the studied mineral were based on the formula above. To study the mineral purity of the
75 sepiolite, different modern methods were used.

76 **X-ray diffraction study.** The X-ray pattern (Fig. 1) was obtained with a powder
77 diffractometer "STOE-STADI MP" (Germany) with curved Ge (111) primary

78 monochromator (λ Cu K α) in the range of $2\theta = 10$ - 100° . The analysis showed no impurities of
79 other minerals in the sample, and allowed to define the parameters of the unit cell of sepiolite:
80 $a = 13.48(1)$ Å, $b = 26.82(2)$ Å, $c = 5.2791(10)$ Å, $V = 1908.7(1)$ Å³; space group Pncn. The
81 derived values are consistent with those included in the Russian crystallographic database
82 MINCRYST (card number 6899, 7070, 8120) (Chichagov et al. 2001).

83 **FTIR examination.** An IR-spectrum was recorded at the Fourier-spectrometer “FSM
84 1201” (Russia) with a resolution of 4 cm^{-1} in transmission mode in the 400 - 4000 cm^{-1} spectral
85 range at an ambient air and room temperature. The spectrum was recorded with the
86 suspension of mineral powder in petrolatum oil. The sample was dried at 55°C to remove
87 excess of adsorbed water. The IR-spectrum of sample sepiolite (Fig. 2) was in a good
88 agreement with the spectrum of natural pure sepiolite from Hawthorne (Nev., U.S.A.), cited
89 in the Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures (Van der Marel
90 and Beutelspacher 1976). All of the registered absorption bands in the spectrum belong to
91 sepiolite. Other mineral impurities in the sample were not found. The absorption spectrum in
92 the high frequency region has a complex profile. This is due to the superposition of several
93 absorption bands relating to the stretching vibrations of OH-groups. The sharp peak at 3685
94 cm^{-1} is attributed to the stretching vibrations of hydroxyl groups associated with Mg^{2+} -cations
95 from octahedral positions. This band supports the trioctahedral character of this mineral. The
96 bands at 3640 and 1620 cm^{-1} are assigned to the stretching and bending vibrations of water
97 molecules of bound type respectively. The absorption bands at 3625 , 3563 , 3382 , 3249 , and
98 1660 cm^{-1} are assigned to the stretching and deformation (last) vibrations of molecules of the
99 zeolitic, and the minor amount of adsorbed water (Hayashi et al. 1969). The bands group in
100 the 1200 - 970 cm^{-1} interval corresponds to the stretching vibrations of Si-O bonds in the
101 tetrahedral sheet. In the range of 900 - 600 cm^{-1} the absorption bands can be attributed to the

102 vibrations of hydroxyl groups associated with octahedral Mg^{2+} and water molecules of the
103 bound type. The bands placed at 466 (with shoulders at 535 and 500 cm^{-1}) and 437 cm^{-1} are
104 related to the deformation vibrations in tetrahedral sheets.

105 **TG, DTG and DSC analyses.** The thermal behavior of sepiolite was studied using
106 “NETZSCH TG 209 F1” and “NETZSCH DSC 204 F1” devices (Germany) in a stream of
107 dry air (20 $ml \cdot min^{-1}$) with $10^{\circ} \cdot min^{-1}$ heating rate in the range from room temperature to 1000
108 and to 600°C respectively. TG and DTG experiments were carried out in a corundum
109 crucible, DSC experiments were performed in aluminum crucible with pierced lid. The
110 specimens’ weights were 10-11 mg. The DSC apparatus was calibrated with the enthalpies
111 and temperatures of the phase transitions of standard substances (C_6H_{12} , Hg, Ga, In, Sn, Bi,
112 Zn, and benzoic acid). The resulting thermogram (Fig. 3) is typical of sepiolite, and is in good
113 agreement with the results of thermal studies of this mineral (Nagata et al.1974; Kiyohiro and
114 Otsuka 1989; Frost and Ding 2003; Giustetto et al. 2011). Four stages of mass loss were
115 recorded on the TG and DTG curves, first three of which characterize various stages of the
116 dehydration process, while the fourth one represents the process of sepiolite dehydroxylation.
117 The first stage (up to 150°C) corresponds to the joint removal of adsorbed and zeolitic water.
118 Loss of bound water associated with magnesium cations occurs in two steps: in the intervals
119 150-340, and 340-650°C. The first interval corresponds to removal of half of the bound water
120 and simultaneous compression of the structure. The second stage is characterized by a
121 significantly lower removal rate of bound water remaining from the compressed structure.
122 According to X-ray studies (Nagata et al. 1974; Giustetto et al. 2011) the formation of the
123 dehydrated sepiolite (sepiolite-II) takes place during this step. The dehydroxylation of
124 sepiolite occurs with further heating to 650-875°C. The DSC curve (Fig. 4) shows three
125 endothermic effects, associated with the dehydration of this mineral. The largest thermal

