Experimental study of thermodynamic properties and phase equilibria in Na_2CO_3 - K_2CO_3 system

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Abstract

Sodium and potassium carbonates and their mixtures are important for different applications, e.g. for latent thermal energy storage, die-casting processes and molten carbonate fuel cells. In this work the phase diagram and thermodynamic properties of Na_2CO_3-K_2CO_3 system were studied by differential thermal analysis, differential scanning calorimetry and high temperature X-ray diffraction. Three carbonate mixtures (56, 25 and 75 mol% of Na_2CO_3) have solid-solid transition in a wide temperature range between 648 K and 823 K. The high temperature XRD analysis has shown that this transition is a continuous process of changing of the unit cell volume without structural changing of the hexagonal lattice. This phenomenon has also been observed on the measured heat capacity curves. The obtained experimental results were compared with calculations performed using the previous thermodynamic datasets. The comparison of these results shows that further thermochemical assessment of this system needs to be performed to achieve better agreement with the available experimental data.

Keywords: phase change materials, potassium, sodium, carbonates, enthalpy increment, heat capacity

Highlights

- Solid-solid phase transition temperatures in Na_2CO_3-K_2CO_3 system have been measured.
- Heat capacity and enthalpy increments of 3 carbonate mixtures (25, 56 and 75 mol% of Na_2CO_3) obtained.
- Continuous solid-solid transition of hexagonal structure was characterized by DSC and XRD.
- New experimental results should be considered for further thermochemical assessments of the Na_2CO_3-K_2CO_3 system.

1. Introduction

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Thermodynamic properties of the Na_2CO_3 – K_2CO_3 system are important for the development of high temperature technologies, e.g. new generation of solar power plants [1-10], die-casting processes [11, 12], and molten carbonate fuel cells (MCFC) [13, 14]. Knowledge on the thermodynamic properties of the carbonate system is helpful for understanding and control of the processes under different conditions (composition, temperature, pressure). According to the CALPHAD methodology the available experimental information (phase equilibria, thermodynamic properties) is used for generation of the thermodynamic dataset containing the proper Gibbs energies for all phases in the system. This system was assessed three times [12, 15, 16], and the corresponding description of liquid and solid phases have been given. In the assessment of Yaokawa et al. [12] the necessity of further experimental study and more adequate thermodynamic description was mentioned because of missing reliable experimental data on transformations concerning solid phases. The existing experimental data on the phase diagram of the Na_2CO_3 – K_2CO_3 system are presented in Fig. 1. The data from different authors [17-19] for solid-liquid transitions in the temperature range from 1000 K to 1200 K are in a good agreement, but this data for solid-solid transitions has considerable discrepancies. For example Reisman [18] using differential thermoanalysis (DTA) and X-ray diffraction (XRD), and Makarov et al. [19] with the method of heating curves found phase transition in the temperature range around 900 K[†]. Later, Christmann et al. [17] has not confirmed this transition by XRD and DTA analysis. Moreover, the discrepancies between the data of Christmann et al. [17] and Reisman [18] and Makarov et al. [19] are observed for solid-solid transition in the temperature range from 400 K to 700 K in the K_2CO_3 reach region. Therefore, the current study aims to perform detailed thermal and calorimetric analyses of the solid phases in the Na_2CO_3 – K_2CO_3 system for further reassessment and improving the thermodynamic database.

[†] These values are omitted in Fig. 1

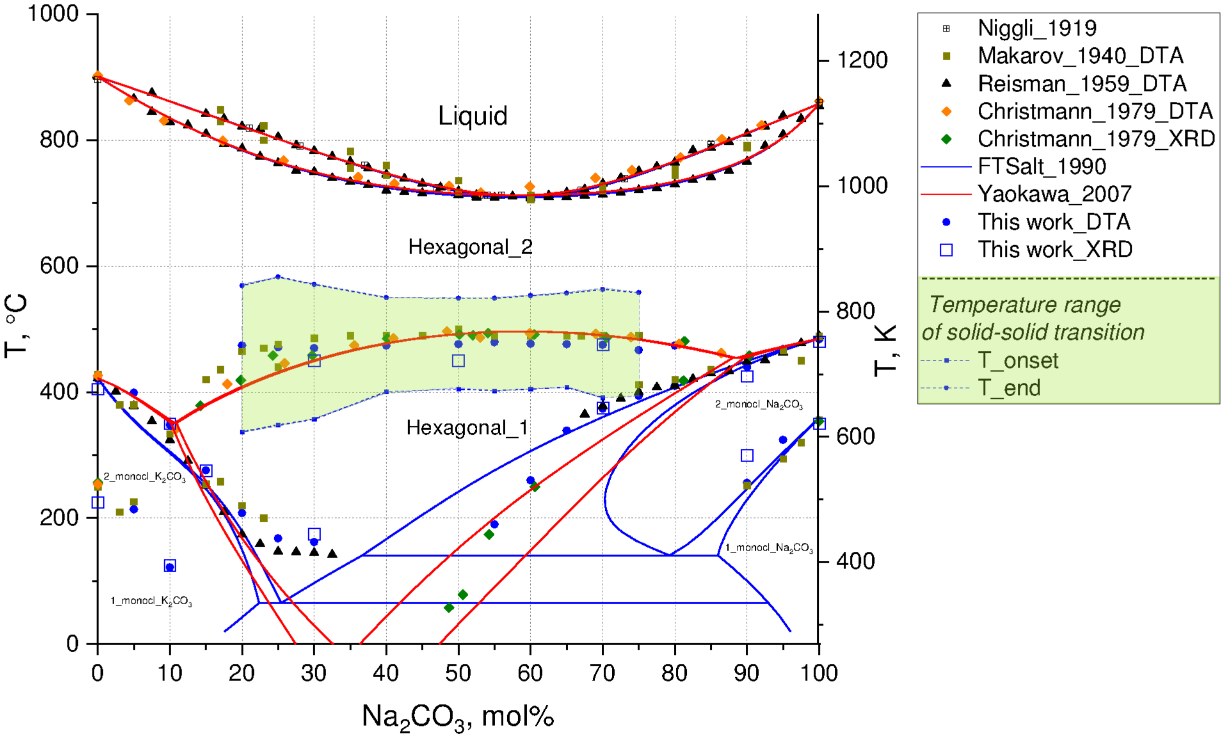

Fig. 1 Phase diagram of the Na_2CO_3-K_2CO_3 system: experimental data from the literature (Niggli - [20], Christmann – [17], Reisman – [18], Makarov – [19]); calculations with the avaiable databases (black lines – calculation with FactSage (FTsalt) [21], red lines – calculations with the data of Yaokawa [12]), and the experimental data obtained by DTA and HTXRD in the present work

