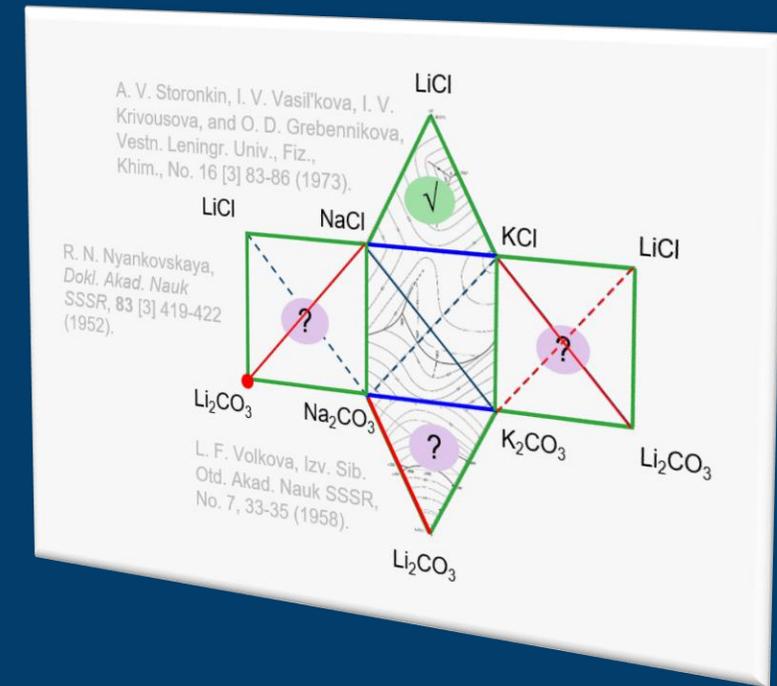


EXPERIMENTAL STUDY AND THERMODYNAMIC ASSESSMENT OF THERMODYNAMIC PROPERTIES OF Li^+ , Na^+ , $\text{K}^+//\text{Cl}^-$, CO_3^{2-} SYSTEM FOR THERMAL ENERGY STORAGE

GTT USERS' MEETING 2022

30.06.2022 | JIA QI

Institute of Energy and Climate Research, IEK-2
Forschungszentrum Jülich GmbH



Jia Qi, D. Sergeev, E. Yazhenskikh, M. Ziegner, G. Wu, M. Müller

OUTLINE

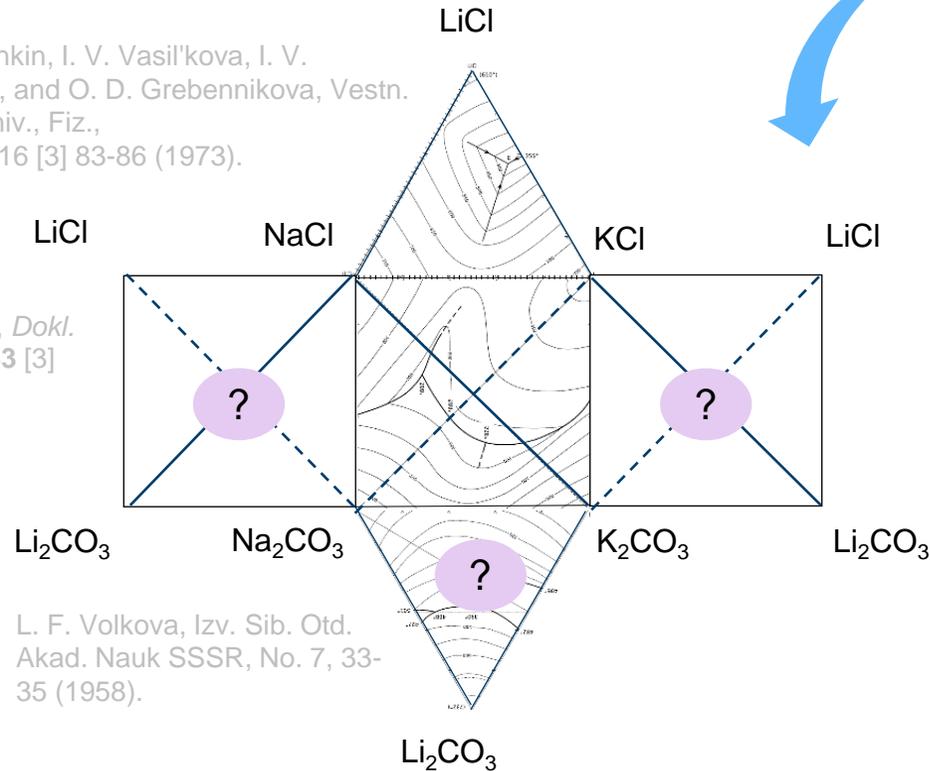
- Introduction
- Modelling Method
- Results and Discussion
- Conclusion and Outlook

INTRODUCTION

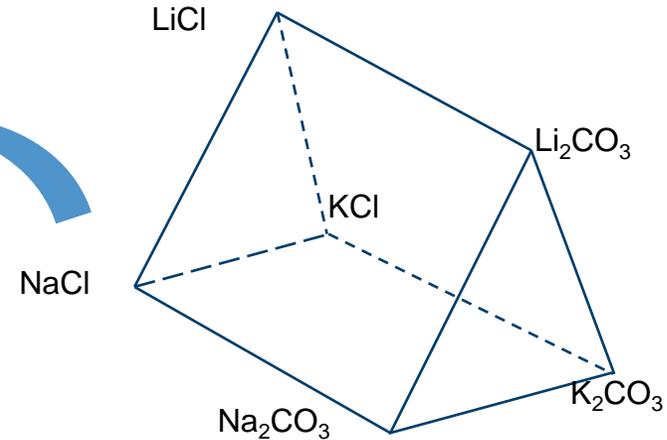
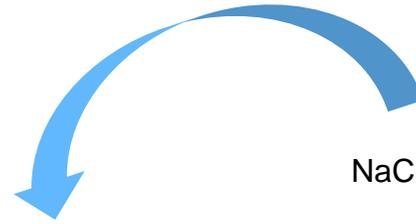
Li⁺, Na⁺, K⁺ // Cl⁻, CO₃²⁻ system

A. V. Storonkin, I. V. Vasil'kova, I. V. Krivousova, and O. D. Grebennikova, *Vestn. Leningr. Univ., Fiz., Khim.*, No. 16 [3] 83-86 (1973).

R. N. Nyankovskaya, *Dokl. Akad. Nauk SSSR*, **83** [3] 419-422 (1952).



L. F. Volkova, *Izv. Sib. Otd. Akad. Nauk SSSR*, No. 7, 33-35 (1958).



Application

- Phase Change Material (PCM) for Concentrating Solar Power (CSP)
- Salt bath treatment (as coolant)
- Electrochemical deposition of carbon materials
- Molten carbonate fuel cell
- Molten salts oxidations of wastes

Modelling method

CALPHAD

Pure substances: gas, liquid, solid (s1,s2,s3...)



In the binary, ternary... system:

- pure substance phase
- Solution phase
 - liquid solution
 - solid solution
- Intermediate compound

✓ **Liquid: modified associate species model using Redlich-Kister-Muggianu equation**

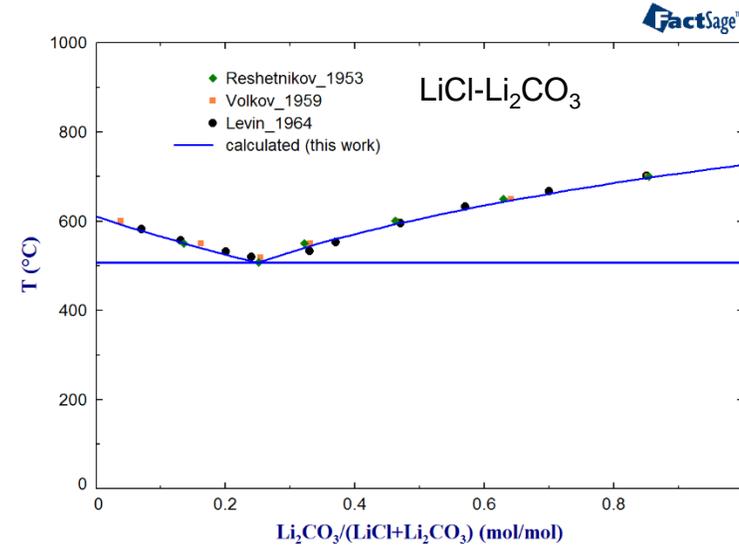
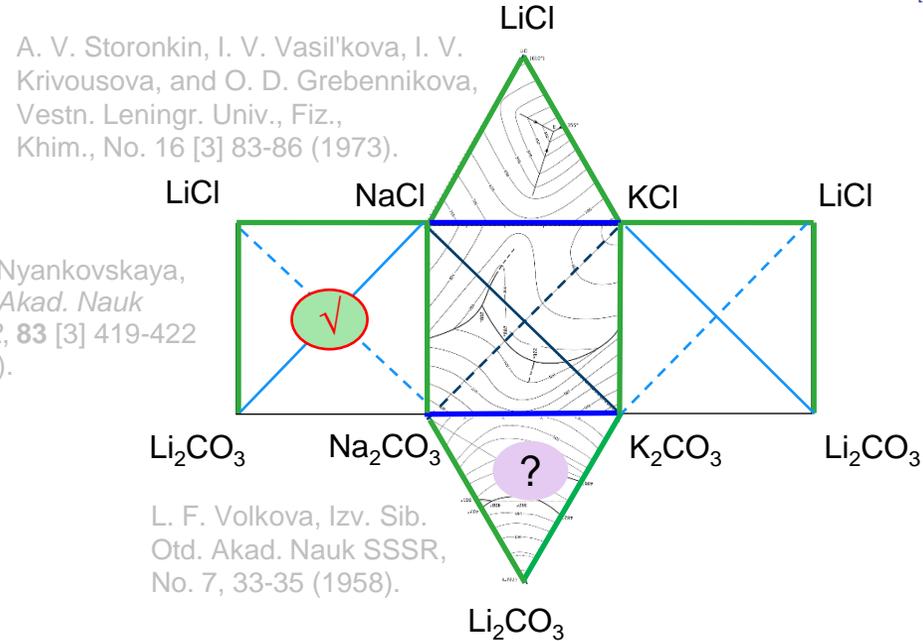
$$G_m = \sum x_i G_i^0 + RT \sum x_i \ln x_i + \sum_{i < j} \sum_{v=0} x_i x_j L_{ij}^{(v)} (x_i - x_j)^v \dots +$$

✓ **Solid solutions: sublattice approach (CEF)**

$$G_m = \sum_{I_0} P_{I_0} Y_{I_0}^0 G_{I_0}^0 + \sum_{s=1}^n a_s RT \sum_{i=1}^{n_s} y_i^s \ln(y_i^s) + \sum_{I_1} P_{I_1} Y_{I_1} (L_{I_1}) + \sum_{I_2} P_{I_2} Y_{I_2} (L_{I_2}) +$$

Overview of the system

$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}$

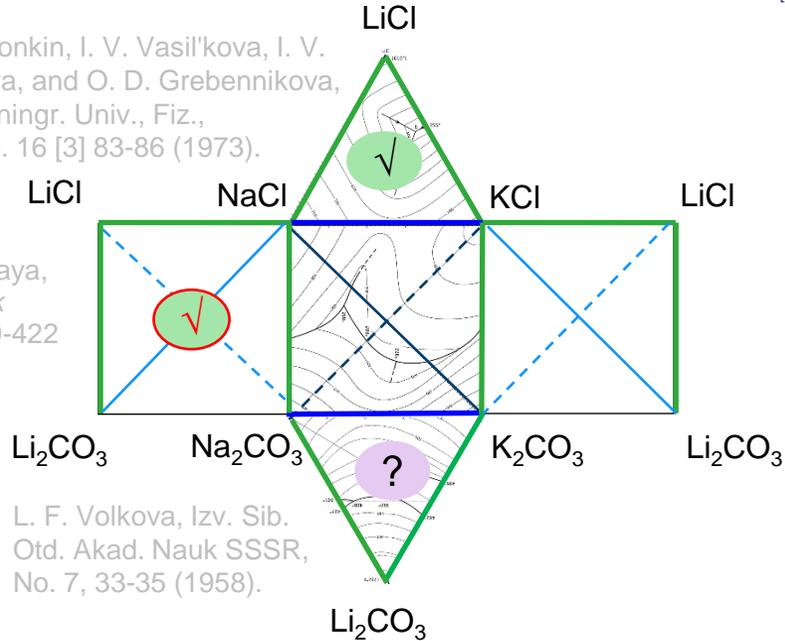


Overview of the system

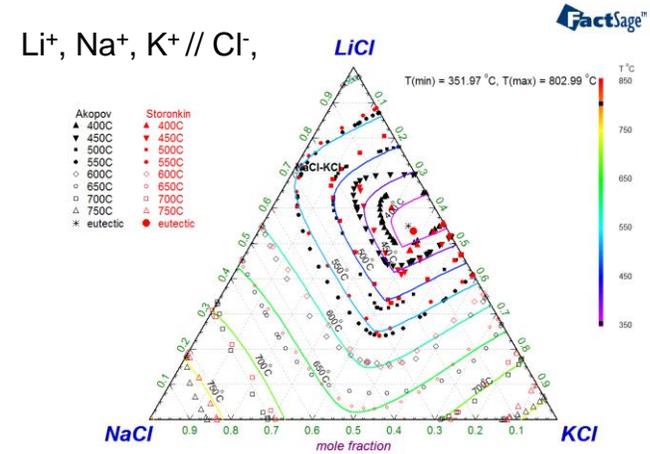
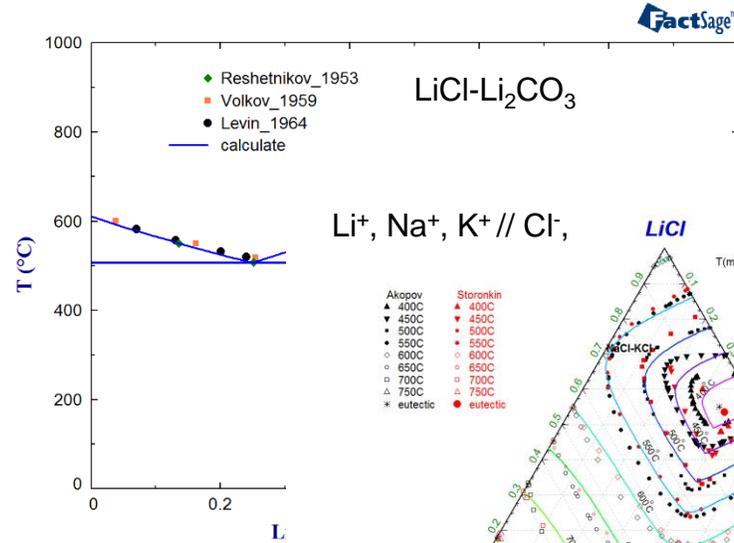
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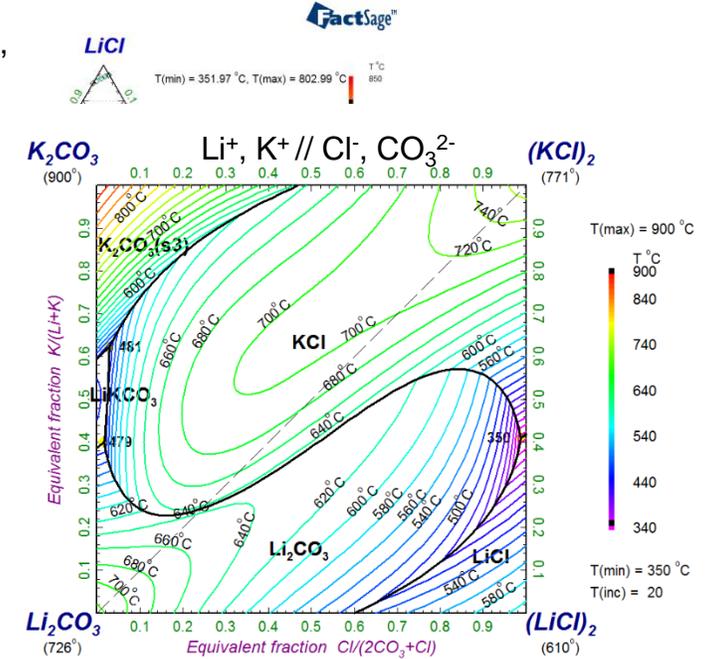
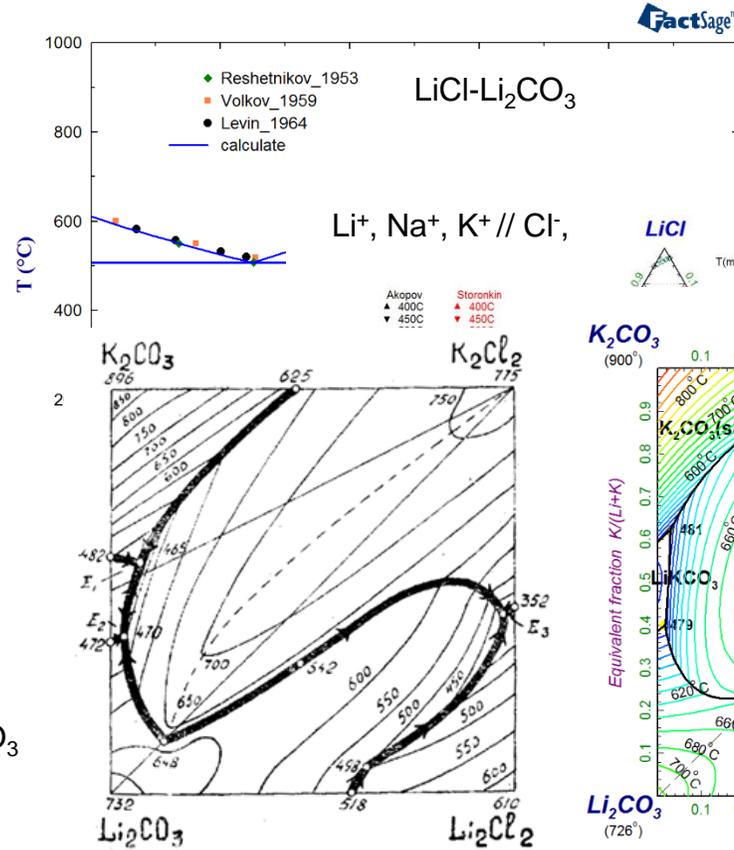
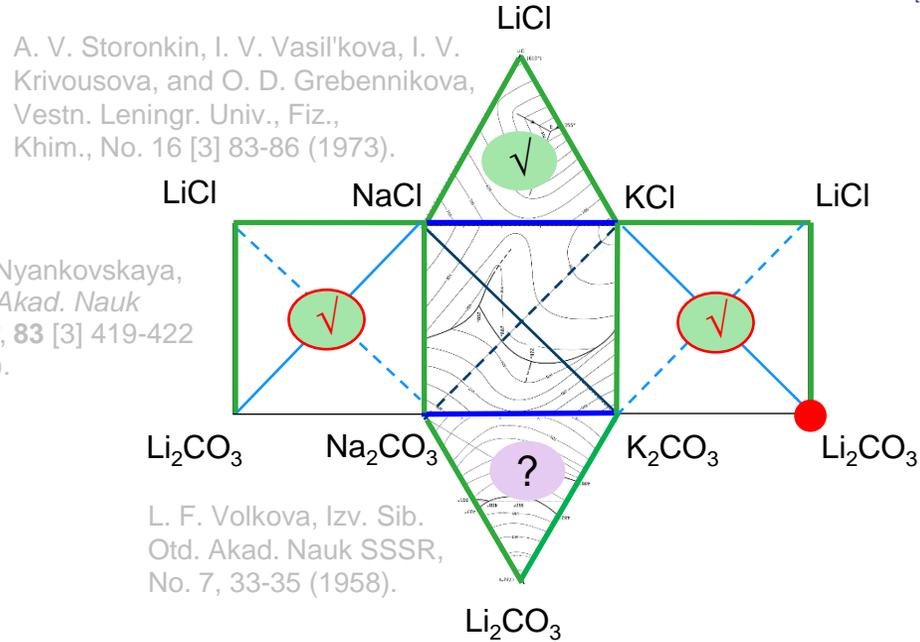