126 effect corresponds to the removal of large amounts of adsorbed and zeolitic water. The second
127 and the third effects relate to the removal of bound water. The third effect is considerably
128 smaller than the second one, because it involves both an endothermic effect of the residual
129 bound water removal (heat absorption) and exothermic effect of a new phase (sepiolite-II)
130 formation (heat release).

131

132 **Calorimetric methods**

133 The thermochemical study of sepiolite was performed on the high temperature heat-flux Tian-
134 Calvet microcalorimeter ("Setaram", France) using two experimental methods. The enthalpies
135 of formation were determined by melt solution calorimetry using a thermochemical cycle,
136 taking into account the dissolution of the mineral and its constituent components: the oxides
137 and the magnesium hydroxide. In order to dissolve crystal fragments of the sepiolite weighing
138 4-12 ($\pm 2 \times 10^{-3}$) mg were dropped from room temperature into solvent-melt with composition:
139 $2\text{PbO} \cdot \text{B}_2\text{O}_3$, located in a platinum crucible in the calorimeter at $T = 973$ K. The heat effect
140 measured was the sum of the sample heat absorption and its dissolution [$H^0(973 \text{ K}) -$
141 $H^0(298.15 \text{ K}) + \Delta_{\text{sol}} H^0(973 \text{ K})$]. Using 30-35 grams of the solvent for 6-8 solution
142 experiments the ratio of dissolved substance – solvent can be attributed to an infinitely diluted
143 solution with mixing enthalpy close to zero. Determination of the enthalpies of the sepiolite
144 dehydration was carried out by the "double step drop" method. At the first step crystal
145 fragments of sample weighing 6-15 ($\pm 2 \times 10^{-3}$) mg were dropped from room temperature
146 (25°C) into an empty platinum crucible in the calorimeter at $T = 359$ K (86°C) and 565 K
147 (292°C) and the total heat effect, associated with the heat absorption of the sample and its
148 dehydration [$H^0(T) - H^0(298.15 \text{ K}) + \Delta_{\text{dehyd.}} H^0(T)$] was measured. At the second stage the
149 dehydrated sample was dropped from room temperature back into the calorimeter at the above

150 mentioned temperatures ($T = 359$ and 565 K), thus the values of its heat absorption [$H^0(T)$ -
151 $H^0(298.15$ K)] were measured. Before this stage dehydrated samples were warmed up to the
152 suitable calorimetric experiment temperatures to avoid a rehydration process and were
153 weighed immediately. The water content was monitored by weighing the samples before and
154 after the calorimetric experiments, and before and after heating.

155 The calibration of the calorimeter was performed by dropping pieces of the reference
156 substances – platinum wire (in the solution experiments) and corundum α - Al_2O_3 (in the
157 dehydration experiments), and using their reference enthalpy increments data (Robie and
158 Hemingway 1995). The experimental data are presented in the Tables 1, 2.

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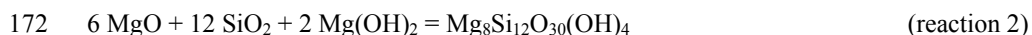
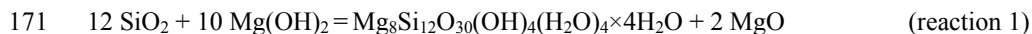
Results and discussion

161

The enthalpies of formation

163 Determination of the standard enthalpies of formation was made for both - the studied
164 sepiolite and the dehydrated hydroxyl-containing sepiolite. In the first case the natural mineral
165 was dried at 55°C for 30 min to remove adsorbed water (7.9 %). In the second case the natural
166 mineral was calcined for 1 h at $T = 873$ K (600°C) corresponding to the complete removal of
167 the molecular water (18.8 %), that was confirmed by weighing the samples before and after
168 the calcination.

