



Experimental study and thermodynamic assessment of the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system

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ABSTRACT

In this study, the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system was investigated experimentally and a new thermodynamic dataset for this system was established using the CALPHAD approach. Thermodynamic data from literature were collected and critically analyzed. The phase equilibria of this system were further investigated experimentally by Differential Thermal Analysis (DTA) measurements and High temperature X-ray Diffractometry (HTXRD): three solid solution phases based on three solid modifications of pure Na_2CO_3 were determined. The heat capacity of Na_2CO_3 and the intermediate compound LiNaCO_3 was obtained experimentally by three types of Differential Scanning Calorimeter (DSC) devices. The Gibbs energies of the studied compounds and solutions were evaluated using available literature data together with our experimental results. The new dataset for the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system can improve the accuracy of phase diagram calculations and the prediction of thermodynamic properties for various applications.

1. Introduction

The salt mixtures of the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system have many applications in different fields such as molten carbonate fuel cells [1,2] and thermal storage [3], etc. However, the current commercial databases for this system are neither complete nor sufficiently precise. Therefore, it is necessary to develop a more reliable thermodynamic dataset to enable better utilization of the salt system. The $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system was investigated extensively in the past, when comparing the calculated results from the commercial database FTsalt [4] with the literature data, we found some vulnerabilities in both experimental data and the calculations. For example, a solid solution phase based on the high temperature modification of Na_2CO_3 (called HT) is shown in the phase diagram calculated with FTsalt database, but the corresponding experimental description is lacking in the literature, which might be caused by the lower precision of the previous instruments. For the pure substance Na_2CO_3 , the heat capacity was reported many times in the literature, but there is some inconsistency, the information needs to be checked. Despite of numerous experimental data on the intermediate compound LiNaCO_3 from literature, no thermodynamic information is available in the commercial database and it is lacking in the calculated phase

diagram. Therefore, in the present work Differential Thermal Analysis (DTA) and High temperature X-ray Diffractometry (HTXRD) were used to investigate different compositions in the system and complete the phase diagram. Besides, Differential Scanning Calorimetry (DSC) was used to measure the heat capacity of Na_2CO_3 and LiNaCO_3 . After collecting and analysis of available literature data and own experimental results, the thermodynamic data (standard enthalpy of formation, standard entropy and heat capacity) of the pure substance Na_2CO_3 and intermediate compound LiNaCO_3 was described in the new PCM database [5–7]. The pure substance Li_2CO_3 has already been described in our previous work [8]. Based on the experimental data of the phase diagram and different thermodynamic properties (such as mixing enthalpy and enthalpy increment) from the literature and this work, the Gibbs energy function of the liquid phase and solid solutions in the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system were generated in the new database. Consistent with previous work [5–7], the liquid phase was assessed with the modified associate species model [9], while the solid solutions were described using the sub-lattice model [10].

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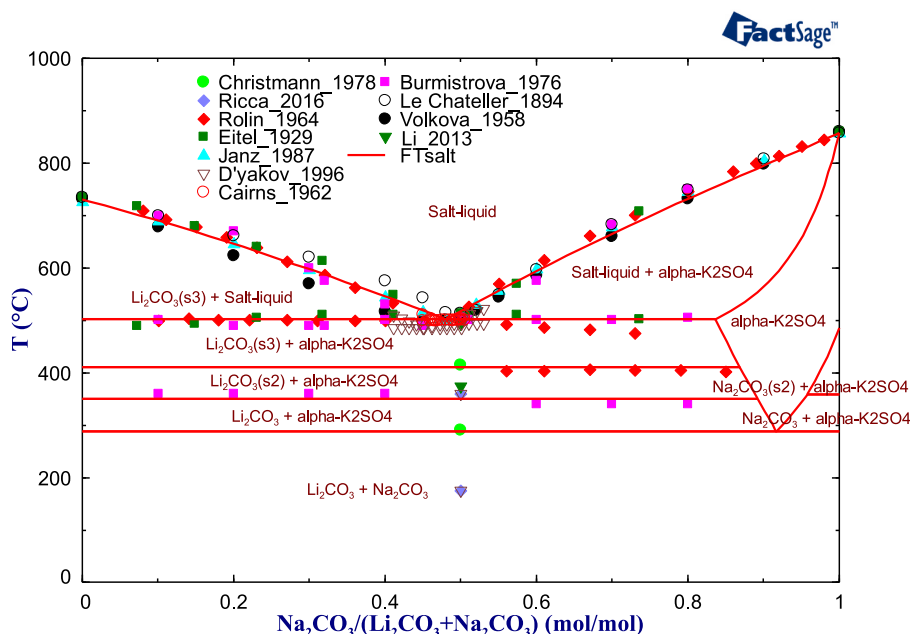


Fig. 1. Comparison of the phase diagram of the Li_2CO_3 - Na_2CO_3 system calculated by FTsalt database with experimental data.

2. Literature data analysis of Li_2CO_3 - Na_2CO_3 system

The system Li_2CO_3 - Na_2CO_3 was investigated extensively in the past [11–21]. The experimental data on the phase equilibria from the literature and calculation using the FTsalt database are summarized in Fig. 1. In the phase diagram, the liquidus lines from different investigators agree well. However, there are different opinions about the type of phase diagram, namely concerning the formation of the intermediate compound LiNaCO_3 and the solid solubilities.

Janz and Lorenz [17] and Rolin and Recapet [16] concluded that this salt system is a simple eutectic system, both the intermediate compound LiNaCO_3 and solid solutions were not considered. According to the measurement of Eitel and Skaliks [19], Burmistrova and Volozhanina [22] and Volkov and Volkova [23], the intermediate compound LiNaCO_3 was considered melting congruently. While LiNaCO_3 was detected melting incongruently in the study of Volkova [18], Volkov and Shvab [24] and D'yakov et al. [25]. Particularly, Cairns and Macdonald [26] measured this system by a highly sensitive ($\pm 0.003^\circ\text{C}$) thermal analysis equipment and confirmed that the intermediate compound LiNaCO_3 melts incongruently.

Dessureault et al. [13] assessed the Li_2CO_3 - Na_2CO_3 system with the quasi-chemical model for the liquid and the sub-lattice model for the solid solution. In their assessment, the existence of LiNaCO_3 was not considered due to the uncertainty of the XRD data obtained before. A solid solution called “alpha- K_2SO_4 ” in FTsalt database based on Na_2CO_3 (high temperature modification, HT) with maximum solubility at 0.88 M fraction of Na_2CO_3 was introduced by the analysis of the slope of liquidus line near Na_2CO_3 and the experimental data of Khlapova and Elenevskaya [27], in which the solubility of Li_2CO_3 in Na_2CO_3 was actually not mentioned. Chen et al. [12] assessed the Li_2CO_3 - Na_2CO_3 system as an eutectic system with the cell model for the liquid phase according to the experimental results from Janz and Lorenz [17] and Rolin and Recapet [16], and in that assessment the solid solubility was not considered. Similar to the assessment of Dessureault et al. [13], the intermediate phase LiNaCO_3 is absent in the commercial FTsalt database and no corresponding thermodynamic data are available in the literature. Besides, the calculated result suggests a solid solution based on Na_2CO_3 (HT) with maximum solubility at 0.84 M fraction of Na_2CO_3 .

When comparing the results calculated using the FTsalt database with the literature data (Fig. 1), uncertainties were observed in both

experimental data and the calculated results. Firstly, the experimental description of the solid solution phase based on Na_2CO_3 (HT) is missing. Additionally, there is only one solid solution based on Na_2CO_3 (HT) introduced in the FTsalt database, while the possible solid solutions based on the medium- and low-temperature modifications, Na_2CO_3 (MT) and Na_2CO_3 (LT), correspondingly, were not considered. It is reasonable, that the solubility based on the lower temperature modifications of Na_2CO_3 can also exist along with the solid solution based on Na_2CO_3 (HT). Therefore, the solubility of Li_2CO_3 in Na_2CO_3 (MT) and Na_2CO_3 (LT) should be checked experimentally.

Additionally, the points shown at around 350°C measured by Burmistrova and Volozhanina [22] as well as the points at around 400°C measured by Rolin and Recapet [16] (see Fig. 1) were explained as the two solid-solid phase transitions of Li_2CO_3 in the FTsalt database. If this is the case, the data points measured by Rolin and Recapet [16] at around 400°C should appear when the composition is close to pure Li_2CO_3 . There is a noticeable temperature difference split by $x(\text{Na}_2\text{CO}_3) = 0.5$ for points shown at around 350°C measured by Burmistrova and Volozhanina [22], which means that they are not raised by the same reaction or phase transition in the phase diagram. According to the assessment of the pure Li_2CO_3 in our previous work [8], the solid-solid phase transitions at around 350°C and 400°C do not exist, so that these phase transition temperatures need to be analyzed further.

In the present work, in order to clarify this contradictory and incomplete information, experimental work was carried out using various experimental techniques, and thermodynamic assessment was done resulting in a new thermodynamic database for the Li_2CO_3 - Na_2CO_3 system.

3. Experimental

3.1. Samples

The pure salts Li_2CO_3 (Acros Organics, 99.999%) and Na_2CO_3 (Fluka, 99.9999%) were used for preparing samples for all the measurements. Li_2CO_3 was purified in CO_2 gas at 650°C for 1 h before the experiment. All samples were weighed in a glove box under a dry argon atmosphere. LiNaCO_3 samples for HTXRD were prepared by melting Li_2CO_3 and Na_2CO_3 in a 1:1 M ratio in a furnace at 550°C and grinding them to a powder with a mortar and pestle in a glove box after cooling to room

Table 1

All information of samples.

Composition (Na ₂ CO ₃ in molar fraction)	Method
0.5 (LiNaCO ₃ , sample 1)	DSC, HTXRD, DTA
0.5 (LiNaCO ₃ , sample 2)	DSC
0.975	HTXRD, DTA
0.4, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95	DTA
1 (Na ₂ CO ₃)	DSC, HTXRD

Table 2

Parameters of DSC devices.

Instrument	DSC 404C-HT	DSC 404C-LT	mHTC 96
Company	Netzsch	Netzsch	Setaram
Temperature range	25-1600 °C	-180-650 °C	25-1400 °C
Atmosphere	He, 10 ml/min	He, 10 ml/min	He, 10 ml/min
Heating rate for LiNaCO ₃	20 K/min	20 K/min	4 K/min
Heating rate for Na ₂ CO ₃	15-20 K/min	15-20 K/min	2 K/min

Table 3Comparison of lattice parameters of α_1 and α_2 at room temperature.

Phase	a, Å	b, Å	c, Å	α , °	β , °	γ , °	Reference
α_1	14.30	14.30	3.32	89.21	91.66	119.98	This work
α_2	14.30	14.30	3.32	88.42	91.68	119.94	This work
α	14.265	14.261	3.305	88.41	91.7	119.95	Ricca et al. [28]
α	14.28	14.29	3.31	89.00	91.70	120.00	Yatsenko et al. [29]
α	14.27	14.27	3.31	88.41	91.70	119.95	Yatsenko et al. [30]

temperature. Because the LiNaCO₃ samples always show extra Li₂CO₃ (which is called sample 1), sample 2 was prepared with extra Na₂CO₃ with the molar ratio 0.49:0.51 (Li₂CO₃:Na₂CO₃). All the information of different samples used in this work are listed in Table 1.

3.2. Differential thermal analysis (DTA)

STA 449F3 Jupiter (Netzsch) was used to measure the phase transformation temperatures of the mixtures in the Li₂CO₃-Na₂CO₃ system. In order to obtain reproducible data, each sample was heated and cooled at 5 K/min for three cycles. The phase transition temperatures retrieved from the third cycle was used for the description of the phase diagram. A CO₂ atmosphere was used to inhibit carbonate decomposition, with a gas flow rate of 20 mL/min. The measurements were carried out in Al₂O₃ crucibles, calibrated using pure metals (In, Sn, Bi, Zn, Al, and Ag). After calibration using standard reference materials, the temperature uncertainty was estimated to be within ± 3 K.