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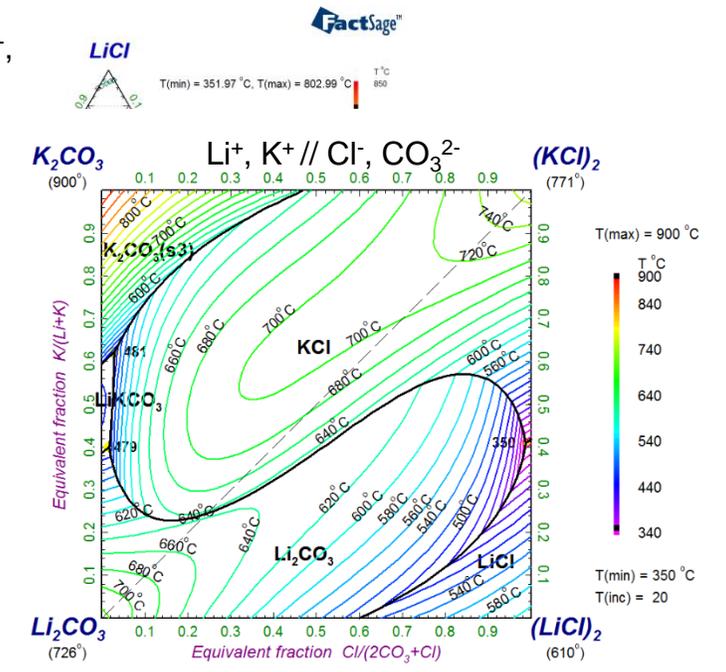
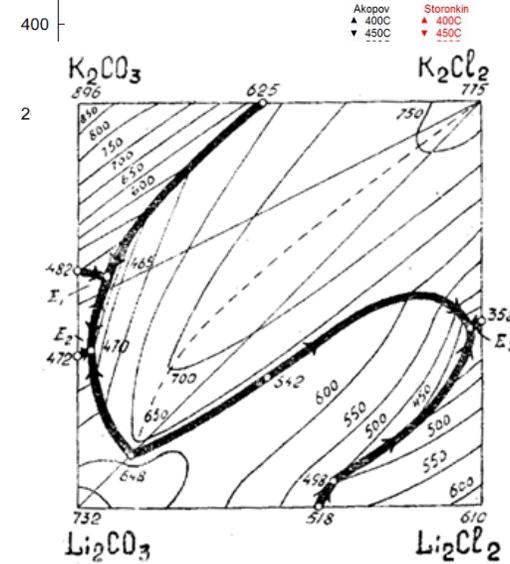
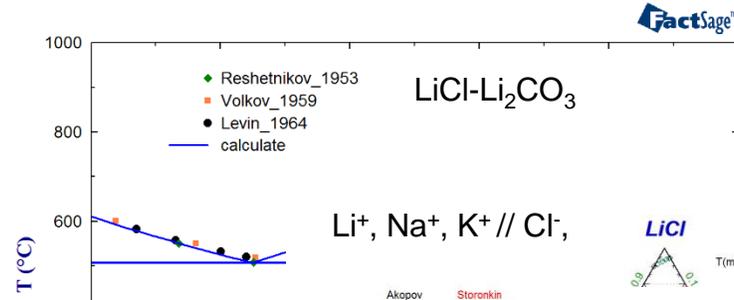
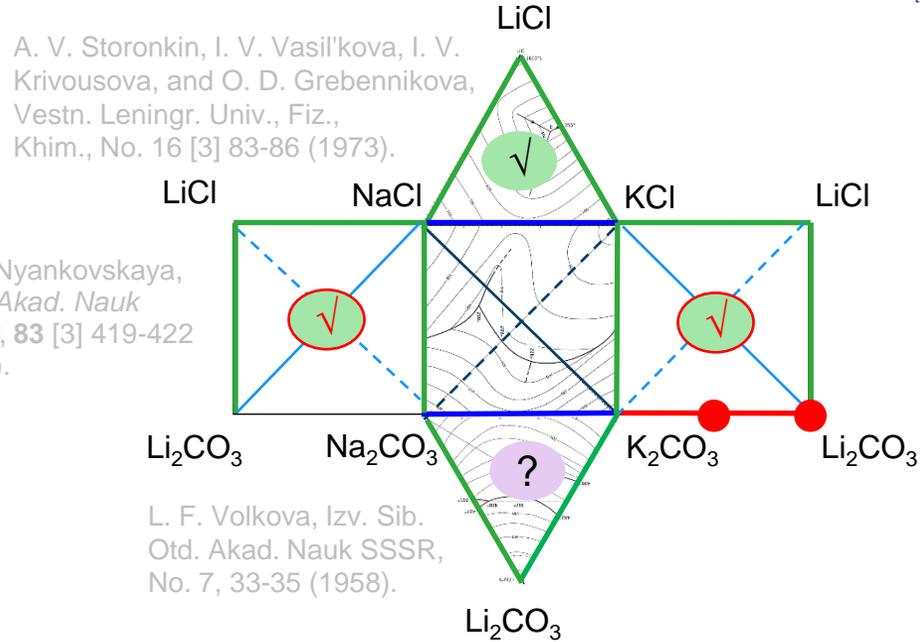
$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}$



➤ The Pure Li_2CO_3

Overview of the system

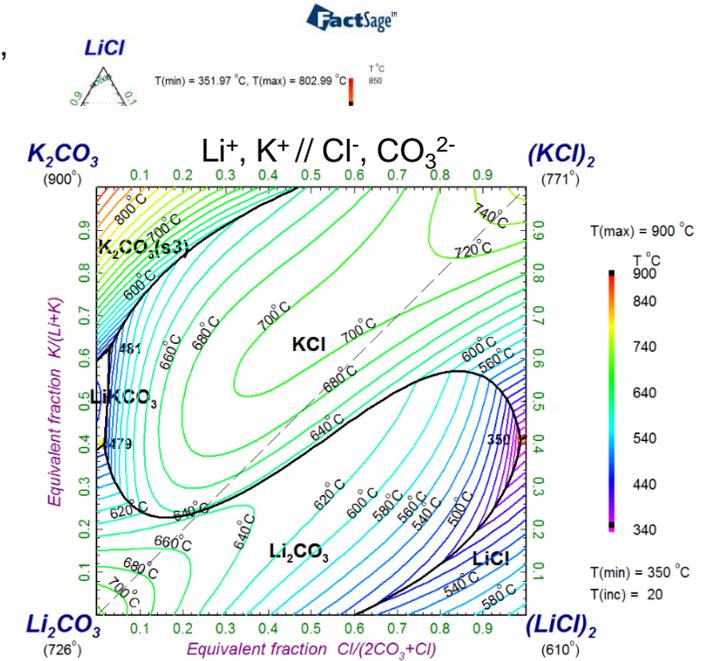
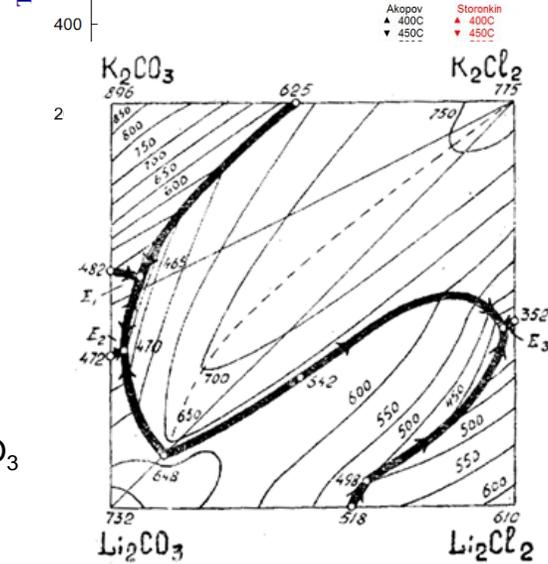
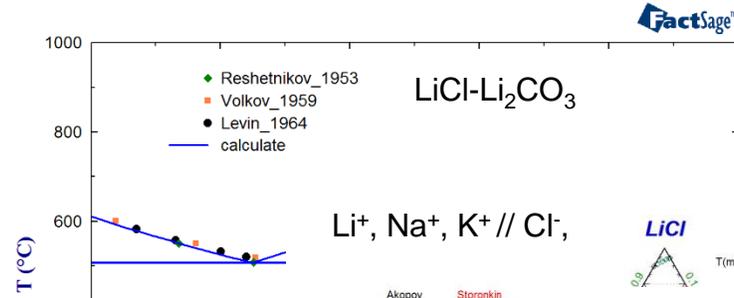
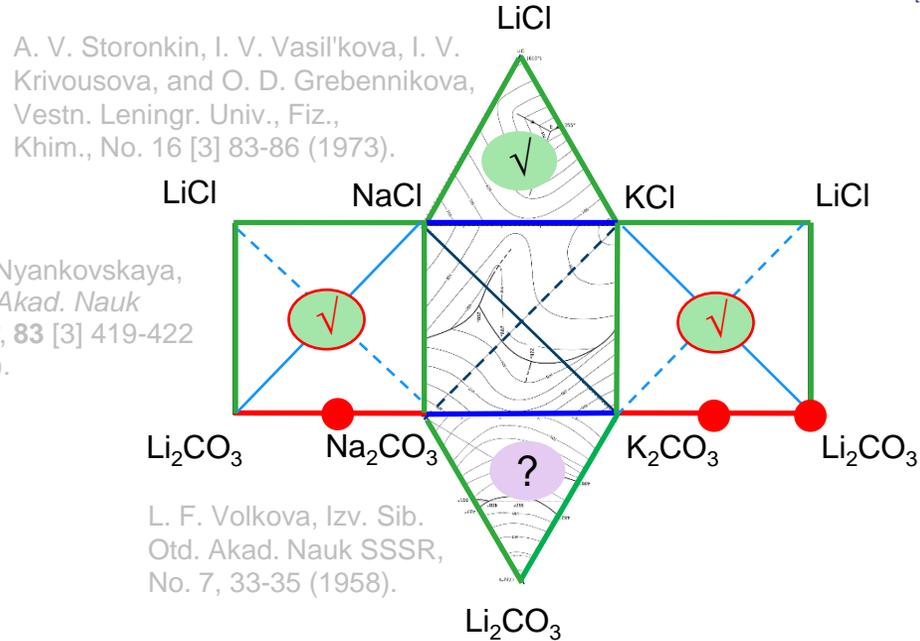
$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}$



- The Pure Li₂CO₃
- System Li₂CO₃-K₂CO₃
 - LiKCO₃

Overview of the system

$\text{Li}^+, \text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{CO}_3^{2-}$



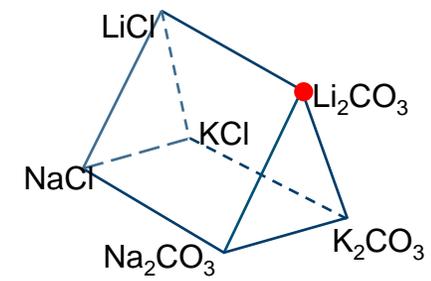
- The Pure Li_2CO_3
- System $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$
 - LiKCO_3
- System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$
 - LiNaCO_3

Pure Li_2CO_3

Solid-solid phase transition

Literature data

Reaction type	T_{tr} ° C (K)	method	Reference
solid \leftrightarrow solid	410 (683)	DTA	[Reisman, 1958]
	407-420 (680-693)	DTA	[Klement and Cohen, 1975]
	415 (688)	DTA	[Otsubo and Yamaguchi, 1961]
	410 (683)	database	SGPS , FTsalt
	416 (689)	DTA (Impurities)	This work
	Not detected		Drop
calorimetry			[Rolin and Recapet, 1964]

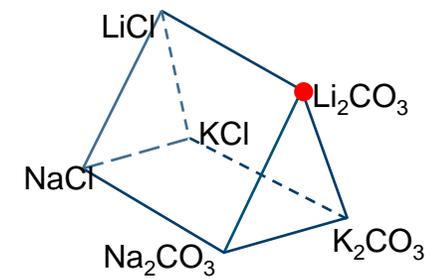


Pure Li_2CO_3

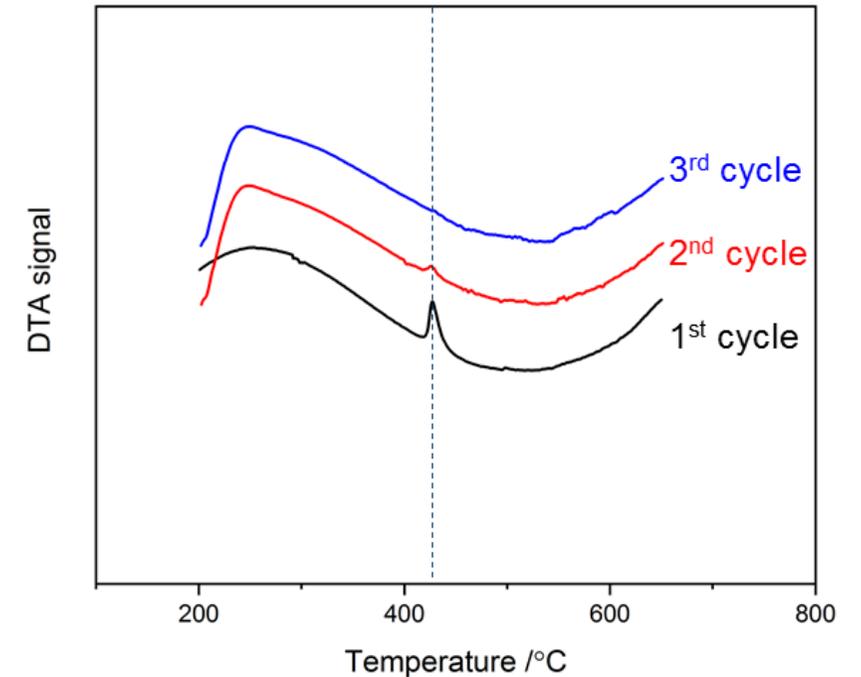
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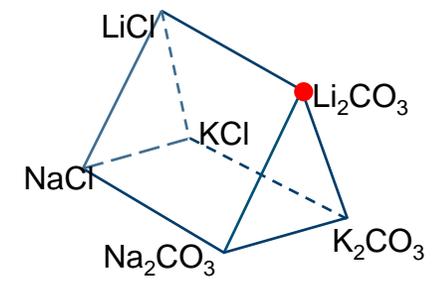
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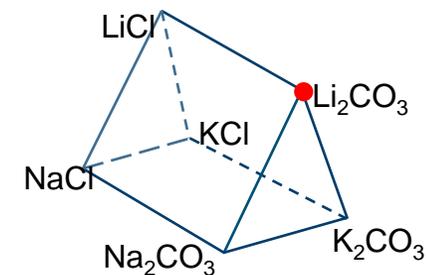
DTA (open crucible, Ar)