169 Values of the standard enthalpies of formation of sepiolites from the elements were calculated
170 in accordance with the reactions 1, 2 and Eq. 3, 4 using the dissolution calorimetric data



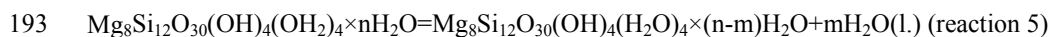
173 $\Delta_{r(1,2)}H^0(298.15 \text{ K}) = \sum v_i \Delta H_{\text{component}_i} - \Delta H_{\text{sepiolite}}$; (Eq. 3)

174 $\Delta H_f^0(298.15 \text{ K}) \text{ sepiolite} = \Delta_{r(1,2)} H^0(298.15 \text{ K}) + \sum v_i \Delta H_f^0(298.15 \text{ K}) \text{ component}_i$, (Eq. 4)
175 where v_i – the stoichiometric coefficients in the equations (1, 2), $\Delta H = [H^0(973 \text{ K}) - H^0(298.15$
176 $\text{ K}) + \Delta_{sol} H^0(973 \text{ K})]$ – the calorimetric data for the sepiolite studied (Table 1), and the
177 corresponding oxides and magnesium hydroxide (Table 3); the values of $\Delta H_f^0(298.15 \text{ K})$ of
178 the components of these reactions needed for calculations are also shown in the Table 3. First
179 experimental determinations are the obtained values of the enthalpies of sepiolite formation
180 (Table 1).

181

182 **The enthalpies of dehydration**

183 The calorimetric study of the dehydration processes (removal of molecular form of water in
184 sepiolite) was performed at two temperatures: at 359 K (86°C) in order to remove the low
185 temperature water (adsorbed and zeolitic), and at 565 K (292°C) in order to remove the higher
186 temperature bound water. Since the content of the low-temperature water is highly dependent
187 on the ambient humidity, the experimental dehydration studies were carried out using both the
188 initial sample and the sample dried at 55°C for 30 min to remove the bulk of the adsorbed
189 water (in this case the enthalpy of the removal of mainly zeolitic water was measured). The
190 water content in the sample was reduced by 7.9% during drying, which corresponded to a loss
191 of about 5.9 moles of the water in the sepiolite formula. Based on the reaction 5 and Eq. 6 the
192 enthalpies of the molecular form water removal were calculated.



194 sepiolite dehydrated sepiolite

195 $\Delta_{r(5)} H^0(298.15 \text{ K}) = [H^0(T) - H^0(298.15 \text{ K}) + \Delta_{\text{dehydr.}} H^0(T)] \text{sepiolite} -$

196 $[H^0(T) - H^0(298.15 \text{ K})] \text{dehydrated sepiolite} - m[H^0(T) - H^0(298.15 \text{ K})] \text{H}_2\text{O}(l)$, (Eq. 6)

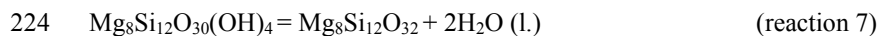
197 where n is number of the moles of water in the sample; m is number of the moles of the water
198 removed during the calorimetric experiment; $(n-m)$ – the number of moles of water in the
199 dehydrated sample; $[H^0(T)-H^0(298.15\text{ K})+\Delta_{\text{dehydr.}}H^0(T)]$ sepiolite, and $[H^0(T)-H^0(298.15\text{ K})]$
200 dehydrated sepiolite - obtained in the present work experimental data (Table 2); $[H^0(T)-$
201 $H^0(298.15\text{ K})]$ H₂O(l.) – the reference data (Robie and Hemingway 1995). The obtained
202 results are listed in Table 2. The values of the enthalpies of dehydration calculated per one
203 mole of H₂O at $T=298.15\text{ K}$ are shown in Table 2 as well. Removal of the water from
204 sepiolite related to chain-structure clays was accompanied by the endothermic effects of about
205 15 kJ per mole of the adsorbed water (the value given in Table 2 was recalculated using the
206 enthalpy of the removal of the zeolitic water); about 28 kJ per mole of the zeolitic water and
207 about 39 kJ per mole of the bound water associated with the magnesium cations in the
208 octahedral sheet. Previously we have studied the dehydration process of a typical
209 phyllosilicate – montmorillonite (containing only the adsorbed and the interlayer water), and
210 have obtained the following values of the enthalpy of dehydration: about 6 and about 11
211 kJ·(mol H₂O)⁻¹ respectively (Ogorodova et al. 2013). Thus, obtained results show that in
212 sepiolite with the chain structure water molecules are stronger connected with the structure of
213 the mineral than in the ordinary layered clays.

