Electrical conductivity, DSC, XRD, and $^7$Li NMR studies of rotator crystals $n$-$C_{21}H_{43}$COOLi$_x$K$_{(1-x)}$ $(0.33 \leq x \leq 0.50)$, $n$-$C_m$H$_{(2m+1)}$COOLi, and $n$-$C_m$H$_{(2m+1)}$COOK ($m = 13, 15, 17, 19, \text{and} 21$)

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Abstract Differential scanning calorimetry (DSC) thermograms, X-ray diffraction (XRD) analysis, electrical conductivity ($\sigma$), and $^7$Li NMR spectroscopy characterization of $n$-$C_m$H$_{(2m+1)}$COOM solids ($M = \text{Li, Na, K}; m = 13, 15, 17, 19, 21$) and mixed crystals $n$-$C_{21}H_{43}$COOLi$_x$K$_{(1-x)}$ $(0.25 \leq x \leq 0.75)$ was performed as a function of temperature. DSC thermograms of $n$-$C_m$H$_{(2m+1)}$COOM revealed several solid-solid phase transitions with large entropy changes. Electrical conductivity studies established that $n$-$C_m$H$_{(2m+1)}$COOLi crystals are poor electrical conductors. In contrast, $n$-$C_m$H$_{(2m+1)}$COOK salts were found to have $\sigma$ values of $10^{-7}$–$10^{-8}$ S·cm$^{-1}$. Since the crystal structures and phase-transition temperatures of both $n$-$C_m$H$_{(2m+1)}$COOLi and $n$-$C_m$H$_{(2m+1)}$COOK crystals were similar, they were able to form mixed crystals with the structure $n$-$C_{21}H_{43}$COOLi$_x$K$_{(1-x)}$. DSC thermograms of the mixed crystals showed a small entropy change at the melting point ($\Delta S_{\text{mp}} < 13$ J K$^{-1}$ mol$^{-1}$), in addition, large $\Delta S$ values at the solid-solid phase transition temperature. The $\sigma$ values obtained for mixed crystals were roughly one order of magnitude greater than those determined for $n$-$C_{21}H_{43}$COOK crystals. $^7$Li NMR spectra of the mixed crystals recorded at various temperatures suggested that the self-diffusion of Li$^+$ ions was excited in the highest-temperature solid phase. Based on these results, we have classified these mixed crystals as rotator crystals.

Keywords Rotator phase · Ion conductor · $^7$Li NMR · Mixed crystal
1 Introduction

Li ion cells are recently used for compact and high-energy density batteries of mobile computers and phones, etc. To further improve their safety and performance, much effort has been put into the development of new solid electrolytes to replace the organic and polymer solvents currently employed in Li ion cells. One promising candidate arising from these investigations is ionic plastic crystals [1], in which ionic self-diffusion has been detected. In plastic-crystal phases, the molecular orientation is fused, meaning that small entropy changes are observed at each melting point (<20 J K$^{-1}$ mol$^{-1}$) [2] and large changes are detected at the phase transition temperature from low-temperature solid-phase to the plastic phase. MNO$_2$ (where M = K, Rb, Cs, TI, or NH$_4$) salts have been shown to form ionic plastic crystals with high electrical conductivity [3–16]; in contrast, Li and Na salts exhibit no plastic phases [3, 17–24]. This difference is because the former contains a planer ion similar in size to the counter-ion that can undergo low-energy isotropic rotations in crystals. This structural requirement makes it difficult to prepare simple ionic plastic crystals of LiX where X is an anion.

Rotator crystals are classified in the family of plastic crystals. Rotator phases are frequently detected in salts that contain several long-chain molecular ions and a monoatomic counter ion [25–42]. In this phase, two-dimensional rotation about the molecular chain is found as well as two-dimensional translational self-diffusion. In plastic-crystal phases, there is three-dimensional rotation of molecules; therefore, rotator crystals are called two-dimensional plastic-crystal. Thermodynamic properties of rotator crystals is similar to plastic crystals, e.g. small and large entropy changes are detected at melting point and the phase transition temperature from low-temperature solid-phase to the rotator phase, respectively. In the example of $n$-C$_m$H$_{(2m+1)}$COOLi (where $m = 7–18$; hereafter abbreviated to C$_m$Li), it is reported that some of the potential structures (12 < $m$ ≤ 18) have rotator phases [43–45]. Reported differential scanning calorimetry (DSC) measurements indicate that the entropy change at the melting point ($\Delta S_{mp}$) is smaller than the total entropy-change ($\Delta S_{total}$) detected at solid-solid phase transition temperatures above room temperature ($\Delta S_{mp} = 28.43 < \Delta S_{total} = 38.37$ J K$^{-1}$ mol$^{-1}$ for C$_{15}$Li and $\Delta S_{mp} = 33.14 < \Delta S_{total} = 49.48$ J K$^{-1}$ mol$^{-1}$ for C$_{17}$Li). For C$_{13}$Li, however, the opposite relationship ($\Delta S_{mp} = 27.67 > \Delta S_{total} = 17.9$ J K$^{-1}$ mol$^{-1}$) has been reported [45]. X-ray diffraction (XRD) spectra obtained at ambient temperature have revealed that these crystals belong to the triclinic crystal system in the $P\bar{1}$ space group, and that the $n$-alkyl chains are uniformly in the trans-conformation with the Li$^+$ ions forming a layer perpendicular to direction of long chains [44]. Infrared (IR) and $^{13}$C NMR spectra recorded at room temperature have provided information about the interactions among the longer $n$-alkyl chains of C$_m$Li ($m \leq 18$) [45]. In contrast to C$_m$Li, other rotator crystals of the form $n$-C$_y$H$_{(2y+1)}$NH$_3$Cl (where $y \geq 4$) exhibit the relationship of $\Delta S_{mp} < \Delta S_{total}$ and $\Delta S_{mp} < 20$ J K$^{-1}$ mol$^{-1}$ [42]. These $n$-alkylammonium halides salts have tetragonal crystal structures in the rotator phase in which ionic self-diffusion has been detected using electrical conductivity and solid-state NMR characterization. These salts and C$_m$Li compounds have similar molecular structures, i.e., both compounds comprise an $n$-alkyl group and a monoatomic ion, therefore, the C$_m$Li crystals are also expected to exhibit ionic conductivity. However, no data relating to the electrical conductivity of C$_m$Li
DSC, XRD, and $^7$Li NMR studies of rotator crystals

Crystals have yet been reported, prompting us to carry out in this study. In addition, because arachidic acid ($n$-C$_{19}$H$_{39}$COOH) and behenic acid ($n$-C$_{21}$H$_{41}$COOH) are easily obtained commercially, we were able to synthesize and characterize C$_{19}$Li and C$_{21}$Li crystals as well. We considered C$_m$Li species where $11 \leq m \leq 21$ and $m$ was an odd number, as $n$-alkyl compounds frequently display even-odd effects [46–48]. In addition, impurities in plastic crystals have often been found to increase electrical conductivity [1], and therefore, we also considered mixed crystals containing K salts in this study. Hereafter, the mixed crystals of the form $n$-C$_m$H$_{(2m+1)}$COOLi$_x$K$_{(1-x)}$ will be abbreviated to C$_m$Li$_x$K$_{(1-x)}$ ($0 < x < 1$). In order to determine the ionic dynamics of Li$^+$ ions, $^7$Li NMR measurements were also carried out. Since the $^7$Li nucleus has a quadrupole moment, $^7$Li NMR spectroscopy is often employed to characterize Li$^+$ dynamics in solid samples [17]. Additionally, DSC and XRD were also employed to characterize the $n$-C$_m$H$_{(2m+1)}$COOK crystals, which are components of the mixed crystals.

2 Experimental

C$_m$Li (where $m$ is an odd number from 11 to 21, inclusive) crystals were prepared using the following protocol: $n$-C$_m$H$_{(2m+1)}$COOH and LiOH were separately dissolved in ethanol at 70 °C and then mixed. The solution was maintained at this temperature with stirring overnight, followed by cooling to produce white C$_m$Li crystals. The crude products were redissolved in ethanol at 70 °C and recrystallized to improve the purity, then dried at 80 °C overnight. C$_m$Na and C$_m$K crystals were prepared using the same process, beginning with NaOH and KOH, respectively, instead of LiOH.

Mixed crystals of C$_m$Li$_x$K$_{(1-x)}$ ($0 < x < 1$) were prepared by combining C$_m$Li and C$_m$K in ethanol at 70 °C with stirring for 30 min. The solution was cooled slowly to 10 °C to yield crystals, which were then dried in an oven at 80 °C for one day. The same preparation was attempted for C$_m$Li and C$_m$Na mixed crystals, but did not obtain usable product; XRD spectra of the product reveals peaks only for the starting materials, C$_m$Li and C$_m$Na.

DSC analysis was performed using a Shimadzu DSC-60 calorimeter with a reference sample of Al$_2$O$_3$. The heating rate was maintained at 10 °C·min$^{-1}$ for experiments above room temperature. For those at low temperature, liquid nitrogen was used to cool samples. From these results, we determined melting points ($T_{mp}$) and some transition temperatures in solid phase as well as entropy changes at these transition temperatures.

Electrical conductivity measurements at 1 kHz were carried out from room temperature to just below $T_{mp}$ employing a two-terminal method using an Andou AG-4303 LCR meter equipped with silver electrodes. The powdered sample was pressed into a disc 1 cm in diameter and ~1 mm thick. XRD spectra of the powdered samples at and above room temperature were obtained using a Rigaku RINT-2100 and Bruker D8 ADVANCE equipped with a Cu anticathode, respectively. Spectra were recorded using a scan range of 5–50° with a step size of 0.02° at room temperature and at 0.01° in high temperature ranges.

$^7$Li ($I = 3/2$) NMR spectra were recorded at 233.23 MHz using a Bruker Avance 600 spectrometer (14.10 T). For $^7$Li MAS NMR measurements, a spinning rate of 1 kHz was maintained throughout the free-induction-decay (FID) acquisition.
powdered samples were packed in a ZrO rotor with an outer diameter of 4.0 mm. Pulse sequences of $^7\text{Li}$ were designed without a $^1\text{H}$ decoupling pulse, and a recycle time of 5 s was employed. $^7\text{Li}$ MAS NMR spectra were obtained through Fourier transformation of FID signals recorded after a single pulse. Chemical shifts were calibrated using an external reference of LiCl powder ($\delta = 0$ ppm). $^7\text{Li}$ NMR spectra in high temperature ranges were recorded using a JEOL CMX300 spectrometer (7.01 T). Samples were sealed in Pylex glass tubes with an outer diameter of 5.0 mm.

3 Results and discussion

XRD spectra of $n\text{-C}_m\text{H}_{(2m+1)}\text{COOLi (C}_m\text{Li)}$ and $n\text{-C}_m\text{H}_{(2m+1)}\text{COOK (C}_m\text{K)}$ observed at room temperature are shown in Fig. 1. The spectra obtained for $C_m\text{Li}$ (where $m = 11, 13, 15, 17$) are in agreement
DSC, XRD, and $^7\text{Li}$ NMR studies of rotator crystals

DSC thermograms of $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COOLi}$ ($C_m\text{Li}$), $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COONa}$ ($C_m\text{Na}$), and $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COOK}$ ($C_m\text{K}$) with heat process. (a) $C_m\text{Li}$ (below RT), (b) $C_m\text{Li}$ (above RT), (c) $C_m\text{Na}$, (d) $C_m\text{K}$

Fig. 2 DSC thermograms of $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COOLi}$ ($C_m\text{Li}$), $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COONa}$ ($C_m\text{Na}$), and $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COOK}$ ($C_m\text{K}$) with heat process. $a$ $C_m\text{Li}$ (below RT), $b$ $C_m\text{Li}$ (above RT), $c$ $C_m\text{Na}$, $d$ $C_m\text{K}$

with previous reports [43], and the $C_{19}\text{Li}$, $C_{21}\text{Li}$, and $C_{21}\text{K}$ crystals yielded similar patterns. These results suggest that $C_m\text{Li}$ ($m = 11\sim21$) and $C_{21}\text{K}$ crystals have similar molecular arrangements.

DSC thermograms of $C_m\text{Li}$, $C_m\text{Na}$, and $C_m\text{K}$ recorded above room temperature and thermograms of $C_m\text{Li}$ recorded below the ambient temperature with heat process are shown in Fig. 2. The largest peak in each line, except that for $C_{15}\text{Na}$, has been set to unity. The variation appearing around 300 K in Fig. 2b–d and 200 K in Fig. 2a is due to instrument noise. The symbols $T_{\text{tr1}}$, $T_{\text{tr2}}$, etc., are used to indicate the transition temperatures in solid phases moving from higher to lower temperatures; Phase I, Phase II, etc., are used to designate the solid phases moving from higher to lower temperatures. Thermograms of $C_m\text{Li}$ ($m = 11\sim17$) recorded above ambient temperature show transition temperatures similar to those previously reported [43–45] as listed in Table 1.

In the previously reports, however, thermograms for $C_{19}\text{Li}$, $C_{21}\text{Li}$, and for $C_m\text{Li}$ at low temperatures have not been shown. In addition, no exothermic processes were observed at temperatures just below $T_{\text{tr1}}$ as displayed in Fig. 2. Melting points determined for $C_m\text{Li}$ crystals ($m = 11, 13, 15, 17, 19, 21$) linearly decreased with increasing carbon chain length, and the pre-melting transition temperatures ($T_{\text{tr1}}$) of $C_m\text{Li}$ ($m \geq 13$) also decreased (Fig. 2b). Based on this trend, we expected that the highest-temperature solid phase (Phase I), which is reported to be the rotator phase [44], can be formed using $C_m\text{Li}$ ($m \geq 23$). In contrast, the temperatures for $T_{\text{tr2}}$ detected around 360 K showed the opposite dependence on $T_{\text{tr1}}$ and $T_{\text{mp}}$. Therefore, $C_m\text{Li}$ crystals ($m \geq 23$) are interesting samples, but unfortunately, we could not obtain $n$-$\text{C}_m\text{H}_{(2m+1)}\text{COOH}$ ($m \geq 23$) commercially. For $C_{11}\text{Li}$, we found
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**Table 1** Melting and phase transition temperatures and entropy changes of $n$-$C_{m}H_{(2m+1)}COOLi$

that $T_{tr1}$ accorded with $T_{mp}$, and Phase I disappeared, and therefore, we used samples of $C_{m}Na$ and $C_{m}K$ with $m \geq 13$ in this study. Some phase transitions of $C_{m}K$ crystals were recorded until melting points, as shown in Fig. 2d. The melting temperature of $C_{m}K$ exhibited a trend similar to that observed for $C_{m}Li$ but at slightly lower temperature. This fact suggests that attractive interactions between $K^{+}$ and $n$-alkylcarbonate ions are weaker and/or repulsion energies among the ions are larger than those in the highest-temperature solid-phase of the $C_{m}Li$ crystals. This point will be discussed in detail in a later section. Three phase transitions in solids for $C_{m}K$ ($m \leq 17$) above room temperature were recorded in addition to one transition detected for $C_{m}K$ ($m \geq 19$). The largest enthalpy change in $C_{m}K$ was observed at $T_{tr3}$, which increased with the length of the carbon chain. The temperature range around 350 K corresponds to $T_{tr2}$ of $C_{m}Li$. Based on these results, including that large heat changes were detected at similar temperatures for Li and K compounds and that their transition temperatures exhibited similar dependence on carbon length, we hypothesized that $C_{m}K$ crystals have similar thermodynamic properties as $C_{m}Li$ crystals. For $C_{m}Na$, however, a more complex dependence on chain length was observed, especially for $C_{15}Na$ crystals, which decomposed at around 500 K with the exothermic peak as shown in Fig. 2c. In addition, XRD analysis revealed that $C_{m}Na$ formed no mixed crystals with $C_{m}Li$. Therefore, we did not pursue any further characterization of $C_{m}Na$ crystals in this study. The entropy changes associated with each phase transition for $C_{m}Li$ and $C_{m}K$ ($13 \leq m \leq 21$) are listed in Tables 1 and 2, respectively. Some of the $\Delta S$ values for $C_{m}Li$ that we determined disagree with those previously reported [45]. This difference may arise from the fact that the reported DSC thermograms have exothermic peaks just below $T_{tr1}$ with heat process [44, 45], while no such irregular signals were found in our thermograms of $C_{m}Li$. The experimentally obtained $\Delta S_{mp}$ values of 21–27 J K$^{-1}$ mol$^{-1}$ are similar to those of previously reported rotator crystals [42]. However, the values for total entropy changes in solid phase ($\Delta S_{tr1} + \Delta S_{tr2}$) are smaller than $\Delta S_{mp}$ except for $C_{21}Li$; the results obtained for $C_{21}Li$ crystals satisfied the requirements of rotator crystals. If another transition associated with a large entropy change was detected below room temperature, other $C_{m}Li$ compounds could also classified as rotator crystals. Therefore, DSC measurements from $\sim$200 K to ambient temperature were carried out. However, as shown in Fig. 2a, the resulting thermograms revealed only
DSC, XRD, and $^7$Li NMR studies of rotator crystals

### Table 2

Melting and phase transition temperatures and entropy changes of $n$-$C_mH_{(2m+1)}COOK$

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**Fig. 3** Electrical conductivities of $n$-$C_{15}H_{31}COOKi$ ($C_{15}K$ (▲)), $n$-$C_{17}H_{35}COOKi$ ($C_{17}K$ (○)) and $n$-$C_{21}H_{42}COOK$ ($C_{21}K$) (●) as a function of temperature.

Minor heat changes. In contrast, large total entropy changes ($\Delta S_{tr1} + \Delta S_{tr2} + \Delta S_{tr3}$) as compared to $\Delta S_{mp}$ were observed for $C_mK$ crystals, as shown in Fig. 2d and Table 2. These results suggest that ionic motions with a large degree of freedom were excited in solid phases above 360 K.

In order to detect ionic diffusion in solid phases of $C_mLi$ and $C_mK$, electrical conductivity measurements were performed. For $C_mLi$ (13 ≤ $m$ ≤ 21), our LCR meter measured large resistances greater than 10 MΩ over the whole temperature range except at each melting point. In contrast, the $C_mK$ crystals exhibited small resistances above room temperature. The experimentally-determined $\sigma$ values for $C_{17}K$ and $C_{21}K$ crystals as a function of temperature are shown in Fig. 3. Upon heating, the $\sigma$ values measured for $C_{15}K$, $C_{17}K$ and $C_{21}K$ reached $\sim 1 \times 10^{-8}$, $3 \times 10^{-8}$ and $2 \times 10^{-7}$ S cm$^{-1}$, respectively. In a case of $C_{19}K$, large resistances were obtained. The results of DSC analysis of $C_{21}Li$ crystals provided the needed information to classify them as rotator crystals, but the very small $\sigma$ values measured over the whole temperature range except for the melting points were unexpected.

In order to investigate the cationic motions in the $C_{21}Li$ crystals, $^7$Li NMR analysis was carried out. Line shapes characteristic of quadrupole interactions were observed at room temperature, as shown in Fig. 4a. Since $^7$Li nuclei have a spin of 3/2, the central peak observed at 0 ppm and the satellite lines around ±40 ppm are assignable to the transitions between spins of 1/2 and −1/2 and between ±3/2 and ±1/2, respectively. The central transition signal was fitted using a Lorentzian function.
with 1.2 kHz of full line-width at a half-height of the peak. This value enabled the simulation of the line shape of the satellites peaks by theoretical curves convoluted by Lorentzian broadening. The theoretical curves yielded a quadrupole coupling constant \((e^2 Q_{\text{qh}}^{-1})\) of 60.6 kHz and an asymmetry parameter \((\eta)\) of 0.38, as shown in Fig. 4b. The spectrum was modified using a magic-angle-spinning (MAS) ratio of 1 kHz with \(^1\text{H}\)-decoupling pulse-sequence, as shown in Fig. 4c. In contrast, when no decoupling pulses were employed, line shapes similar to those observed in the static spectrum (Fig. 4a) were obtained as displayed in Fig. 4d. This result suggests that the line-width of 1.2 kHz was largely caused by \(^1\text{H}^\text{7}\)Li dipole-dipole coupling. This interaction can be described by the following equation.

\[
\Delta \nu = \frac{\gamma_7 \text{Li} \gamma_1 \text{H} h}{\pi r^3}
\]

Here, \(\Delta \nu\), \(\gamma\), and \(r\) are the full line-width at half-height of the peak, the gyromagnetic ratio of each nucleus, and the average distance between \(\text{Li}^+\) ions and \(\text{H}\) atoms in a crystal, respectively. Substituting 1.2 kHz for \(\Delta \nu\) in the equation yields \(r = 498\) pm. This length is similar to the distance between \(\text{Li}^+\) cations and \(\text{H}\) atoms bonded to the \(\alpha\)-carbon of \(n\)-alkyl carbonate in the crystal. Therefore, we concluded that the \(\text{Li}^+\) ions are localized in the solid phase at room temperature.

In general, impurities in a sample increase electrical conductivity. Since the \(\text{C}_{21}\text{K}\) crystals exhibited the highest \(\sigma\) value measured in this study, and DSC analysis
indicated that the \( n \)-alkyl carbonate ions move with a large degree of freedom in both \( C_{21}K \) and \( C_{21}Li \) crystals, we anticipated even higher electrical conductivity in mixed crystals of \( C_{21}Li \) and \( C_{21}K \). In addition, XRD spectra of both samples revealed similar crystal structures, as shown in Fig. 1. Therefore, mixed crystals of \( C_{21}Li_xK_{(1-x)} \) were prepared. XRD spectra obtained for the mixed crystals are shown in Fig. 5, where the highest count in each graph has been scaled to unity. Some of these diffraction patterns recorded in the \( 2\theta \sim 25^\circ \) range revealed that the mixed crystals were produced in molar ratios such that \( 0.25 \leq x \leq 0.60 \) in \( C_{21}Li_xK_{(1-x)} \).

Results of DSC analysis are shown in Fig. 6, where the most strength peak in each thermogram has been normalized; variation observed around 300 K is due to instrument noise. Based on the fact that new phase transitions were detected in the mixed crystals, it can be concluded that mixed crystals of the \( C_{21}Li_xK_{(1-x)} \) structure are successfully obtained. In samples where \( x = 0.60 \) and 0.67, exothermic peaks were observed at \( \sim 430 \) K with heat process. This temperature is just above the melting temperatures observed for the other mixed crystals characterized, suggesting that the endothermic peak observed just below this exothermic signal in \( C_{21}Li_{0.60}K_{0.40} \) and \( C_{21}Li_{0.67}K_{0.33} \) crystals could not be identified as either a melting point or solid-solid transition. Large enthalpy changes observed at \( \sim 380 \) K in \( C_{21}Li_xK_{(1-x)} \) where \( 0.25 \leq x \leq 0.50 \) suggested that mixed crystals of this composition were successfully produced, as no phase transition at this temperature was detected for the starting
Fig. 6  DSC thermograms of \(n\text{-C}_{21}\text{H}_{43}\text{COOLi}_{x}\text{K}_{(1-x)}\) (\(\text{C}_{21}\text{Li}_{x}\text{K}_{(1-x)}\)) with heat process.

Table 3  Melting and phase transition temperatures and entropy changes of \(n\text{-C}_{21}\text{H}_{43}\text{COOLi}_{x}\text{K}_{(1-x)}\).

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The material (\(C_m\text{Li}\) and \(C_n\text{K}\) crystals). Hereafter, \(T_{tr1}\) and \(T_{tr2}\) will be used to indicate the phase transition temperatures around 405 and 380 K, respectively. Since additional endothermic peaks observed just below \(T_{tr1}\) of \(\text{C}_{21}\text{Li}_{0.25}\text{K}_{0.75}\), \(\text{C}_{21}\text{Li}_{0.33}\text{K}_{0.67}\), and \(\text{C}_{21}\text{Li}_{0.40}\text{K}_{0.60}\) crystals were very small, we did not characterize them further. An additional transition for \(\text{C}_{21}\text{Li}_{0.33}\text{K}_{0.67}\) was observed at 415.2 K with an associated entropy change of \(\Delta S = 20.4\) J K\(^{-1}\)mol\(^{-1}\). Entropy changes estimated for \(T_{tr1}\), \(T_{tr2}\), and melting temperatures are listed in Table 3. That \(\Delta S_{tr2}\) was greater than \(\Delta S_{mp}\) suggests that some motions with large degrees of freedom were excited in Phases I and II. Based on the facts that \(\Delta S_{mp} < 20\) J mol\(^{-1}\)K\(^{-1}\) and \(\Delta S_{mp} < (\Delta S_{tr1} + \Delta S_{tr2})\), we can conclude that Phase I and/or Phase II are rotator phases.
In order to detect ionic diffusion, the temperature dependence of electrical conductivity was characterized. The results obtained are plotted in Fig. 7, which reveals higher $\sigma$ values for the mixed crystals as compared with C$_{21}$K; as anticipated, C$_{21}$Li exhibited a large resistance over 10 M$\Omega$. The C$_{21}$Li$_{0.33}$K$_{0.67}$ crystals particularly electrifies 1 order comparing with C$_{21}$K. The discontinuity of $\sigma$ values recorded around 380 and 402 K corresponds with the phase-transition temperatures of $T_{tr2}$ and $T_{tr1}$. By plotting ln($\sigma T$) versus $T^{-1}$, activation energies of 25.3, 93.4, 41.4, and 30.8 kJ mol$^{-1}$ were determined for C$_{21}$Li$_x$K$_{(1-x)}$ where $x = 0.25, 0.33, 0.40$, and 0.50, respectively. These are similar to reported activation energy values for rotator and isotropic plastic crystals [42].

In order to obtain information about the molecular dynamics in the crystals, $^7$Li NMR measurements were carried out. A MAS rate of 1 kHz was used even though the use of high speed spinning is known to reduce the first order interaction of quadrupole coupling. Our apparatus, unfortunately, requires that a non-zero MAS rate be used in order to allow control over sample temperature. The $^7$Li MAS NMR spectrum of the C$_{21}$Li crystals obtained using a spinning rate of 1 kHz without $^1$H decoupling pulse exhibited the same line shapes as the static spectrum demonstrated in Fig. 4, and so we applied this method to the mixed crystals. $^7$Li NMR spectra of the mixed crystals obtained at room temperature show characteristic indications of quadrupole interactions (Fig. 8).

The line width of the central transition was independent of temperature below $T_{tr2}$ except for C$_{21}$Li$_{0.25}$K$_{0.75}$ crystals, although the peak difference between the satellite signals ($\Delta \nu$) decreased with increasing temperature. This result suggests that the dipole-dipole interactions between $^7$Li and $^1$H nucleus occurred in Phase III of the C$_{21}$Li$_x$K$_{(1-x)}$ crystals where $0.33 \leq x \leq 0.50$. The half-height line-width was estimated as 1.2 kHz from the central transition signal. Employing this value, the line simulation of satellite signals using a Lorentzian function gave the $e^2Qqh^{-1}$ and $\eta$ values listed in Table 4. The trend of decreasing $e^2Qqh^{-1}$ and $\eta$ values with increasing temperature may arise from thermal vibrations by which the EFG values at the $^7$Li nucleus in mixed crystals are averaged. Above $T_{tr2}$, at which the largest
entropy change is detected for each mixed crystal, a component giving rise to a narrow line width appeared on the central signal of each $^7$Li MAS NMR spectrum. Because this component did not produce any satellite peaks, we propose that the EFG anisotropy of the Li$^+$ ion was averaged by ionic motions (in other words, that the quadrupole interaction was dynamically averaged out), and/or the Li$^+$ ions were located at a site that gave statistically equivalent EFG values as the $xx$, $yy$, and $zz$ components. In order to better understand the crystal structure in Phase II, XRD analysis at some temperatures was carried out. The resulting spectra revealed that only minor changes in crystal structures occurred after the phase transition at $T_{tr2}$, as shown in Fig. 9. Based on this result, we concluded that the component giving the sharp signal is assignable to diffusing Li$^+$ ions, consistent with our conductivity results showing that $\sigma$ values increased from Phase II (Fig. 7).
Fig. 9  Temperature dependence of XRD spectra of \( n\)-C\(_{21}\)H\(_{43}\)COOLi\(_x\)K\(_{(1-x)}\) (C\(_{21}\)Li\(_x\)K\(_{(1-x)}\))
4 Conclusion

Using DSC, XRD, electrical conductivity, and $^7\text{Li}$ NMR, we characterized mixed crystals with the structure $C_{21}\text{Li}_x\text{K}_{(1-x)}$ ($0 < x < 1$) and $C_m\text{Li}$ and $C_m\text{K}$ crystals where $m = 13, 15, 17, 19, 21$. $C_{m}\text{Li}$ ($m = 13, 15, 17$) crystals exhibited similar transition temperatures and crystal structures, as assessed using DSC and XRD, as those published in the literature [43–45]; however, our DSC thermograms did not exhibit any exothermic error peaks with heat process. The entropy changes $\Delta S_{\text{mp}}$ observed at the melting points were larger than the total entropy changes $\Delta S_{\text{total}}$ between solid phases, except in $C_{21}\text{Li}$ crystals. Electrical conductivity measurements revealed that $C_m\text{Li}$ crystals were poor conductors, while the analysis of $C_{21}\text{K}$ crystals yielded $\sigma$ values of $\sim 2 \times 10^{-7}$ S·cm$^{-1}$. Crystal structures and phase transition patterns of $C_m\text{K}$ and $C_m\text{Li}$ were similar to one another but dissimilar enough from $C_m\text{Na}$ such that $C_m\text{Li}/C_m\text{K}$ mixed crystals could be obtained but neither compound would form mixed crystals with $C_m\text{Na}$. DSC thermograms of $C_{21}\text{Li}_x\text{K}_{(1-x)}$ crystals revealed some endothermic peaks. A small entropy change ($\Delta S_{\text{mp}} < 20$ J K$^{-1}$ mol$^{-1}$) at the melting temperatures and large $\Delta S$ values were obtained at the solid-solid phase transition. In addition, self-diffusion of Li$^+$ ions was detected using electrical conductivity and $^7\text{Li}$ NMR spectral analysis. These results suggest that the $C_{21}\text{Li}_x\text{K}_{(1-x)}$ mixed crystals are rotator crystals.

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