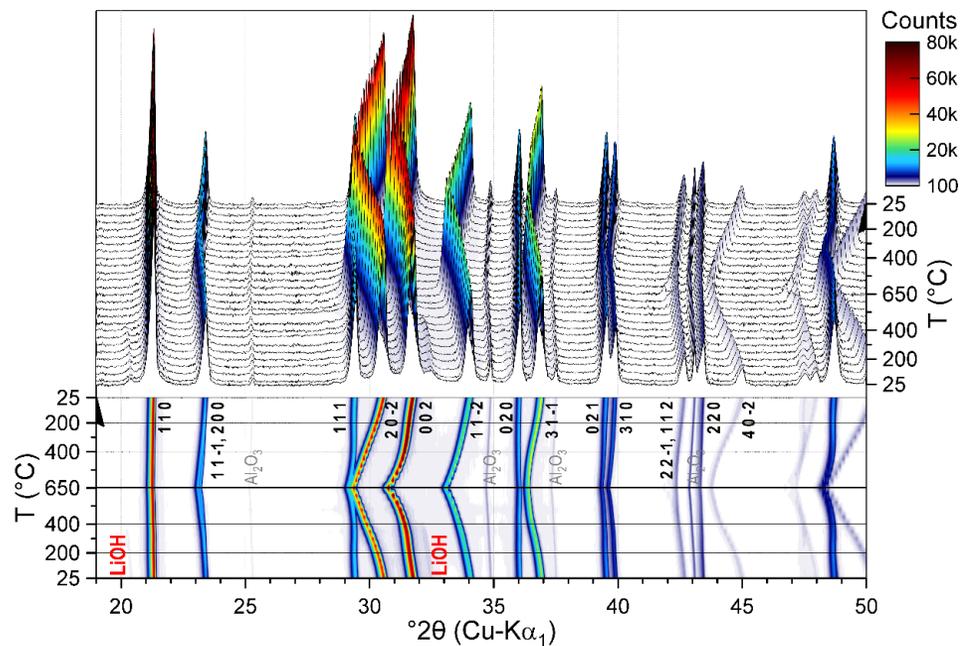
Pure Li_2CO_3



Pure Li_2CO_3



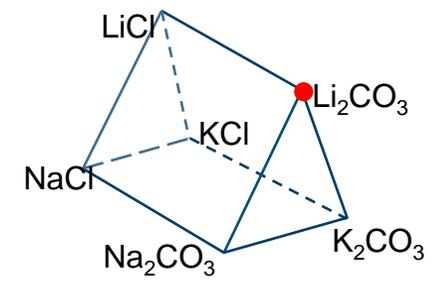
HTXRD



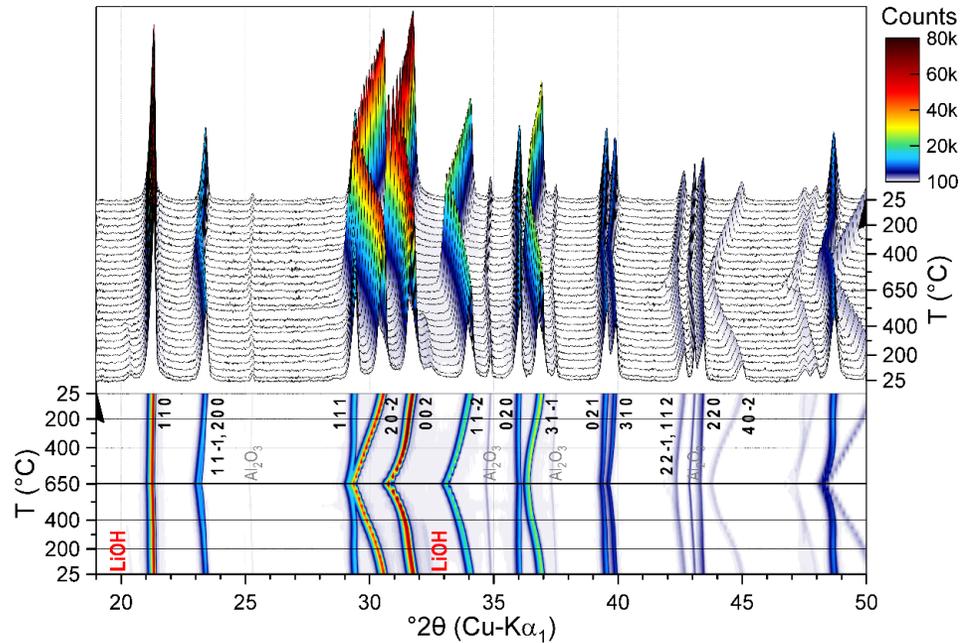
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- Eutectic temperature of $\text{LiOH-Li}_2\text{CO}_3$ -----419 °C [1].

[1] R. Cohen-Adad et al., *Bulletin de la Societe Chimique de France*. 1961:356-359.

Pure Li₂CO₃



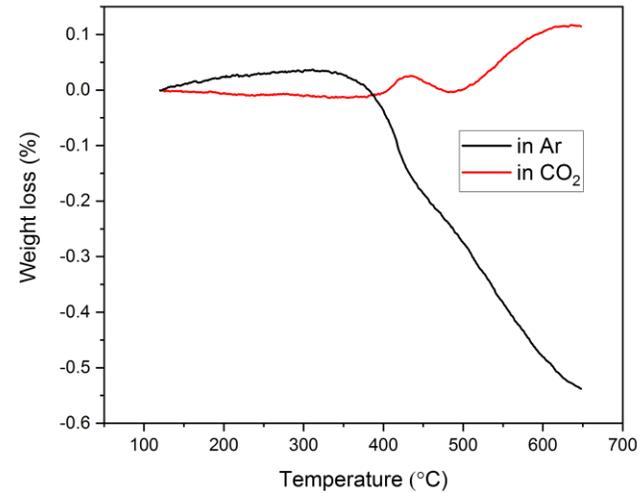
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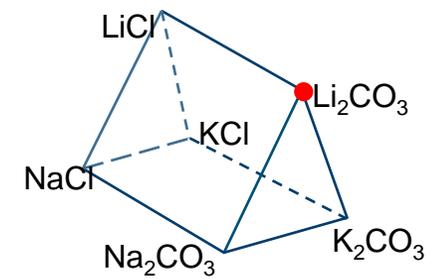
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TG

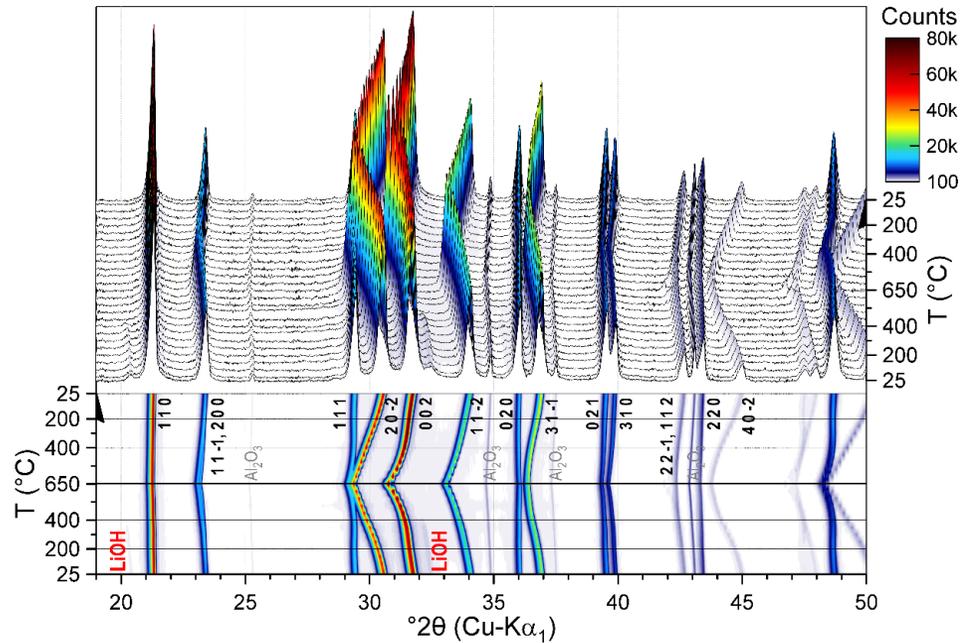


Vaporisation of LiOH

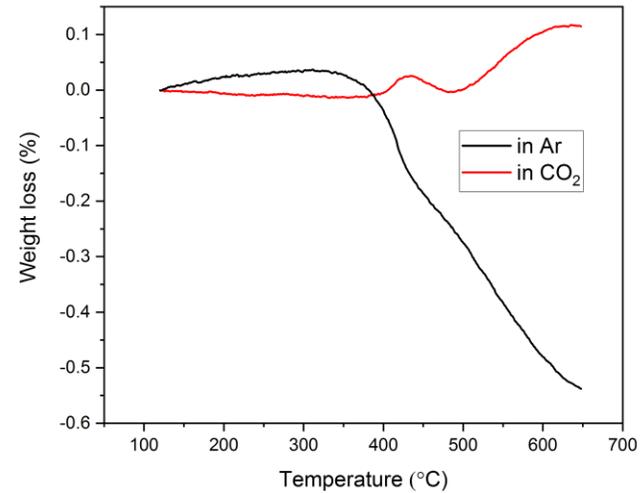
Pure Li_2CO_3



HTXRD

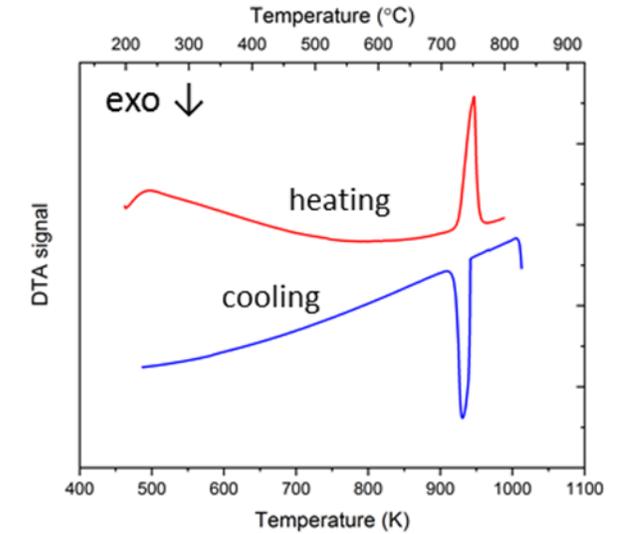


TG



Vaporisation of LiOH

DTA

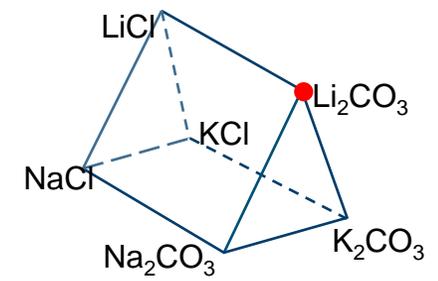


under CO_2 at 650 °C for 1 h to purify

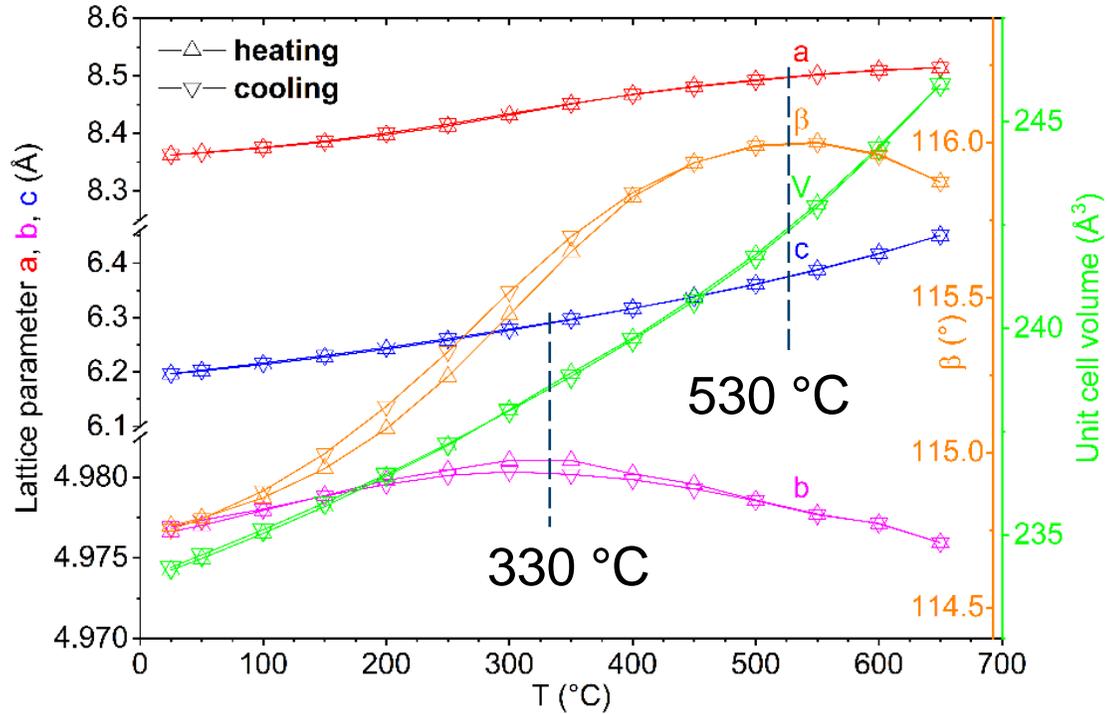
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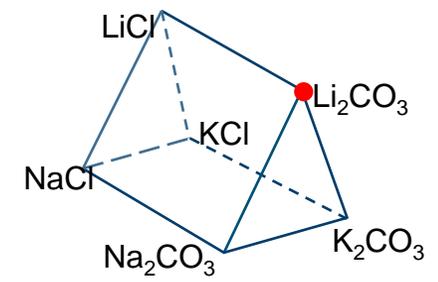


HTXRD

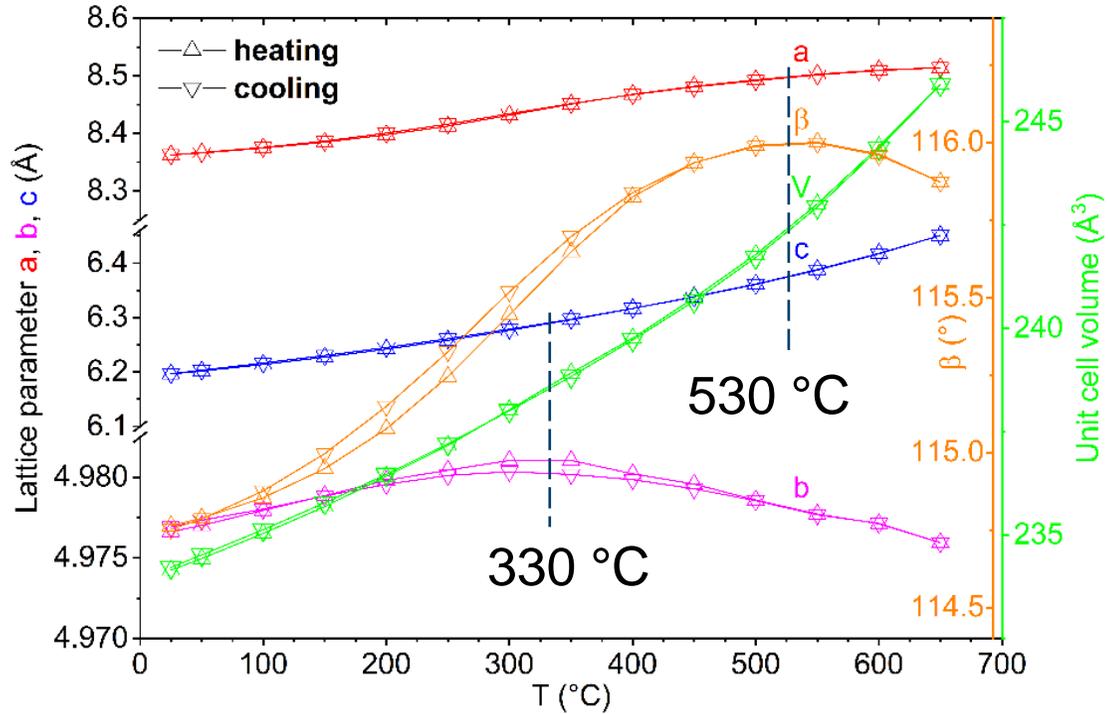


Slight phase transitions at 330 $^{\circ}\text{C}$ and 350 $^{\circ}\text{C}$ were noticed, but their thermal effect is too small to be detected.

Pure Li_2CO_3

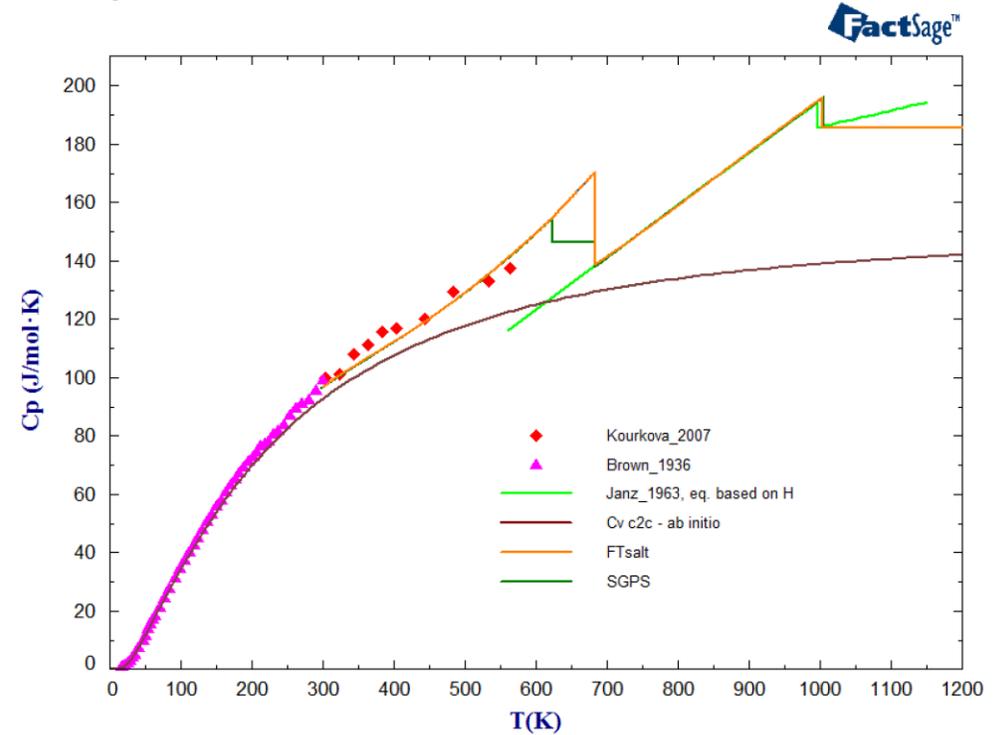


HTXRD



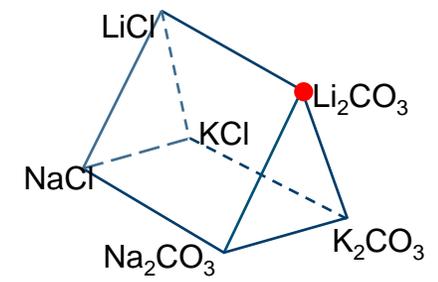
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C_p literature data

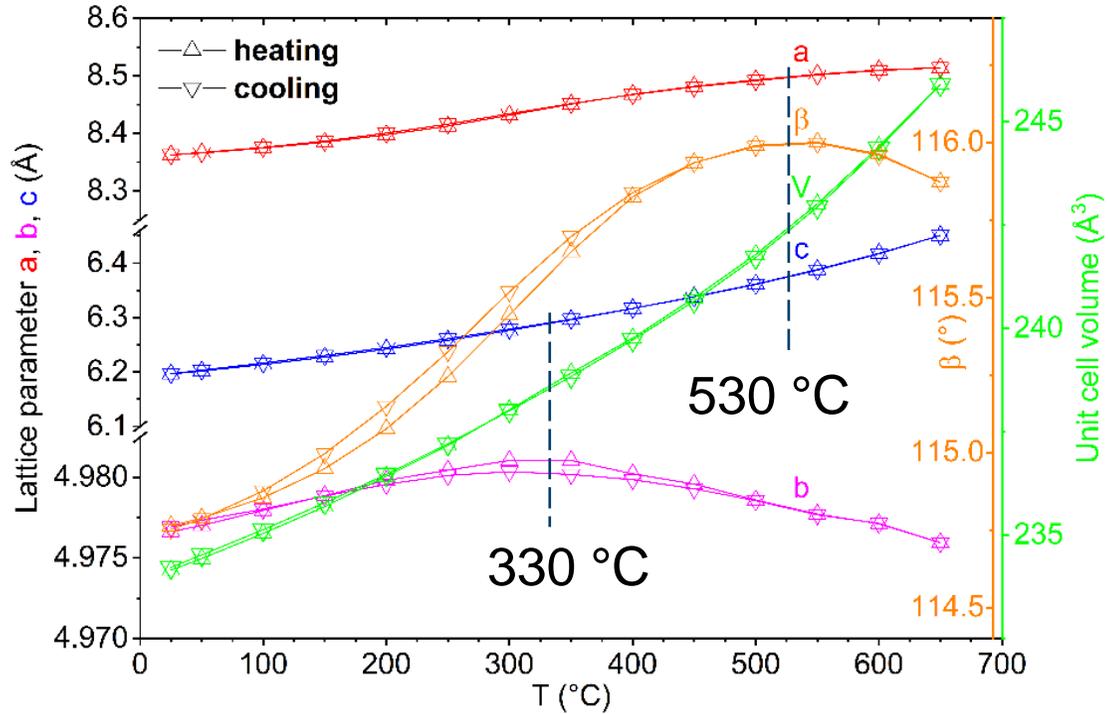


From equation based on enthalpy [Janz, 1963], which can be not accurate.

