

Synthesis and Crystal Structure of KNaCO_3

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Synopsis Single crystals of KNaCO_3 were grown from a melt, leading to a structure determination in the space group $C2/c$, with unique atomic sites for K and Na. The structure of powders synthesized in solid state from K_2CO_3 and Na_2CO_3 precursors was also consistent with this structure, as demonstrated through a refinement using the Rietveld method.

Abstract Potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3) are useful inorganic alkali salts with a multitude of uses, although both can be unstable at room temperature. The focus of this work was to react these two carbonates together to form KNaCO_3 single crystals, and to determine the structure of the resulting crystals. The symmetry of the crystals was assigned to the monoclinic space group $C2/c$ (No. 15), with lattice parameters of 5.4546(7), 9.462(1), 6.1282(7), and $\beta=95.209(4)$. The K and Na are located on fully occupied, unique atomic positions. The phase evolution of K_2CO_3 and Na_2CO_3 to form KNaCO_3 was also examined using *in situ* high temperature X-ray diffraction. The final compound in both single crystal and powder form was found to be stable over time at room temperature.

Keywords: Potassium sodium carbonate; phase transitions; monoclinic crystal structure; X-ray crystallography

1. Introduction

Potassium and sodium carbonate are useful inorganic salts in a wide variety of industrial applications, such as for glass, brick, and soap production, food processing, cleaning products such as stain removers, disinfectants, toothpaste, in agriculture, photography, and many more (1,2). Hygroscopicity is a property that is common to both salts, but particularly K_2CO_3 . The materials' hygroscopicity has been used to advantage in applications such as in agrochemical fertilizers. In recent research, these carbonates are being explored for carbon capture (3), as a catalyst for oxidative coupling of methane (4), and as a molten carbonate media in direct coal fuel cells (5).

However, in the development of new applications, the instability of K and Na (as they both lie in column 1 on the periodic table, and therefore have one valence electron) means the use of starting materials based on these elements can be challenging. In particular, the hygroscopicity of the carbonates, and the fact that certain combinations of K and Na can result in a liquid phase at room temperature, means that starting materials are difficult to combine to form stoichiometric combinations, both by themselves and in combination with other components (6). If heating for calcination or sintering purposes, the instability can lead to volatilization, chemical inhomogeneity, and/or abnormal grain growth in the products (7).

There are few published studies focused on the crystal structure of KNaCO_3 . In the Powder Diffraction File (PDF-5, 8), there are currently 5 entries. Hanawalt *et al.* from 1938 (9) includes no structural details (PDF#00-001-1038). The remaining 4 entries relate to one publication by Christmann and Papin from 1979 (10). In PDF#00-045-0871, the room temperature space group of KNaCO_3 is stated as $C2/c$ (No. 15), with lattice parameters $a=5.501 \text{ \AA}$, $b=9.516 \text{ \AA}$, $c=6.15 \text{ \AA}$, $\beta=94.4^\circ$, and no crystal structure details, such as atom positions, site occupancies, or isotropic or anisotropic displacement values. This entry was updated in PDF#04-027-8949 with space group $C2/m$ (No. 12), with a note that the space group in PDF#00-045-0871 is a misprint. The lattice parameters are $a=9.52 \text{ \AA}$, $b=5.515 \text{ \AA}$, $c=6.16 \text{ \AA}$, $\beta=94.5^\circ$. This entry included atom positions, namely 3 equally shared special positions for K/Na, one special Carbon atom position, and 2 Oxygen atom positions. All isotropic displacement parameters were set at 0.5. The other two PDF entries relate to the high temperature hexagonal phase of KNaCO_3 . PDF#00-045-0870 was measured at 573 K, with lattice parameters of $a=5.4777 \text{ \AA}$, and $c=6.156 \text{ \AA}$. PDF#04-027-8948 also refers to Christmann and Papin (10) with a measurement temperature of 773 K, the hexagonal space group of $P6_3/mmc$ (No. 194), lattice parameters of $a=5.43 \text{ \AA}$ and $c=7.19 \text{ \AA}$, and some crystal structure details.

This work presents a comprehensive crystal structure solution and refinement from single crystals grown from a melt, including the space group, atom positions and occupancies which vary significantly from the previous work (9, 10), and isotropic and anisotropic displacement parameters. Since the carbonates are also commonly used as precursor powders, especially on industrial scales, we performed further experiments to determine if KNaCO_3 could be synthesized through solid state reaction. When combined in powder form, *in situ* high temperature X-ray diffraction (*in situ* XRD) enables a detailed phase evolution study of the primary carbonates (K_2CO_3 and Na_2CO_3) to the high temperature phase of KNaCO_3 , and upon cooling, the phase transition to the final stable crystal structure at room temperature.

2. Experimental

Laboratory reagents of K_2CO_3 (99.99%, Alfa Aesar) and Na_2CO_3 (99.99%, Alfa Aesar) were stored in an oven at 150°C to minimize the adsorption and absorption of water into the powders, which could otherwise result in variations from ideal stoichiometry due to errors in weighing the starting materials. The powders were weighed to form a 50:50 stoichiometric mixture, which was placed in an alumina

crucible and covered with an alumina lid. From our previous *in situ* studies, it was determined that the melting temperature of the mixture is 710°C. This temperature agrees with previous studies of the K₂CO₃-Na₂CO₃ phase diagram (11), which show a solid solution from 650°C to the liquid phase at 710°C for an equimolar mixture.

The crucible was placed in a furnace and heated at 10°C/min to 725°C. It was held at that temperature for 60 mins, then cooled at 1°C/hour, until 650°C, and then furnace cooled. The product was removed from the crucible, and after selecting several possible crystals for single crystal study, a portion of the product was finely ground for X-ray fluorescence (XRF) elemental data collection. XRF was carried out to ensure that final composition in the crystals remained in the 50:50 stoichiometric ratio.

For the single crystal data collection, a small block-shaped crystal of approximately 0.04 μm was selected. This was fixed to a MiTeGen crystal mount and loaded into a Bruker D8 Venture single crystal diffractometer equipped with an area detector and a Mo-Kα micro-focus sealed X-ray tube with a wavelength of 0.71073 Å. A full crystal reflection set was collected at room temperature, followed by data reduction using Apex4 (Bruker AXS, 2021). The structure solution was carried out using SHELXS 86 (12), and the refinement was performed using Olex2 1.3 (13). A crystallographic information file (CIF) and a structure factor file (FCF) were generated at the completion of the structure refinement in Olex2.

In situ XRD was performed using a PANalytical Empyrean X-ray diffractometer equipped with an HTK-1200 temperature chamber. As the melting temperature for the mixed carbonates is 710°C, the heating program used was a constant rate 1°C/min to 650°C and cooling to room temperature was at the same rate. These heating and cooling rates were used for all the *in situ* XRD data collections in the current work. At the same time, XRD patterns were collected at 1 min intervals. For the *in situ* XRD with the mixture of K₂CO₃ and Na₂CO₃, the same protocol was followed for heating and cooling, however the furnace temperature was held constant for 2 h at 650°C to allow for the complete diffusion and mixing of the carbonates. Following each data collection, the XRD patterns were compiled into a single figure using a contour plot, so that the phase evolution could be observed with changes in temperature.

3. Results and Discussion

3.1. Single crystal structure

The single crystal structure and refinement converged with a Bragg-R factor of 2.62%. The space group is monoclinic *C2/c* (No. 15), with lattice parameters of $a=5.4546(7)$ Å, $b=9.462(1)$ Å, $c=6.1282(7)$ Å, and $\beta=95.209(4)^\circ$. This structure was submitted to the CCDC with a catalogue number of 2352733.

The experimental details are given in Table 1, and the structural details are presented in Table 2.

Table 1 Experimental details for single crystal synthesis(?) and diffraction measurements.

<u>Crystal data</u>	
Chemical formula	$K_1Na_1C_1O_3$
M_r	? Melting point 983
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	298
a, b, c (Å)	5.4546 (7), 9.462 (1), 6.1282(7)
β (°)	95.209 (4)°
V (Å ³)	314.98 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	?
Crystal size (mm)	0.04 x 0.04 x 0.04
<u>Data collection</u>	
Diffractometer	Bruker D8 Venture Apex4
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
T_{min}, T_{max}	0.938
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2945 ?
R_{int}	
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	
<u>Refinement</u>	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	
No. of reflections	413
No. of parameters	31
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	

Computer programs: *APEX4* and *SAINT* (14), *SHELXS97* (12), *CrystalMaker* (15).

Table 2 Lattice constants, fractional atomic sites and their coordinates and U_{iso}/U_{eq} values (Å²)^a for the KNaCO₃ single crystal structure.

Lattice constants: $a = 5.4546$ (7) $b = 9.462$ (1) $c = 6.1282$ (7)Å, $\beta = 95.209$ (4)°							
Atom	Wyckoff position	Site Symmetry	S.O.F.	x	y	z	U_{iso}^*/U_{eq}
K1	4e	2	1	0	0.66729 (5)	0.25	0.0240 (2)
Na1	4a	a	1	0	0	0	0.0242 (3)
C1	4e	-1	1	0	0.3338 (2)	0.25	0.0172 (4)
O1	8f	1	1	0.1991 (2)	0.4016 (1)	0.2219 (2)	0.0276 (3)
O2	4e	2	1	0	0.1986 (2)	0.25	0.0301 (4)

Anisotropic displacement parameters and interatomic distances are included in the supplementary CIF.

Table 2 reports that each of the site occupancy factors, S.O.F., are equal to 1. During the refinement, each atom S.O.F. was allowed to deviate from full occupancy. Nevertheless, the crystal structure refinement showed that the K and Na atom site are independent, and fully occupied by the lone atom (i.e. there was no indication of site mixing between K and Na). This result agrees with the XRF results that showed that, after single crystal growth, the initial 50:50 stoichiometry is maintained.

To visualize the crystal structure, the CIF was opened in Mercury 3.8 (Build RC2, © CCDC 2001-2016). The model is presented in Figure 1. The model was then converted to a powder XRD pattern, and this is presented in Figure 2. The primary purpose for Figure 2 is for comparison with the *in situ* XRD experiments presented in Section 3.2.

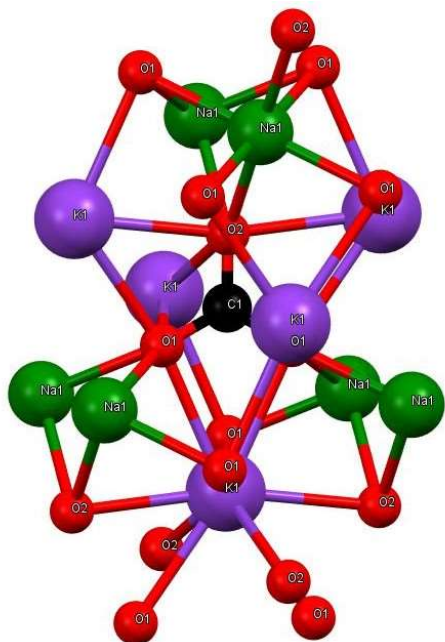


Figure 1 Model of the single crystal structure in Mercury showing the atom positions and the isotropic displacement parameters.

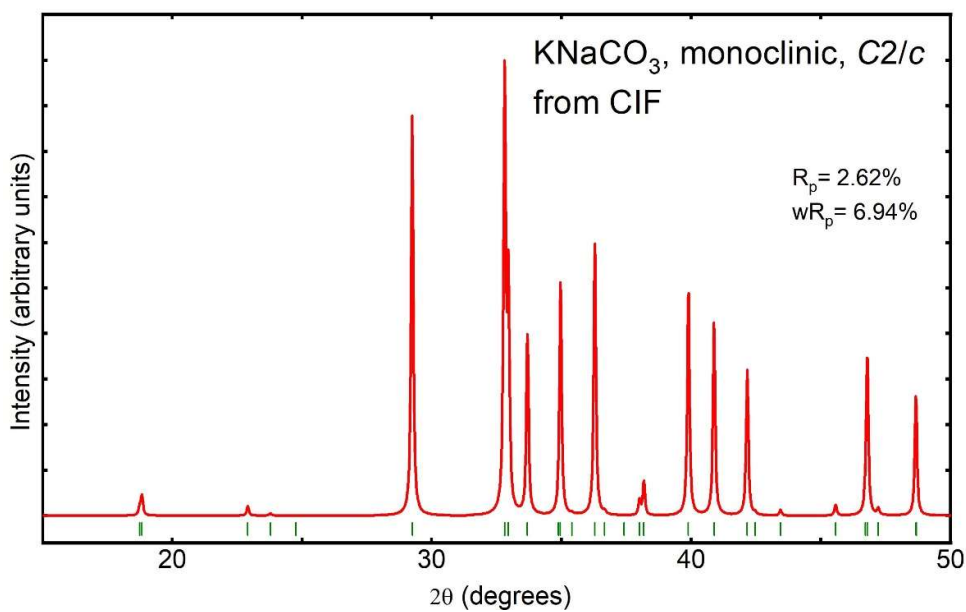


Figure 2 Powder XRD pattern generated from single crystal CIF using Mercury. The FWHM=0.1, 15-50°2θ with a step-size of 0.02°. The wavelength was converted to Cu Kα1 radiation (1.54056 Å).

3.2. *In situ* XRD

The phase evolution with increasing and decreasing temperature of powders was examined using *in situ* XRD. For this study, melting of the sample was undesirable, and the highest temperature was therefore restricted to 650°C. The carbonates were first individually heated and then subsequently cooled. The results are shown in Figure 3, a contour plot of the XRD patterns in the range $20^\circ < 2\theta < 55^\circ$, as the samples were heated. Both Na_2CO_3 and K_2CO_3 are monoclinic at room temperature, although they are assigned to different space groups: K_2CO_3 has space group $P2_1/c$ (No. 14), consistent with prior reports, such as PDF#04-012-7109; Na_2CO_3 belongs to $C2/m$ (No. 12), also consistent with results, such as PDF#05-001-0004. The similarities between the heating profiles are evident, e.g., the evolution of the 002 reflection in both carbonates, and the high temperature phase transition to the $P6_3/mmc$ space group. The differences are also apparent. For example, the 2θ position of the 002 reflection is in a significantly different 2θ position. In the K_2CO_3 heating profile, the position is at much lower 2θ , indicating a larger lattice parameter in K_2CO_3 . Another interesting observation is that the phase transition in K_2CO_3 to the hexagonal structure occurs at $\sim 400^\circ\text{C}$, whereas in the Na_2CO_3 case, the phase transition occurs at $\sim 480^\circ\text{C}$. The data measured during cooling (not shown here) shows the complete reversibility of the phases to their original structure upon cooling.

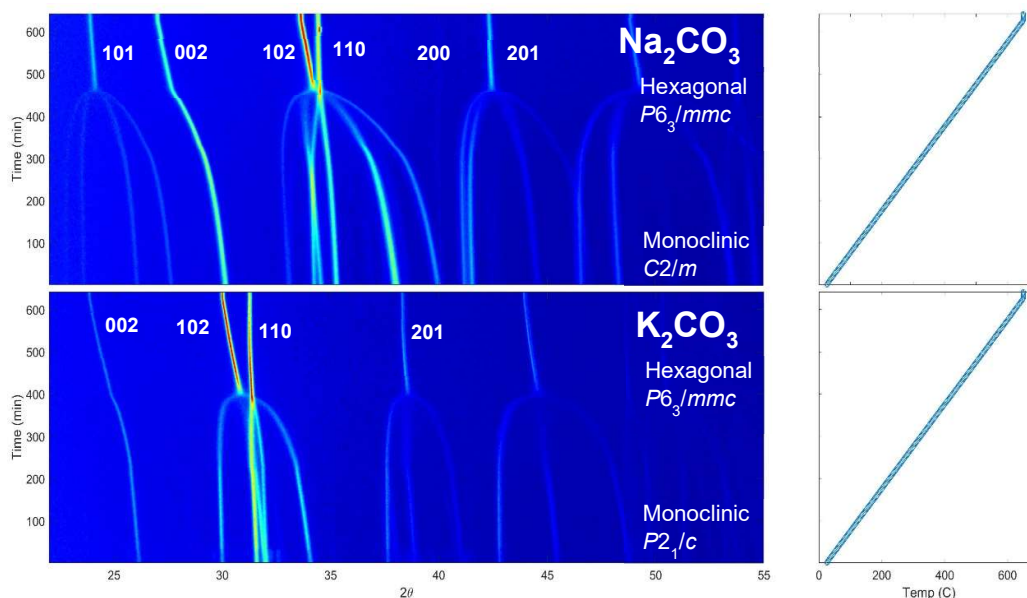


Figure 3 Heating of Na_2CO_3 and K_2CO_3 to 650°C , showing the phase transition from the low temperature monoclinic symmetry to the high temperature hexagonal symmetry.

The equimolar combination of Na_2CO_3 and K_2CO_3 heated to 650°C is presented in Figure 4. This figure includes heating to 650°C (bottom panel), a 2 h hold at 650°C (middle panel), and then subsequent cooling to room temperature (top panel). The 2θ range in this figure is limited to $22^\circ < 2\theta < 44^\circ$ so that the major features can be more easily observed. The monoclinic crystal structures of the individual

carbonates are observable in the bottom panel, as are the phase transitions of the individual carbonates to the high temperature hexagonal phases. Interestingly, at the start of the *in situ* run (in the first few XRD patterns with increasing temperature), there are several small areas of intensity (e.g. just below $2\theta=30^\circ$). These extra peaks appear because a hydrated carbonate forms due to the strong affinity of moisture to K_2CO_3 that occurs in the short amount of time required to load the sample into the diffractometer furnace. Inspection of the higher temperatures in the bottom panel shows that above 500°C , there is an area of interdiffusion, during which the carbonates start to react. During the 2 h hold at 650°C , there is further interdiffusion, with the appearance and disappearance of some reflections. During cooling, it is apparent that the final phase does not match any of the earlier observed phases. After completion of the *in situ* experiment, the sample was removed from the furnace. It was observed that, in contrast to the starting carbonates, the KNaCO_3 product was stable at room temperature. i.e. it did not require oven storage to prevent water absorption.

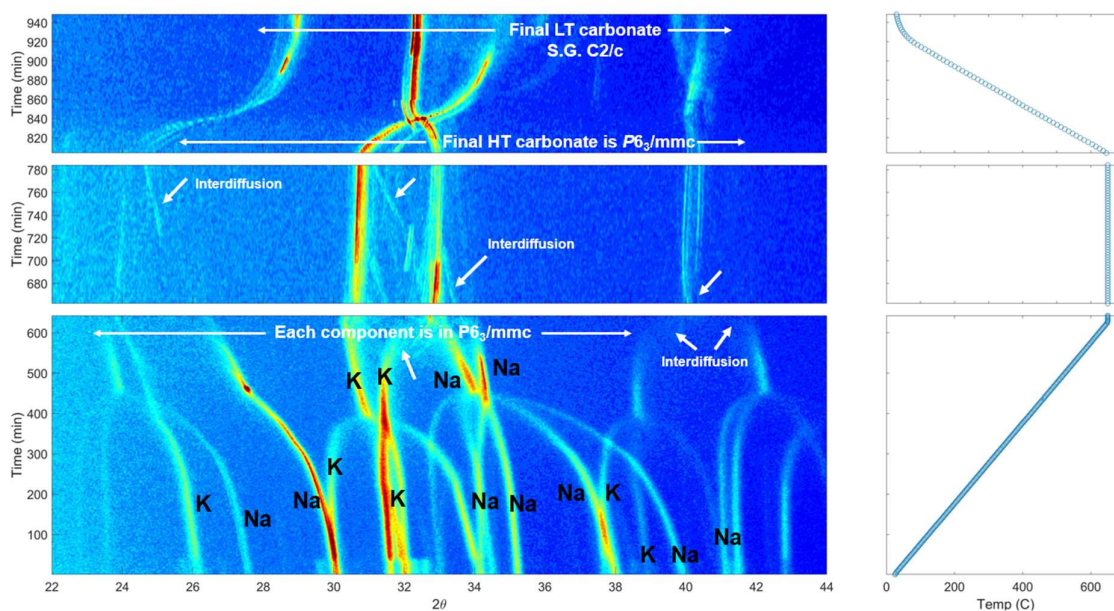


Figure 4 Phase evolution in K_2CO_3 and Na_2CO_3 using *in situ* XRD during heating, holding at high temperature, and cooling. Monoclinic space group $C2/c$ (No. 15).

To examine the crystal structure of the final powder, an XRD pattern was recorded using a Rigaku Smartlab powder diffractometer equipped with a graphite monochromator and crossbeam optics to maximize the resolution while minimizing the background. The pattern collection parameters were $10^\circ < 2\theta < 90^\circ$, 0.02° step, and 10 s per step counting time. A Rietveld refinement was carried out using GSAS (16) with 12 background parameters, peak shape function 4 to model the peak asymmetry, and the starting crystal structure parameters from the single crystal structure solution in Part A. The occupancies of the K and Na atom positions were trialed with mixtures of the two atoms, and, like the

single crystal analysis, each atom site was found to be independently and fully occupied. The fit of modeled data to experimental data resulting from the Rietveld refinement is presented in Figure 5, and the refined structural parameters are tabulated in Table 3. The XRD pattern was well-modeled using the Rietveld refinement and therefore the crystal structure is assigned $C2/c$, equivalent to the space group determined from the single crystal.

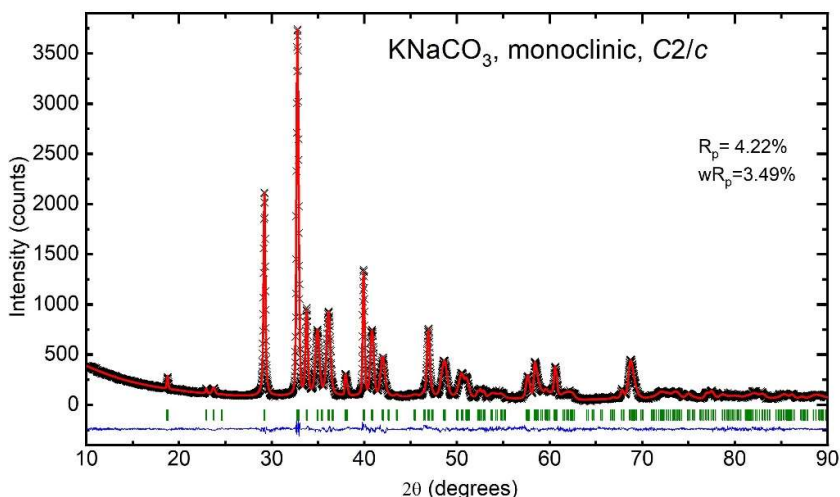


Figure 5 Rietveld refinement of the XRD pattern recorded following the *in situ* XRD scan.

Table 3 Refined crystal structure data for KNaCO_3 powder in space group $C2/c$ from Rietveld refinement and $U_{\text{iso}}/U_{\text{eq}}$ values (\AA^2)^a for the structure.

Lattice constants: $a = 5.4608 (2)$, $b = 9.4712 (3)$, $c = 6.1257 (2)\text{\AA}$, $\beta = 94.724 (2)^\circ$							
Atom	Wyckoff position	Site Symmetry	S.O.F.	x	y	z	$U_{\text{iso}} \times 100$
K1	4e	2	1	0	0.6641 (2)	0.25	2.68 (6)
Na1	4a	a	1	0	0	0	1.15 (5)
C1	4e	-1	1	0	0.3233 (6)	0.25	0.38 (14)
O1	8f	1	1	0.1923 (5)	0.4041 (2)	0.2215 (2)	4.49 (9)
O2	4e	2	1	0	0.1855 (4)	0.25	4.02 (13)

A comparison between the refined structure from powders in Table 3 and the single crystal structure refinement in Table 2 shows that the values vary in only the second or third decimal place. The agreement between the powder and single crystal structural parameter values is a good indication that the single crystal and powder diffraction structures are consistent.

Conclusions

Single crystals and powders of KNaCO_3 were synthesized and single crystal and powder X-ray diffraction were used to study the crystal structure of KNaCO_3 in both forms. The space group for both single crystals and powders was determined to be $C2/c$, and the refined crystallographic parameters are

consistent between the single crystal and powders. Finally, whereas the initial carbonate reactants are very hygroscopic, KNaCO_3 is relatively stable in air. As these carbonates are useful in industry, this more stable product could find application in various areas.

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Conflicts of interest The authors have no conflicts of interest to declare.

Data availability The CIF and FCF with results from the single crystal refinement presented in this work can be retrieved from the Cambridge Structural Database (CSD) (17) (deposition number: CCDC 2352733).

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