2. Experimental

2.1 Samples

The pure compounds Na_2CO_3 (Fluka, anhydrous, 99.9999%) and K_2CO_3 (Aldrich, anhydrous, 99.99%) were used for the preparation of mixtures. The mixtures were synthesized according to the molar fractions with the accuracy of the weighed portion of 0.1 mg in closed platinum tubes with an amount of about 500 mg. The tubes were heated up to 1173 K (900 °C) and held for one hour to prepare the homogeneous mixtures, because both components are melted at this temperature. The homogeneity was confirmed by DTA during heating – cooling cycles. All measurements showed good reproducibility. All manipulations with the samples were carried out in a glove box under dry argon atmosphere.

2.2 Instruments

2.2.1 Differential scanning calorimeter (DSC)

A differential scanning calorimeter DSC 404C Pegasus (Netzsch), Pt-Rh oven (25 °C -1600 °C), and type S thermocouple (Pt/PtRh10%) was used for determining the phase transition temperatures and heat capacity of both solid and liquid phases for the 56 mol% Na_2CO_3-44 mol% K_2CO_3 system. The sample holder with a specific design was used for precise measurements of heat capacity. Temperature calibration was performed with the pure compounds C_6H_5COOH (395 K), $RbNO_3$ (437 K), $KClO_4$ (574 K), Ag_2SO_4 (699 K) and CsCl (749 K). The average temperature deviation was ± 2 K. The same instrument was used for measurements of phase transition temperatures in a DTA mode. The He and Ar atmosphere with gas flow of 15 ml/min was used. No weight loss was detected at temperatures lower than 973 K, which is also related to the vapor pressures of pure substances studied in our previous paper [22].

A differential scanning calorimeter (404 F1 Pegasus®, Netzsch) was used to identify the specific heat capacity of the solid phases in the salt mixture of Na_2CO_3-K_2CO_3 at 75mol% and 25mol% of Na_2CO_3. The sample powder of 30-40 mg, loaded in the platinum pan, is subjected to a heating rate of 20 K/min under nitrogen with a flow of 20 ml/min.

The heat capacity (C_p°, J·mol^{-1}·K^{-1}) of a sample was calculated by the following equation:

$$C_{p(s)}^\circ = \frac{n_r}{n_s} \cdot \frac{DSC_s - DSC_b}{DSC_r - DSC_b} \cdot C_{p(r)}^\circ \,, \qquad (1)$$

where subscripts s – sample, r – reference and b – baseline, n – mole fraction of the substance (mol), DSC – signal of thermopile (μV). $C_{p(r)}^\circ$ of sapphire was taken from the Netzsch database delivered with the software [23]. The standard procedure with three separate steps (baseline, sample and reference) was performed. The mass of the samples was around 45-60 mg. A scanning rate of 10-15 K min^{-1} was chosen according to standard conditions for DSC measurements. At the end, the stability of the baseline was checked with another three runs: sample without baseline, baseline and reference. The measurement precision for sapphire was 0.8 %.

A Calvet-type DSC calorimeter, model mHTC 96 (Setaram), was used for more precise determination of heat capacity of the 56 mol% Na_2CO_3-44 mol% K_2CO_3 mixture. The weight of sample powder was 400-500 mg, which was loaded in the platinum pan. The heating rate of 2 K/min under helium with a flow of 5 ml/min was applied.

2.2.2 High temperature X-ray diffractometry (HTXRD)

An Empryean diffractometer from PANalytical equipped with a Cu-LFF X-ray tube (operated at 40 kV, 40 mA), BBHD mirror, a PIXcel3D detector and a high temperature oven chamber Anton Paar HTK 1200N was used for HTXRD analysis. A continuous flow of synthetic air was applied during the experiment. The lattice parameters and the number of secondary phases were determined through Rietveld refinement using the profile analysis software TOPAS version 4.2 from Bruker AXS. Crystal structures were obtained from the Inorganic Crystal Structure Database (ICSD). The uncertainty for molar volume was estimated to be ±0.02 cm^3/mol and for temperature ±2 K.

3. Experimental results and discussion

3.1 Solid-solid phase transitions in the Na_2CO_3-K_2CO_3 system

The existing experimental data on the phase diagram have considerable discrepancies below the azeotropic equilibria between the liquid and solid phases. The differential thermal analysis (DTA) of the system has been performed to proof the phase diagram. The pure Na_2CO_3 and K_2CO_3 exist in three crystallographic forms. The high temperature phase with hexagonal structure form a continuous solid solution, while the low-temperature modifications of Alk_2CO_3 having monoclinic structure display the limited solubility in the solid state. The enthalpies of these *solid→solid* transitions are relatively low. Therefore, a special sample holder was used for precise measurements of heat capacity. The DTA signal was corrected according to the measured baseline for each sample to reduce the influence of instrumental conditions.

The obtained DTA curves for 18 various compositions are shown on Fig. 2 and the corresponding phase transition temperatures are given in Table 1. These results allow tracking the changes of the phase transitions. More detailed analysis of this data is given in the supplementary material (Part_1), where the reproducibility of the measured heating curves and the selected phase transition temperatures are shown. Additionally, HTXRD analysis for eight compositions was performed. The experimental data are summarized in the supplementary material (Part_2). The selected values of phase transition temperatures are shown in Fig. 1 and in Table 1.

Potassium carbonate transforms from the low temperature modification (space group P21/c) to other monoclinic structure (C2/c) at 526 K, which undergoes at 694 K to the high temperature modifications with hexagonal structure (P63/mmc). The similar transformations are found for sodium carbonate: the first transition between two low temperature modifications with space groups C2/m(α0γ)0s and C2/m occurs at 627 K, the second transformation is at 757 K to the high temperature hexagonal phase P63/mmc. Phase transition temperatures for pure Na_2CO_3 and K_2CO_3 are given in Table 2**Fehler! Verweisquelle konnte nicht gefunden werden.**. Our values obtained by DTA show good agreement with most literature data (Table 2) in the frame of experimental uncertainties of different methods, which confirms the reliability of our results and proves the calibration of the device. Our values obtained by HTXRD analysis show relatively large deviations (28 K and 16 K) in the case of K_2CO_3. The main aim of performing HTXRD analysis was the determination of the structure of existing phases. Furthermore, it is technically difficult to determine exact phase transition temperatures due to the step-wise technique; at each temperature with steps of 5-20 °C a XRD scan should be performed, which is more time-consuming compared to DTA. Therefore, we consider our HTXRD results rather qualitatively for determination of phase structures.

The first transitions of the K_2CO_3 and of the Na_2CO_3 can be seen only in the mixtures within 90% mole fraction of the pure compounds due to the rapid decreasing of enthalpy of these transitions. It should be noted that in the previous studies these transitions were considered only by Makarov at el. [19]. The second transitions of K_2CO_3 and Na_2CO_3 were visible up to 70% and 55% of the pure compounds, respectively. Temperatures of phase transitions from the Na_2CO_3 side have good agreement with the previous studies using DTA [18, 19] and XRD [17]. On the other hand, the XRD data of Christmann [17] regarding the phase transition on the K_2CO_3 side does not agree, neither with our results nor with the DTA data of Makarov and Reisman [18, 19].

One more transition was detected at 750 K with concentration of Na_2CO_3 between 15% and 80%. This transition was related to the formation of the solid solution with hexagonal structure (Hexagonal_1 on Fig. 1), that is located below the continuous solid solution based on the high temperature modifications of both carbonates (Hexagonal_2 on Fig. 1) [17]. This transition has a relatively wide temperature range (up to 175 °C), which is unusual for ordinary first order transition. Therefore, we have obtained three temperatures being “onset”, “peak”, and “end” for this transformation. These values are given in Table 1 (P63/mmc to P63/mmc). Examples of the selected temperatures are shown in the supplementary material (Part_1). The uncertainty for determination of “onset” and “end” temperature is estimated to be 20 K. The uncertainty of the “peak” temperature is 3 K (Table 1), which is based on calibration values of the device (Section 2.2.1) and standard deviation of obtained signals. To represent this wide temperature range of phase transition in the phase diagram (Fig. 1) we decided to show the “peak” temperature as points, which are also in a good agreement with literature data [17] [19] . The “onset” and “end” temperatures are shown as dashed lines and the whole range of this phase transition is highlighted with transparent green color.

The maximum of the enthalpy of this transition corresponds to the mole fraction 55-65% of the Na_2CO_3. Previously this transition was confirmed also by DTA [17, 19] and XRD [17], but in the work of Reisman [18] this transition was found at higher temperature of 883 K. Makarov at el. [19] have also mentioned about exothermal effect at this temperature, but it can be due to impurities in the initial compounds.

Table 1. Phase transition temperatures (in K) in the system Na_2CO_3-K_2CO_3 obtained with DTA[a] and HTXRD[b]

Mol %	P21/c to C2/c		C2/c to P63/mmc		P63/mmc to P63/mmc				C2/m to P63/mmc		C2/m(α0γ) to C2/m	
					Peak		Onset[c]	End[c]				
Na_2CO_3	DTA	XRD	DTA	XRD	DTA	XRD	DTA	DTA	DTA	XRD	DTA	XRD
K_2CO_3	526	498	694	678	-				-		-	
5	487		672		-				-		-	
10	395	398	621	623	-				-		-	
15	-		549	548	748				-		-	
20	-		481		747		610	842	-		-	
25	-		441		744		621	856	-		-	
30	-		435	448	743	723	630	844	-		-	
40	-		-		747		674	823	-		-	
50	-		-		749	723	678	822	-		-	
55	-		463		752		675	822	-		-	
60	-		533		750		678	826	-		-	
65	-		612		749		681	830	-		-	
70	-		647	648	748	748	664	836	-		-	
75	-		-		740		-	831	667		-	
80	-		-		747		-	-	683		-	
90	-		-		-		-	-	713	698	529	573
95	-		-		-		-	-	741		596	
Na_2CO_3	-		-		-		-	-	757	753	627	623

Note: [a] - the standard uncertainty (u) is u(T) = 3 K; [b] - the standard uncertainty (u) is u(T) = 3 K; [c] – estimated temperatures with estimated uncertainty u(T) = 20 K

Table 2. Solid-solid phase transition temperatures (in K) of pure Na_2CO_3 and K_2CO_3

Na_2CO_3		Method	Ref.	K_2CO_3		Method	Ref.
C2/m(α0γ) to C2/m	C2/m to P63/mmc			P21/c to C2/c	C2/c to P63/mmc		
627	757	DTA	This work	526	694	DTA	This work
623	753	HTXRD	This work	498	678	HTXRD	This work
623	767	HTXRD	Ballirano_2011 [24]	526	693	Raman	Maciel_1981 [25]
605	754	HTXRD	Arakcheeva_2005 [26]				
-	754	Neutron Powder Diffr.	Swainson_1995 [27]				
633	753	DTA/ HTXRD	Christmann_1979 [17]	526	696	DTA/ HTXRD	Christmann_1979 [17]
634	762	DTA	Reisman_1959 [18]	-	695	DTA	Reisman_1958 [18]
623	750	DTA	Popov_1951 [23]				
629	759	DTA	Makarov_1940 [19]	523	711	DTA	Makarov_1940
623	752	Database	IvtanThermo [28]	-	693	Database	IvtanThermo [28]
-	723	Database	SGPS [21]	-	693	Database	SGPS [21]
632	758	Database	FactPS/FTsalt [21]	-	695	Database	FactPS/FTsalt [21]
593	723	Database	NIST-JANAF [29]				

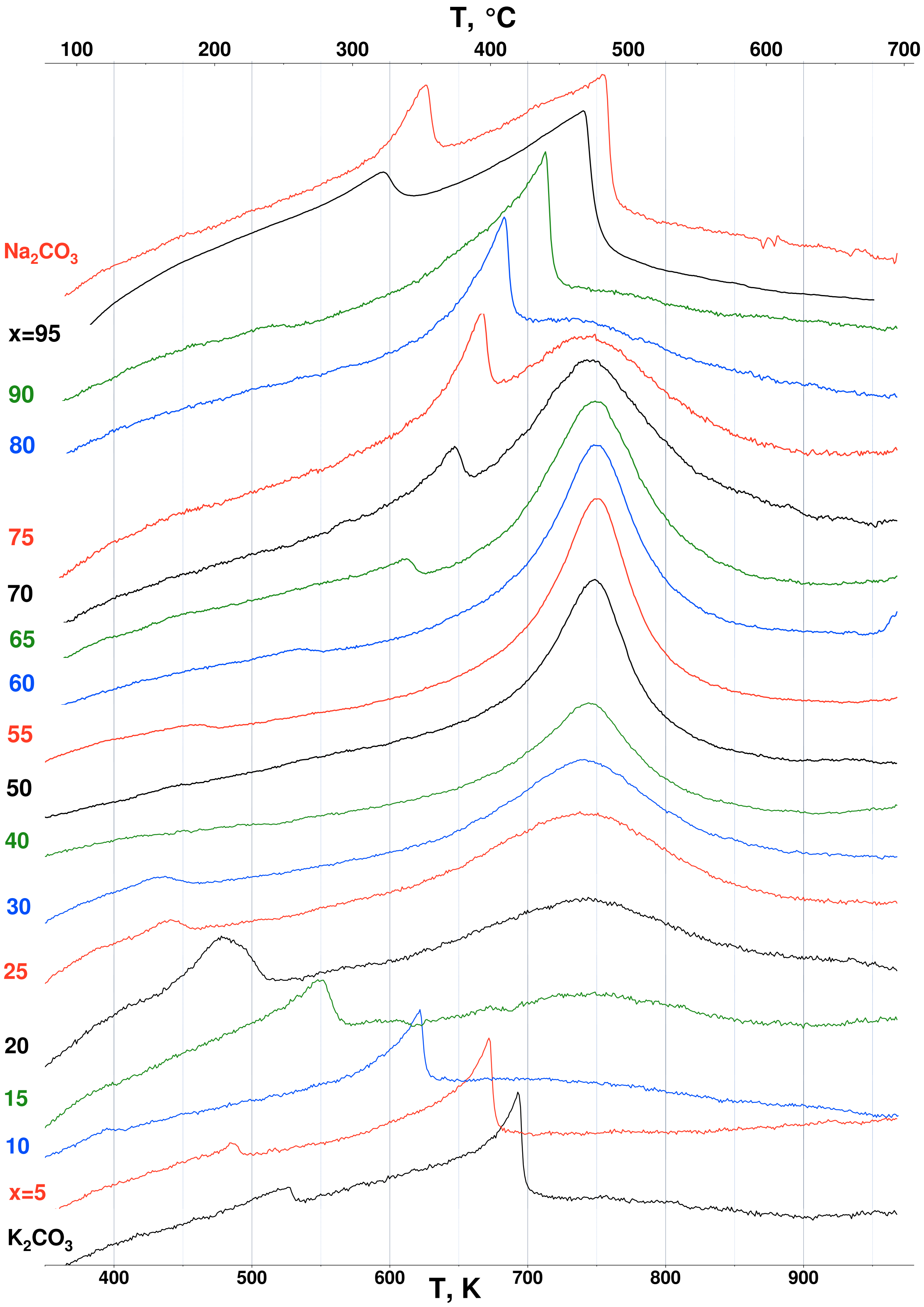

Fig. 2 Heating DTA-curves for various compositions in the Na_2CO_3 – K_2CO3 system

HTXRD analysis was performed for the sample with composition $50Na_2CO_3$-$50K_2CO_3$ in the temperature range from 298 K to 923 K to clarify the type of the phase transition at 750 K. Fig. 3 shows the results of HTXRD measurements. It was found out, that both phases before and after 750 K are hexagonal (space group P63/mmc). The difference between these two phases is only the size of the unit cells. The lattice parameter *a* starts to decrease at around 648 K. At the same temperature parameter *c* was significantly increasing. This changing process was continued until 823 K, which indicates a continuous phase transition in a wide temperature range of 175 K. The same effects were observed on the DTA curves (Fig. 2) for the mixtures between 15% to 80% of Na_2CO_3.

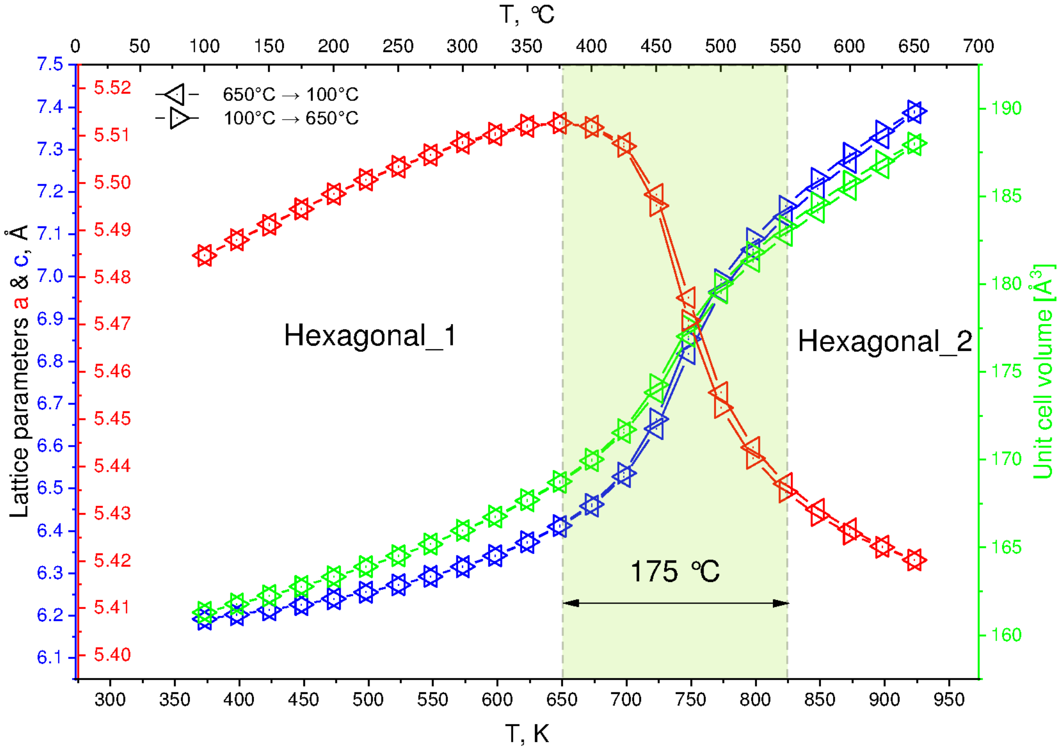

Fig. 3 HTXRD results for the $50Na_2CO_3$ – $50K_2CO_3$ mixture

3.2 Enthalpy increment and heat capacity

The enthalpy increment of $56Na_2CO_3$ – $44K_2CO_3$ mixture was experimentally studied by Janz et al. [30]. These results were compared with the calculations performed using the available datasets from FTSalt database [15, 16, 21] and from the data reported by Yaokawa et al. [12] in Fig. 4. The enthalpy increment of the $56Na_2CO_3$ – $44K_2CO_3$ mixture was not predicted properly by using both datasets (blue and red lines, correspondingly). The difference between the experimental results of Janz et al. [30] and the calculated values are significant. Especially, the evident deviation is observed in the temperature range from 648 K to 823 K, where the continuous phase transition was detected by DTA and XRD in the present work. As a result of these discrepancies the difference between calculations based on the dataset [12] and experimental data [30] at 976 K is 13 kJ/mol (Fig. 4). Also the difference of the fusion enthalpies is significant: the experimental value is 19.7 ± 0.5 kJ/mol [30], the value calculated by Yaokawa is 24.7 kJ/mol [12] and that from FTSalt database is 23.44 kJ/mol. Therefore, the detailed experimental study of enthalpy increment using different methods is necessary for further comparison.

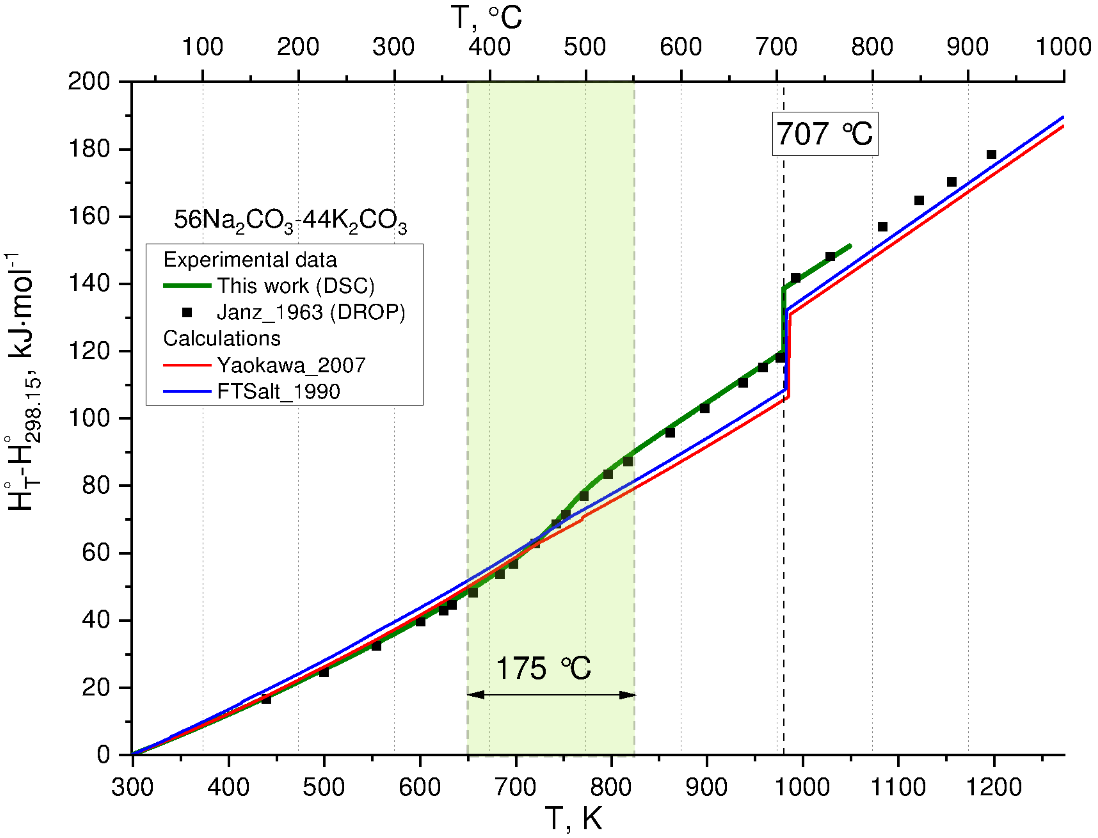

Fig. 4 Enthalpy increment of the $56Na_2CO_3$-$44K_2CO_3$ mixture obtained from the DSC and SHRTA results in comparison with literature data: experiments of Janz_1963 [30]; calculations based on the dataset of Yaokawa_2007 [12] and the commercial database FTSalt_1990 [15, 16, 21]