Pure Li_2CO_3

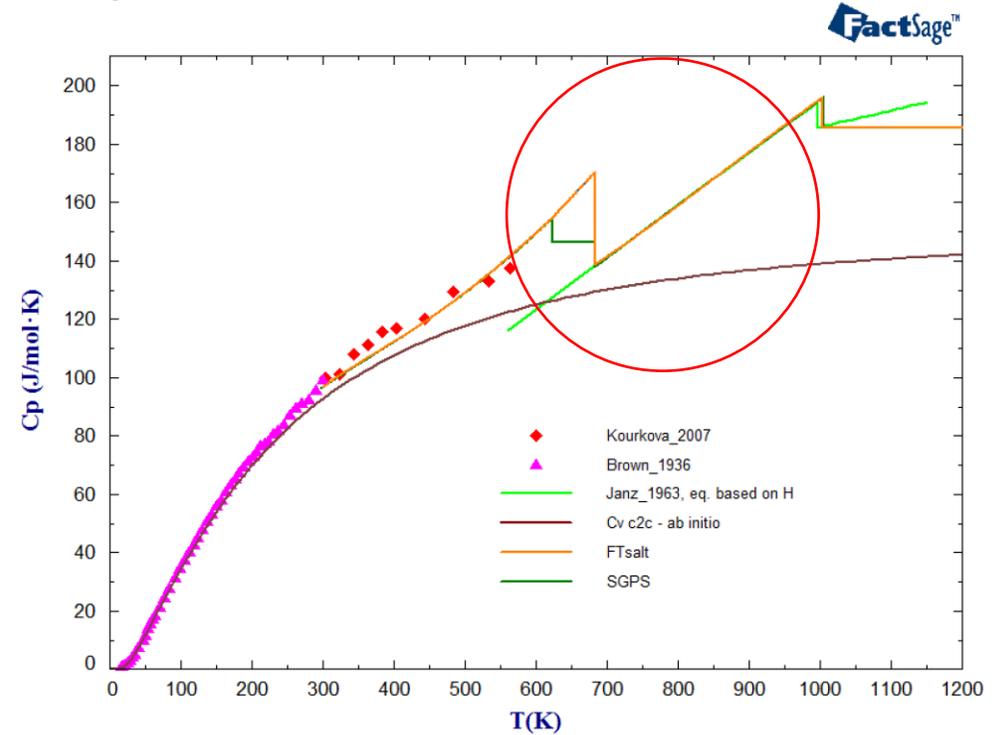


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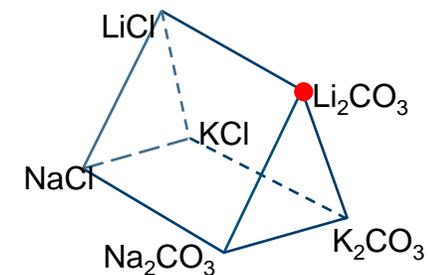
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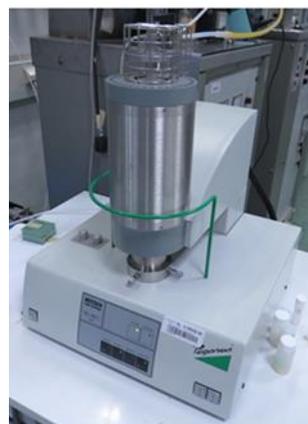
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Pure Li_2CO_3

C_p measurement-DSC devices



Liquid N_2



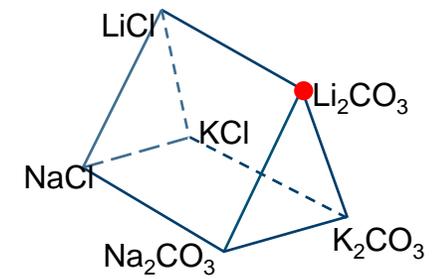
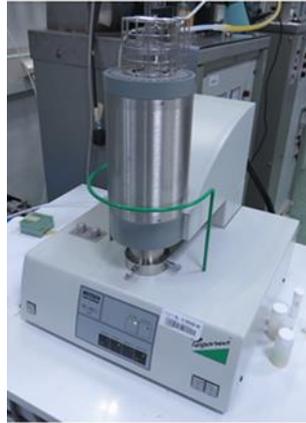
Instrument	DSC 404C_low_T	DSC 404C_high_T	mHTC 96
Company	Netzsch	Netzsch	Setaram
Temperature range	-180 - 650 ° C	25 - 1600 ° C	25 - 1400 ° C
Heating rate	20 K/min	20 K/min	4 K/min
Crucible	Pt with Al_2O_3 liner	Pt with Al_2O_3 liner	Pt with Al_2O_3 liner
Atmosphere	He, 10 mL/min	He, 10 mL/min	He, 10 mL/min

Pure Li_2CO_3

C_p measurement-DSC devices



Liquid N_2



Crucible selection

Pt : good thermal conductivity,
but react with Li_2CO_3 [1]

[1] R. Kasuya et al., *Journal of the Ceramic Society of Japan*.
2013;121(1418):884-890.

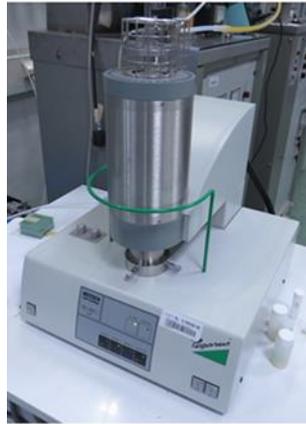
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Pure Li_2CO_3

C_p measurement-DSC devices

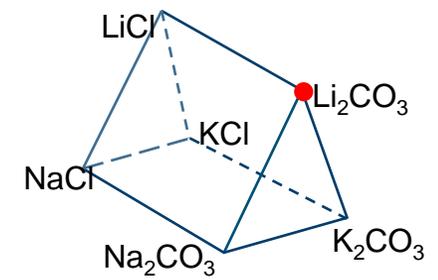


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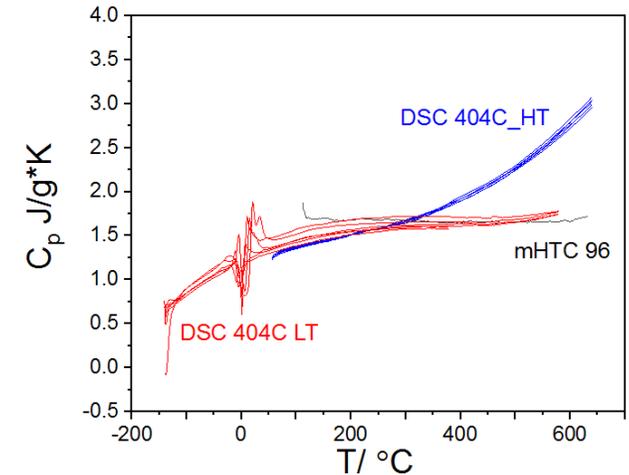
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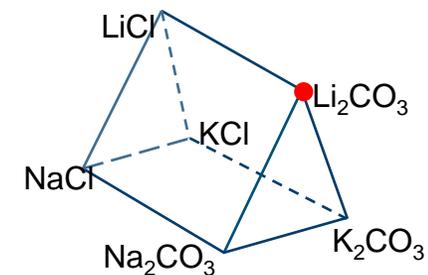
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Al_2O_3 : thermal conductivity not good



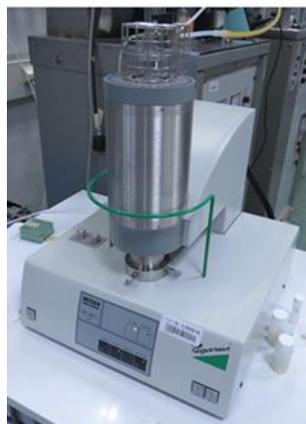
Pure Li_2CO_3



C_p measurement-DSC devices



Liquid N_2



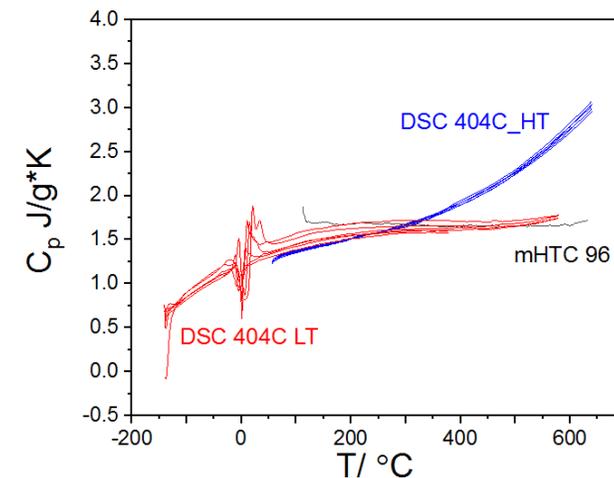
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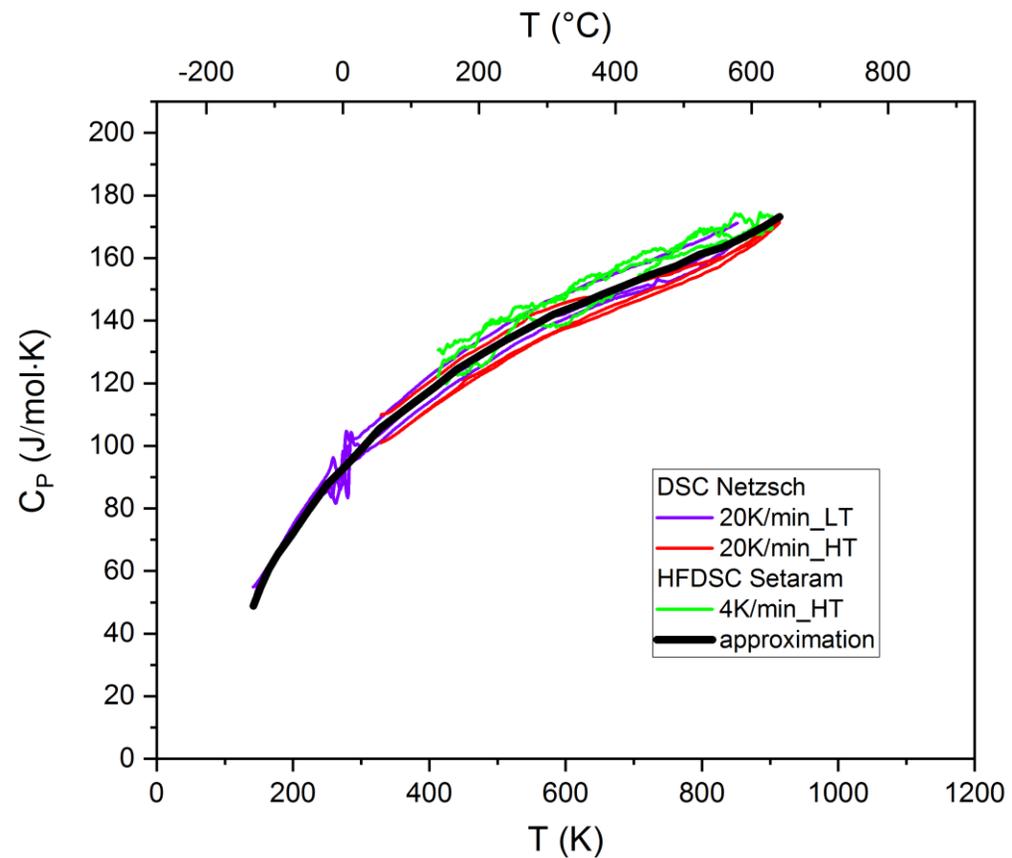
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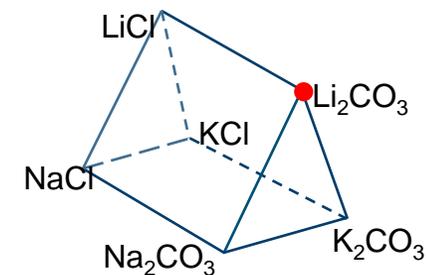
Pt + Al_2O_3 liner

Pure Li_2CO_3

C_p measurement

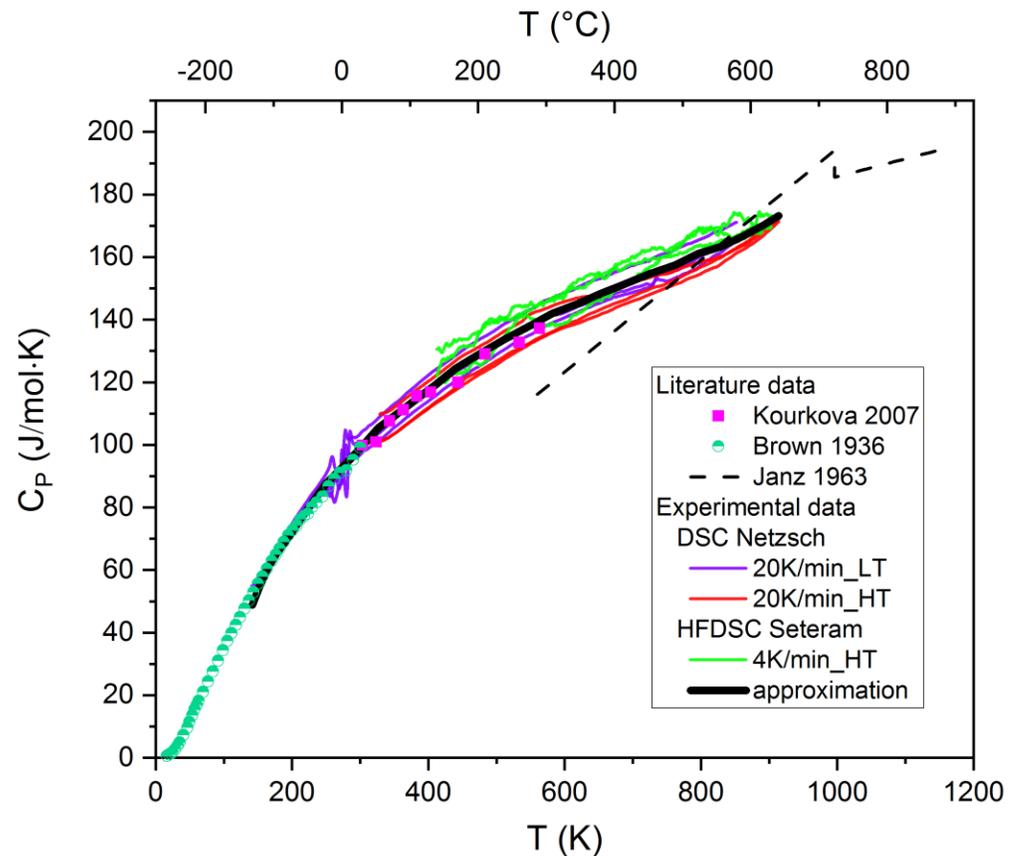


C_p optimisation

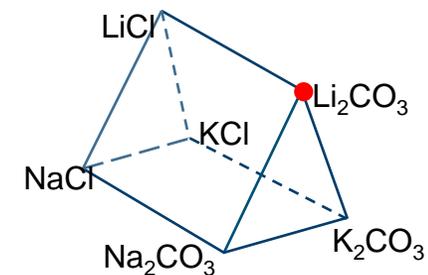


Pure Li_2CO_3

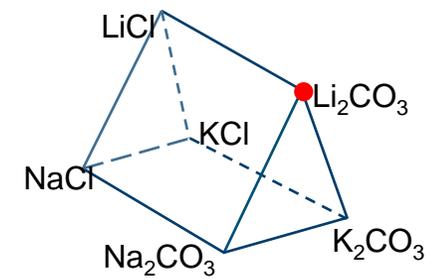
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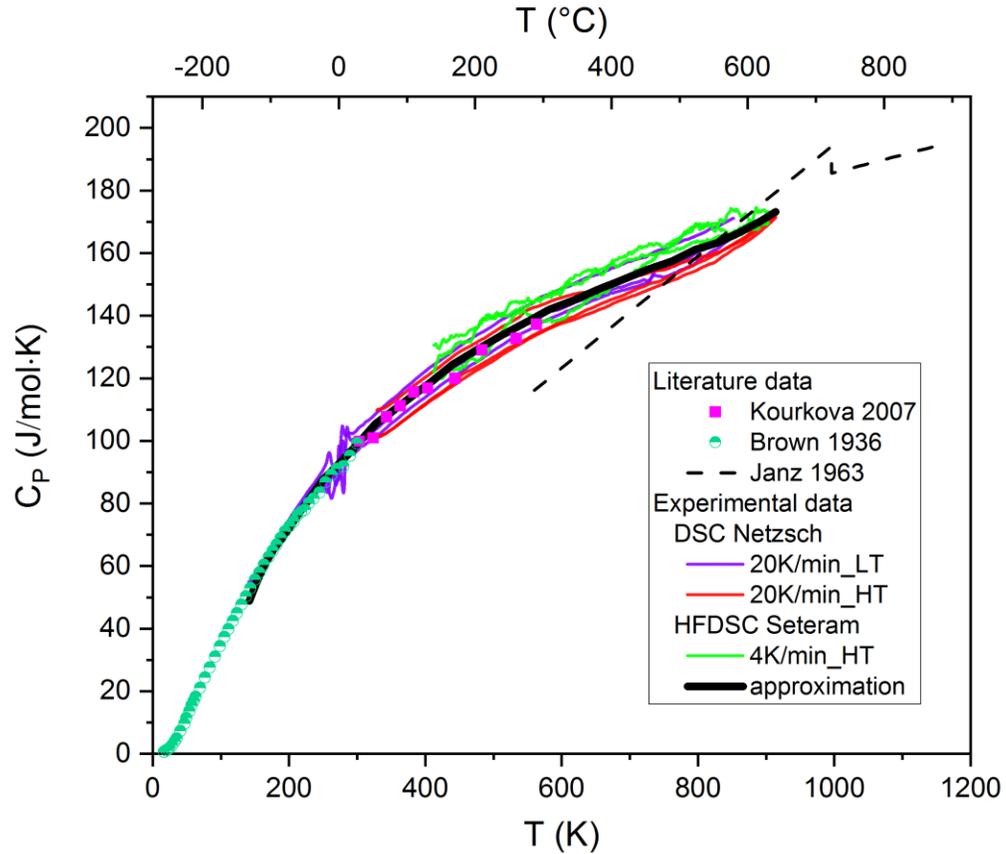
C_p optimisation