3.3. Differential scanning calorimetry (DSC)

Three types of DSC devices (Netzsch 404C-HT, Netzsch 404C-LT and Setaram mHTC 96) were used to measure the heat capacity of LiNaCO₃ and Na₂CO₃. The parameters of the devices are introduced in Table 2. Pt crucibles were used for the C_p measurement of Na₂CO₃, while Pt crucibles with Al₂O₃ liner were used for LiNaCO₃. The determination process of the heat capacity was introduced in details in the previous work [8]. The heat capacity $C_p(T)$ was obtained according to the following Eq. (1):

$$C_p(T) = \frac{HF_{sample} - HF_{blank}}{HF_{ref} - HF_{blank}} \cdot \frac{Mass_{ref}}{Mass_{sample}} \cdot C_{p,ref}(T), \quad (1)$$

where HF_{sample} is the heat flow of the sample, HF_{blank} is the heat flow of the empty crucible as baseline, HF_{ref} is the heat flow of the reference

material sapphire, $Mass_{ref}$ is the mass of the reference material sapphire, $Mass_{sample}$ is the mass of the sample and $C_{p,ref}(T)$ is the heat capacity of the reference material sapphire.

3.4. High temperature X-ray diffractometry (HTXRD)

High temperature XRD was used to detect the phase change temperatures during the heating and cooling process and determine the crystal structure of different phases. The EMPYREAN (Malvern Panalytical, Almelo, Netherlands) diffractometer and Cu LFF X-ray tube (operated at 40 kV and 40 mA) was applied for the measurement in this work. For the composition 0.975 Na₂CO₃-0.025 Li₂CO₃ (molar ratio), the measurement was carried out over the temperature range 25-650 °C with 2 cycles of heating and cooling in synthetic air (continuous flow of 10 ml/min). Heating and cooling rate was 2 K/min. Two types of temperature steps were applied: (i) measurements of 5 min at every 5 K (20 range: 10–80°, step size: 0.0263°, time per step: 0.1 s), and (ii) measurements of 5 min and 22.5 min at every 25 K (20 range: 5–90°, step size: 0.0131°, time per step: 0.2 s). The short 5-min measurements every 5 K replaced the dwell time before long measurements and helped to identify narrower temperature ranges for phase changes, while the long measurements provided more accurate lattice parameters. The lattice parameters were determined with Pawley fits using the β -Na₂CO₃ space group C2/m for the low temperature modifications (Software used: TOPAS V6, Bruker AXS). For the composition LiNaCO₃, the measurement conditions were identical to the composition 0.975 Na₂CO₃-0.025 Li₂CO₃ with the exception of the 450 °C maximum temperature.

4. Thermodynamic modelling

4.1. Description for stoichiometric compounds

The thermodynamic data (standard enthalpy of formation $\Delta H_{298,f}^0$, standard entropy (S_{298}^0) and heat capacity) of Li₂CO₃ has already been described in the PCM database based on the literature data and own experimental results in our previous work [8]. In this work, the thermodynamic function of Na₂CO₃ and LiNaCO₃ is assessed according to the measured heat capacity data by DSC as well as the available data from literature. The heat capacity of stoichiometric compounds are represented by power series in T (K), as given in Eq. (2).

$$C_p = A + B \cdot T + C \cdot T^{-2} + D \cdot T^2 + E \cdot T^3 + \quad (2)$$

4.2. Description for solutions

The liquid solution phase (Liquid) is described with the modified associate species model [9] and the Gibbs energy is shown in Eq. (3) including the terms of pure substances, ideal-mixing and excess Gibbs energy. The latest term is expressed with the Redlich-Kister polynomial. $L_{ij}^{(v)}(T)$ is the empirical coefficient related to the interactions between pure components i and j . Consistent with the previous works on the salt systems [5,31], pure liquid Alk₂CO₃/1.5 (Alk = Na, Li) are considered as solution components without any additional associate. The stoichiometry of carbonates was modified in accordance with Besmann and Spear [9] where the stoichiometry of the end-members is chosen in order to obtain two non-oxygen atoms per formula unit, allowing equal weighting with regard to each species ideal entropic contribution. The interaction parameters between these species are introduced for description of the non-ideal mixing properties of the solution.

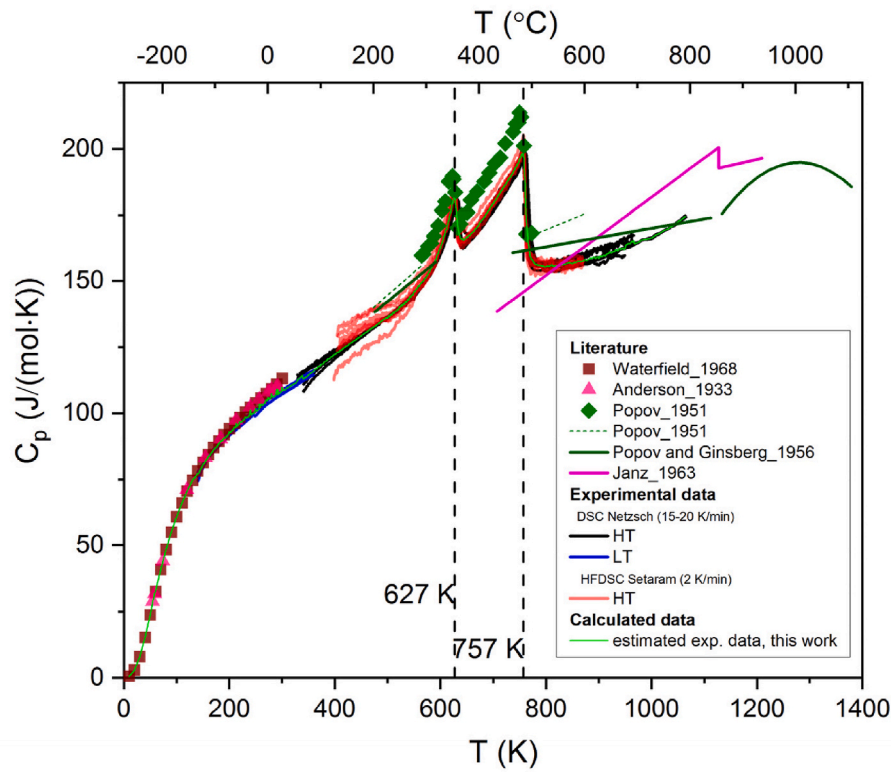


Fig. 2. Experimental data of the heat capacity of Na_2CO_3 .

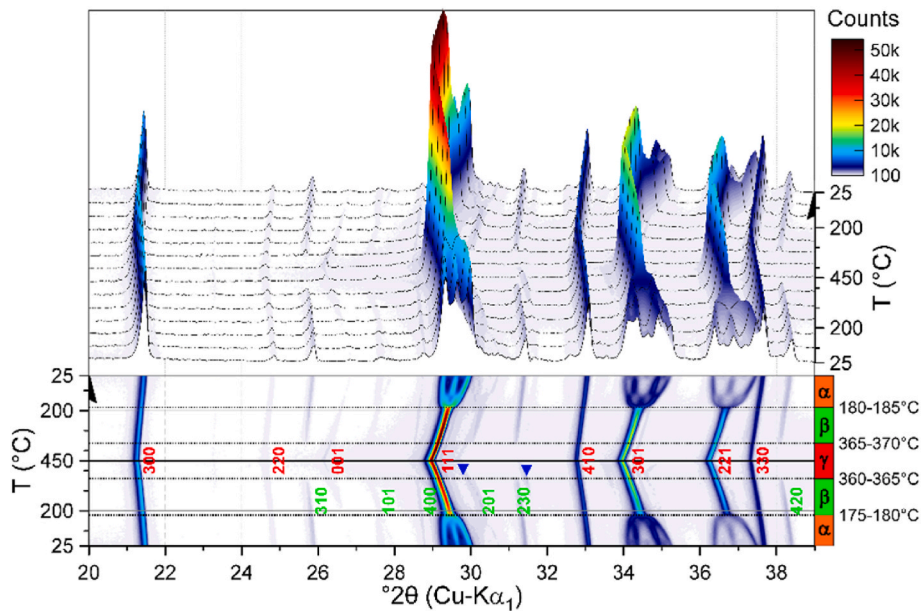


Fig. 3. HTXRD result of the composition $0.5\text{Na}_2\text{CO}_3\text{-}0.5\text{Li}_2\text{CO}_3$.

$$G_m(T, x_i) = \sum_i^n x_i \sum_i^n x_i^0 G_i + RT \sum_i^n x_i \ln x_i + \sum_i \sum_{j < i} x_i x_j \sum_{v=0}^{n_{ij}} L_{ij}^{(v)}(T) (x_i - x_j)^v \quad (3)$$

Three solid solution phases based on three solid modifications of Na_2CO_3 were detected experimentally in the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ system and introduced in the database. HEXA, MONA, and MOLT correspond to the solid solution phases based on the high-, medium- and low-temperature

modifications of Na_2CO_3 , respectively. The names of phases relate to their crystallographic structure, hexagonal and monoclinic. All solid solutions are described using the formula $(\text{Na}^{1+}, \text{Li}^{1+})_2(\text{CO}_3^{2-})_1$. The sublattice model [10] was used to describe these solid solutions, the Gibbs energy of solutions is shown in Eq. (4), the molar excess Gibbs energy is expressed by Redlich-Kister polynomial in Eq. (5), where the interaction parameter between cations on the first sublattice are described using Eq. (6).

Table 4

Phase transition temperatures in the system $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ obtained by DTA, HTXRD and DSC.

Na ₂ CO ₃ , Molar fraction	T, C							source
	1	2	3	4	5	6	7	
0.4	-	-	364	-	498	-	541	DTA
0.5	-	-	363	405	497	-	-	DTA
	180- 185	-	365- 370	-	-	-	-	HTXRD
	170	-	360	-	-	-	-	DSC
0.6	-	-	373	407	500	-	597	DTA
0.7	-	337	366	403	498	-	678	DTA
0.75	-	338	370	405	491	-	714	DTA
0.8	-	336	367	404	476	560	746	DTA
0.85	-	339	367	404	460	612	776	DTA
0.9	-	335	-	402	410	693	799	DTA
0.95	-	335	-	398	433	774	838	DTA
0.975	-	339	-	-	462	819	853	DTA
Na ₂ CO ₃	-	330	-	-	450	-	-	HTXRD
	-	354	-	-	480	-	-	DTA [46]
	-	350	-	-	480	-	-	HTXRD [46]

Table 5

Transition data of Na_2CO_3 .

Reaction	Reaction type	Temperature of transition			Heat of transition			
		T _{tr} , °C (K)	method	Reference	ΔH _{tr} , kJ/mol	Reference		
Na ₂ CO ₃ (LT) ↔ Na ₂ CO ₃ (MT)	solid↔solid	290-365 (563-638)	calorimetry	Popov 1951 [30]	0.368	in CO ₂ atmosphere		
		361 (634)	DTA	Reisman 1959 [31]				
		350 (623)	DTA	Billhardt 1969 [32]				
		360 (633)	DTA	Ovechkin et al., 1971 [33]				
		360 (633)	HTXRD	Christmann and Papin 1979 [34]				
		332 (605)	estimation	Arakcheeva 2005 [35]				
		350 (623)	HTXRD	Ballirano 2011 [36]				
		359 (632)	database	FactPS				
		350 (623)	HTXRD	Sergeev et al. [46]				
		354 (627)	DTA	Sergeev et al. [46]				
		354 (627)	database	This work	1.781	This work		
		430 (703)	DTA	Amadori 1912 [37]	2.09	in CO ₂ atmosphere		
		356 (629)	DTA	Makarov and Shulgina 1940 [38]				
		477 (750)	calorimetry	Popov 1951 [30]			T _{tr} – max of peak	
		489 (762)	DTA	Reisman 1959 [31]				
440-460 (713-733)	Drop	Rolin and Recapet 1964 [39]						
480 (753)	DTA	Billhardt 1969 [32]						
485 (758)	DTA	Ovechkin et al., 1971 [33]						
Na ₂ CO ₃ (MT) ↔ Na ₂ CO ₃ (HT)	solid↔solid	480 (753)	HTXRD	Christmann and Papin 1979 [34]	2.09	in CO ₂ atmosphere		
		481 (754)	Neutron diffraction	Swainson et al., 1995 [40]			Suggest the second order transformation	
		481 (754)	estimation	Arakcheeva 2005 [35]				
		494 (767)	HTXRD	Ballirano 2011 [36]				
		450 (723)	database	SGPS				0.69
		485 (758)	database	FactPS	2.536	FactPS		
		480 (753)	HTXRD	Sergeev et al. [46]	3.651	This work		
		484 (757)	DTA	Sergeev et al. [46]				
		484 (757)	database	This work				
		854 (1127)	DTA	Amadori 1912 [37]				
		854 (1127)	DTA	Reisman 1959 [31]				
		Na ₂ CO ₃ (HT) ↔ Na ₂ CO ₃ (Liq)	melting	856 (1129)	DTA	Ovechkin et al., 1971 [33]	28.03 ± 0.84	Janz et al. [45]
				858 (1131)	DTA	Tegman and Warnqvist 1972 [41]		
				860 (1133)	HTXRD	Christmann and Papin 1979 [34]		
				858 (1131)	Drop	Janz et al. [45]		
858 (1131)	Drop			Rolin and Recapet [42]				
850 (1123)	database			SGPS	29.664	SGPS		
858 (1131)	database			FactPS	29.665	FactPS, used in this work		

$$G_m(T, y_i) = y_{\text{Na}^{1+}}^i {}^0G_{\text{Na}_2\text{CO}_3} + y_{\text{Li}^{1+}}^i {}^0G_{\text{Li}_2\text{CO}_3} + 2RT(y_{\text{Na}^{1+}}^i \ln y_{\text{Na}^{1+}}^i + y_{\text{Li}^{1+}}^i \ln y_{\text{Li}^{1+}}^i) + G_m^{\text{ex}} \quad (4)$$

$$G_m^{\text{ex}} = y_{\text{Na}^{1+}}^i y_{\text{Li}^{1+}}^i \sum_{k=0}^{n_{ij}} L_{\text{Na,Li:CO}_3}^{(k)}(T) (y_{\text{Na}^{1+}}^i - y_{\text{Li}^{1+}}^i)^k \quad (5)$$

$$L_{\text{Na,Li:CO}_3}^{(k)} = A + BT + CT \ln(T) + DT^2 + ET^3 + F/T \quad (6)$$