In the present study, the DSC measurements of the $56Na_2CO_3$-$44K_2CO_3$ mixture were performed to evaluate the experimental results reported by Janz et al.[30] . The heat capacity was measured in the temperature range from 330 K to 1053 K by two different DSC devices described in section 2.2.1 with different heating rates (2 and 15 K/min). The results are shown in Fig. 5. Three phase transitions can be seen: the first and second are related to the *solid→solid* reaction, which occurs at 480 K and in temperature range from 648 K to 823 K, respectively. The comparison of DSC curves obtained at different heating rates demonstrates good agreement, which confirms the reliability of our DSC results at 15 K/min and they can be considered for thermodynamic modelling. The transition at 980 K is related to the *solid→liquid* reaction (melting). The weight loss after heating up to 1073 K was less than 0.1%. The deviation of experimental data is not higher than 5.3% in the temperature range from 330 K to 823 K, while after the second phase transition the deviation is increased up to 10 % at temperatures higher than 823 K. The comparison of calculated heat capacity from the available databases [12, 15, 16] with experimental data shows acceptable agreement, if the part of latent heat of phase transitions is excluded from the consideration. The average value of obtained heat capacity was recalculated to enthalpy increment and compared with the results of Janz et al. [30] (Fig. 4). It shows good agreement in the whole temperature range, which also indicates on the reliability of different experimental techniques with different heating rates (Janz et al. [30] used DROP calorimetry, which assumes heating rate equal 0 K/min). Therefore, it can be concluded that results of the previous assessments [12, 15, 16] cannot be used for accurate prediction of thermodynamic properties of the Na_2CO_3-K_2CO_3 system. A new thermochemical assessment of the system should be performed based on the obtained average heat capacity (Fig. 5 and supplementary material (Table)).

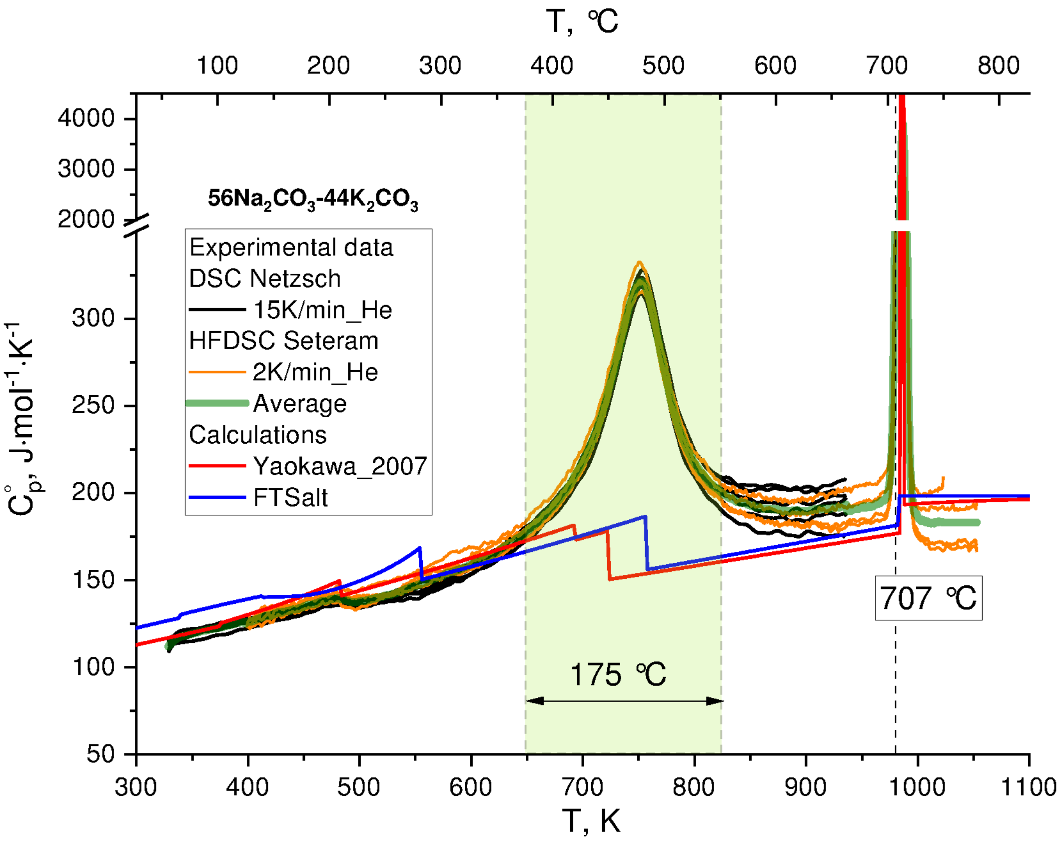

Fig. 5 Heat capacity of the $56Na_2CO_3$-$44K_2CO_3$ mixture measured by two different DSC devices and comparison with calculated heat capacity from the available databases [12, 15, 16]

In the present work, the heat capacity of two additional carbonate mixtures was studied in detail to provide more reliable information about thermodynamic properties in the system. The obtained results of 75 mol% Na_2CO_3-25mol% K_2CO_3 and 25 mol% Na_2CO_3-75mol% K_2CO_3 over the temperature range between 50 °C and 625 °C are presented in Fig. 6 - Fig. 8. The average heat capacity was obtained from the value of 5 or 6 DSC measurements. The average value shows a deviation of less than 5% and 10% with that of experimental values for using 75 and 25 mol % of Na_2CO_3, respectively. The comparison of obtained heat capacity of $75Na_2CO_3$-$25K_2CO_3$ with the calculated data predicted by both available datasets shows better agreement at low temperatures, before the phase transitions in the temperature range from 600 K to 900 K. This phase transformation cannot be reproduced by calculation, as it was shown also on the phase diagram (Fig. 1). After the phase transition the absolute value of calculated heat capacity is 7% lower than experimental values at 880 K.

The DSC results for $25Na_2CO_3$-$75K_2CO_3$ mixture (Fig. 6) show a small sharp peak at the temperature between 150 °C and 220 °C with a maximum temperature of 190 °C. This transition is associated with the solid-solid transition between monoclinic and intermediate phase (hexagonal 1) (Fig. 1). The next wide peak, which starts at 330 °C with a maximum temperature of 480 °C, corresponds to another solid-solid transition from hexagonal 1 to hexagonal 2 (Fig. 1). The similar transitions have been detected for the sample $75Na_2CO_3$ (Fig. 7), but the peak temperatures are closer together in compassion with that measured for $25Na_2CO_3$. These results also agree with DTA measurements obtained in the current work (Fig. 2). The enthalpy increments of the salts at different contents of Na_2CO_3 (75 and 25 mol %) were calculated based on the present measurements of heat capacity in the temperature range between 25 °C and 625 °C and presented in Fig. 9 and Fig. 8, respectively. These data demonstrate better agreement with the calculated results in comparison to the data for the $56Na_2CO_3$-$44K_2CO_3$ mixture. The maximum difference between the calculated enthalpy increment of $75Na_2CO_3$-$25K_2CO_3$ using FTSalt database and the experimental data achieve 10.85% (5.3 kJ/mol) at 658 K and 5.87% (2.9 kJ/mol) between the calculations with the database of Yaokawa [12]. These discrepancies are also related to the uncorrected description of thermodynamic functions of the corresponding phases and, consequently, to inaccurate prediction of solid-solid transitions. In the case of the $25Na_2CO_3$-

$75K_2CO_3$ mixture the deviation is 10.32% (5.1 kJ/mol) at 672 K comparing to FTSalt database and 12.7% (6.25 kJ/mol) comparing to the calculations with dataset by Yaokawa [12].

The comparison of obtained experimental results with existing datasets for the Na_2CO_3-K_2CO_3 system shows, that the larger deviation of enthalpy increment is observed in case of the $56Na_2CO_3$-$44K_2CO_3$ mixture. The main reason for that is an inaccurate description of the corresponding phases and the enthalpy of the continuous solid-solid transition in the temperature range between 648 and 823 K.

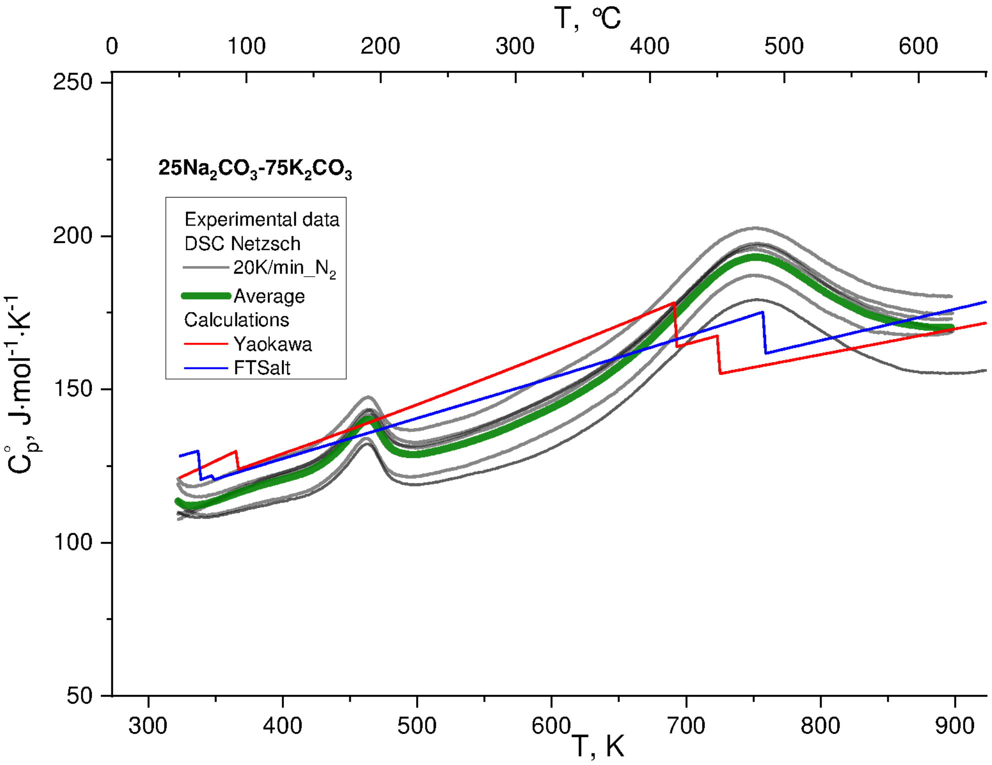

Fig. 6. Experimental results of the heat capacity of solid phase for the 25 mol% Na_2CO_3-$75K_2CO_3$ mixture and comparison with calculated values from the available databases [12, 15, 16]

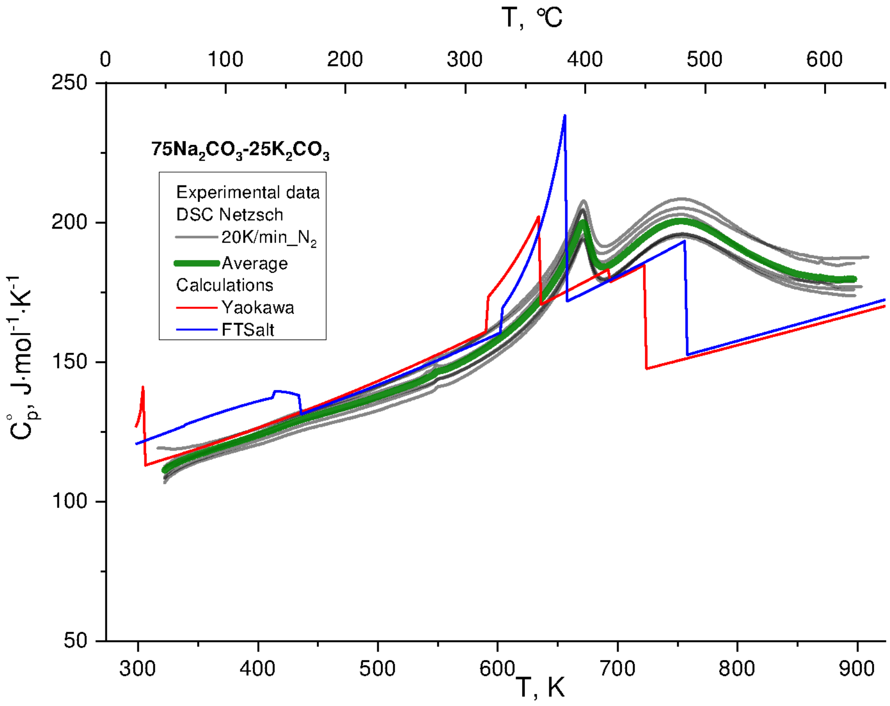

Fig. 7. Experimental results of the heat capacity of solid phase for the 75 mol% Na_2CO_3-25K_2CO_3 mixture and comparison with calculated values from the available databases [12, 15, 16]

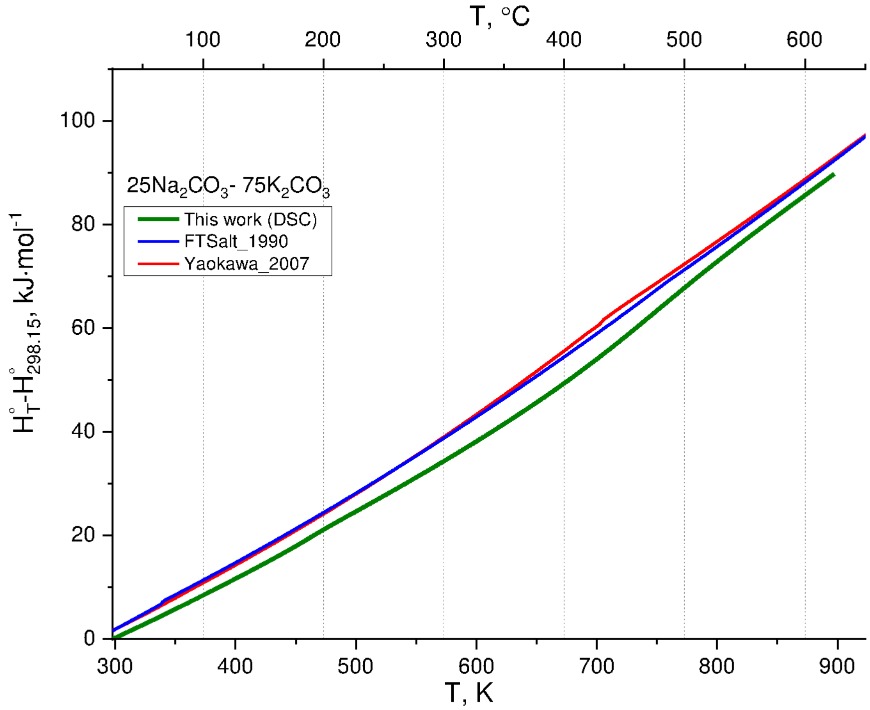

Fig. 8. Experimental results of the enthalpy increment of solid phase for the 25 mol% Na_2CO_3-75K_2CO_3 mixture and comparison with calculated values from the available databases [12, 15, 16]

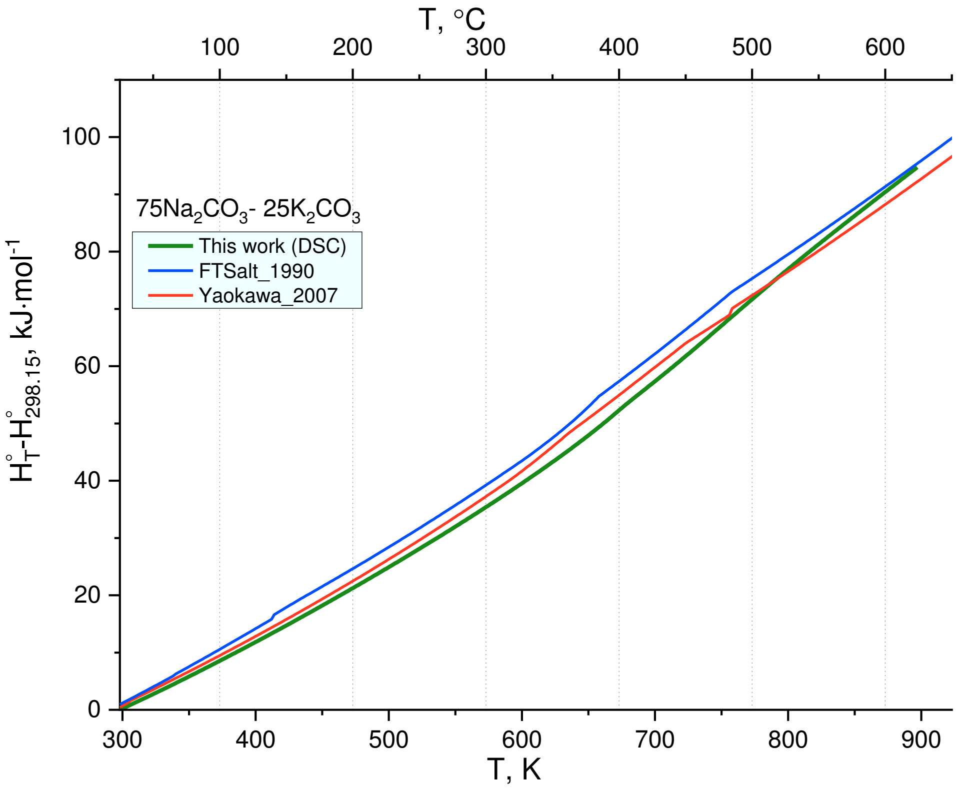

Fig. 9. Experimental results of the enthalpy increment of solid phase for the 75 mol% Na_2CO_3-25K_2CO_3 mixture and comparison with calculated values from the available databases [12, 15, 16]

4. Conclusions

The phase diagram of the Na_2CO_3-K_2CO_3 system and thermodynamic properties of three compositions were studied using DTA, HTXRD and DSC with the purpose to clarify the transformation behaviour of the solid phases. The combination of different methods and devices allowed performing comprehensive analysis of the obtained results. It was found that all three studied compositions have a solid-solid transition in a wide temperature range between 648 K and 823 K. This transition was not characterised previously. High temperature XRD analysis confirms that this transition is a continuous process of changing the volume of the unit cell, but without structural changing of the hexagonal lattice. This phenomenon was not considered in the previous thermodynamic assessments. Therefore, the calculations of enthalpy increment using the existing datasets from the literature [12, 15, 16] cannot reproduce the experimental results. The thermodynamic database containing the description for all phases should be improved in terms of accurate prediction of the solid-solid transformations. The present measured data on the alkali carbonate system are useful for further assessments with the purpose of database improvements.

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Data availability

The raw and processed data required to reproduce these findings are available to download from [supplementary material].

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