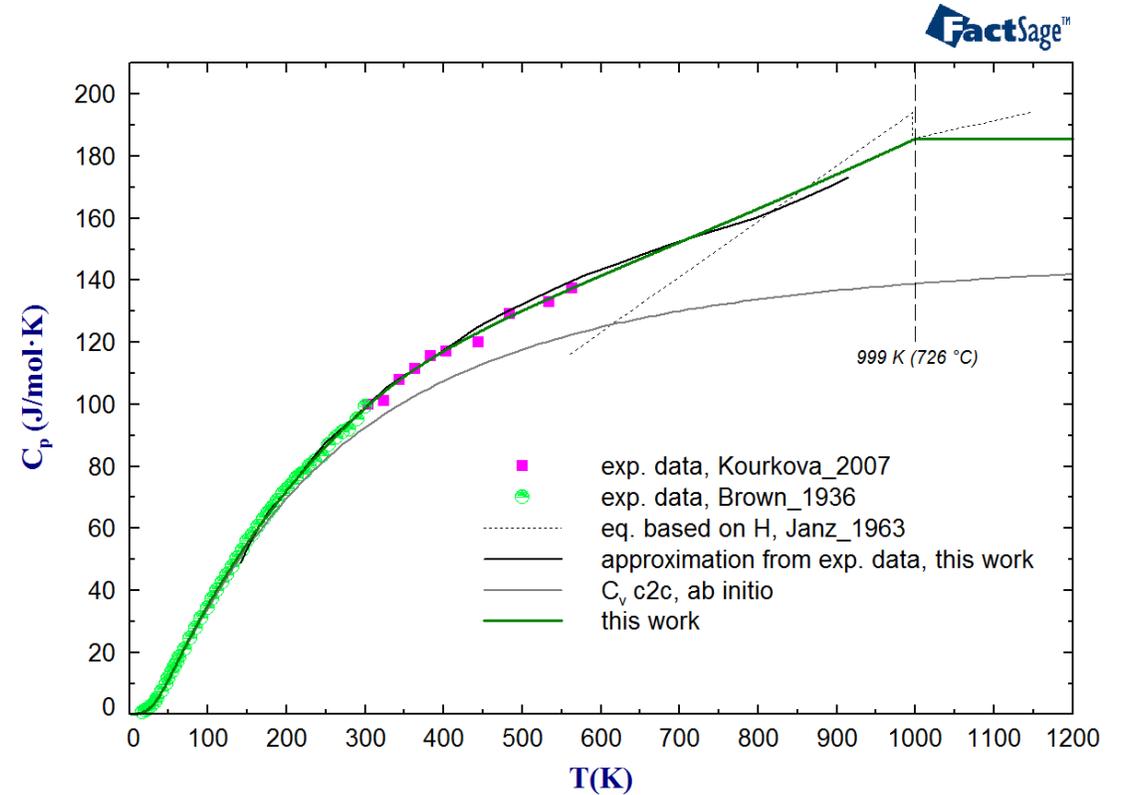
Pure Li_2CO_3



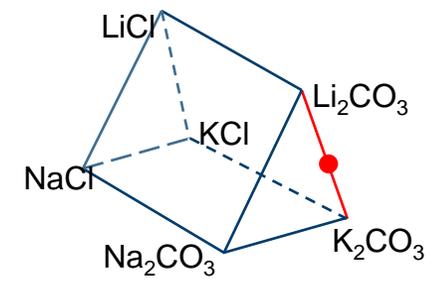
C_p measurement



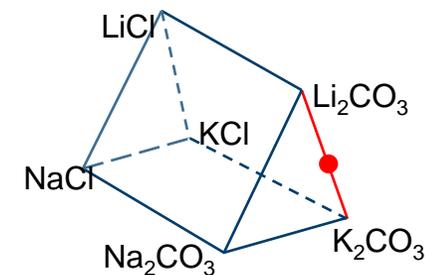
C_p optimisation



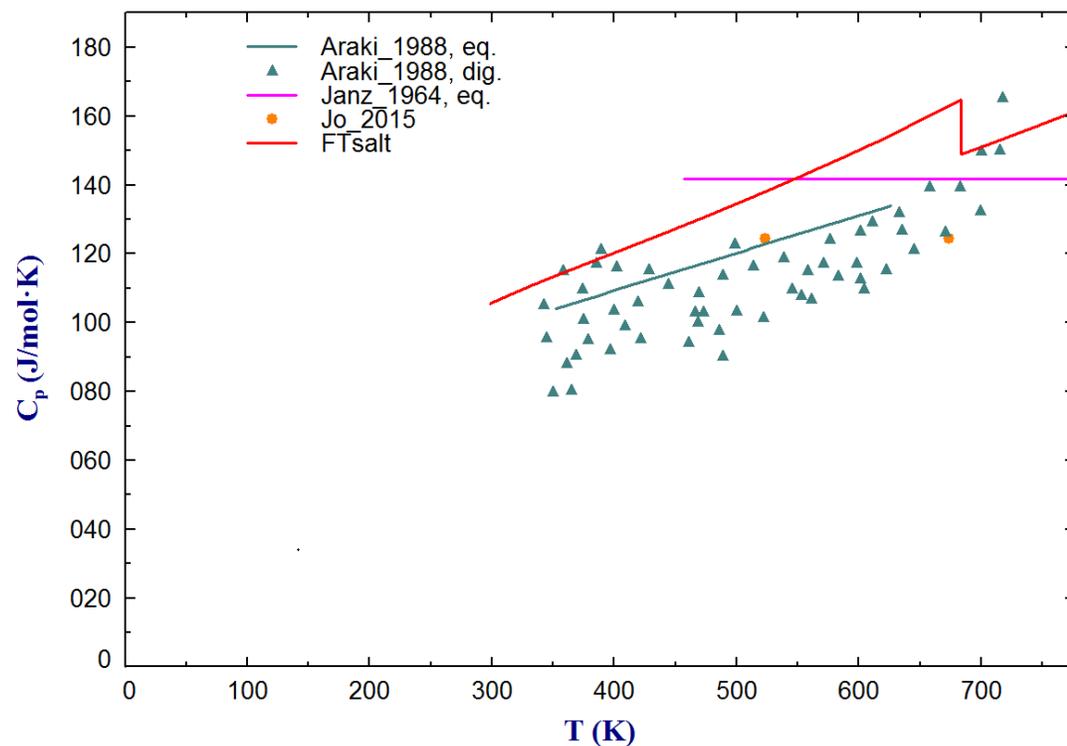
Intermediate compound LiKCO_3



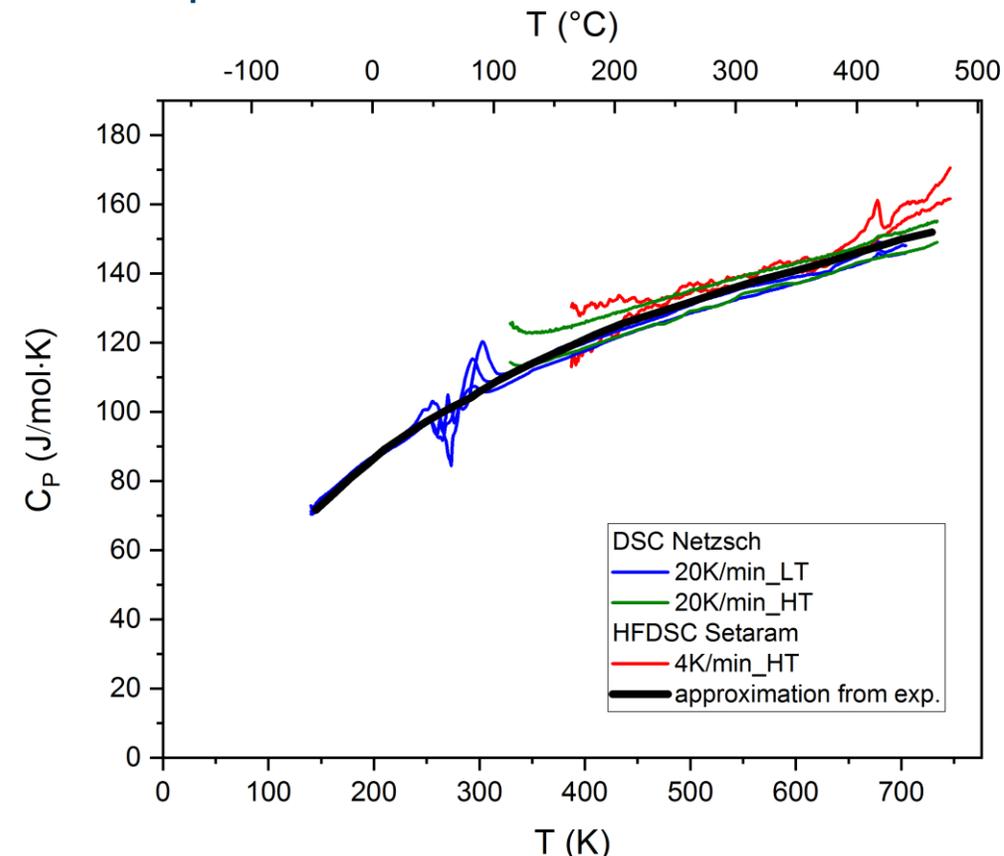
Intermediate compound LiKCO_3



C_p of LiKCO_3 literature data

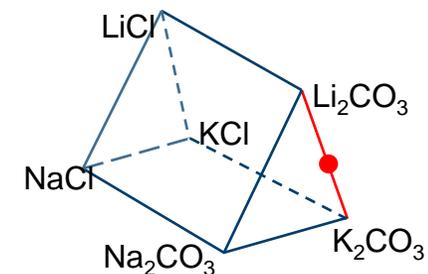


C_p measurement

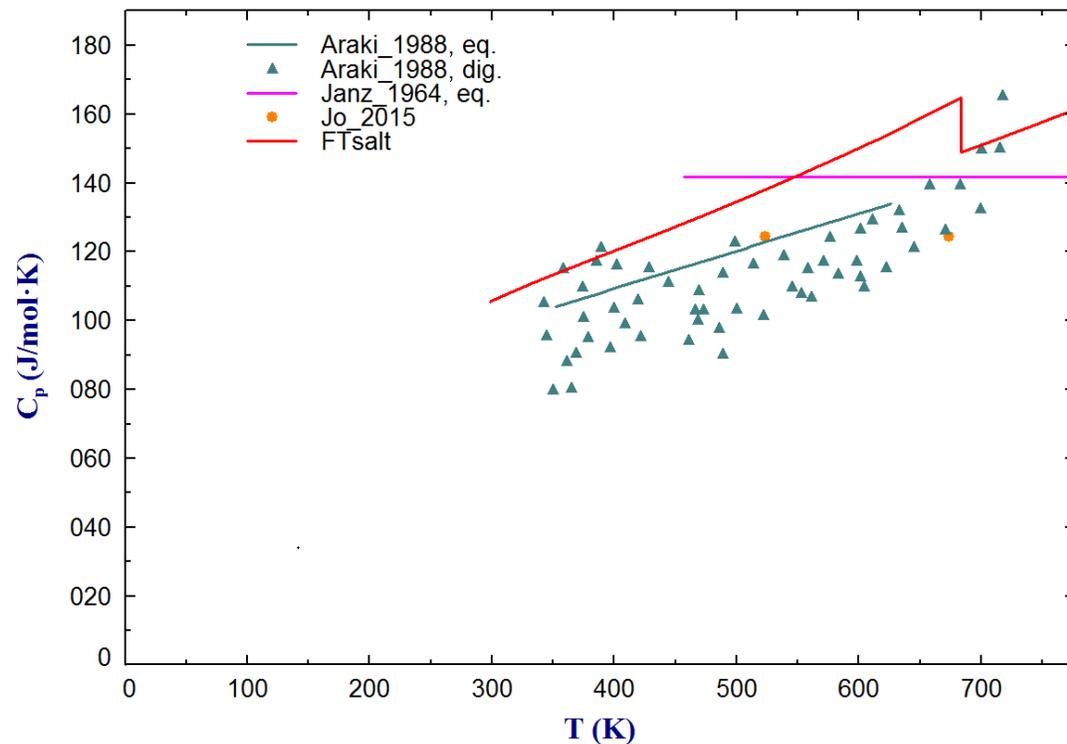


A peak was shown in the C_p curve at 404 °C

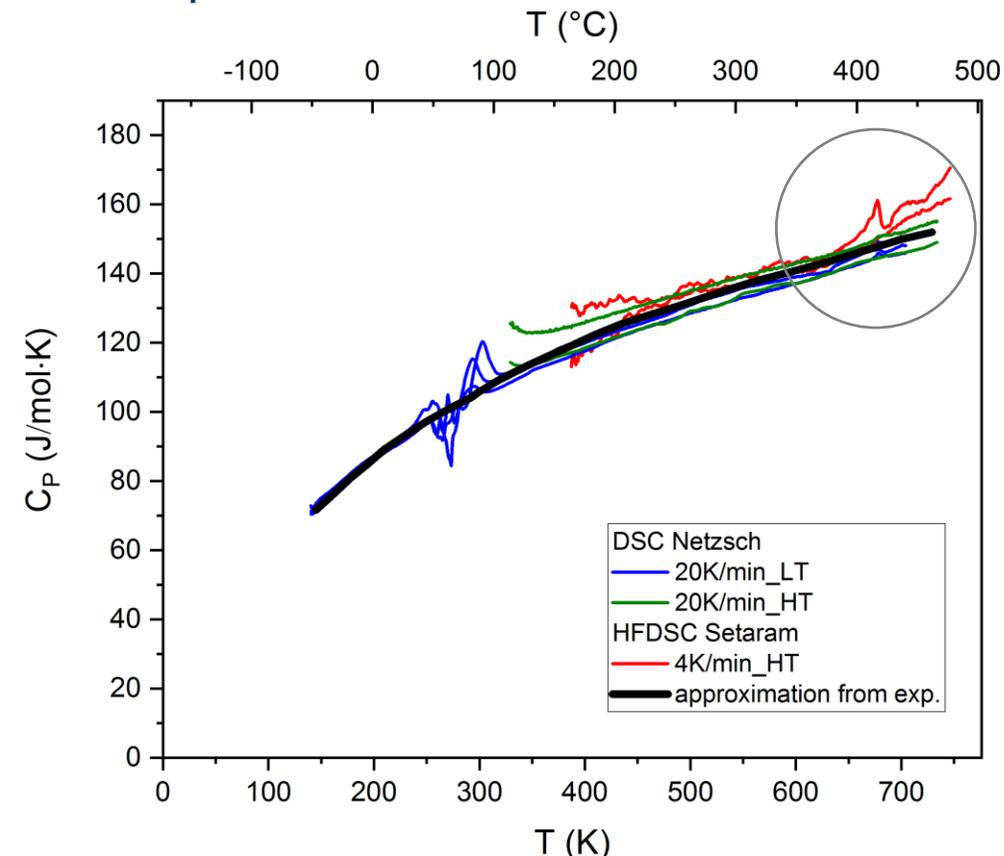
Intermediate compound LiKCO_3



C_p of LiKCO_3 literature data