In the above Equations, G_m is the Gibbs energy of solution phases, x_i (y_i) and ${}^0G_i^{\text{ref}}$ means the molar fraction (site fraction) and Gibbs energy of the solution component i , R is the molar gas constant, T is the temperature in Kelvin. The term of ${}^0G_{\text{Na}_2\text{CO}_3}$ is the Gibbs energy of the corresponding modification of solid sodium carbonate without any modifications, whereas the value ${}^0G_{\text{Li}_2\text{CO}_3}$ is related to the Gibbs energies of lithium carbonate and was optimized along with the interaction parameters ($L_{\text{Na,Li:CO}_3}^{(k)}$) for all solid solutions according to the phase diagram information in the system $\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3$.

4.3. Assessment of Gibbs energy parameters

The assessment of the binary system was performed using available

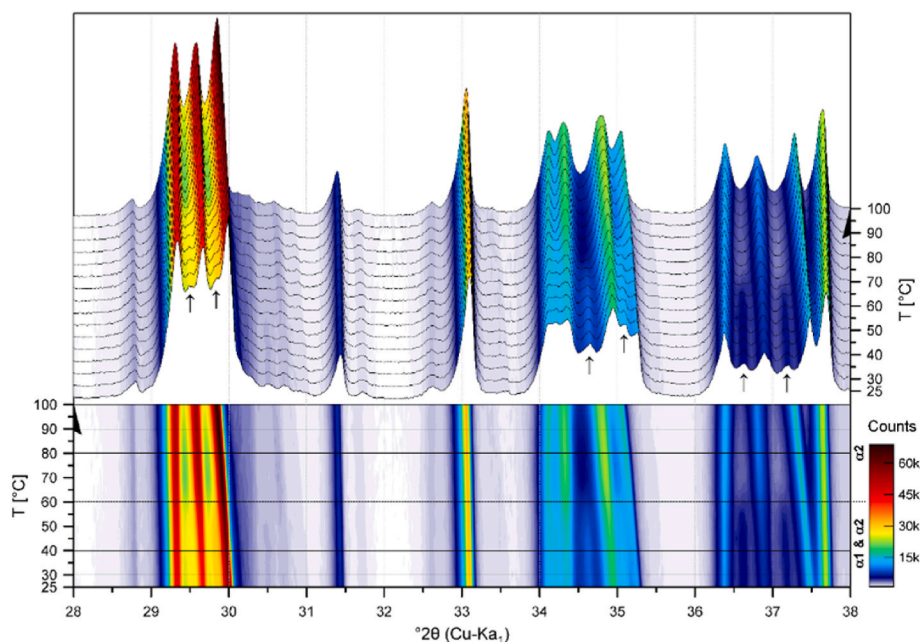


Fig. 4. HTXRD result of the LiNaCO_3 in the temperature range of 25–100 °C.

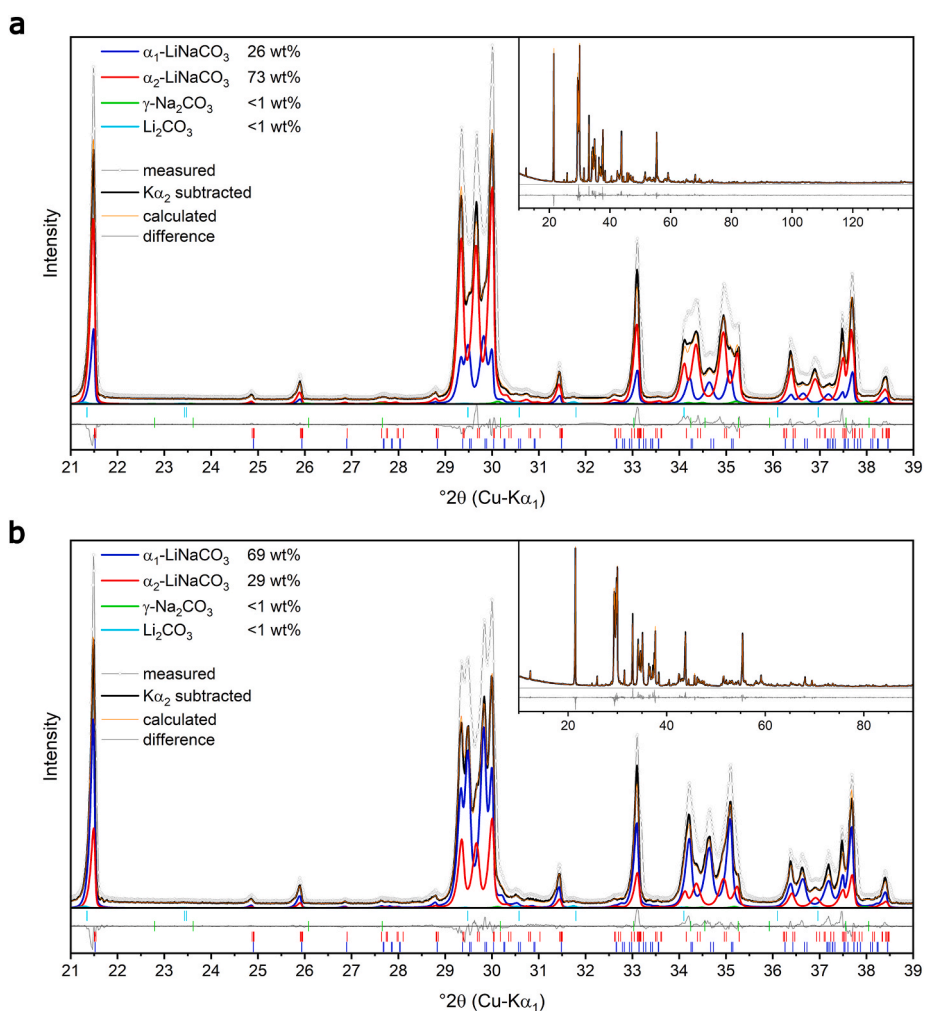


Fig. 5. XRD patterns of LiNaCO_3 a) in initial state and b) after HTXRD measurement.

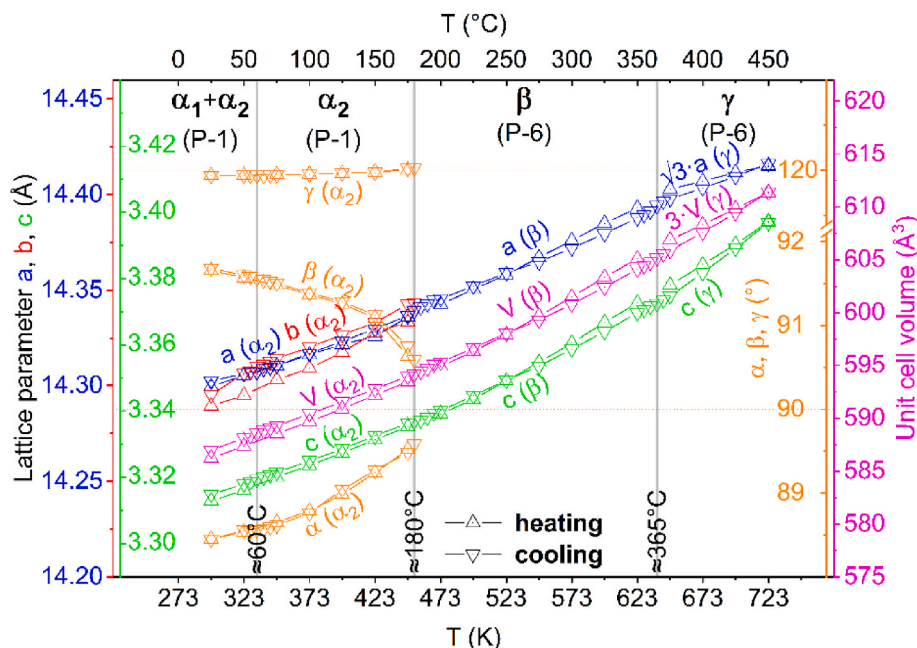


Fig. 6. Temperature dependence of lattice parameters of LiNaCO_3 .

experimental information on the phase diagrams and thermodynamic properties (mixing enthalpy, enthalpy increment). The standard enthalpy of formation and the standard entropy, ΔH_{298}^0 , S_{298}^0 of the intermediate compound and end-members of the solution phases as well as the various binary interaction parameters $L_{ij}^{(v,k)}$ between species both in the liquid and solid solutions were optimized. The C_p functions of pure compounds were assessed before the optimization and kept constant. The introduction of non-ideal interactions between the solid respectively liquid solution components Na_2CO_3 and Li_2CO_3 was required in order to obtain correct representations of the solubility regions. Under these conditions, a satisfactory description of the solid solutions could be obtained. The optimization of the chosen solution parameters based on the available experimental data including own measurements was performed using the optimizer module OptiSage included in the FactSage software [32].

5. Results and discussion

5.1. Experimental

5.1.1. Na_2CO_3

The crystal structure and phase transition temperature of Na_2CO_3 was studied extensively in the past [33–45]. In our previous work, DTA and HTXRD were used for the determination of the crystal structure and phase transition temperature of Na_2CO_3 [46], and the vaporization behavior was studied [47]. According to the literature, Na_2CO_3 exhibits three distinct crystallographic modifications: a low-temperature monoclinic phase (space group C2/m ($\alpha 0\gamma$)), which undergoes a phase transition to a second monoclinic structure (C2/m) at 627 K, and subsequently to a high-temperature hexagonal phase ($\text{P6}_3/\text{mmc}$) at 797 K. These phases are conventionally designated as Na_2CO_3 (LT), (MT), and (HT), respectively. The transition information is summarized in Table 5.

The heat capacity of Na_2CO_3 was reported by different authors [33, 45, 48–50] (See Figs. 2 and 12). It was measured by Anderson [48] and Waterfield et al. [49] at low temperatures (from 55 K to 290 K, from 10 K to 300 K, separately) and by Popov et al. [33], at high temperatures (from 473 K to 873 K) using calorimetry. It was found out that Na_2CO_3 has two reversible polymorphic transformations in the temperature range from

563 K to 773 K with the maximal temperatures at 623 K (estimated enthalpy of transition 0.84 kJ/mol) and 750 K (1.88 kJ/mol) [33]. In the temperature range 750–850 K, there are heat capacity data from estimated equations by Popov et al. [33], Popov and Ginzburg [50] and Janz et al. [45], but they are not consistent with each other. Therefore, new heat capacity measurements are necessary to obtain more reliable data.

In the present work, the heat capacity of Na_2CO_3 was measured using three DSC devices (140 – 360 K with 404C_LT, 340 – 1060 K with 404C_HT, and 400 – 870 K with mHTC 96). The obtained results are compared with literature data in Fig. 2. The two peaks at 627 K and 757 K in the C_p curves correspond to solid–solid phase transitions, as reported by Popov et al. [33]. These peaks originate from the transition enthalpies associated with the phase transformations. A good agreement is achieved between the results obtained from 404C_HT and mHTC 96, both of which are lower than the experimental values reported by Popov et al. [33] during the two reversible polymorphic transformations. There is a smooth transition between the measurement data of 404C_HT and 404C_LT, i.e., the data are consistent in the overlapping temperature range (340–360 K). Besides, the data from DSC 404C_LT are in good agreement with the literature data from Anderson [48] and by Waterfield et al. [49], especially in the lower temperature range. In the temperature range from 400 K to around 500 K, the results obtained with mHTC 96 device exhibit uncertainties of $\pm 8 \text{ J}/(\text{mol}\cdot\text{K})$. Outside this range, the average uncertainty is approximately $\pm 4 \text{ J}/(\text{mol}\cdot\text{K})$. The overall relative uncertainty is estimated to be about 4%. The estimated experimental data was taken from the average of the measured data in this work and the experimental data from Anderson [48] and by Waterfield et al. [49], which was used for the assessment of the heat capacity polynomials.

5.1.2. LiNaCO_3

As mentioned in Section 2, although the intermediate compound LiNaCO_3 was not considered in the commercial database FTSalt, it was reported extensively in the literature. The structure of LiNaCO_3 at room temperature was determined by Eitel and Skalijs [19] by XRD. Due to the poor formation of the crystal faces, it was assumed to be probably hexagonal. Christmann et al. [51] measured LiNaCO_3 with high temperature XRD and reported three solid phases from low temperature to high temperature: α phase (monoclinic, 25–290 °C), β phase (hexagonal,

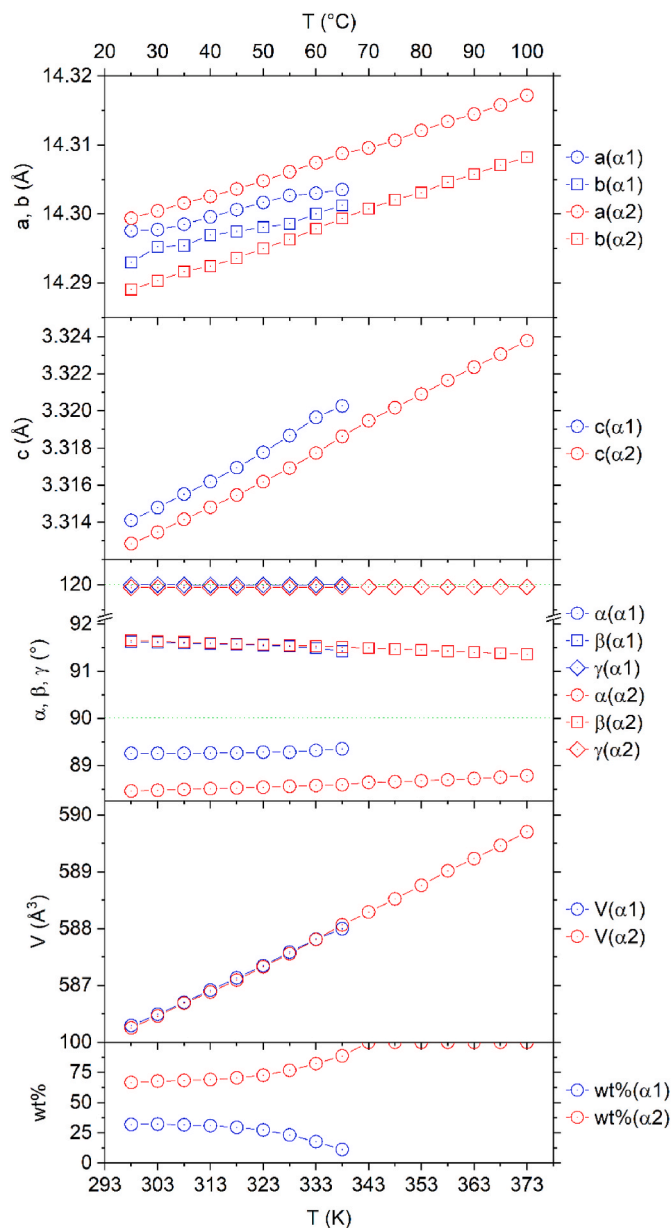


Fig. 7. Lattice parameters of LiNaCO_3 in the temperature range of 25–100 °C.

290–415 °C) and γ phase (hexagonal, 415–500 °C). Yatsenko et al. [29, 30] investigated the crystal structures of α phase (triclinic, 25–175 °C) and β phase (hexagonal, 175–360 °C) by XRD with single crystal samples. Zhukov et al. [52] confirmed the crystal structures of γ phase (hexagonal, 360–500 °C). D'yakov et al. [25] detected two solid-solid phase transitions of LiNaCO_3 at 175 °C and 360 °C by DTA. Li and Zhang [53] measured one solid-solid transition at 373 °C by DTA.

In this work, the phase transition temperatures of LiNaCO_3 were determined using DTA, DSC, and HTXRD measurements. The crystal structures were analyzed by XRD/HTXRD, and the heat capacities were measured by DSC. The DTA results are discussed in Section 5.1.3.

The HTXRD results of LiNaCO_3 are shown in Fig. 3 ($\text{K}\alpha_2$ peaks and background were removed, and the intensity is in square root scaling for clarity). Three solid phases with different structures from low temperature to high temperature were detected, i.e., α phase (triclinic), β phase (hexagonal) and γ phase (hexagonal), respectively. The solid-solid phase transition temperatures were measured to be 180–185 °C and 365–370 °C from HTXRD, which are consistent with the corresponding DTA and DSC data listed in Table 4. The results obtained in this work are in

good agreement with the measurements reported by Yatsenko et al. [29, 30] and Zhukov et al. [52]. All phase transition temperatures of LiNaCO_3 are listed in Table 8. The results from Christmann et al. [51] deviate significantly from the other data, therefore, it was not taken into consideration for the assessment of LiNaCO_3 .

From the HTXRD results, it can be seen that below 60 °C, a new phase seems to appear and the position of its peaks are indicated as upward arrows in Fig. 4. Therefore, in our work, instead of only one α phase, two phases α_1 and α_2 were detected coexisting in the temperature range below 60 °C, which is not mentioned in the work of Yatsenko et al. [29]. The difference of the XRD patterns of these two phases at room temperature is shown in Fig. 5.

As shown in Fig. 5, the difference of α_1 and α_2 can be recognized in their XRD pattern at room temperature. When 2θ is in the range of 29–30°, α_1 has four peaks and α_2 has three peaks. While in the range of 34–35°, the number of peaks is switched for α_1 and α_2 . In addition, when 2θ is at 36–38°, α_1 has five peaks and α_2 has four peaks.

According to the ratio of the intensity of the corresponding peaks, the amount of α_1 and α_2 can be calculated. The calculated weight ratio between α_1 and α_2 according to the measured XRD intensity is different in the initial state (Fig. 5a) and after HTXRD (Fig. 5b). Besides, the XRD measurement in this work shows that the weight ratio of the α_1 phase increased after grinding. Therefore, the coexistence of α_1 and α_2 is assumed to be caused by kinetic effects. The phase transition between α_1 and α_2 happened at a relatively low temperature and it may be a continuous process. There might be a temperature, below which only the α_2 phase exists but it was not detected due to the temperature limitation of the XRD device.

The lattice parameters of the α phase at room temperature from this work and the literature are shown in Table 3. The main difference between α_1 and α_2 is the angle α , which is 89.2° for α_1 and 88.4° for α_2 . It can be seen, that the phase α_2 has the same angle $\alpha = 88.4^\circ$ as the phase calculated by Ricca et al. [28] with ab initio method and the phase of the single crystal sample measured by Yatsenko et al. [30]. While the angle $\alpha = 89.2^\circ$ in the α_1 phase detected in this work is close to the angle $\alpha = 89.0^\circ$ measured in another work of Yatsenko et al. [29], where the sample did not have a single crystal structure.

The temperature dependence of the lattice parameters of different phases is shown in Fig. 6. Here, the phase transformation temperatures (180 °C and 365 °C) are illustrated obviously. The lattice parameters of the high temperature modification $\gamma\text{-LiNaCO}_3$ in Fig. 6 are recalculated for a better comparability. The relations between the lattice parameters are as follows: $a_{\alpha, \text{tc}} = b_{\alpha, \text{tc}} = a_{\beta, \text{hex}} = a_{\gamma, \text{hex}} \cdot \sqrt{3}$, $c_{\alpha, \text{tc}} = c_{\beta, \text{hex}} = c_{\gamma, \text{hex}}$, $V_{\text{UC } \alpha, \text{tc}} = V_{\text{UC } \beta, \text{hex}} = V_{\text{UC } \gamma, \text{hex}} \cdot 3$, where hex = hexagonal, tc = triclinic. The $\beta \leftrightarrow \gamma$ transition is a conventional solid-solid phase transition between two hexagonal phases and can be interpreted as an order-disorder transition, as reported by Zhukov et al. [52]. The observed lattice relationship, $a_{\beta, \text{hex}} = a_{\gamma, \text{hex}} \cdot \sqrt{3}$, indicates an in-plane unit-cell multiplication and suggests that the β phase can be described as a superstructure of the γ phase. While the lattice parameter of phase α_1 and α_2 are enlarged and shown in Fig. 7.

The heat capacity of the intermediate compound LiNaCO_3 has not been reported before. In this work, it was measured by three different types of DSC mentioned in section 3.3. The heat capacity of LiNaCO_3 Sample 1 was measured using all three instruments. Sample 2 was measured only with the Netzsch 404C HT to assess the possible effect of the slight compositional deviation of Sample 1 from the stoichiometric LiNaCO_3 composition. The difference in the measured heat capacities of the two samples was found to be within the experimental uncertainty, indicating that the compositional variation has a negligible effect on the measured heat capacity. The experimental results are shown in Fig. 8. The green line (20 K/min HT) and the blue line (20 K/min HT-2) in Fig. 8 are the sample 1 and sample 2 (the compositions are slightly different, see section 3.1) measured with Netzsch HT, and they show good agreement. Two solid-solid phase transitions were observed, as indicated by the peaks at 170 °C and 360 °C in all DSC curves. The peaks

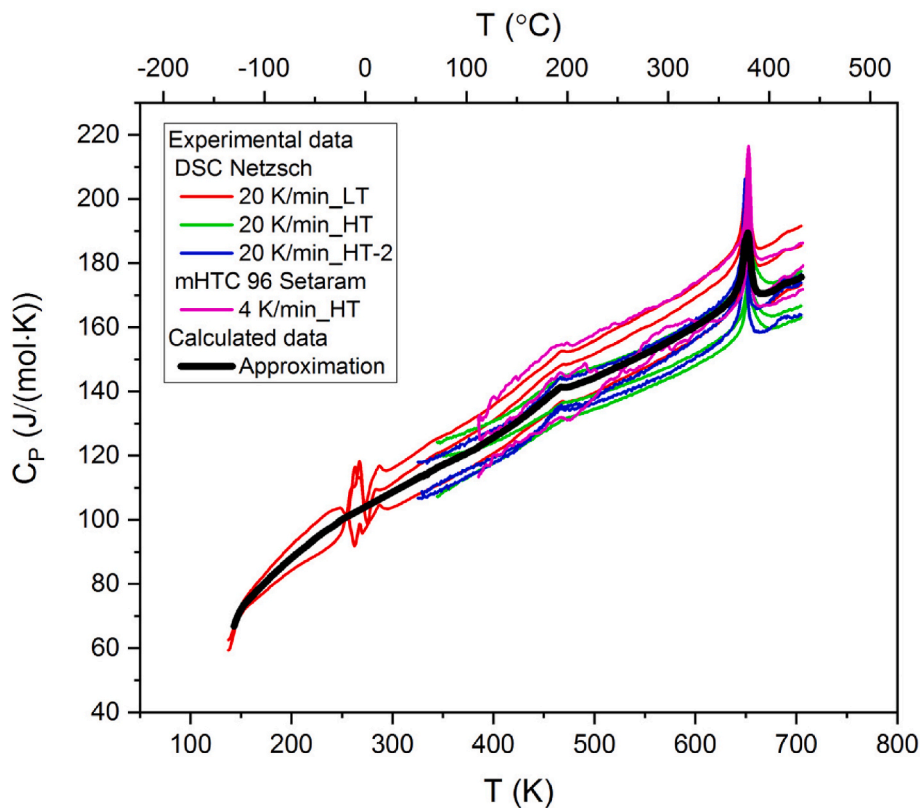


Fig. 8. Heat capacity of LiNaCO_3 determined by three different types of DSC.

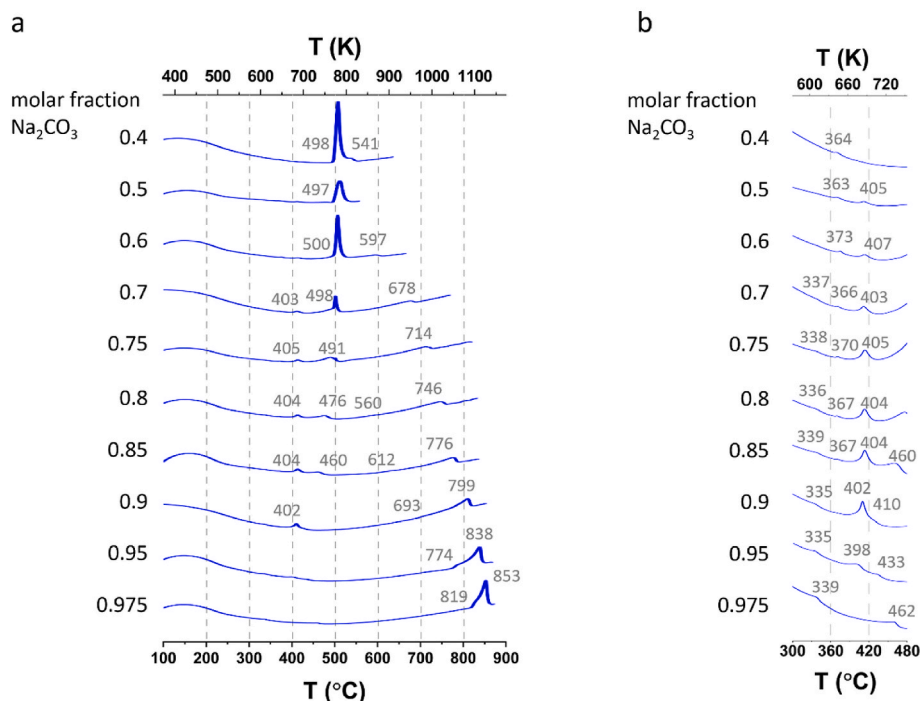


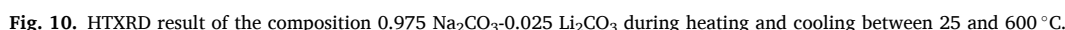
Fig. 9. a) Heating DTA-curves for various compositions in the Li_2CO_3 - Na_2CO_3 system, b) enlarged part in the temperature range 300–480 °C.

in the curve measured with Netzsch_LT from -30°C to 50°C were not taken into consideration because they are already shown in the baseline due to some artificial signal of the sample holder. The approximation was obtained according to the average results, which was used to find an appropriate polynomial of the C_p in the new database. The uncertainty

of the data is around $\pm 13 \text{ J}/(\text{mol}\cdot\text{K})$, corresponding to a relative uncertainty of about 10%.

5.1.3. Phase transition temperatures of the Li_2CO_3 - Na_2CO_3 system

The Li_2CO_3 - Na_2CO_3 system is characterized by significant



Group 7 details the liquidus temperatures. Below the liquidus, in the Na₂CO₃-rich region ($x(\text{Na}_2\text{CO}_3) = 0.8$ to 0.975), subtle thermal events were also detected (**Group 6**).

Other complex solid-state transitions were observed. A peak near 500 °C for compositions of $x(\text{Na}_2\text{CO}_3) = 0.4\text{--}0.7$ shifts to $\sim 410^\circ\text{C}$ at x

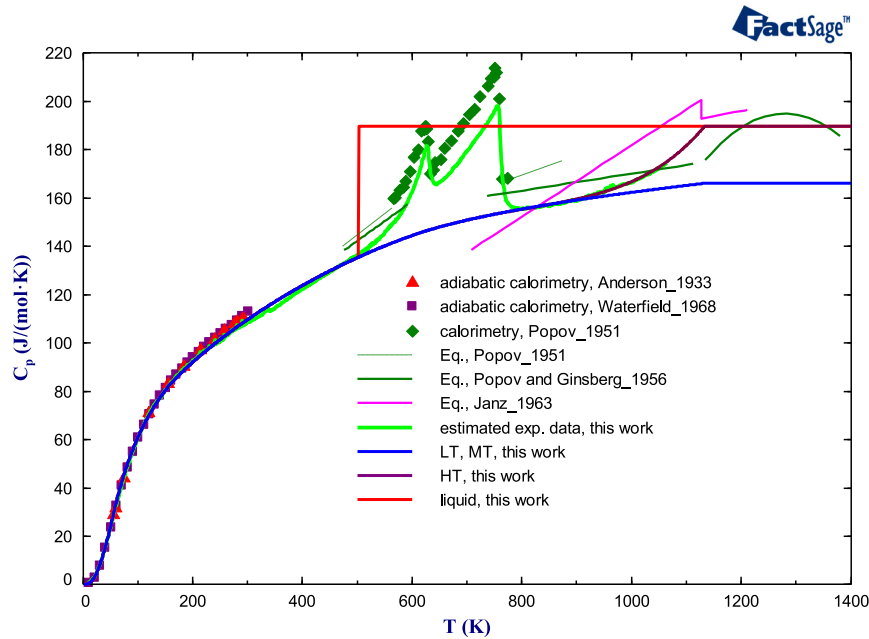


Fig. 12. Comparison of the calculated heat capacity data of Na_2CO_3 with the experimental data from this work and the literature.

Table 6

Thermodynamic parameters of Na_2CO_3 .

Phase	$\Delta H_{298,f}^0$ J/mol	S_{298}^0 J/(mol·K)	T, K	C_p , J/(mol·K)	Reference
Na_2CO_3 (LT)	-1130768	134.4	1-45	$4.51329906 \cdot 10^{-4} \cdot T^3 - 5.26713589 \cdot 10^{-6} \cdot T^4$	This work
			45-158	$95.5112473 + 0.14335091 T + 83564.4144 T^2 - 1.41399772 \cdot 10^{-4} \cdot T^2 - 5574.95743 \cdot T^{-1}$	This work
			158-627	$57.72815 + 0.21161 T - 143034.69275 \cdot T^{-2} - 1.10897 \cdot 10^{-4} \cdot T^2$	This work
			627-1131	$157.12833 + 6.52 \cdot 10^{-3} T - 6603187.4863 \cdot T^{-2} + 5.1708 \cdot 10^{-6} \cdot T^2$	This work
			LT $\rightarrow$ MT $H_{tr} = 1781.4$ J/mol at 627 K		This work
Na_2CO_3 (MT)	-1128986.6	137.4	1-45	$4.51329906 \cdot 10^{-4} \cdot T^3 - 5.26713589 \cdot 10^{-6} \cdot T^4$	This work
			45-158	$95.5112473 + 0.14335091 T + 83564.4144 T^2 - 1.41399772 \cdot 10^{-4} \cdot T^2 - 5574.95743 \cdot T^{-1}$	This work
			158-627	$57.72815 + 0.21161 T - 143034.69275 \cdot T^{-2} - 1.10897 \cdot 10^{-4} \cdot T^2$	This work
			627-1131	$157.12833 + 6.52 \cdot 10^{-3} T - 6603187.4863 \cdot T^{-2} + 5.1708 \cdot 10^{-6} \cdot T^2$	This work
			MT $\rightarrow$ HT $H_{tr} = 3650.8$ J/mol at 757 K		This work
Na_2CO_3 (HT)	-1125335.8	142.06	1-45	$4.51329906 \cdot 10^{-4} \cdot T^3 - 5.26713589 \cdot 10^{-6} \cdot T^4$	This work
			45-158	$95.5112473 + 0.14335091 T + 83564.4144 T^2 - 1.41399772 \cdot 10^{-4} \cdot T^2 - 5574.95743 \cdot T^{-1}$	This work
			158-627	$57.72815 + 0.21161 T - 143034.69275 \cdot T^{-2} - 1.10897 \cdot 10^{-4} \cdot T^2$	This work
			627-757	$157.12833 + 6.52 \cdot 10^{-3} T - 6603187.4863 \cdot T^{-2} + 5.1708 \cdot 10^{-6} \cdot T^2$	This work
			757-1131	$80.20523 + 0.19338 T - 2894310.40701 \cdot T^{-2} - 1.22239 \cdot 10^{-4} \cdot T^2 + 1.82335 \cdot 10^{-23} \cdot T^8$	This work
			1131-3500	189.535	FactPS
			HT $\rightarrow$ Liq $H_{tr} = 29664.6$ J/mol (SGPS) at 1131 K (FactPS)		Refs
Na_2CO_3 (Liq)	-1116049.32	139.7	1-45	$4.51329906 \cdot 10^{-4} \cdot T^3 - 5.26713589 \cdot 10^{-6} \cdot T^4$	This work
			45-158	$95.5112473 + 0.14335091 T + 83564.4144 T^2 - 1.41399772 \cdot 10^{-4} \cdot T^2 - 5574.95743 \cdot T^{-1}$	This work
			158-501	$57.72815 + 0.21161 T - 143034.69275 \cdot T^{-2} - 1.10897 \cdot 10^{-4} \cdot T^2$	This work
			501-3000	189.535	FactPS

(Na_2CO_3) = 0.75–0.9, before increasing again toward the transition temperature of pure Na_2CO_3 (Group 5). Another transition appeared near 400 °C in the range of $x(\text{Na}_2\text{CO}_3)$ = 0.5–0.95 (Group 4), while small peaks at around 337 °C were detected only for $x(\text{Na}_2\text{CO}_3)$ $\geq$ 0.7 (Group 2). The relatively small size of the peaks in Groups 2, 3, and 4 indicates that these solid-state transitions have lower enthalpies than the melting and eutectic reactions, which was enlarged in the temperature range 300–480 °C, as shown in Fig. 9b.

To further confirm the solid solution phases, HTXRD measurement was performed for the composition of 0.975 Na_2CO_3 –0.025 Li_2CO_3 . Fig. 10 shows the measured diffractograms for the composition $x(\text{Na}_2\text{CO}_3)$ = 0.975 and it was compiled to a 3D surface plot with a corresponding plan plot for the whole investigated temperature range. Three solid-solution phases were further confirmed, corresponding to the low-, medium-, and high-temperature polymorphs of Na_2CO_3 (LT,

MT, and HT, respectively). These phases are denoted as MOLT, MONA, and HEXA, respectively, and exhibit the same crystal structures as the corresponding Na_2CO_3 polymorphs, namely monoclinic γ , monoclinic β , and hexagonal α (Fig. 10). At lower temperatures (25 – ~340 °C on heating, ~290 – 25 °C on cooling) a weak Bragg reflection at ~21.3° 2 θ was measured, which is assumed to belong to LiNaCO_3 indicated as a pink point in Fig. 10. Therefore, at lower temperature for the composition 0.975 Na_2CO_3 –0.025 Li_2CO_3 , the intermediate compound LiNaCO_3 and the solid solution phase γ coexisted. When the temperature was above 340 °C, the intermediate compound LiNaCO_3 disappeared. That is because when the temperature increases, the solubility of Li_2CO_3 in Na_2CO_3 becomes larger, and the intermediate compound LiNaCO_3 dissolved into the solid solution γ phase. The average structure (approximant) of the γ phase is isostructural to that of the β phase. Both phases have the same metric of the unit cell and very similar diffraction

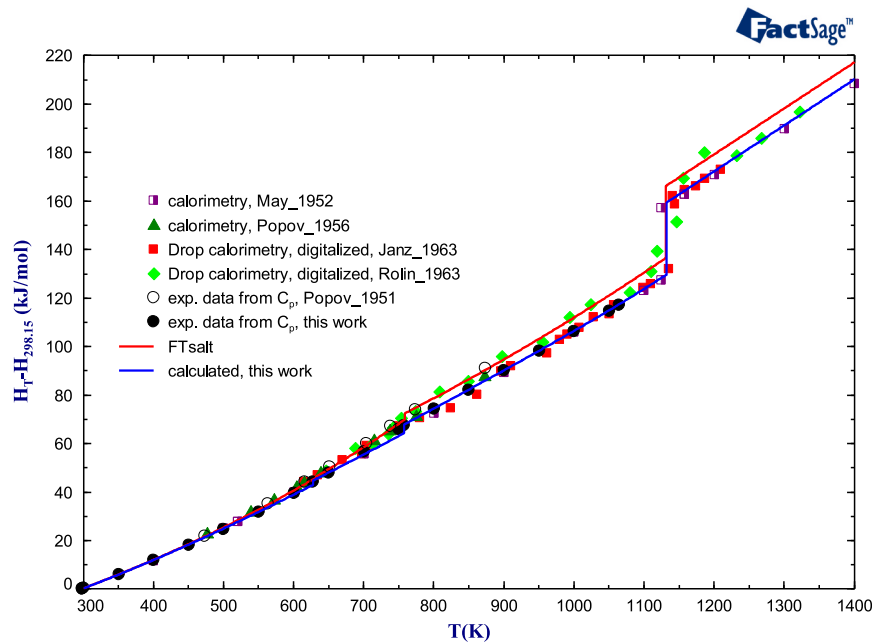


Fig. 13. Comparison of the calculated enthalpy increment of Na_2CO_3 with the experimental data from this work and the literature.