214

215 **The enthalpy of dehydroxylation**

216 Additional experiments on the dissolution of sepiolite calcined for 1 h at $T=1123\text{ K}$ (850°C)
217 were performed in order to determine the enthalpy of dehydroxylation of sepiolite (removing
218 the constitutional water located in the structure of the mineral in the form of hydroxyl
219 groups). According to the results of thermal analysis and IR spectroscopy, complete removal
220 of all types of water (including constitutional water) takes place at this temperature, product

221 destruction of sepiolite was an amorphous phase with signs of clinoenstatite crystallization
222 [Guistetto et al. 2011]. The enthalpy of dehydroxylation was calculated for the reaction 7 by
223 Eq. 8.



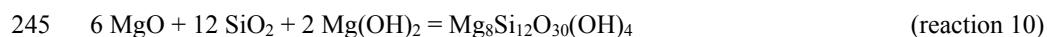
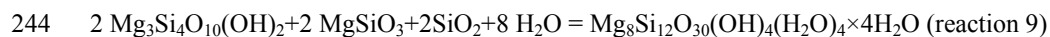
$$225 \Delta_{\text{r}(7)}H^{\circ}(298.15 \text{ K}) = \Delta H_f^{\circ}(298.15 \text{ K})\text{Mg}_8\text{Si}_{12}\text{O}_{32} + 2 \Delta H_f^{\circ}(298.15 \text{ K})\text{H}_2\text{O}(\text{l}) -$$
$$226 \Delta H_f^{\circ}(298.15 \text{ K})\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4. \quad (\text{Eq. 8})$$

227 The enthalpy of formation of fully dehydrated sepiolite was calculated by equations similar to
228 Eq. 5, 6; it is given in Table 1. On the basis of our data on $\Delta H_f^{\circ}(298.15 \text{ K})$ for sepiolite and
229 the reference data for $\Delta H_f^{\circ}(298.15 \text{ K})\text{H}_2\text{O}(\text{l})$ (Robie and Hemingway 1995) the value of the
230 enthalpy of dehydroxylation process was found to be $290 \pm 28 \text{ kJ}\cdot\text{mol}^{-1}$. The value of
231 $\Delta_{\text{dehydroxyl}}H^{\circ}(298.15 \text{ K})$ calculated per one mole of H_2O ($145 \pm 14 \text{ kJ}$) is significantly greater
232 than the given above enthalpies of the removal of the other water types . This fact indicates
233 higher bond energies of the hydroxyl groups in the structure of sepiolite. The obtained data
234 are close to the previously determined value of dehydroxylation enthalpy for montmorillonite
235 ($166 \pm 10 \text{ kJ}\cdot(\text{mol H}_2\text{O})^{-1}$) (Ogorodova et al. 2013).

236

237 **The Gibbs energies of formation**

238 In order to calculate Gibbs energy of studied sepiolites formation, one needs to have the
239 values of standard entropies, which cannot be found in the literature. Evaluation of these
240 values was made on the basis of the reactions 9 and 10 using the values of the entropies of
241 talc, enstatite, quartz, and magnesium oxide (Robie and Hemingway 1995), and entropy
242 contributions of the bound and zeolitic water, that are assumed to be equal to 39.3 and 50.2 J·
243 $(\text{K}\cdot\text{mol})^{-1}$ respectively (Fyfe et al. 1962).



246 We calculated the values of $\Delta G_f^0(298.15 \text{ K})$ for these minerals: $-17280 \text{ kJ}\cdot\text{mol}^{-1}$
247 $(\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \times 4\text{H}_2\text{O})$ and $-15383 \text{ kJ}\cdot\text{mol}^{-1}$ $(\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4)$ using the estimated
248 values of $S^0(298.15 \text{ K})$ equals to 1095 and $737 \text{ J}\cdot(\text{K}\cdot\text{mol})^{-1}$ respectively and enthalpies of
249 formation of the hydrous and the anhydrous sepiolites obtained in this study.