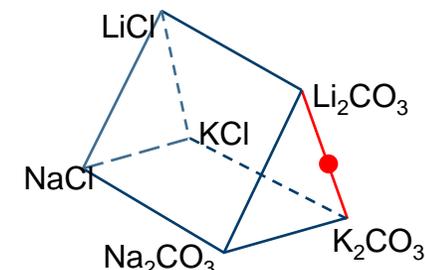


C_p measurement



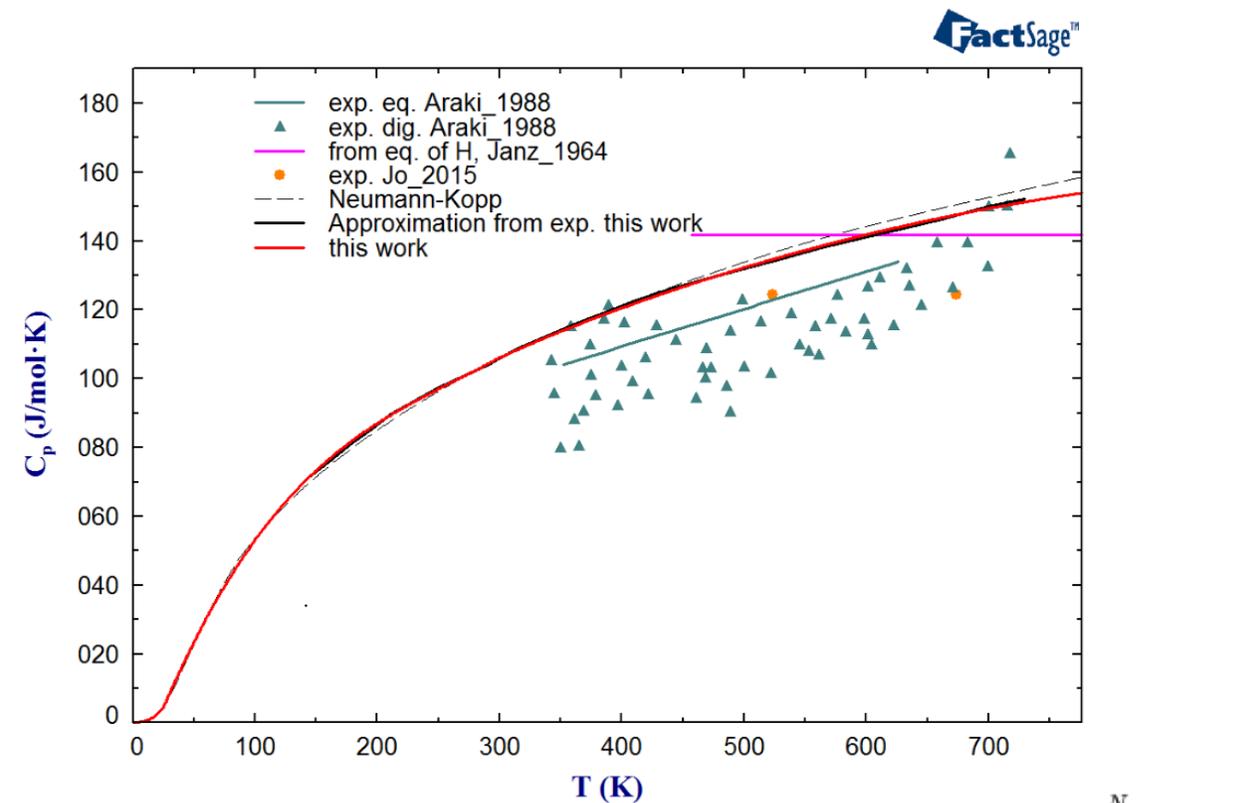
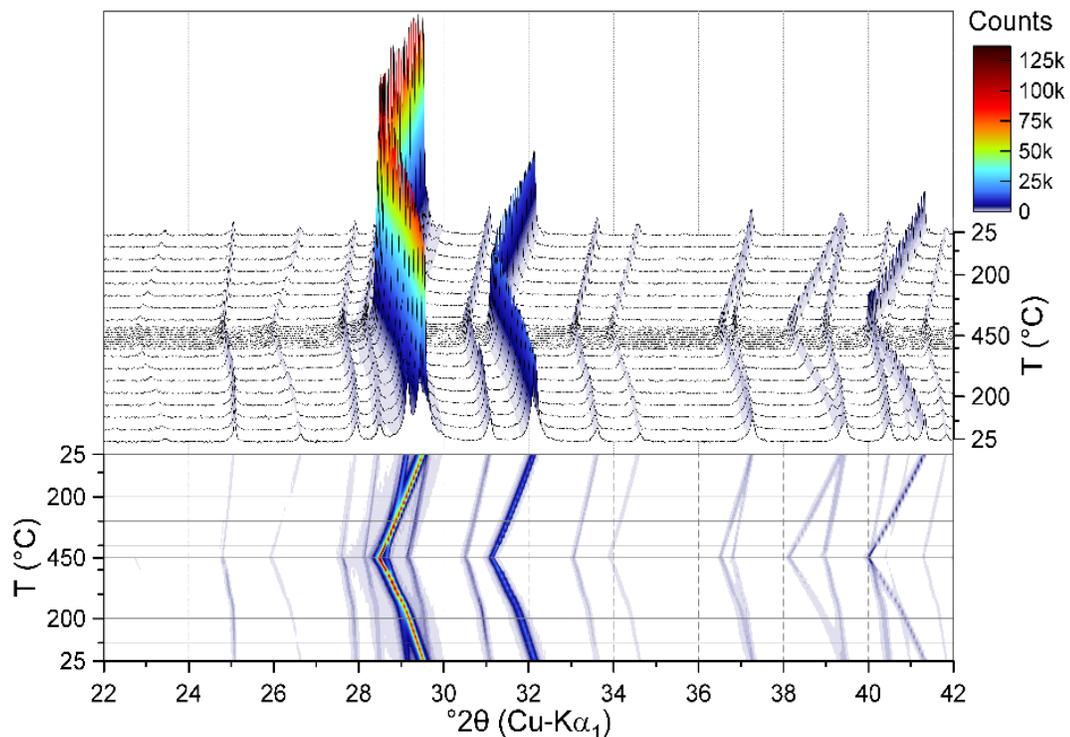
A peak was shown in the C_p curve at 404 °C

Intermediate compound LiKCO_3



HTXRD of LiKCO_3

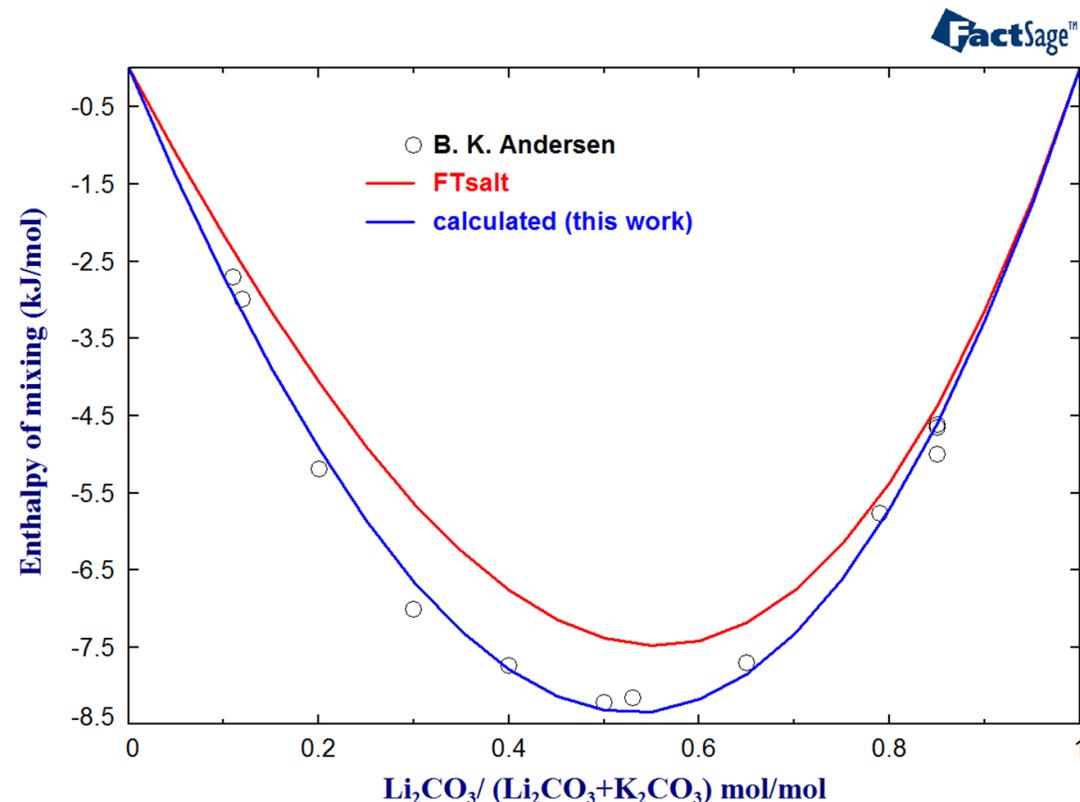
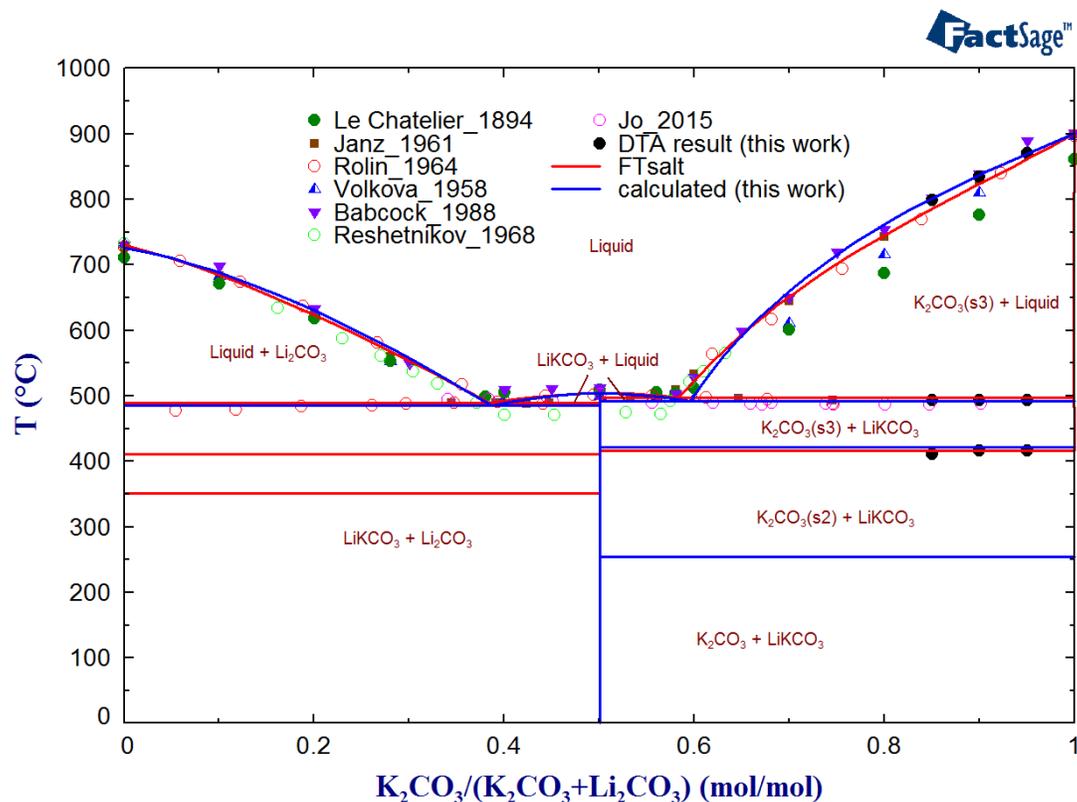
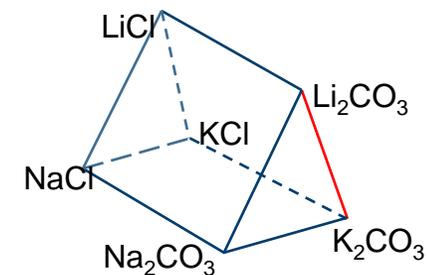
C_p optimisation



Low temperature C_p : calculated from Neumann-Kopp $C = \sum_{i=1}^N (C_i \cdot f_i)$

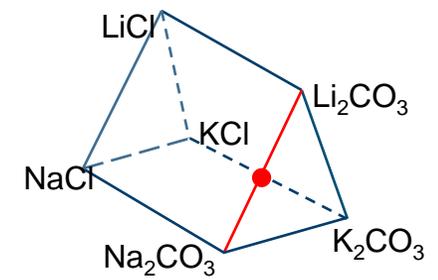
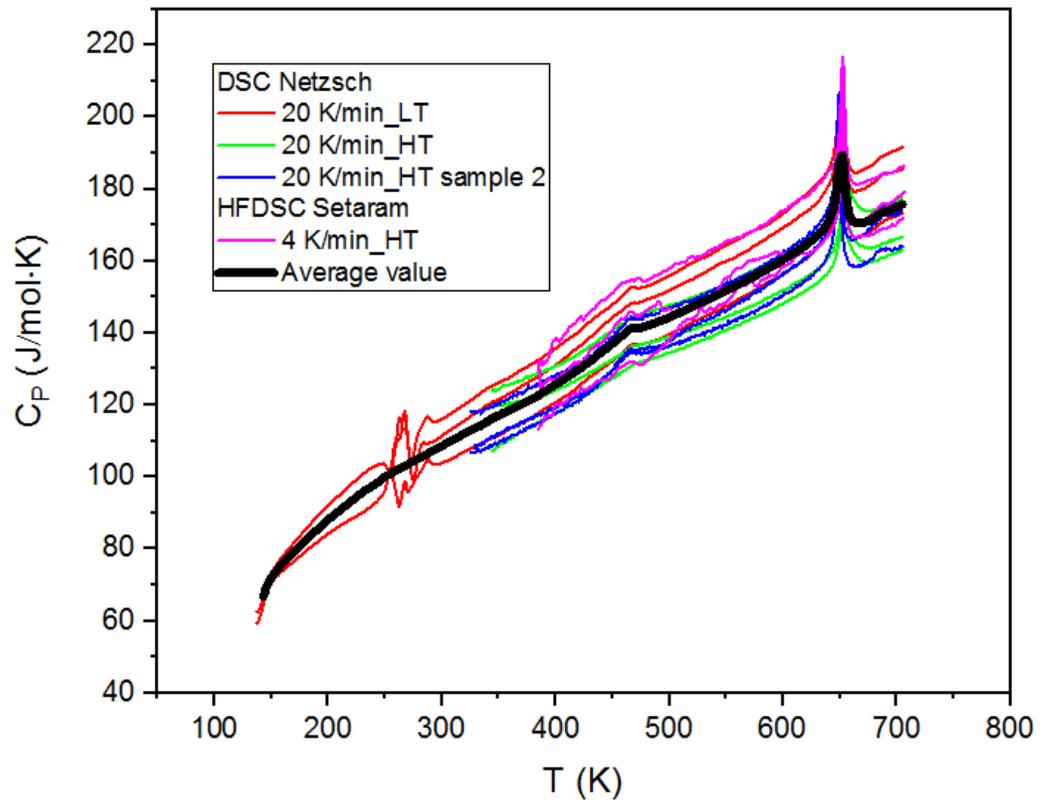
System $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$

