Fast and Slow Components in the Crystallization of a Model Multicomponent System, NaKCa(NO₃): The Role of Composition Fluctuations

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ABSTRACT: We use calorimetrically detected crystal nucleation and growth studies to broaden the discussion of fluctuation-induced nucleation processes to include composition fluctuations in ionic complex-forming systems. We use the model system Ca(NO₃)₂–KNO₃ with NaNO₃ introduced as a third component, so that crystallization kinetics can be controlled by change of alkali cation at constant mole fraction of Ca(NO₃)₂. At fixed NaNO₃ content, we find separate and thermodynamically anomalous kinetics for the crystallization of NaNO₃ and Ca(NO₃)₂, which we attribute to the importance of slow concentration fluctuations in the latter case. The “nose” of the time–temperature–transformation TTT curve for crystallization of the Ca(NO₃)₂ occurs at much higher temperatures and longer times than that for NaNO₃ and the shape of the curve is different. Above the metastable liquidus surface of NaNO₃, supercooled ternary melts can persist for long times. Suppression of the fast NaNO₃ crystallization, by replacement of Na⁺ by K⁺, is a prerequisite for easy vitrification in this system.

INTRODUCTION

Glasses form when crystals are unable to nucleate and grow to visible proportions during the process of cooling the liquid from its stable state to the final temperature of the experiment, (taken to lie below the glass transition temperature, Tₘ₉)⁴–₇ Tₘ₉ is commonly defined as the temperature at which the heat capacity of a glass starts to increase abruptly during steady heating at 20 K/min. In most cases it is easily determined by differential scanning calorimetry or differential thermal analysis.⁵,⁶

It is a common observation that liquids that vitrify on cooling will crystallize when they are reheated at the same rate as they were cooled, though it is often not properly understood why.⁷ “Good” glassformers are those that do not crystallize either on cooling to Tₘ₉ or on reheating anywhere above it. “Ideal” glassformers may be defined as those rare cases that are incapable of crystallizing at any temperature because they are thermodynamically stable as they enter the glassy state. For the latter type of glassformer, an example of which is the eutectic in the system H₂O · H₂Cr₂O₇ · 6H₂O system,⁸ the conventional discussion of glass formation in terms of slowdown of crystal nucleation processes, is irrelevant.⁹

In this paper we deal with the usual case of avoided crystallization and consider the interesting case where the crystallization of the thermodynamically preferred phase exhibits a different and slower kinetics than does that of a less preferred phase of different composition. The thermodynamically preferred phase only appears after the barrier is lowered as a result of the composition change that has occurred, an interesting multicomponent version of the Ostwald “law of stages”. To study this question, we use a variant of the much-studied¹⁰–¹⁷ system Ca(NO₃)₂–KNO₃ in which NaNO₃ is included as a third component.¹⁸

To set up the problem, it will be convenient to discuss the glass formation in terms of relative time scales for the competing processes that determine the outcome of a cooling experiment. For a glass to form, the liquid structure must become arrested (and incapable of further evolution) before a detectable level of crystallization has occurred.¹⁹ The onset glass temperature determined in this manner is generally found to correspond to the temperature at which the structural relaxation time (called here the internal relaxation time) of the liquid reaches 100 s.²⁰

The internal relaxation time of the system is easily determined by dielectric relaxation spectroscopy for molecular liquids. For ionic and metallic glassformers, mechanical or thermal relaxation studies are needed. These various relaxation times are usually

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very similar in magnitude when measured for the same substance, though there are some striking exceptions. The reason that the internal relaxation time becomes long (often with spectacular temperature dependence) is an issue quite separate from the suppression of crystallization and will not be discussed in this paper.

To compare with the internal relaxation time, a characteristic time for crystallization can also be determined by calorimetry. In scanning calorimetry, a crystallization onset temperature is routinely reported, and used in the discussion of supercooled liquid stability, but it has not been linked to a crystallization time. A crystallization time has been defined from isothermal calorimetry studies in which an exothermic peak is observed as crystals nucleate and then grow. The peak corresponds to the maximum crystallization rate but we should note that the completion of the peak only means that the sample is completely crystalline in the case of pure substances. In multicomponent systems, crystallization is terminated by the arrival of the composition at the saturation line (i.e., liquidus line) for the component that is crystallizing, unless the residual (depleted) material becomes too viscous to crystallize. For three dimensional (spherical) growth of the crystal, MacFarlane et al. showed that, under the Avrami nonimpingement assumption, the peak time was reached when the crystallization was 45% complete.