250

251

Implications

252 Our pioneer thermodynamic data on the enthalpies and Gibbs energies of formation for the
253 natural hydrous and anhydrous sepiolites, and the quantitative heat characteristics of its
254 dehydration processes can be used for the physicochemical study of the clay minerals'
255 formation in the system magnesium-silica-water, and conversion of smectite to sepiolite in the
256 sedimentary rocks and the weathering crusts, as well as for determination of conditions for
257 sepiolite rock formation. The obtained data are useful for the thermodynamic modeling of
258 processes in the field of environmental studies and synthesis of the nano-composite materials
259 with the sepiolite structure and predetermined sorptive, catalytic and other properties.

260

261

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341 **Table 1.** Results of sepiolite study by solution calorimetry method ^a

Composition of sample	Molar mass (g·mol ⁻¹)	$[H^0(973\text{ K})-H^0(298.15\text{ K})$		$-\Delta H_f^0(298.15\text{ K})$ (kJ·mol ⁻¹)
		$+\Delta_{\text{sol}}H^0(973\text{ K})]^b$ (J·g ⁻¹)	(kJ·mol ⁻¹)	
Mg ₈ Si ₁₂ O ₃₀ (OH) ₄ (H ₂ O) ₄ ×4H ₂ O	1223.60	1077.3±15.4 (5)	1318±19	18773±28
Mg ₈ Si ₁₂ O ₃₀ (OH) ₄	1079.49	883.5±15.1 (6)	954±16	16426±21
Mg ₈ Si ₁₂ O ₃₂	1043.46	563.3±11.2 (5)	588±12	15565±18

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343 *Note:* ^a The correction for the minor difference in the compositions of studied sample and
344 sepiolite of ideal formula was made with the required thermochemical data for calcium oxide
345 [Kiseleva et al. 1979], iron trioxide [Kiseleva 1976], nickel oxide [DiCarlo et al. 1994] and
346 corundum [Ogorodova et al. 2003] and found to be 4.1±0.1 kJ, this value was not taken into
347 account because it was significantly lower than the error of the experimental results; ^b
348 uncertainties are calculated using Student's *t*-distribution with a 95% confidence interval, in
349 brackets the number of determinations is given.

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$$\begin{array}{cccccccc} \text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 & H^0(T)-H^0(298.15\text{ K}) & 565 & 2.6 & 316.5\pm 10.1 & 356.5\pm 11.4 & 0 & 2.6 \\ (\text{OH}_2)_{2.6}^g & & & & & & & (6) \end{array}$$

M.m.=1126.33

360

361 *Note:* ^a Uncertainties are calculated using Student's *t*-distribution with a 95% confidence interval, in brackets the number of determinations
362 is given; *n*, *m*, (*n*-*m*) -the number of moles of water in the initial sample, removed in calorimetric experiment and in dehydrated sample,
363 respectively; ^b the value relates to process of removal of all adsorbed (5.9 moles) and part of zeolitic (1.9 moles) water, this value was
364 recalculated taking into consideration the enthalpy of the removal of the zeolitic water ($28\pm 8\text{ kJ}\cdot(\text{mol H}_2\text{O})^{-1}$) to the enthalpy of removal of
365 adsorbed water, which was found as $\sim 15\text{ kJ}\cdot(\text{mol H}_2\text{O})^{-1}$; ^c sample in the initial state; ^d sample after drying at 55°C for 30 min; ^e after
366 heating at 86°C (359 K) for 1 h; ^f after heating at 200°C for 1 h; ^g after heating at 292°C (565 K) for 1 h.

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369 | **Table 3.** Thermochemical data used in calculation of the enthalpies of formation of sepiolite
 370 studied ($\text{kJ}\cdot\text{mol}^{-1}$)

Component	$[H^0(973\text{ K})-H^0(298.15\text{ K}) + \Delta_{\text{sol}}H^0(973\text{ K})]$	$-\Delta H_f^0(298.15\text{ K})^{\text{a}}$
MgO(s.)	$36.38\pm 0.59^{\text{b}}$	601.6 ± 0.3
SiO ₂ (quartz)	$39.43\pm 0.21^{\text{c}}$	910.7 ± 1.0
Mg(OH) ₂ (brucite)	$111.5\pm 1.6^{\text{d}}$	924.5 ± 0.4

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 372 *Note:* ^a Reference data (Robie and Hemingway 1995); ^{b,c} – calculated using reference data on
 373 $[H^0(973\text{ K})-H^0(298.15\text{ K})]$ (Robie and Hemingway 1995) and experimental data on
 374 $\Delta_{\text{sol}}H^0(973\text{ K})$: ^b (Navrotsky and Coons 1976), ^c (Kiseleva et al. 1979); ^d by data (Kiseleva
 375 and Ogorodova 1984).

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389 **Figures captions**

390 **Figure 1.** XRD pattern of sepiolite

391 **Figure 2.** FTIR spectra of sepiolite

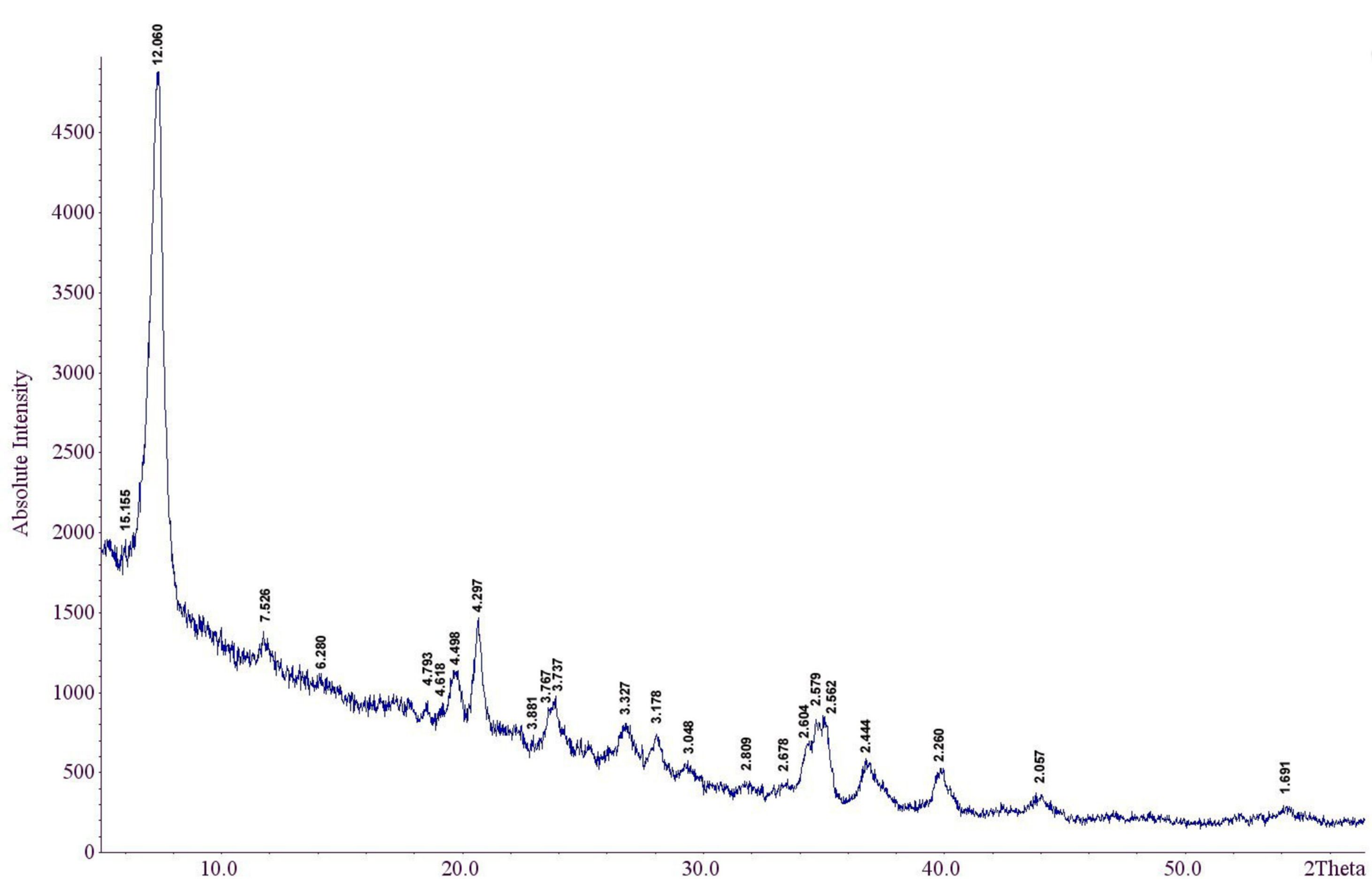
392 **Figure 3.** TG and DTG curves of sepiolite

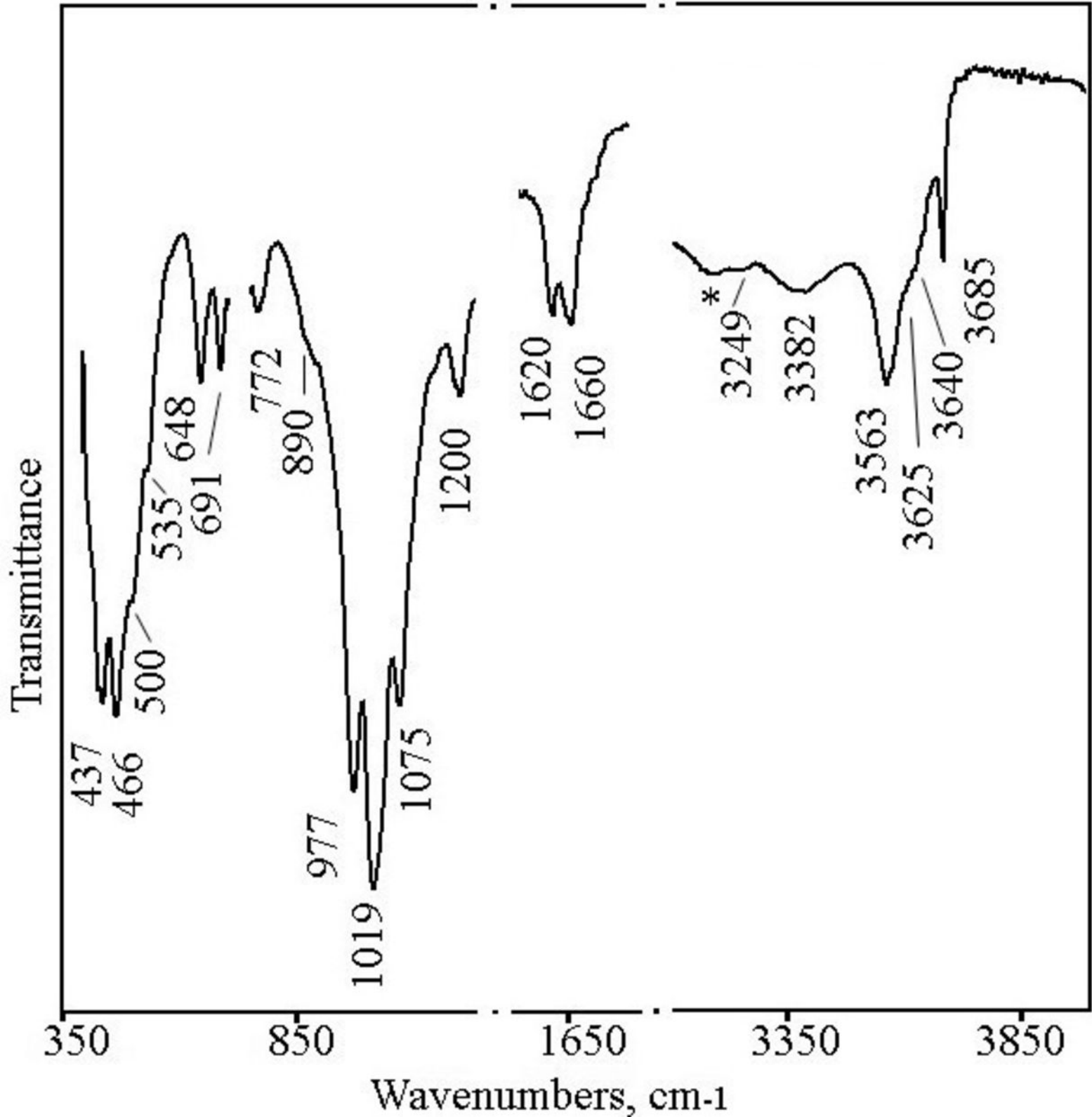
393 **Figure 4.** DSC curve of sepiolite