Assessment of the system



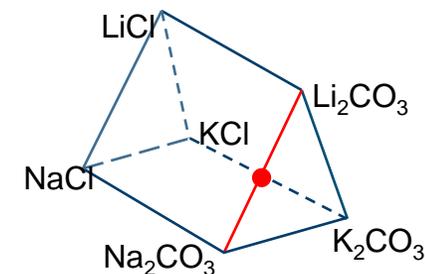
Intermediate compound LiNaCO_3

C_p measurement

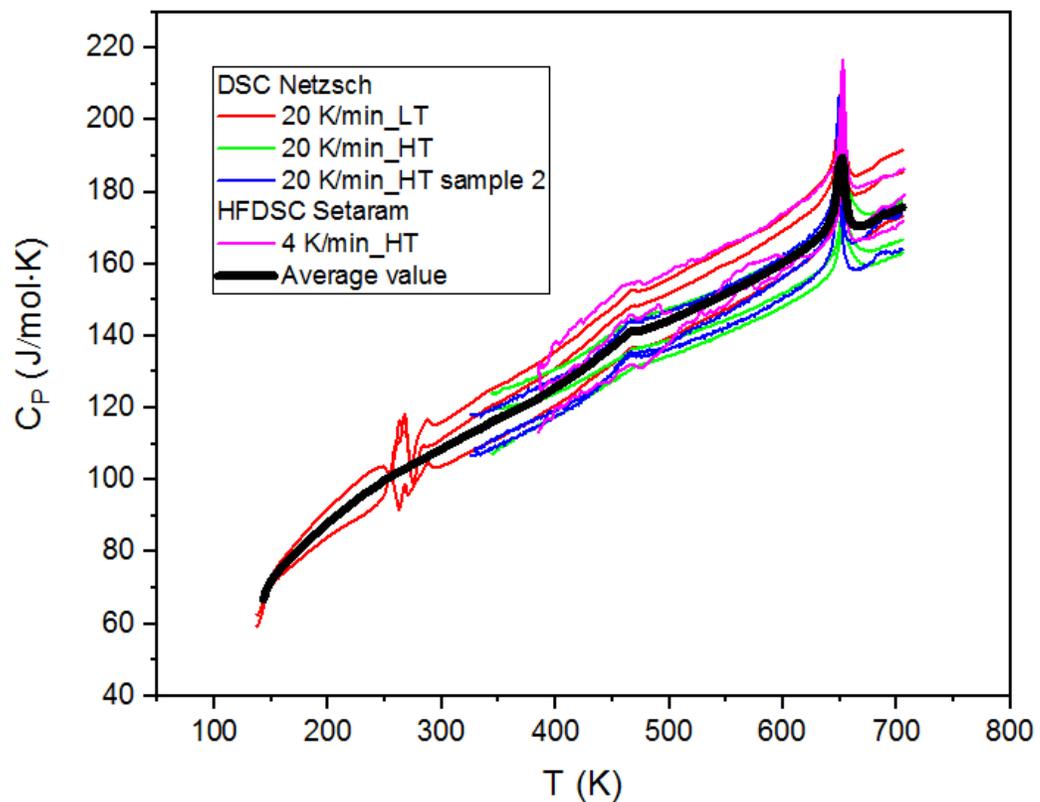


$$C = \sum_{i=1}^N (C_i \cdot f_i)$$

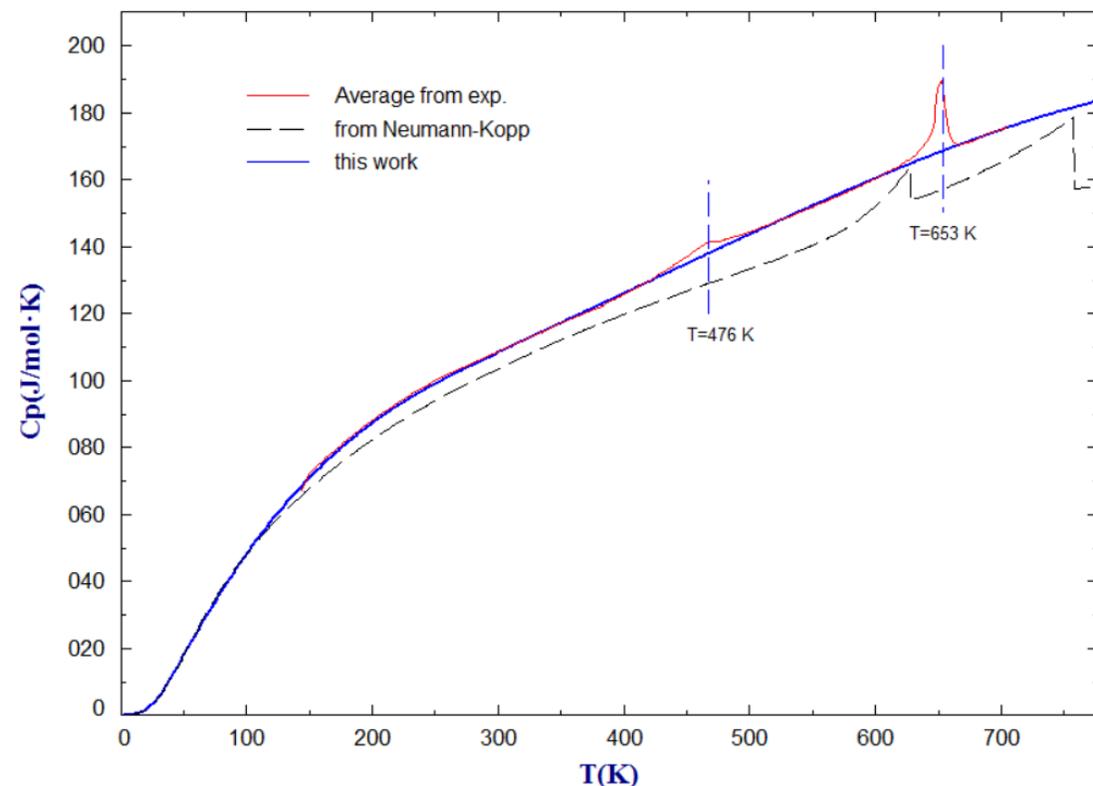
Intermediate compound LiNaCO_3



C_p measurement



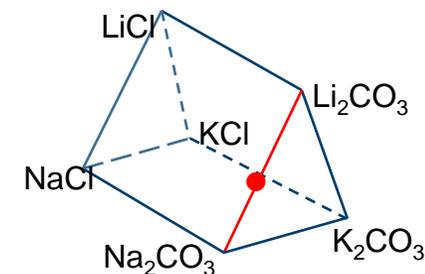
C_p optimisation



Low temperature C_p : calculated from Neumann-Kopp

$$C = \sum_{i=1}^N (C_i \cdot f_i)$$

Intermediate compound LiNaCO_3



HTXRD

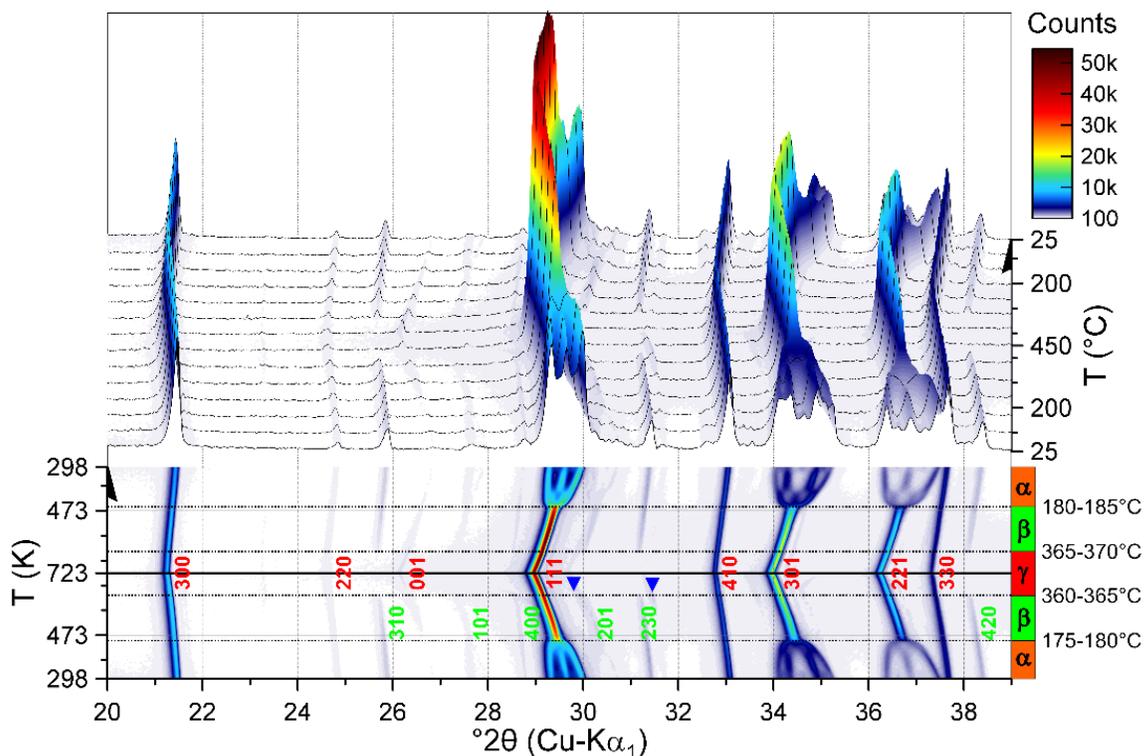


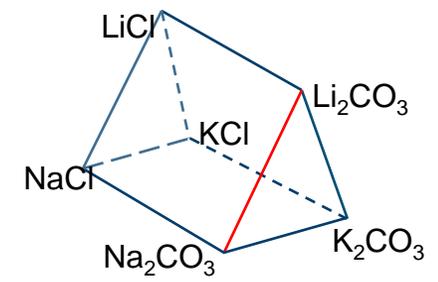
Table. Solid phase crystal structure and phase change temperature of LiNaCO_3 from different authors.

	M. Christmann	C. Ricca	This work
α phase	monoclinic	triclinic	triclinic
α phase \rightarrow β phase	290 °C	175 °C	180-185 °C
β phase	hexagonal	hexagonal	hexagonal
β phase \rightarrow γ phase	415 °C	360 °C	365-370 °C
γ phase	hexagonal	hexagonal	hexagonal

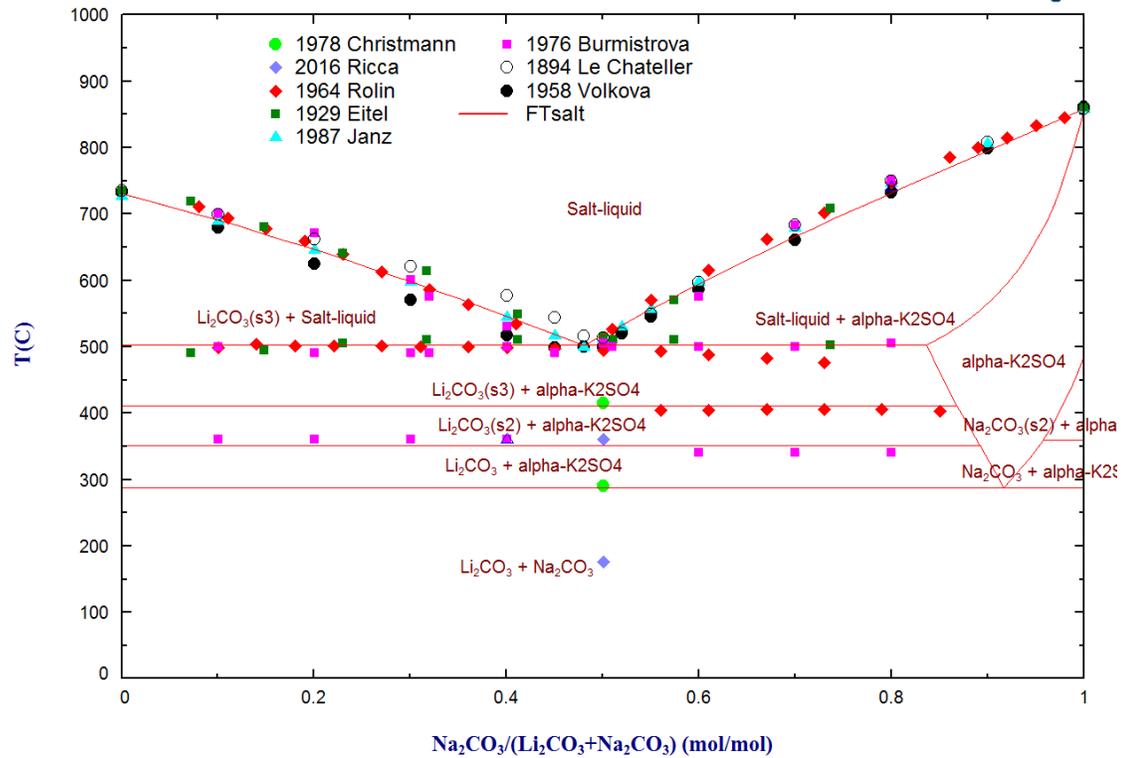
M. Christmann et al., Revue de Chimie Minerale, 15 (1978) 312-317.

C. Ricca et al., Surface Science, 647 (2016) 66-77.

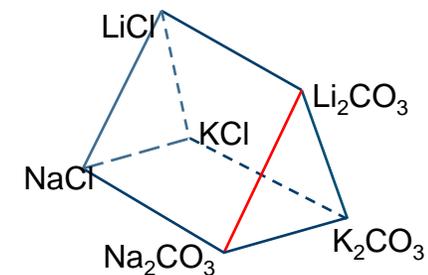
System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$



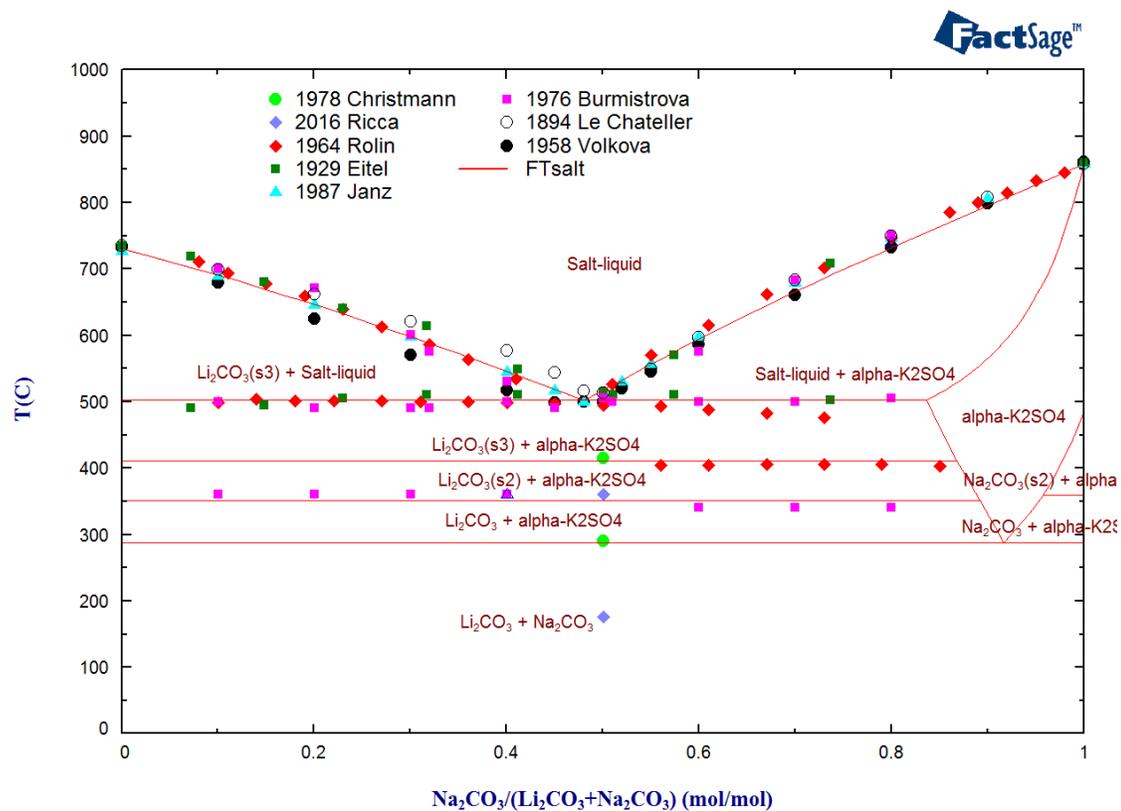
literature data



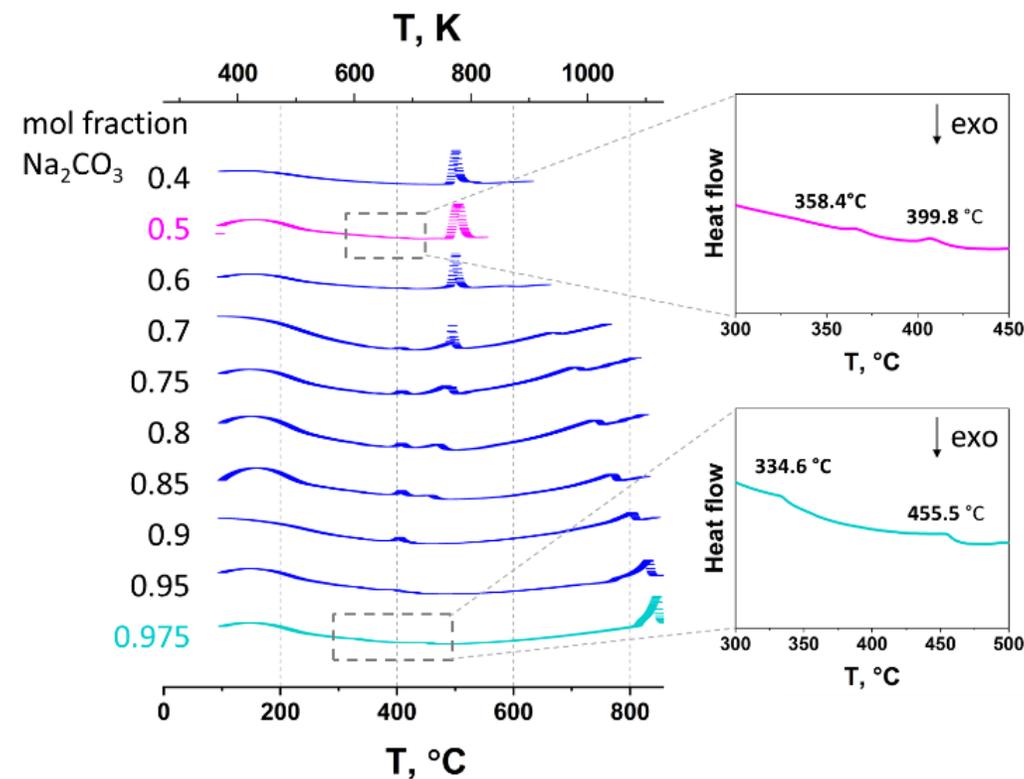
System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$