Table 7

Thermodynamic parameters of LiNaCO_3 .

Phase	$\Delta H_{298,f}^0$ J/mol	S_{298}^0 J/(mol·K)	T, K	C_p , J/(mol·K)	Reference
LiNaCO_3 (LT)	-1179383.56	104.25	1-36	$2.84134483 \cdot 10^{-4} \cdot T^3 - 2.633567945 \cdot 10^{-6} \cdot T^4$	This work
			36-298	$-25.1235 + 0.95137 \cdot T + 3607.62964 \cdot T^{-2} - 2.46 \cdot 10^{-3} \cdot T^2 + 2.56407 \cdot 10^{-6} \cdot T^3$	This work
			140-776	$98.574 - 0.04924 \cdot T - 607145.59959 \cdot T^{-2} - 4.38747 \cdot 10^{-4} \cdot T^2 - 3.00294 \cdot 10^{-7} \cdot T^3$	This work
			LT $\rightarrow$ MT $H_{tr} = 154$ J/mol at 443 K		
LiNaCO_3 (MT)	-1179229.56	104.59	1-36	$2.84134483 \cdot 10^{-4} \cdot T^3 - 2.633567945 \cdot 10^{-6} \cdot T^4$	This work
			36-298	$-25.1235 + 0.95137 \cdot T + 3607.62964 \cdot T^{-2} - 2.46 \cdot 10^{-3} \cdot T^2 + 2.56407 \cdot 10^{-6} \cdot T^3$	This work
			140-776	$98.574 - 0.04924 \cdot T - 607145.59959 \cdot T^{-2} - 4.38747 \cdot 10^{-4} \cdot T^2 - 3.00294 \cdot 10^{-7} \cdot T^3$	This work
			MT $\rightarrow$ HT $H_{tr} = 275$ J/mol at 633 K		
LiNaCO_3 (HT)	-1178954.56	105.02	1-36	$2.84134483 \cdot 10^{-4} \cdot T^3 - 2.633567945 \cdot 10^{-6} \cdot T^4$	This work
			36-298	$-25.1235 + 0.95137 \cdot T + 3607.62964 \cdot T^{-2} - 2.46 \cdot 10^{-3} \cdot T^2 + 2.56407 \cdot 10^{-6} \cdot T^3$	This work
			140-776	$98.574 - 0.04924 \cdot T - 607145.59959 \cdot T^{-2} - 4.38747 \cdot 10^{-4} \cdot T^2 - 3.00294 \cdot 10^{-7} \cdot T^3$	This work

patterns. The main Bragg reflections of both phases are identical. The γ phase originates relatively weak additional reflections, which cannot be simulated with a standard Rietveld or Pawley/Le Bail fit. The γ - β phase transition can only be tracked by observing the formation/vanishing of the mentioned weak additional reflections, which are indicated in orange letter γ in Fig. 10. The β - α phase transition is much easier to be tracked by observing the merging of several monoclinic reflections into one hexagonal reflection. The phase transition temperatures are collected in Table 4.

The lattice parameters are presented in Fig. 11. For better comparability, the monoclinic lattice parameters in the diagram were recalculated. The high-temperature hexagonal phase (HEXA) can also be described in terms of the lower-symmetry monoclinic structures of the low-temperature phases (MONA and MOLT). In this representation, the unit cell volume (V_{UC}) of the monoclinic structures is doubled relative to the hexagonal unit cell, while the monoclinic angle β becomes 90° .

The relations between the lattice parameters are as follows:

$c_{\text{hex}} = c_{\text{mon}}$, $a_{\text{hex}} = a_{\text{mon}}/\sqrt{3} = b_{\text{mon}}$, $V_{UC \text{ hex}} = V_{UC \text{ mon}}/2$, where hex = hexagonal, mon = monoclinic. Additionally, the lattice parameters of pure Na_2CO_3 reported by Sergeev et al. [46] are included for comparison with the present results.

It can be easily noticed, that the lattice parameters measured are very close to the pure substance, and the crystal structure did not change,

which means the solutions are formed based on the structures of the pure substance Na_2CO_3 . In addition, the type of the solid solutions is substitutional solid solution, where Li atoms replaces the Na atoms, which causes the difference between the solution phase and the pure substance Na_2CO_3 . The unit cell volume of all three solid solution phases is lower than that of the pure Na_2CO_3 , because the atom size of Li is smaller than that of Na. The lattice parameters a , b and β are smaller than those of pure Na_2CO_3 , while lattice parameter c is larger than that of Na_2CO_3 , which results from the interactions between the atoms. The difference of the lattice parameters between solid solutions and pure Na_2CO_3 become larger with increasing temperature. For the low temperature phase γ , they are very close to those of pure Na_2CO_3 (LT), which is due to the low solubility at this temperature. The phase change temperature of the solution phase is lower than that of the pure Na_2CO_3 , the comparison is shown in Table 4. It can be seen that the difference of the data from DTA and HTXRD are consistent, with an error of 10°C .

From the DTA and HTXRD measurements in the present work, three solid solutions based on modifications of Na_2CO_3 (HEXA, MONA, and MOLT) were confirmed, and their phase boundaries were determined in the phase diagram (Fig. 15).

For the HEXA phase, the solidus temperature was described by DTA data in Group 6 (Table 4). While the phase transition temperature in Group 5 (Table 4) at around 500°C did not extend over the entire

Table 8Experimental and calculated phase transitions in the system Li_2CO_3 - Na_2CO_3 .

Reaction	Reaction type	Molar fraction Na_2CO_3	T, °C	method	Reference
Liquid $\leftrightarrow$ Li_2CO_3 + Na_2CO_3 (HT)	eutectic	0.48	500	Cryometric	Rolin and Recapet [16]
		0.48	500	TA	Janz and Lorenz [17]
		0.48	495	Calculated	Chen et al. [12]
Liquid $\leftrightarrow$ Li_2CO_3 + $\alpha\text{-K}_2\text{SO}_4$ ^a	eutectic	0.48	500	Calculated	Dessureault et al. [13]
		0.48	498.7	Calculated	FTsalt [4]
Liquid $\leftrightarrow$ Li_2CO_3 + LiNaCO_3	eutectic	0.46	497	Visual-polythermal	Zakhvalinskii and Belykh [58]
		0.47	510	TA	Eitel and Skalikis [19]
		0.45	496	Visual-polythermal	Volkov and Shvab [24]
		0.471	497	Visual-polythermal	Volkov and Volkova [23]
		0.467	499.754 $\pm$ 0.057	Highly sensitive TA	Cairns and Macdonald [26]
		0.45	485	DTA	D'yakov et al. [25]
		0.464	499.5	Calculated	This work
LiNaCO_3 (LT) $\leftrightarrow$ LiNaCO_3 (MT)	solid-solid	0.5	175	HTXRD	Zhukov et al. [52]
		0.5	175	DTA	D'yakov et al. [25]
		0.5	290	HTXRD	Christmann et al. [51]
		0.5	180-185	HTXRD	This work
		0.5	170	DSC	This work
		0.5	180	Calculated	This work
		0.5	360	HTXRD	Zhukov et al. [52]
LiNaCO_3 (MT) $\leftrightarrow$ LiNaCO_3 (HT)	solid-solid	0.5	360	DTA	D'yakov et al. [25]
		0.5	415	HTXRD	Christmann et al. [51]
		0.5	360	DSC	Li and Zhang [53]
		0.5	360	DSC	This work
		0.5	360-365	HTXRD	This work
		0.5	363	DTA	This work
		0.5	360	Calculated	This work
LiNaCO_3 (HT) $\leftrightarrow$ Liquid	congruently melting	0.5	501	Visual-polythermal	Zakhvalinskii and Belykh [58]
		0.5	481	DSC	Sang et al. [59]
		0.5	503	Visual-polythermal	Rea [60]
		0.5	514	TA	Eitel and Skalikis [19]
		0.5	500.757 $\pm$ 0.005	Highly sensitive TA	Cairns and Macdonald [26]
$\text{LiNaCO}_3 \leftrightarrow \text{Na}_2\text{CO}_3$ + Liquid	incongruently melting (peritectic point)	0.499	510	Visual-polythermal	Volkov and Volkova [23]
		0.5	493	DTA	D'yakov et al. [25]
		0.5	494.2	DTA	Li and Zhang [53]
$\text{LiNaCO}_3 \leftrightarrow \text{HEXA}$ + Liquid	incongruently melting	0.5	500.7	Calculated	This work
Liquid $\leftrightarrow$ Na_2CO_3 + LiNaCO_3	eutectic	0.51	501	Visual-polythermal	Zakhvalinskii and Belykh [58]
		0.52	510	TA	Eitel and Skalikis [19]
Solubility limit in HEXA	-	0.5	501	Visual-polythermal	Volkov and Shvab [24]
		0.88		Modeling	Dessureault et al. [13]
		0.84	498.7	Calculated	FTsalt [4]
		0.68	500.7	Calculated	This work
$\alpha\text{-K}_2\text{SO}_4^* \leftrightarrow \text{Na}_2\text{CO}_3$ + Li_2CO_3	eutectoid	0.92	287	Calculated	FTsalt [4]
		-	404	DTA	This work
HEXA $\leftrightarrow$ MONA + LiNaCO_3 (HT)	eutectoid	-	408.7	Calculated	This work
Solubility limit in MONA	-	0.96	408.7	Calculated	This work
MONA $\leftrightarrow$ MOLT + LiNaCO_3 (MT)	eutectoid	-	337	DTA	This work
		0.98	338.0	Calculated	This work
Solubility limit in MOLT	-	0.98	338.0	Calculated	This work

^a Solid solution phase in the FTsalt [4] containing Na_2CO_3 (HT).

composition range. Instead, a lower temperature was detected when $x(\text{Na}_2\text{CO}_3) \geq 0.75$. The larger the composition $x(\text{Na}_2\text{CO}_3)$, the lower this temperature will be. These points below 500 °C give the bottom boundary of the HEXA phase in the phase diagram. In the measurement of Rolin and Recapet [16], this phase transition temperature was also observed decreasing gradually from $x(\text{Na}_2\text{CO}_3) = 0.61$. These data are used to determine the solubility limit of Li_2CO_3 in Na_2CO_3 (HT), it should be around $x(\text{Na}_2\text{CO}_3) = 0.61$ -0.7, which is much lower than the calculated result of $x(\text{Na}_2\text{CO}_3) = 0.88$ from Dessureault et al. [13] and $x(\text{Na}_2\text{CO}_3) = 0.81$ from FTsalt [4] (Table 8). In both measurements of Rolin and Recapet [16] and DTA results of this work (Group 4 in Table 4), in compositions with $x(\text{Na}_2\text{CO}_3) \geq 0.5$ the phase transition at around 400 °C was detected as shown in the phase diagram (Fig. 15). According to the FTsalt database, these data correspond to a solid-solid phase transition in pure Li_2CO_3 . This contradicts our previous work, in which we concluded that this transition does not exist. [8]. Besides,

according to that assumption, this temperature should be detected especially at compositions where $x(\text{Na}_2\text{CO}_3) \leq 0.5$ (close to the pure Li_2CO_3), which contradicts both measurements. According to our new experimental results, this temperature is the eutectoid temperature of the phase HEXA, much higher than 287 °C predicted by the commercial database FTsalt. Therefore, the whole boundary of the HEXA phase is determined and used for the assessment of the phase diagram with the new database.

Moreover, as mentioned in section 2, only one solid solution based on Na_2CO_3 (HT) is adopted in the FTsalt database. If this assumption was taken in this work, the eutectoid line of HEXA at 400 °C should be detected in the composition range of $x(\text{Na}_2\text{CO}_3) = 0.5$ -1. However, the DTA results of the composition $x(\text{Na}_2\text{CO}_3) = 0.975$ reflected in the phase diagram is opposed to it. In addition, other solid solutions (based on the medium- and low-temperature modifications of Na_2CO_3 , called MONA and MOLT, respectively) were detected and confirmed by HTXRD, and

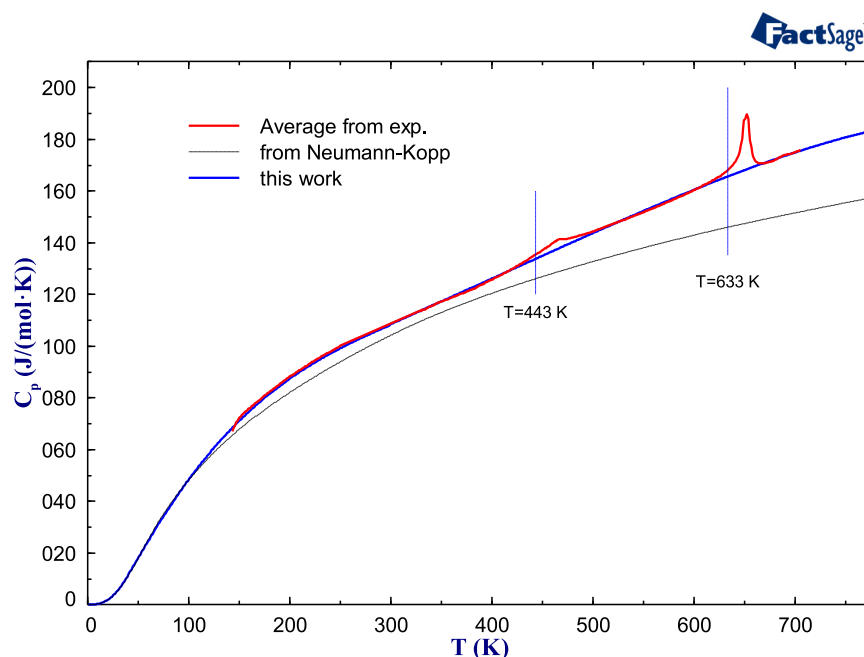


Fig. 14. Heat capacity of the intermediate compound LiNaCO_3 .

the phase transition temperatures are lower than the corresponding temperature for the pure Na_2CO_3 (see Table 4). The eutectoid temperature of MONA was measured around 337°C (group 2 in Table 4) by DTA and 330°C by HTXRD (Table 4), which is used for the assessment of the phase diagram.

In addition, one solid solution based on LiNaCO_3 was reported in the literature by Khlapova and Elenetskaya [27]. In their work, the solubility of Na_2CO_3 in LiNaCO_3 was detected in the composition range $x(\text{Na}_2\text{CO}_3) = 0.5\text{--}0.56$ through the comparison of lattice parameters of different compositions measured by XRD at room temperature. However, according to the XRD measurement of the $0.6\text{Na}_2\text{CO}_3\text{--}0.4\text{Li}_2\text{CO}_3$ composition at room temperature in this work (Supplementary, Fig. S2), besides two modifications $\alpha 1$ and $\alpha 2$ phases of LiNaCO_3 , 0.184 M fraction of Na_2CO_3 was detected in the phase content, which is close to 0.2 M fraction of Na_2CO_3 phase content calculated using lever rule from the phase diagram without consideration of this solubility. In contrast, if the solubility of Na_2CO_3 in LiNaCO_3 was taken into account, the calculated phase content of Na_2CO_3 is 0.09 M fraction at room temperature, which deviated too much from the experimental value. Besides, the solid-solid phase change temperature of LiNaCO_3 (360°C) was detected in a large composition range, which is also against this solubility assumption, because the phase change temperature should be lower than that of pure LiNaCO_3 . Therefore, this solid solution was excluded in the present optimization work.

5.2. Thermodynamic modelling

5.2.1. Na_2CO_3

In the present work three stable solid phases and the liquid phase of sodium carbonate, namely Na_2CO_3 (LT), (MT), (HT) and (Liq) were considered in accordance with all available data. Thermodynamic functions for all stable forms of Na_2CO_3 were generated based on the experimental information from the literature along with the measurements performed in the present work. A similar approach was applied for the thermodynamic description of K_2CO_3 in the previous work [8].

The standard formation enthalpy and the fusion enthalpy of Na_2CO_3 were adopted from the commercial databases, namely SGPS [54] and FactPS [32], which were confirmed by Knudsen effusion mass spectrometry [47].

Fig. 12 demonstrates the heat capacity of sodium carbonate compared with the experimental data from the present work as well as from the literature in the low- [48,49] and high-temperature [33] ranges. As mentioned in Section 5.1.1, the assessment was based on the estimated data points (the same green lines shown in Figs. 2 and 12), which was derived from the literature [48,49] and the average values from the present DSC measurements. The heat capacity was calculated using the C_p polynomials, as shown in Table 6. Multiple temperature ranges and coefficients were used to accurately describe the non-linear thermodynamic behaviour. The polynomial for the temperature range $0\text{--}298\text{ K}$ was introduced based on the present calorimetric measurements combined with the literature values reported by Anderson [48] and by Waterfield et al. [49]. Using this polynomial, the value of standard entropy derived by integration of C_p/T ($133.858\text{ J/mol}\cdot\text{K}$) agrees with the average experimental value based on the present calorimetric measurements ($134.4 \pm 1.1\text{ J/mol}\cdot\text{K}$). The latest value is used in the present database (Table 6).

The heat capacity polynomial for the high temperature range (starting at 298 K) was implemented based on the present DSC measurements. The obtained C_p polynomials present smooth lines (Fig. 12), the specific heat of peaks on the experimental curves was included into the phase transition enthalpy (Fig. 13) in order to avoid an appearance of such peaks for the salt mixtures applying the Neumann-Kopp approach. The C_p polynomials of the low- and medium-temperature modifications were extrapolated up to the melting temperature to provide a reasonable behaviour of the components in the corresponding solid solutions, which can be stable outside the stability ranges of the pure compound. A similar assumption was used for the C_p of the HT phase, whose temperature dependence of C_p was extrapolated below its stability range as a smooth line (Fig. 12).

The heat capacity of the liquid phase ($T_m = 1123\text{ K}$ or 850°C) was adopted from the FactPS database [32]. The heat capacity of the liquid phase was extrapolated to lower temperatures by the method described earlier for nitrates [7], sulphates [55], and carbonates [8]. An estimation of the so-called Kauzmann temperature (T_K) in the terminology used elsewhere [7] was made from the temperature at which the liquid and the solid entropies become the same if the liquid C_p was extrapolated as constant value below the melting point. In the reference book [56], the solid-solid transition temperature (723 K) was assumed as a

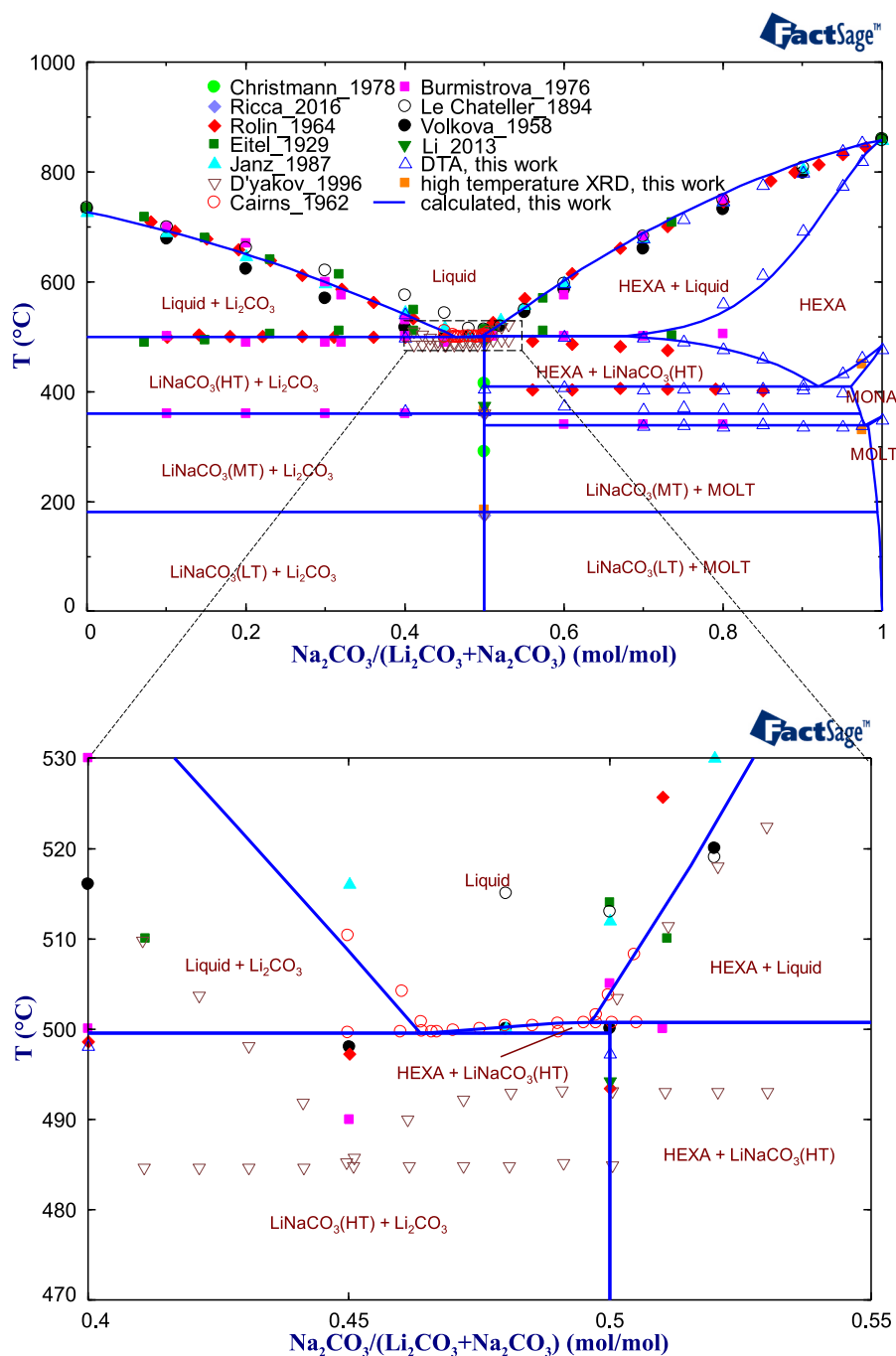


Fig. 15. Comparison of the phase diagram calculated by the present database with the experimental data in the Li_2CO_3 - Na_2CO_3 system. The zoomed part of the phase diagram shows the melting behavior of the compound LiNaCO_3 .

glass transition. In the present work, the Kauzmann temperature for Na_2CO_3 (Liq) was estimated to be 501 K, where the C_p of the liquid phase coincides with the heat capacity for the solid phase at $T < T_K$ and was considered to be constant above this temperature (Table 6, Fig. 12). The constant extrapolation of C_p of liquid below the melting point was used since direct C_p measurements of the supercooled liquid state of the pure salts are not available.

The enthalpy increment of sodium carbonate has been measured in several studies [42,45,50,57]. The enthalpy increment derived from the heat capacity from Popov et al. [33] was calculated for comparison. We have summarized all these results in Fig. 13 as the temperature dependence of enthalpy increment. Additionally, the phase transition enthalpy

data for Na_2CO_3 are collected in Table 5. All of these data agree well within the low-temperature range below 700 K. The data from Popov et al. [33] is around 2-3 kJ/mol lower than the data from Popov and Ginzburg [50] in the temperature range of 735 - 870 K. As the latter study was published by the same group in 1956 by Popov and Ginzburg [50], it is considered more reliable. The results of May [57] and Janz et al. [45] agree well with each other for their whole measured temperature range. While the data of Rolin et al. [42] differ from them [45, 57] in the high temperature range of 800 K - 1185 K and the discrepancy is relatively high. For example, at 1109 K the difference is 5.32 kJ/mol.

The enthalpy increment for Na_2CO_3 (Fig. 13) was calculated based on the present DSC results, and the calculated values agree with the

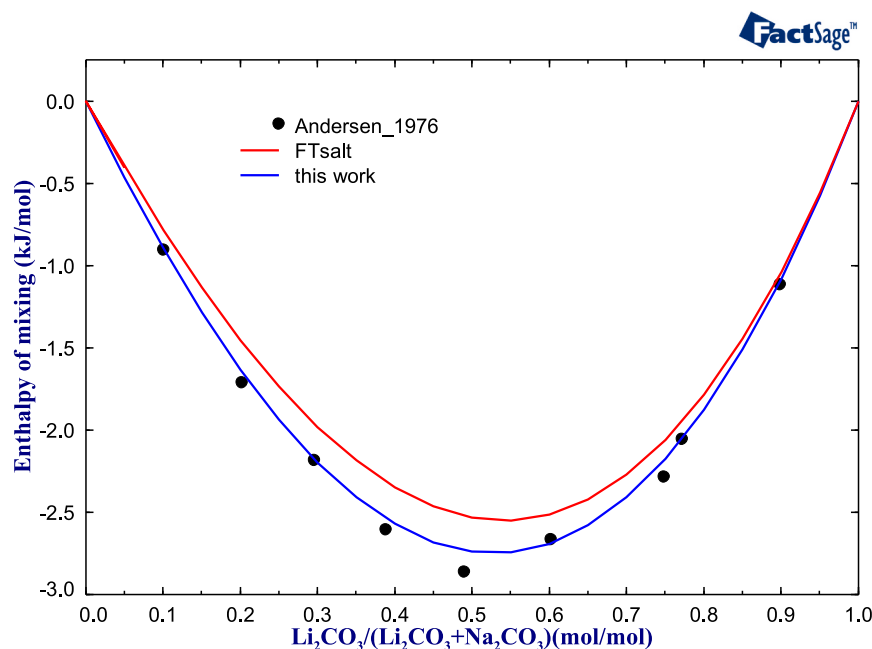


Fig. 16. Mixing enthalpy of the Li_2CO_3 - Na_2CO_3 system.

Table 9

Fusion enthalpy at certain composition in the Li_2CO_3 - Na_2CO_3 system.

Molar fraction Na_2CO_3	T, °C	Fusion enthalpy, kJ/ mol (J/g)	Method	Reference
0.511	499	33.5 ± 2.3 (374 ± 26)	TA	Li et al. [61]
0.491	498	29.85 ± 0.05 (330.8 ± 0.6)	STA	Jiang et al. [62]
0.48	500	31.56 (348.5)	DSC	Ge et al. [63]
0.467	496	33.05 ± 1.65	Drop calorimetry	Janz et al. [64]
0.467	496	31.11(342)	-	Petri et al. [3]
0.48	502	30.8	Calculated	FTsalt [4]
0.464	499.5	31.1	Calculated	This work
0.5	494	32.87 (365.5)	DSC	Li and Zhang [53]
-	-	30.3	Calculated	FTsalt [4]
-	-	31.0	Calculated	This work

measured heat increment for the solid phases, whereas the data on the liquid phase correlate with those determined calorimetrically in Refs. [45,57]. The solid-solid transitions $\text{LT} \rightarrow \text{MT}$, $\text{MT} \rightarrow \text{HT}$ were modelled based on the present study, where the transition temperatures were determined by DTA and HTXRD in the previous work [46], and the corresponding enthalpies of transitions were determined by integrating the C_p curve from the present DSC data (Table 5). The transformations of Na_2CO_3 are considered at 627 K with $\Delta H = 1.781$ kJ/mol and at 757 K with $\Delta H = 3.651$ kJ/mol for the solid-solid transitions $\text{LT} \rightarrow \text{MT}$ and $\text{MT} \rightarrow \text{HT}$, respectively.

The calculated entropy of Na_2CO_3 is compared with the values derived from the adiabatic calorimetry by Waterfield et al. [49] in the temperature range up to 298 K (Supplementary, Fig. S1).

5.2.2. LiNaCO_3

The standard enthalpy of formation and the standard entropy of LiNaCO_3 were optimized based on the Neumann-Kopp estimation enable the thermodynamic optimization of the Li_2CO_3 - Na_2CO_3 system, with particular focus on the incongruent melting behavior of LiNaCO_3 . The optimized values are presented in Table 7. As described in Section

5.1.2, three solid phases of LiNaCO_3 were measured and considered in the thermodynamic assessment, namely LiNaCO_3 (LT), LiNaCO_3 (MT), and LiNaCO_3 (HT). The heat capacities of these phases were assumed to be identical and were optimized based on the DSC measurements obtained in the present work. The calculated heat capacity of LiNaCO_3 is shown in Fig. 14 in comparison with the average experimental data from the present work. Because no other experimental data was found in the literature, the C_p above 150 K was assessed using the experimental results from the DSC measurement, while the C_p below 150 K was obtained according to the calculated data by Neuman-Kopp method. In the whole temperature range for the solid phase, the measured C_p is higher than the Neuman-Kopp estimation. The phase transition enthalpies, $\Delta H = 154$ J/mol at 443 K (170 °C) and $\Delta H = 275$ J/mol at 633 K (360 °C), for the solid-solid transitions $\text{LT} \rightarrow \text{MT}$ and $\text{MT} \rightarrow \text{HT}$, respectively, were determined by integrating the two peaks in the measured C_p curve. These transition enthalpies were treated separately and were therefore not included in the C_p optimization. As a result, the calculated C_p curves are smooth, as shown in Fig. 14. The polynomials of C_p for the three phases in the different temperature ranges are shown in Table 7.

The intermediate compound LiNaCO_3 is considered to be incongruently melting according to the measurement of Cairns and Macdonald [26], the calculation agrees well with the experimental result (see the zoomed part in Fig. 15).

5.2.3. Li_2CO_3 - Na_2CO_3 system

The obtained phase equilibria data from the DTA and HTXRD study along with the literature information are used to generate the Gibbs energy dataset for the system Na_2CO_3 - Li_2CO_3 . The phase transition data regarding the solid solubilities based on Na_2CO_3 measured in the present work were directly used to optimize the interaction parameters in the solid solutions (HEXA, MONA, MOLT). The intermediate compound LiNaCO_3 was introduced into the new dataset. The incongruent melting data of LiNaCO_3 obtained by Cairns and Macdonald [26] were regarded as the most reliable and precise, and thus selected for the optimization. The thermodynamic properties of the compound LiNaCO_3 was generated in accordance with the present experimental results and presented in Section 5.2.2. Excess Gibbs energy parameters for the liquid phase were optimized to describe the solid-liquid equilibria. The obtained dataset allows the correct representation of the phase diagram as well as

Table 10

Thermodynamic description of the liquid and solid solution phases.

Gibbs energy data, J/mol	
Liquid: $(\text{Li}_2\text{CO}_3/1.5, \text{Na}_2\text{CO}_3/1.5)$	
${}^0G_{\text{Na}_2\text{CO}_3} = {}^0G_{\text{Na}_2\text{CO}_3(\text{liquid})}$	
${}^0G_{\text{Li}_2\text{CO}_3} = {}^0G_{\text{Li}_2\text{CO}_3(\text{liquid})}$	
$L_{\text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3}^0 = -7307.82 - 4.92T$, $L_{\text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3}^1 = -842.19$	
HEXA: $(\text{Li}^{1+}, \text{Na}^{1+})_2(\text{CO}_3^{2-})_1$	
${}^0G_{\text{Na}_2\text{CO}_3} = {}^0G_{\text{Na}_2\text{CO}_3(\text{HT})}$	
${}^0G_{\text{Li}_2\text{CO}_3} = {}^0G_{\text{Li}_2\text{CO}_3(\text{solid})} + 2500$	
$L_{\text{Li}^{1+}, \text{Na}^{1+}, \text{CO}_3^{2-}}^{0, \text{HEXA}} = 52131.33 - 36.79T$	
MONA: $(\text{Li}^{1+}, \text{Na}^{1+})_2(\text{CO}_3^{2-})_1$	
${}^0G_{\text{Na}_2\text{CO}_3} = {}^0G_{\text{Na}_2\text{CO}_3(\text{MT})}$	
${}^0G_{\text{Li}_2\text{CO}_3} = {}^0G_{\text{Li}_2\text{CO}_3(\text{solid})} + 8000$	
$L_{\text{Li}^{1+}, \text{Na}^{1+}, \text{CO}_3^{2-}}^{0, \text{MONA}} = 33850.45 - 9.17T$	
MOLT: $(\text{Li}^{1+}, \text{Na}^{1+})_2(\text{CO}_3^{2-})_1$	
${}^0G_{\text{Na}_2\text{CO}_3} = {}^0G_{\text{Na}_2\text{CO}_3(\text{LT})}$	
${}^0G_{\text{Li}_2\text{CO}_3} = {}^0G_{\text{Li}_2\text{CO}_3(\text{solid})} + 20000$	
$L_{\text{Li}^{1+}, \text{Na}^{1+}, \text{CO}_3^{2-}}^{0, \text{MOLT}} = 2349.02 + 26.14T$	

other properties, like mixing enthalpy and enthalpy increment of the eutectic mixture from the literature. The thermodynamic parameters of the liquid and solid solution phases are collected in Table 10.

The calculated phase diagram is in good agreement with the selected experimental data, as shown in Fig. 15. The zoomed part of the phase diagram in Fig. 15 is intended to show the incongruent melting behavior of the intermediate compound LiNaCO_3 . The solid solubility limits are predicted in accordance with the present experimental data. The prediction of the incongruently melting behavior of LiNaCO_3 agrees well with the experimental data of Cairns and Macdonald [26]. A good agreement between the measured and calculated data on phase equilibria (also summarized in Table 8) indicates that the new database provides high accuracy and can be used for reliable predictions on the phase diagram and other properties.

The mixing enthalpy of this system at 1178 K was investigated by Andersen and Kleppa [21] using high temperature calorimetry. It can be seen from Fig. 16 that the results calculated by the new database are in better agreement with the experimental data. In addition, the fusion enthalpy of the eutectic and 0.5:0.5 (LiNaCO_3) compositions were investigated by many authors [3,53,61–64], all these data are listed in Table 9.

For the fusion enthalpy of the eutectic composition, compared with the value from FTsalt (30.8 kJ/mol), the value calculated of this work (31.1 kJ/mol) is relatively closer to the average value from in the literature [3,61–64] (31.8 kJ/mol). While the calculated fusion enthalpy of LiNaCO_3 from this work (31.0 kJ/mol) is also closer to the value from Li and Zhang [53] (32.87 kJ/mol) compared with the value from FTsalt (30.3 kJ/mol).

6. Conclusion

For the salt system $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$, the phase diagram was studied experimentally: three solid solution phases HEXA, MONA and MOLT based on three solid modifications of pure Na_2CO_3 (HT-, MT-, LT-modification, respectively) were confirmed by DTA measurement and high temperature XRD; the eutectoid temperature of the solid solution phases HEXA and MONA was measured to be 409 °C and 338 °C, respectively. The phase transition temperatures and crystal structures of the intermediate compound LiNaCO_3 was confirmed by HTXRD. It is found out that LiNaCO_3 has two phases coexisting below 60 °C, which is assumed to be caused by kinetic effect. Besides, the heat capacity of Na_2CO_3 and LiNaCO_3 were obtained experimentally by three types of DSC. LiNaCO_3 is considered to melt incongruently. The Gibbs energies of Na_2CO_3 , LiNaCO_3 as well as the solution phases (the liquid solution and

three solid solutions) in the binary system $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ were generated based on the own and literature experimental results. Good agreements are achieved between calculations and experimental data on phase equilibria and thermodynamic properties. This indicates that the new database provides high accuracy and can be used for reliable predictions of the phase diagram and related properties.

CRedit authorship contribution statement

Jia Qi: Investigation, Writing – original draft. **Elena Yazhenskikh:** Software, Writing – original draft, Writing – review & editing. **Mirko Ziegner:** Investigation, Writing – original draft. **Guixuan Wu:** Writing – review & editing. **Michael Müller:** Funding acquisition, Supervision, Writing – review & editing. **Dmitry Sergeev:** Funding acquisition, Investigation, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

All references are cited correctly. Only original data are published, the used data are referred in the right way. This work was supported by the Federal Ministry for Economic Affairs and Energy on the basis of a decision by the German Bundestag within the project PCM-Screening 1 and 2 (FKZ 03ET1441D, FKZ 03EN6005D) and by the China Scholarship Council (No. 201804910575).

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Appendix B. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.calphad.2026.102982>.

Data availability

Data will be made available on request.

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