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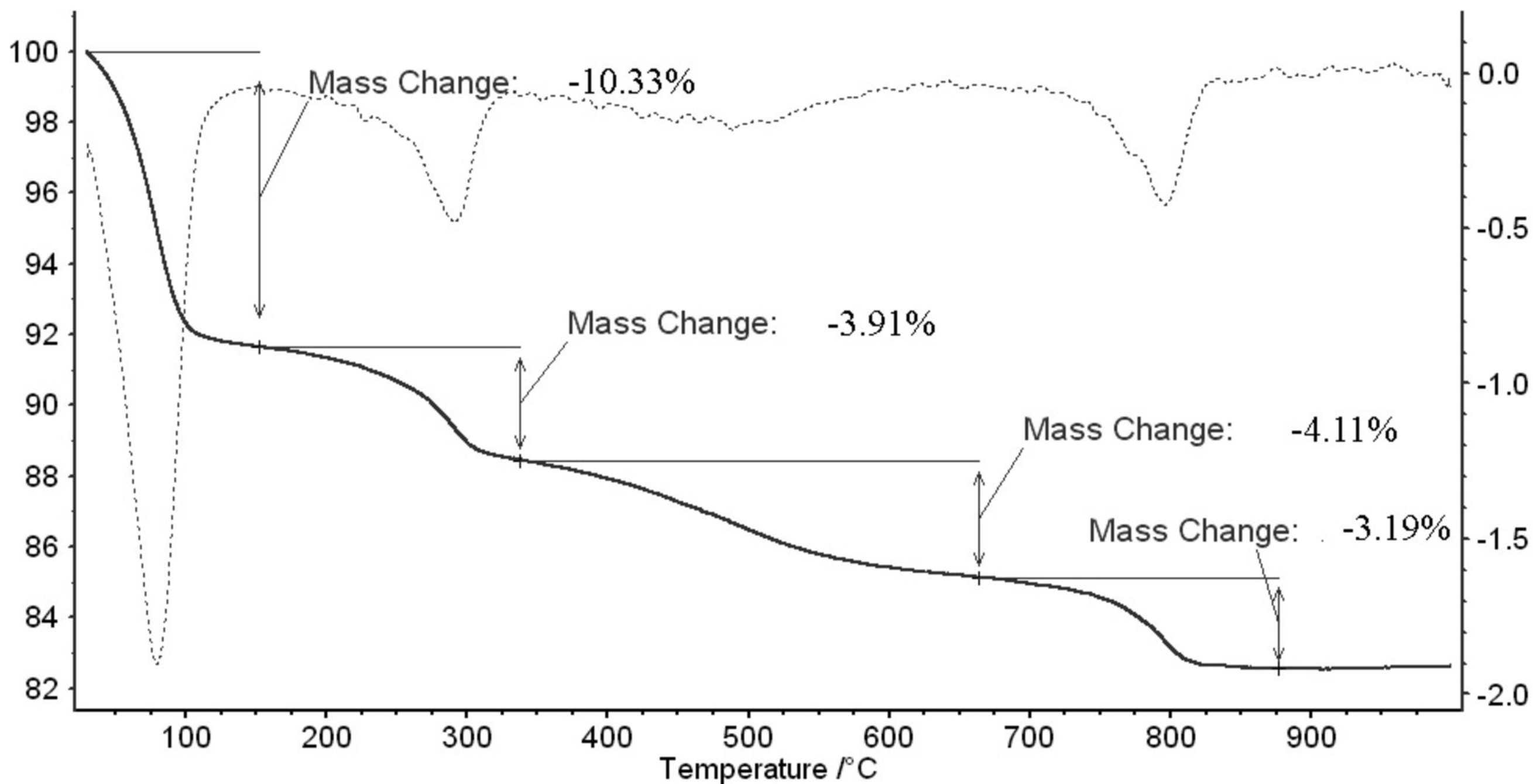
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TG /%

DTG /(%/min)



DSC I (mW/mg)

↑ exo