literature data

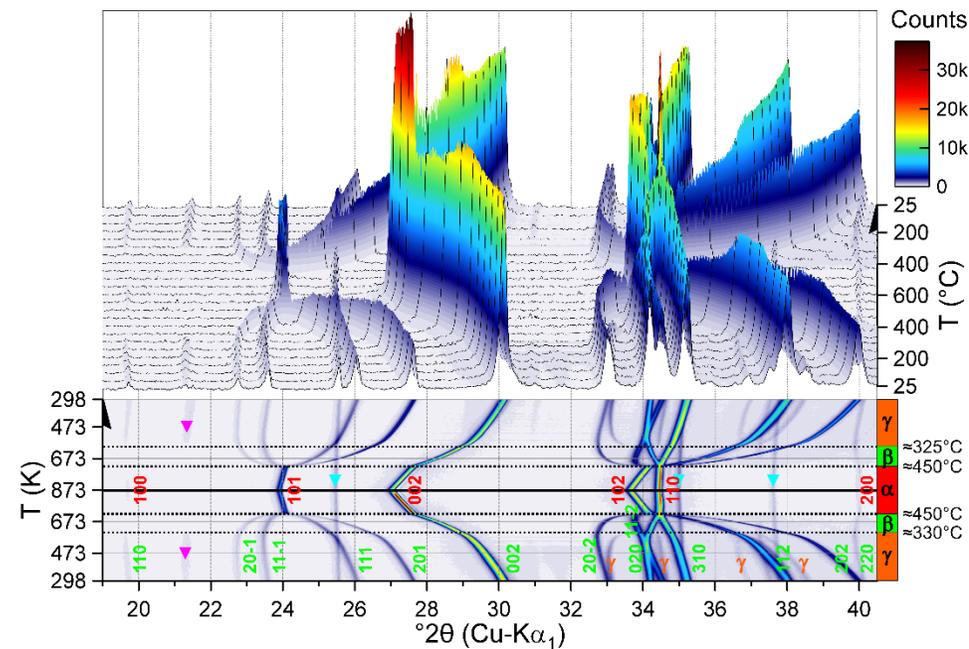
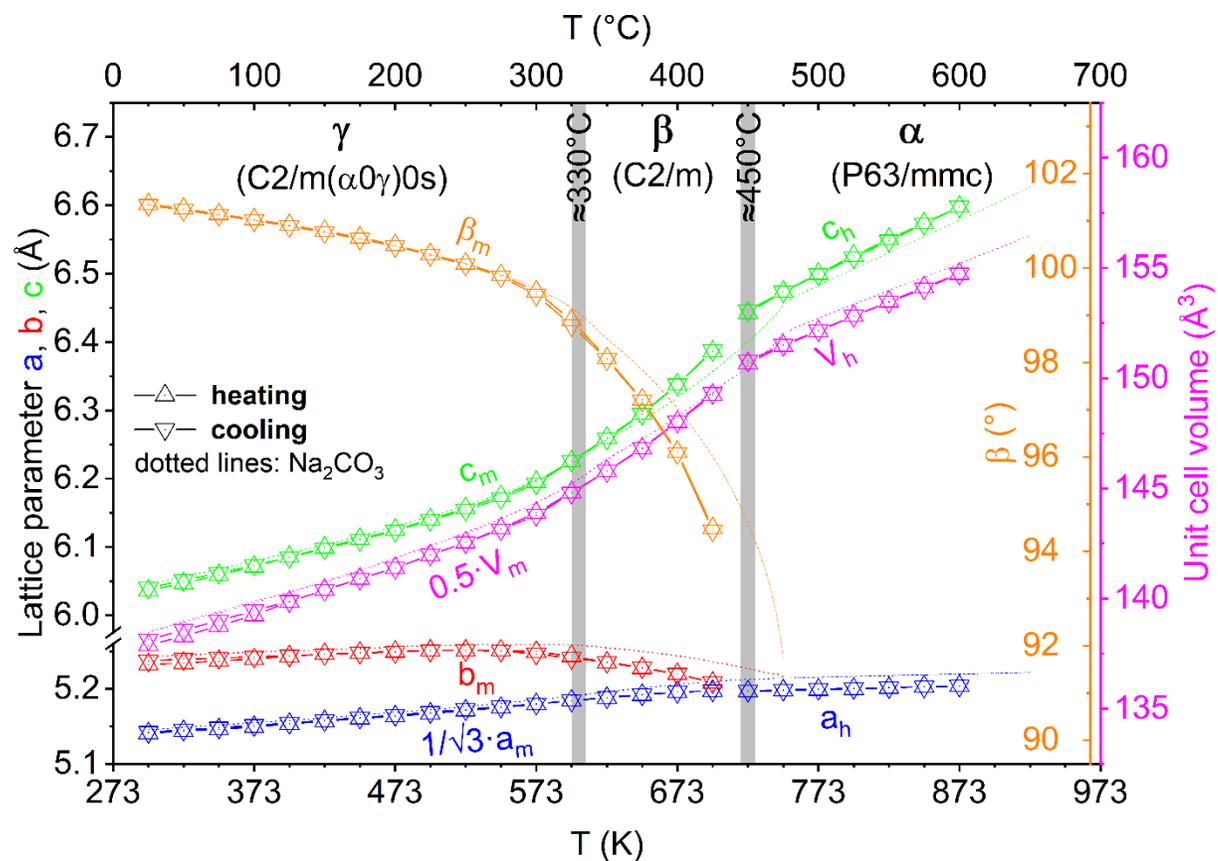
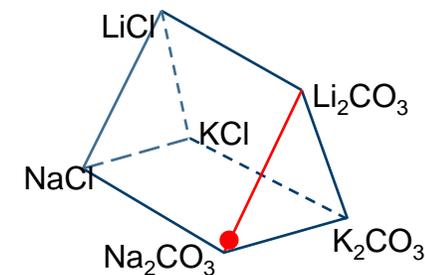


DTA measurement



System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$

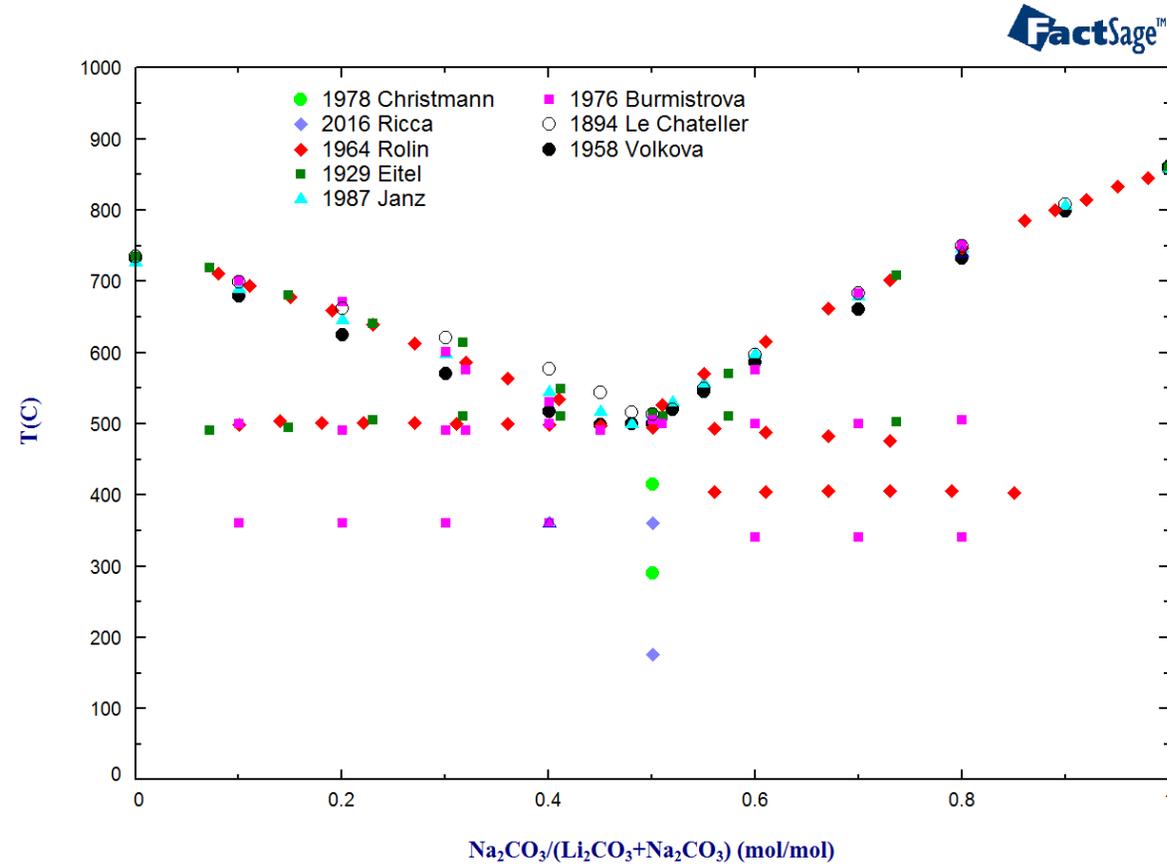
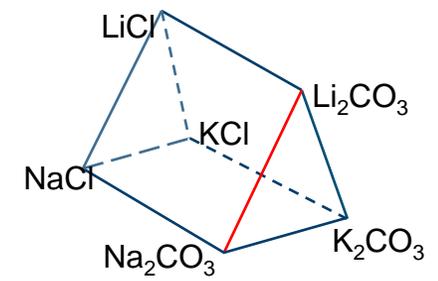
HTXRD of Composition $0.975 \text{ Na}_2\text{CO}_3\text{-}0.025 \text{ Li}_2\text{CO}_3$



Composition	$0.975 \text{ Na}_2\text{CO}_3\text{-}0.025 \text{ Li}_2\text{CO}_3$	Pure Na_2CO_3	
Measurement	DTA	HTXRD	DTA
γ phase \rightarrow β phase	335°C	330°C	348°C
β phase \rightarrow α phase	456°C	450°C	477°C

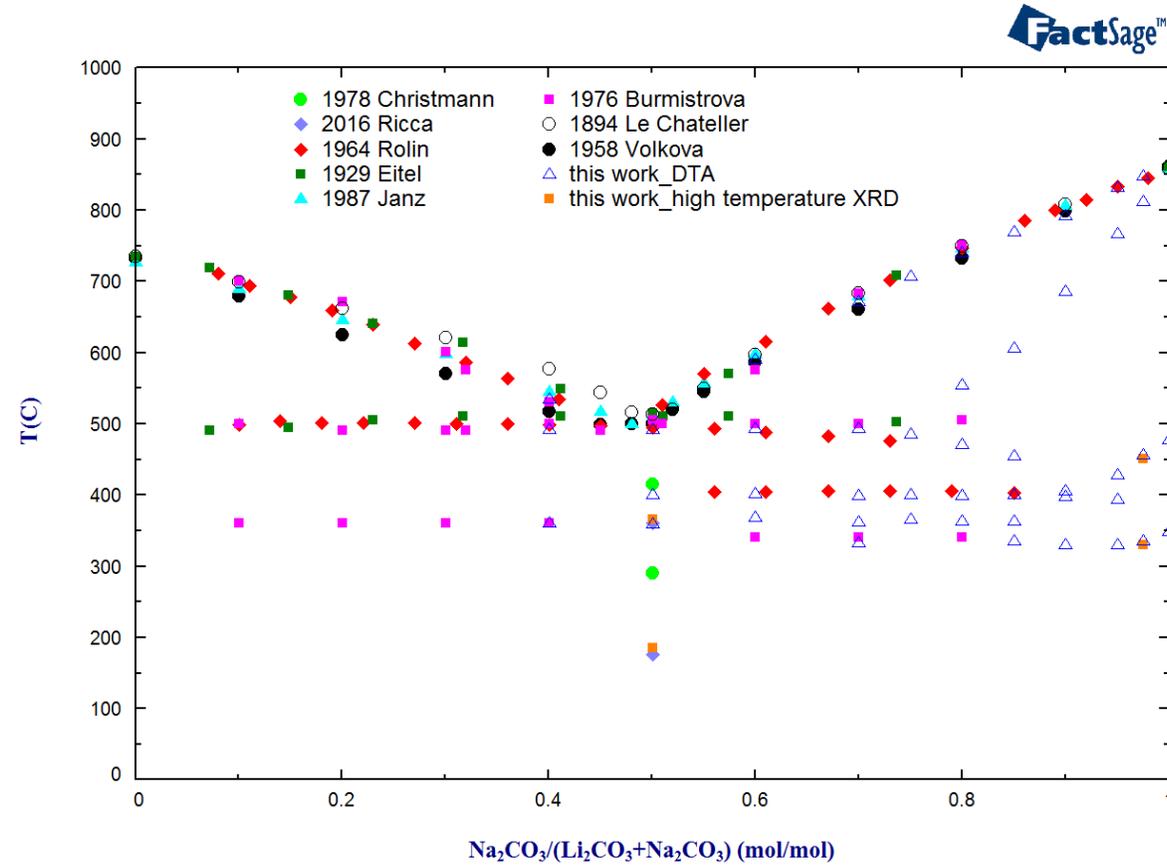
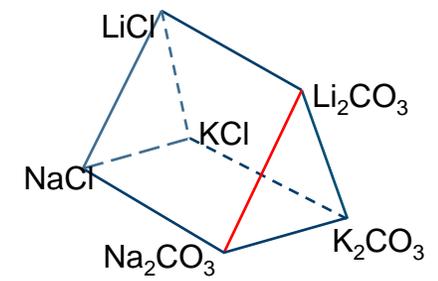
System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$

Assessment of the system



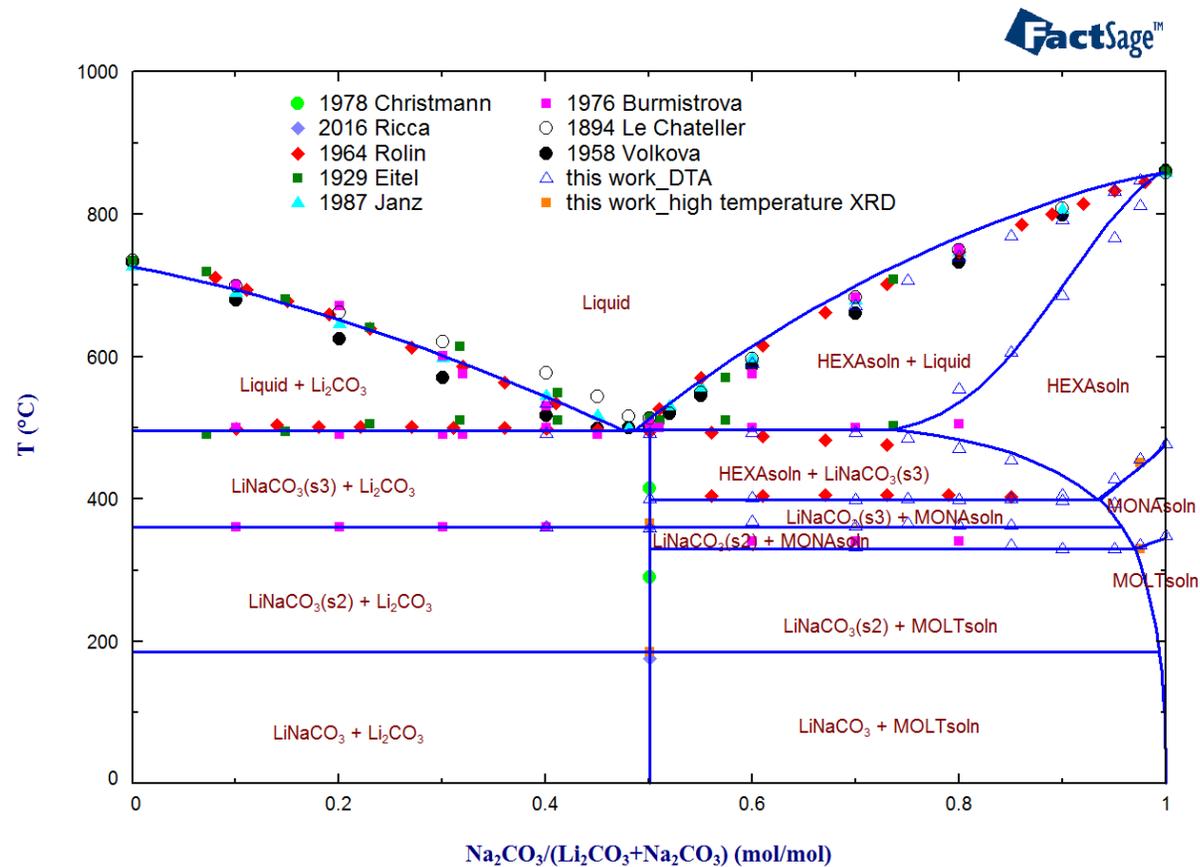
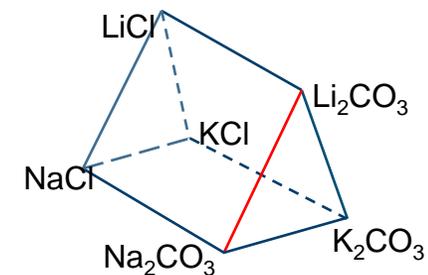
System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$

Assessment of the system



System $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$

Assessment of the system



CONCLUSION AND OUTLOOK

- ✓ Pure Li_2CO_3 has no solid-solid transition at 419 °C
- ✓ Cp measurement for Li_2CO_3 from 300 - 450 °C

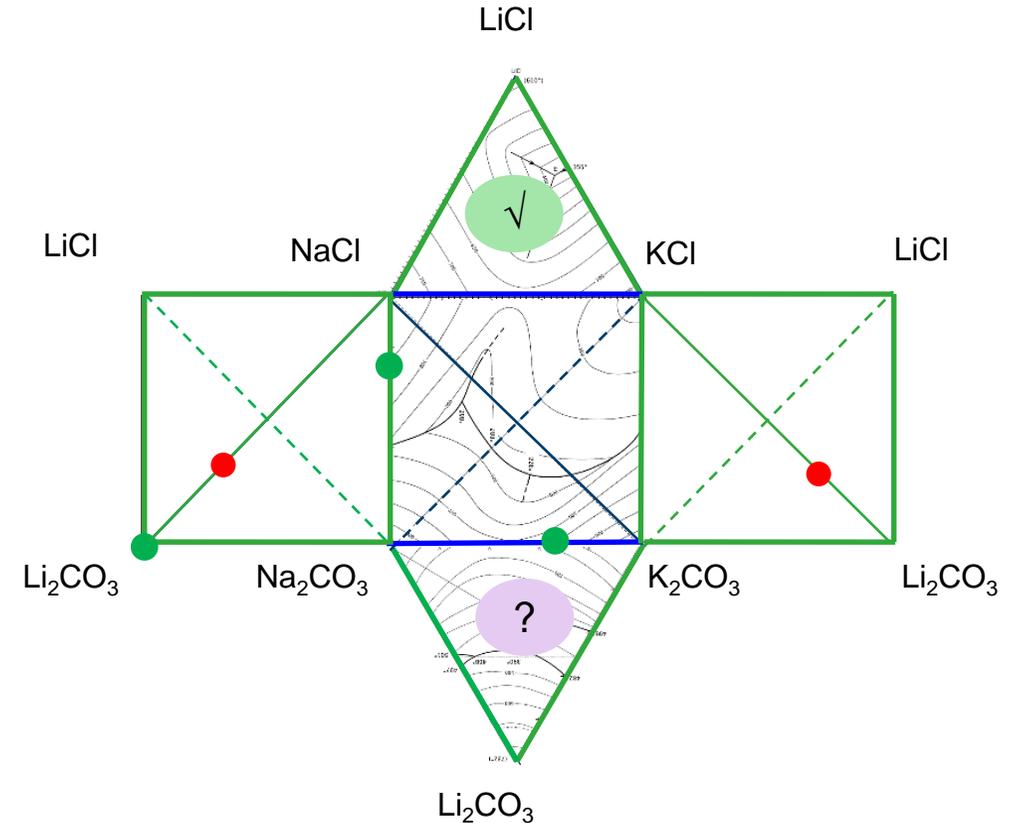
- ✓ Phase diagram of Na_2CO_3 - Li_2CO_3
- ✓ High temperature XRD for Li_2CO_3 - Na_2CO_3

- ✓ Phase diagram of Li_2CO_3 - K_2Cl_2

- ✓ Phase diagram of K_2CO_3 - Li_2Cl_2
- ❑ Enthalpy increment of eutectic point of Li_2CO_3 - K_2Cl_2

- ✓ Phase diagram of Li_2CO_3 - Na_2Cl_2

- ✓ Phase diagram of Na_2CO_3 - Li_2Cl_2
- ❑ Enthalpy increment of eutectic point of Li_2CO_3 - Na_2Cl_2
- ❑ Optimization of ternary system Li^+ , Na^+ , K^+ // CO_3^{2-}



ACKNOWLEDGEMENTS



Supported by:



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In cooperation with:

