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Construction of phase diagram in systems $Na_2CO_3{\cdot}10H_2O$ – $CH_3COONa{\cdot}3H_2O$

The phase diagram in the system of crystalline hydrates $Na_2CO_3{\cdot}10H_2O$ – $CH_3COONa{\cdot}3H_2O$ is constructed with methods of thermal analysis, this diagram is of the eutectic type. Eutectic composition is 66 wt.% $Na_2CO_3{\cdot}10H_2O$ + 34 wt.% $CH_3COONa{\cdot}3H_2O$. Eutectic temperature is of –11±0.7 °C. The enthalpy of melting and crystallization of mixtures relatively to liquidus and solidus lines were measured, which were used for specify the type of phase diagrams. As the eutectic composition is approached, the reduction of supercooling was established. The mixture of eutectic composition was proposed for using as a heat storage material.

Key words: crystalline hydrates, sodium acetate trihydrate, sodium carbonate ten hydrate, thermal analysis, melting, crystallization, phase diagram, liquidus, solidus, eutectic supercooling, enthalpy of phase transition, Tamman triangle, heat storage material.

Crystalline hydrates of sodium acetate trihydrate (AH-3) and sodium carbonate ten hydrates (KH-10) are widely used as a heat storage material (HSM) based on the phase transitions [1–7]. In this case we can predict the compositions, the most satisfying the requirements for HSM. Information about this diagram is not available in the literature. So basic aim of this paper is construction of phase diagrammes of crystalline hydrates KH-10 – AH-3, also investigation of super cooling processes and enthalpy of phase transition of mixtures as basic parameters.

Experimental part

Mixtures containing 0 (I), 10 (II), 20 (III), 30 (IV), 34 (V), 40 (VI), 50 (VII), 60 (VIII), 70 (IX), 80 (X), 90 (XI), 95 (XII), 97 (XIII), 100 (XIV) wt. % AH-3 were investigated. These mixtures were prepared from components of KH-10 and AH-3 (model is «pure»). Additional investigations for compositions different from the eutectic at 0.5 % were carried out in the vicinity of the eutectic composition. Samples were prepared according to procedure [6–7]. All samples having the same weight of 0.1 g, were placed in a test tube with ground-glass lid. Heating and cooling of the samples were performed by a resistance furnace in a temperature range from –25 °C to +80 °C. For this the furnace was placed in a freezer operating at a temperature of –30 °C. Heating and cooling rates were chosen approximately the same and ranged from 0.1–0.2 K/sec.

Liquidus and solidus temperatures of mixtures were mainly determined by the cyclic thermal analysis (CTA) in coordinates «temperature–time», also endo- and exothermic effects were determined by differential thermal analysis (DTA). All mixtures in the system «KH-10 – AH-3» were investigated under conditions in which the individual crystalline hydrates were enough super cooling. These conditions were achieved after heating mixtures of 10÷12 degrees above the corresponding liquidus temperatures. Recording of DTA and CTA curves, also heating-cooling processes was made using meter-regulator TRM-202 from «OVEN» firm and PC. Samples of each composition were prepared not less than 3 times, the number of thermal cycles of each composition consists of at least 10.

The statistical processing was carried out, and the average values of liquidus (T_L), solidus (T_S) and minimum temperatures (T_L^{min}) in cooling at the beginning of crystallization, crystallization enthalpy relatively liquidus (ΔH_L) and solidus (ΔH_S) temperatures were found on the basis of these experiments.

Results and discussion

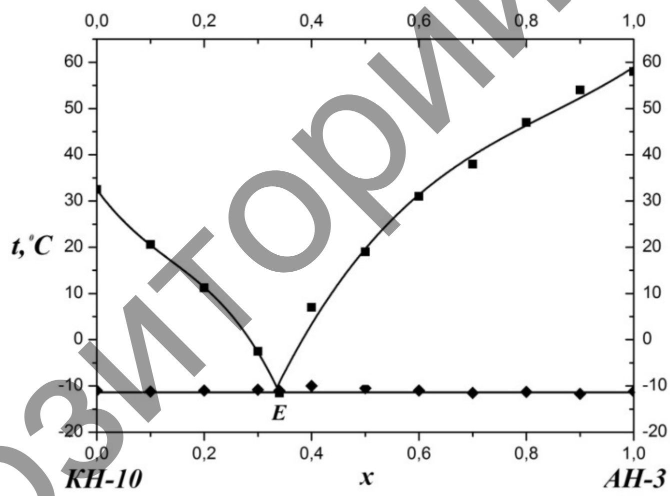
In a first step the samples were heated and cooled in order to determine the liquidus (T_L) and the solidus (T_S) temperatures. Results of mean values of T_L and T_S are shown in Table 1.

Table 1

Composition of samples and their corresponding average liquidus temperature (T_L), the solidus temperature (T_S), the minimum temperature (T_{min}), cooling ΔT_L^- and ΔT_S^- relative to temperature T_L and T_S in system of crystalline hydrates «$Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$»

Sample №	Amount of AH-3 in KH-10, wt.%	$<T_L>$	$<T_L^{min}>$	$<\Delta T_L^->$	$<T_S>$	$<T_S^{min}>$	$<\Delta T_S^->$	ΔH_L	ΔH_S
		ºC						kJ/kg	kJ/kg
I	0.0	32.5	19	13.5				286	0
II	10.0	20.6	9	11.6	–11.2	–14.0	2.8	247	38
III	20.0	11.2	1	10.2	–11.0	–13.8	2.8	225	59
IV	30.0	–2.5	–9	6.5	–10.8	–14.2	3.4	152	131
V(E)	34.0	–11.5	–14	2.5	–11.0	–14.0	3.0	124	124
VI	40.0	7.1	–3	10.1	–10.0	–14.0	4.0	130	151
VII	50.0	19.5	8	11.5	–10.5	–14.1	3.6	156	124
VIII	60.0	31.0	18	13.0	–11.0	–14.2	3.2	184	95
IX	70.0	38.0	22	16.0	–11.5	–14.0	2.5	200	78
X	80.0	47.0	28	19.0	–11.3	–14.0	2.7	218	59
XI	90.0	54.0	31	23.0	–11.7	–13.8	2.1	245	31
XII	95.0	57.5	22.3	35.2	–10.5	–13.5	3.0	247	28
XIII	97.0	57.8	18	39.8	–11.0	–13.5	2.5	263	12
XIV	100	58.0	–20	78.0				274	0

The liquidus and solidus lines for the system $Na_2CO_3 \cdot 10H_2O$ — $CH_3COONa \cdot 3H_2O$ were constructed on evidence derived from Table 1. Obtained phase diagram is was eutectic type diagram (Fig. 1).



A = 58 ºC; B = –75; C = 104; D = –223 for $x > x_E$

Figure 1. Phase diagram of crystalline hydrates «$Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$»

Eutectic composition consists of ~ 66 wt.% KH-10 + 34 wt.% AH-3. Line corresponding to the temperatures T_S, is practically a straight line, corresponding to an average value –11.0 ± 0.7 ºC.

Obtained liquidus lines were fairly well described by the equation:

$$T_L = A + Bx + Cx^2 + Dx^3, \quad (1)$$

where A = 32.5 ºC; B = –160; C = 532; D = –1294.7 for $x < x_E$.

The enthalpy of melting ΔH_{LS} and crystallization ΔH_{SL} were measured by DTA. As has already been intimated that the measured values of melting enthalpy of pure crystalline hydrates KH-10 (286 kJ/kg) and AH-3 (274 kJ/kg) were close to the literature data: it is 286.6 kJ/kg for KH-10 [8, 9], and 280.0 kJ/kg for AH-3 [6].

Bifurcate of exothermic effects of crystallization of mixtures relative to the lines of the liquidus T_L and solidus T_S was established. DTA-curves of compositions with 10 wt.% (II) and 70 wt.% (IX) were given as examples (Fig. 2). Each curve has two peaks of exo-effects, and the main proportion of the thermal effect in the crystallization occurs in the region near the liquidus temperature.

Investigations have shown that the sum of the enthalpies ΔH_L and ΔH_S approximately equal to the total enthalpy of crystallization, i.e. $\Delta H_L + \Delta H_S \approx \Delta H_{SL}$, which in turn is equal to the melting enthalpy ΔH_{LS}, i.e. $\Delta H_{LS} \approx \Delta H_{SL}$.

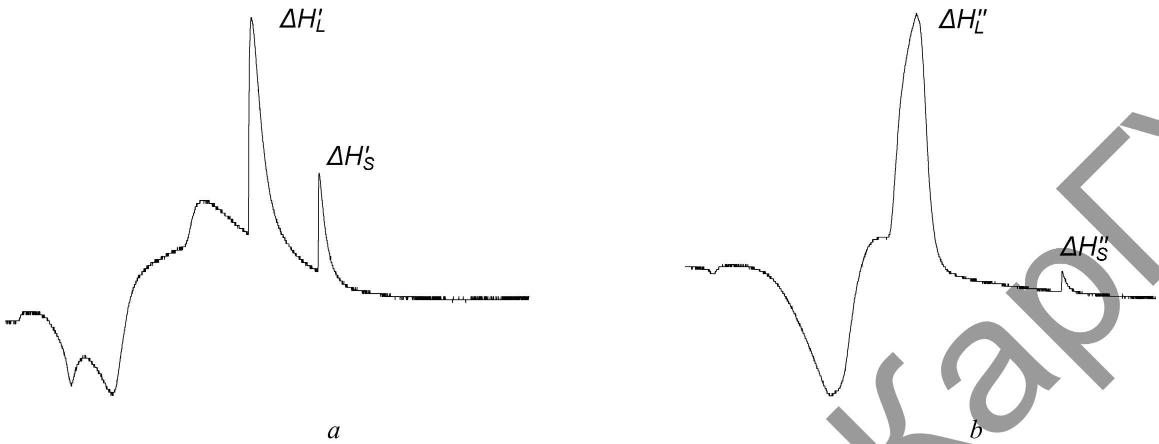


Figure 2. DTA-curves of melting and crystallization for compositions (II) — *a* and (IX) — *b*

Such bifurcating of thermal effects ΔH_{LS} on ΔH_L and ΔH_S may mean that the crystallization mixtures take place in two stages: the first stage is relative to liquidus line when crystals of KH-10 begin to form in the hypoeutectic region, and AH-3 crystals in the hypereutectic region.

Then this process is terminated due to depletion of solutions in molecules Na_2CO_3 and CH_3COONa. And the residues of these molecules in their own water of crystallization form fine mixed crystals of both hydrates in the form of eutectic when approaching the eutectic temperature.

Average values ΔH_L and ΔH_S show in table. Data of ΔH_S were used for refinement of eutectic composition according to Tamman triangle method [8] (Fig. 3).

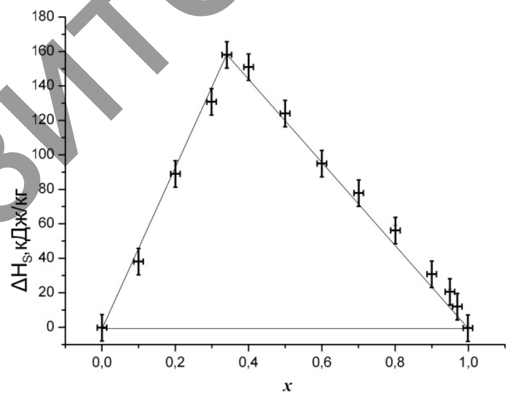


Figure 3. Dependence of the enthalpy ΔH_S of components' concentration in the KH-10 – AH-3

The correlation of eutectic composition with data shown in the diagram (Fig. 1) in the range of 2–3 % is seen from figure 3. Stability of the thermal effects values ΔH_{LS} and ΔH_{SL} to prolonged thermal cycling on a sample of eutectic composition and pure crystalline hydrates KH-10 and AH-3 was checked.

The results showed some decrease in value of ΔH_{SL} after 10 cycles initially, and then almost constant value with further thermal cycling up to 100 thermal cycles. The decrease value of ΔH_{SL} is ~17 % for KN-10 and ~5 % for AN-3, and ~ 3 % for the eutectic composition. The decrease of enthalpy of crystallization may be due to partial dehydration of aqueous solutions with repeated thermal cycling. It is observed, in this case, that the eutectic composition compares favorably to some crystalline hydrates.

At the third stage the precrystallization hypothermia ΔT_L of samples relatively liquidus temperature (for mixtures) and the melting temperature of pure crystalline hydrates was studied. For this, the minimum temperatures in hypothermia field T_L^{min}, in which the spontaneous crystallization was began, was recorded by CTA method. The average values $<T_L^{min}>$ are shown in Table. It also gives the hypothermia relatively to liquidus line $\Delta T_L^- = T_L - T_L^{min}$ and solidus line $\Delta T_S^- = T_S - T_S^{min}$. Dependence of the average hypothermia $<\Delta T_L^->$ from concentration of *x* in the mixture is shown in Figure 4.

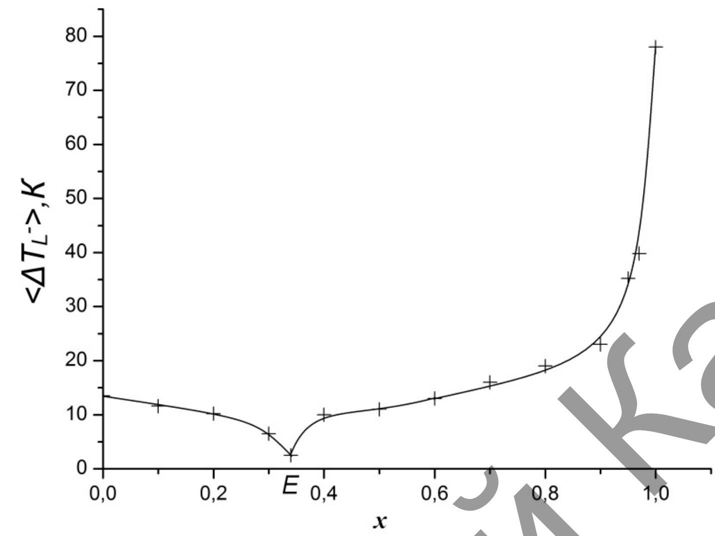


Figure 4. Dependence of average hypothermia of mixture from concentration of AN-3

The figure shows, that as the mixture composition to approach the eutectic (point *E*), hypothermia regularly reduce: in hypoeutectic field from ~13 °C (for pure decahydrate of sodium carbonate), and hypereutectic field from ~78 °C (for pure trihydrate of sodium acetate) until ~3÷4 ºC in eutectic. In addition to all the mixtures the hypothermia ΔT_S^- with respect to solidus temperature T_S were recorded. Average values of $<\Delta T_S^->$ ranged 3.5 ± 0.5 ºC and didn't depend on prior overheating of the liquid phase ΔT^+. Figure 5 provides a comparative graphs of dependence of hydrothermia from pre-overheating of liquid phase to three compositions: (I), (V) and (XV).

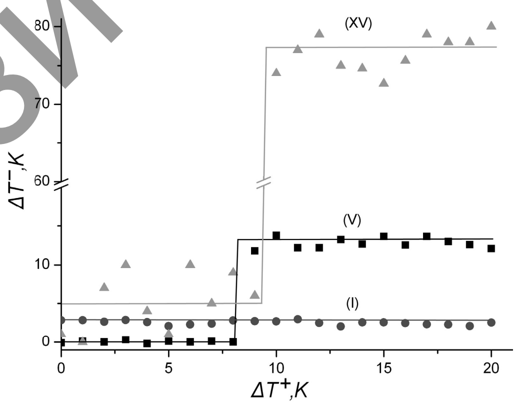
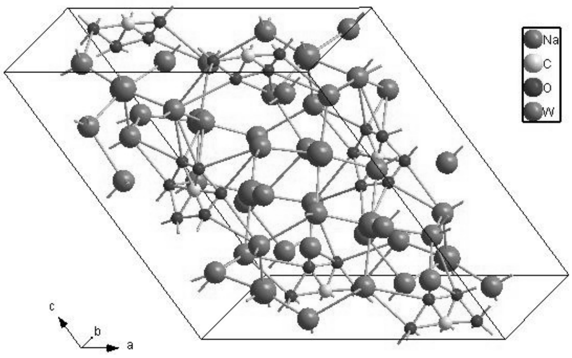


Figure 5. Dependence of hidrotermia from overheating for three compositions KH-10 (I),
the eutectic composition (V), AN-3 (XV)

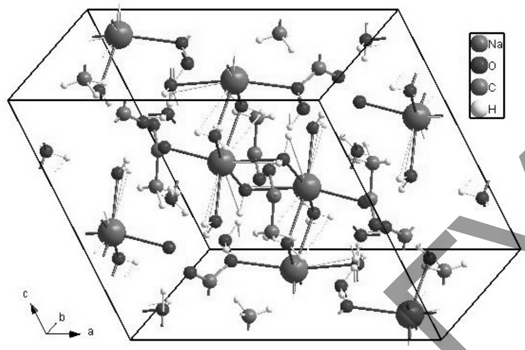
As seen in Figure 4, the eutectic composition has the lowest hydrothermia which doesn't depend on overheating, which makes it more attractive for use as HAM, acting at low temperatures.

Result discussion

The crystal structure of the test substances (Fig. 6) is considered for the interpretation of the results. Both crystalline hydrates have monoclinic type of crystalline lattices [10–11]. According to classical ideas, mixtures of similar substances should lead to the formation of a continuous series of solid solutions. However, in this case two similar crystalline hydrates form mixtures of eutectic type.



a



b

Figure 6. Crystal lattices $Na_2CO_3{\cdot}10H_2O$ (*a*) and $CH_3COONa{\cdot}3H_2O$ (*b*)

Consider the lattice parameters of the crystalline hydrates KH-10 and AN-3 are given in Table 2.

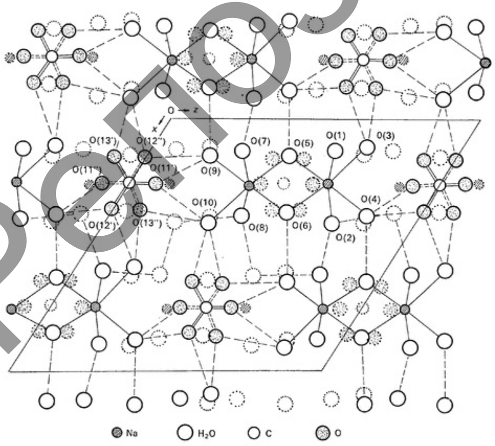
From data shown in Table 2, the difference between the lattice parameters of the KH-10 and AN-3 is not so great. For example, the volume of cells unit difference is only 4.6 %. Same syngony of crystals with similar ratios of parameters of lattices at best could lead to the formation of limited solubility of the components.

Table 2

Crystal lattice parameters of decahydrate sodium carbonate and trihydrate sodium acetate [10–11]

	Lattice type	Coordination number	*a*, Å	*b*, Å	*c*, Å	β, °	V, $Å^3$
KH-10	Monoclinic	4	12,83	9,03	13,44	123	1305,31
AH-3	Monoclinic	4	12,34	10,45	10,41	111,65	1247,8
Parameters differences			4,0 %	13,6 %	29,1 %	10,2 %	4,6 %

The possible reason of formation eutectic mixtures in the system of crystalline hydrates $Na_2CO_3{\cdot}10H_2O$ and $CH_3COONa{\cdot}3H_2O$ can be a significant difference between the structure of molecules, the content of crystallization water in corresponding hydrates, molecular configuration $Na_2CO_3{\cdot}10H_2O$ and $CH_3COONa{\cdot}3H_2O$ and quantities of hydrogen bonds. You can see this if you look at the projections of the lattices of these materials (Fig. 7).



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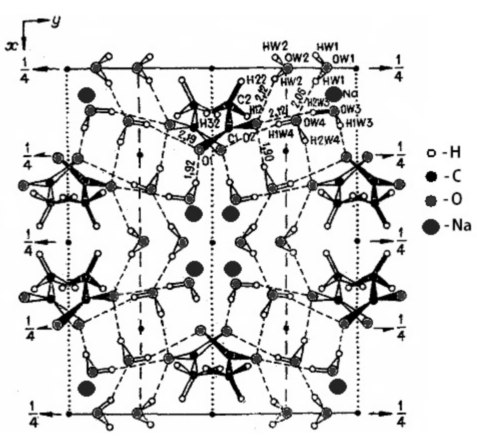

b

Figure 7. Projections of the crystal lattices on the *x–y* plane of decahydrate sodium carbonate (*a*) and trihydrate sodium acetate (*b*). The dotted lines show the hydrogen bonds [10–11]

By incongruent melting of KH-10 and AN-3, there are saturated salt solution Na_2CO_3 and CH_3COONa in their own crystallization water, i.e. their dehydration is by scheme $CH_3COONa·3H_2O → CH_3COONa$ + + $3H_2O$ and $Na_2CO_3·10H_2O → Na_2CO_3 + 10H_2O$. Upon cooling these solutions occurs a reverse process — the water molecules attaching to the respective ions. For solutions in hypoeutectic region dominated Na_2CO_3 molecules, so KN-10 crystals begin to form at the liquidus temperature, and in hypereutectic region AN-3 crystals form, because of the predominance of CH_3COONa molecules. At the same molecules of H_2O in respective crystals form the complex of hydrogen bonds (see dashed lines in Fig. 7). For example, acetate ions form clusters (in the *x–y* plane, four ion into cluster), and methyl groups are oriented inside the cluster, but carboxyl groups are to outward.

With regard to crystallization water in turn to molecular weights of hydrates *M* and components: anhydrous salts of M_1 and water M_2. Their comparison shows (Table 3) that the water amount in the CN-10 is more than water amount of the AN-3 is approximately in 2.6 times. The relative water content in the AN-3 is ~39 %, and RH 10 is ~63 %. The good correlation is observed when comparing these dates with the percentage of AN-3 and KH-10 in the eutectic (~34 wt.% AN-3 + 66 wt.% KH-10).

Table 3

Molecular weights of components of crystalline hydrates, g/mol

Crystalline hydrates	M of hydrate	M_1 of dry salt	M_2 of water	M_1/M	M_2/M	M_1/M_2
$Na_2CO_3·10H_2O$	286	106	180	0,37	0,63	1,70
$CH_3COONa·3H_2O$	136	82	54	0,61	0,39	0,66
Eutectic of 66 wt.% KH-10 + 34 wt.% AN-3	236	98,84	137,16	0,42	0,58	1,40

Having a large amount of total crystallization water in mixtures of KH-10 and AN-3 in the range to ~80 %, which facilitates mobility of molecules of Na_2CO_3, CH_3COONa and H_2O, their association and formation of crystal hydrates, which helps to reduce hypothermia. For example, in the eutectic water content is 58 % in a mixture with crystalline hydrates, and subcooling reaches a minimum value (~3÷4 K). At high concentrations (> 80 %) of AN-3 in the system, the mobility of molecules (especially CH_3COONa) in solution with a low water content creates steric interferences with respect to crystallization and sharply increases supercooling of these solutions, including clean trihydrate sodium acetate.

Conclusion

The phase diagram of two crystalline hydrates: carbonate and sodium acetate is constructed by methods of thermal analysis. The thermal effects of melting and crystallization, and pre-crystallization supercooling of mixtures in the system were investigated. Based on the analysis of the obtained results it is proposed to use a mixture of eutectic composition (66 wt.% of Sodium carbonate + 34 wt % of sodium acetate) as a heat accumulating material.

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Ш.К.Әмерханова, В.Д.Александров, А.Ю.Соболев

$Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$ жүйесінің күй диаграммаларын тұрғызу

Мақалада термиялық сараптама әдісімен $Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$ кристаллогидраттар жүйесінің күй диаграммалары тұрғызылды, олар эвтетикалық типті болды. Эвтектика құрамы: 66 масс.% $Na_2CO_3 \cdot 10H_2O$ + 34 масс.% $CH_3COONa \cdot 3H_2O$. Эвтектикалық температура –11±0,7 ºС. Күй диаграммаларының типін айқындауға қолданылған солидус пен ликвидус сызықтарына қатысты қоспалардың кристалдануы мен балқу энтальпиялары анықталды. Эвтектикалық құрамға жақындау шамасына қарай суытылудың төмендеуі байқалды. Эвтектикалық құрам жылуаккумуляциялық материал ретінде қолданылуға ұсынылды.

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Построение диаграммы состояния системы $Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$

В статье методами термического анализа построена диаграмма состояния в системе кристаллогидратов $Na_2CO_3 \cdot 10H_2O$ – $CH_3COONa \cdot 3H_2O$, которая оказалась диаграммой эвтектического типа. Состав эвтектики: 66 масс.% $Na_2CO_3 \cdot 10H_2O$ + 34 масс.% $CH_3COONa \cdot 3H_2O$. Эвтектическая температура –11±0,7 ºС. Измерены энтальпии плавления и кристаллизации смесей относительно линии ликвидуса и солидуса, которые были использованы для уточнения типа диаграммы состояния. Установлено уменьшение переохлаждений по мере приближения к эвтектическому составу. Эвтектический состав предложен для использования в качестве теплоаккумулирующего материала.

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