Alternative to the peak of the isothermal crystallization exotherm, the onset of the peak may be used, as for the glass transition, to define an onset crystallization time. The isotherm for which this time is 100s should be the temperature at which crystallization commenced when temperature is down-scanned at 20 K/s. We will see the test of this proposition in the Results section of this paper. An accord will be dependent on having bypassed the nose of the TTT curve for nucleation during the initial cooling in the run for which the crystallization onset temperature is determined.

To understand the latter statement, it is necessary to appreciate that the TTT curve determined by isothermal calorimetry, as normally practiced, is a TTT curve for the combined process, nucleation-plus-growth. The process of nucleation involves smaller length scales than nucleation-plus-growth and is intrinsically faster. The two TTT curves are quite separate in most cases. It is important to recognize this when comparing the results of isothermal crystallization studies with (i) those of computer simulations which see only nucleation, or (ii) results of the classical studies on oxide glassformers, in which the studies were executed by carrying out a nucleation step, and then growing the nuclei to visible proportions for counting. The growth step was conducted at a higher temperature where new nuclei would not form at an interfering rate, implying that the TTT curves obtained were also for nucleation alone. Theoretical studies, both classical and more modern density functional approaches, have also been concerned primarily with the nucleation process.

For simple cases where only one crystal is involved (usually single component systems), the form of the TTT curve for nucleation alone can be determined calorimetrically by a different (“two-step”) isothermal crystallization protocol, but we will not be concerned with this separation in the present paper. Rather, we will be concerned with a different separation, namely, the separation in crystallization kinetics (TTT curves) that is encountered in a multicomponent system where more than one type of crystal forms during the crystallization process. We observe an aspect of liquid crystallization kinetics that is not often discussed at a fundamental level because it is not manifested in the single component systems on which most theoretical studies have been made. It is the effect on the diffusion-controlled part of the TTT curve of the longer range diffusion (or more complex composition fluctuation) that is needed to allow a complex-forming cation like the doubly charged Ca$^{2+}$ species of our mixed nitrate system, to extricate itself from a weak field cation second coordination shell so as to generate a pure crystal of the doubly charged cation.

In the variant of the classical Ca(NO$_3$)$_2$-KNO$_3$ system that we use to study these effects (called “CKN” when Ca/K = 4:6), NaNO$_3$ is substituted for KNO$_3$ to make a “poor” glassformer, and then crystallization resistance is “tuned in” systematically at constant alkali content by substituting K$^+$ for Na$^+$. This substitution allows Ca$^{2+}$ to tighten its nitrate anion coordination shell, inhibiting the nucleation of pure Ca(NO$_3$)$_3$.

This constant 60% alkali nitrate join has the special advantage that the glass temperature, $T_g$, at which the internal relaxation time reaches 100 s for a standard 20 K/min scan, is almost independent of the composition studied, while the liquidus temperatures and downscan crystallization temperatures change rapidly with composition. The phase diagram for the system is shown in Figure 1.

Because our findings will require understanding of metastable liquidus surfaces, we provide a detailed presentation of the phase relations in the ternary system. Figure 1a shows a 3D representation of how the liquidus surfaces vary with temperature, while Figure 1b shows the quantitative relationships in a 2D contour diagram from the work of Bergmann et al. Thick lines mark the compositions studied in this work.

The use of constant equivalent compositions, requiring that the alkali nitrate corners be represented by (KNO$_3$)$_2$ and (NaNO$_3$)$_2$, can be a source of confusion. The model glassformer “CKN” that has been the subject of so many glass science studies, has the molar composition 4Ca(NO$_3$)$_2$.6KNO$_3$, which falls at 43% (KNO$_3$)$_2$ on the Figure 1b diagram. Because so much of the present study is concerned with compositions that lie on the isocom connecting this composition to one in which NaNO$_3$ replaces KNO$_3$ we have marked this line conspicuously in Figure 1b. Then we can use the temperature contours of this diagram to understand where the different compositions we study first become supercooled with respect to Ca(NO$_3$)$_3$. Likewise, we can use constant temperature contours on the NaNO$_3$ liquidus surface to find, by extrapolation, where liquids of the 43% (MNO$_3$)$_2$ (60% MNO$_3$) isocom become supercooled with respect to the NaNO$_3$ (the heavy dashed line shows the case of the 170 K isotherm to be encountered later in the paper). Most of the composition variations of this study will involve the variable, x, the fraction of sodium ions in the composition 4Ca(NO$_3$)$_2$.60NaNO$_3$ that have been replaced by potassium ions, hence defined by $x = $ moles KNO$_3$/moles KNO$_3$ + moles NaNO$_3$.

**EXPERIMENTAL SECTION**

The materials used in this work were formed directly by the melting of mixtures of reagent grade NaNO$_3$, KNO$_3$, and Ca(NO$_3$)$_2$. $4\text{H}_2\text{O}$ obtained from Sigma-Aldrich, which were used without further purification. The mass of the mixture was about 5 g. Water in the mixture was removed by holding at 573 K for over 12 h in an oven. Then the mixture was heated to a complete liquid state, and quenched into a solid plate of 1.0 mm thickness using a copper mold. Samples of about 15 mg were
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RESULTS

The present study makes use of results from an initial study of the NaNO$_3$–Ca(NO$_3$)$_2$ binary system, which is being published separately. A phase diagram containing data pertinent to the present study will appear later in this section. Cooling curves and reheating glass transition and crystallization curves are similar to those seen below for ternary melts and it will help in understanding the rather complex relationships of the present work if two key results of the binary system study are revisited here at the start.

First, and remarkably, NaNO$_3$ was found to crystallize without any supercooling, that is, immediately on crossing the equilibrium liquidus line on the phase diagram (seen in Figure 1b) to lie above 50 mol % (NaNO$_3$)$_2$. Furthermore, NaNO$_3$ continued to be the primary crystallizing phase well into the Ca(NO$_3$)$_2$ crystallization field of the phase diagram, including the composition marked 60 mol % NaNO$_3$ in Figure 1b. The reason for this facile crystallization is not well understood, but it is a dominant feature of the present study also. Second, and unexpectedly, when Ca(NO$_3$)$_2$ finally became the primary crystal phase, it appeared with considerable and erratic degrees of supercooling.

Accordingly, the sharp exotherms seen in Figure 2 for heat flow from the samples of different K/Na content, measured during cooling from the stable liquid, with exception of $x = 0$ and probably 0.1, are due to NaNO$_3$ crystallization even though this is not expected from the phase diagram. Then, at fixed mole fraction MNO$_3$, but increasing $K^+/(K^+ + Na^+)$, the exotherms of Figure 2 are due to NaNO$_3$ crystallization though the rate is clearly slowing down as the Na$^+$ is replaced.

In the binary system, there are circumstances near the eutectic composition where the nucleation rates for Ca(NO$_3$)$_2$ and NaNO$_3$ are comparable. But as NaNO$_3$ is replaced by KNO$_3$, Ca(NO$_3$)$_2$ nucleation is suppressed, showing that the Ca(NO$_3$)$_2$ crystallization is conditioned by the second nearest neighbor environment. It is suppressed as the Ca$^{2+}$ ions become more firmly locked into their anion environments because K$^+$ in the second nearest neighbor position is electrostatically less competitive than Na$^+$.

With increasing $x$(KNO$_3$), the nucleation rate for the NaNO$_3$ also decreases. For the cooling rate of Figure 2, 20 K/min, the occurrence of crystallization could be observed at $x = 0.30$ but not beyond. However, as is common, crystallization could be observed in these latter “non-crystallizing” compositions during reheating.

To study the recrystallization during reheating over the whole composition range, samples were initially quenched by dropping the sealed pans into liquid nitrogen (LN$_2$) from above the liquidus temperatures, $T > T_1$. At the 60 mol % alkali nitrate broken from the plate and sealed into aluminum DSC pans after further heating to 570 K to minimize water in the samples.

Thermal analysis of phase changes occurring during both cooling and heating schedules was performed using a Mettler Toledo DSC823e thermal analyzer. To obtain completely glassy samples at any composition, the sealed pans were dropped into liquid N$_2$ from above the liquidus temperatures of Figure 1. Otherwise, the DSC protocols involved cooling from the liquid state at fixed cooling rates, followed by upscans which were conducted in all cases at 20 K/min. According to ref 30, quenching samples in calorimeter pans by dropping into liquid nitrogen produces a cooling rate of 120 K/s or 360 times as fast as our standard 20 K/min heating rate.

XRD studies, that were used to determine the products of initial and secondary crystallization during selected the heating or cooling schedules, will be described in a separate publication focused on the binary NaNO$_3$–Ca(NO$_3$)$_2$ system.
composition of this study, the LN$_2$ quench suppresses crystallization completely except perhaps in the binary (Na$_{40}$Ca$_{40}$) case. Results are shown in Figure 3.

Figure 3 shows the recrystallization steps that occur during reheating at 20 K/min after the initial vitrifying quench. Independent of composition, up to about x = 0.4, the crystallization occurs sharply at about the same temperature i.e. at the same temperature interval above T$_{vp}$ implying viscosity control. According to X-ray data, the initial crystallization is exclusively NaNO$_3$ although it is not the most stable product. The crystallization surfaces of Figure 1 are shown extrapolated metastably beyond the ternary eutectic line to illustrate how this prior crystallization of the less stable phase can be possible.

The crystallization of NaNO$_3$, which seems to be complete after some more 10 K, is followed quickly by a second sharp crystallization peak so long as x(KNO$_3$) remains small. XRD shows the second exotherm to be due to Ca(NO$_3$)$_2$ crystal formation, presumably with more NaNO$_3$ in a pseudoeutectic process. With both crystalline phases present, further heating causes a sharp melting which, at x = 0 and under equilibrium conditions, would occur at the binary eutectic temperature of 506 K, according to Figure 1b. Because of the fast scan and the excess NaNO$_3$ from metastable crystallization we observe this melting at a somewhat lower temperature, 498 K. The remelting temperature decreases with increasing x, following the pseudoeutectic temperature in the ternary system, see Figure 1.

The slower crystallization of Ca(NO$_3$)$_2$ at larger mole fractions of KNO$_3$ is obvious in Figure 3 from the behavior of the second exotherm as the initially sharp peak broadens and becomes shallower before finally disappearing completely at x = 0.45. It becomes very sensitive to upscan rate and is finally suppressed completely. As this happens, an interesting effect develops in the lower temperature part of the upscan, which will be seen more clearly in the next figure. It is that, at x = 0.35, the Ca(NO$_3$)$_2$ crystallization has almost disappeared, the first exotherm (due to NaNO$_3$ crystallization) turns into an endotherm as temperature increases, as if the NaNO$_3$ is remelting. Indeed, in the absence of Ca(NO$_3$)$_2$ crystals for eutectic melting this is exactly what the phase diagram predicts will happen. The NaNO$_3$ liquidus projects under the equilibrium Ca(NO$_3$)$_2$ crystallization surface, and remelting of the NaNO$_3$ will occur as the temperature rises above this liquidus. Figure 1b shows the projection of the 170 °C (443 K) NaNO$_3$ crystallization contour into the metastable composition domain and shows that it intersects our 60% MNO$_3$ composition line at about x = 0.35. This will be remarked on further after the unambiguous results for the composition x = 0.35, seen in Figure 4, have been presented.

The decreasing gap between the equilibrium liquidus temperature (of Figure 1b) and T$_g$ (of Figure 3), as KNO$_3$ replaces NaNO$_3$ along our 60% MNO$_3$ isocom, is important to understanding the development of good glassformer properties in this system. These trends are summarized in Figure 5, where it is seen that the intersection (at x ≈ 0.4) of the cooling crystallization line (T$_c$) and heating crystallization temperatures (T$_c$) determines the beginning of the system glassforming range for studies conducted at 20 K/min. We are interested, ultimately, in the possibility of finding third components that give rise to such an intersection even for scans of infinitely slow rate. This would imply that we had engineered an "ideal glassformer". Progress toward such an objective will be described in a separate paper.  

Figure 4 shows the consequences of annealing LN$_2$-quenched samples a little above T$_g$ for different periods (to encourage the rapidly nucleating process) before recooling and conducting the usual 20 K/min upscans. The upscans now show that, unless the annealing has continued for more than 10 minutes, Ca(NO$_3$)$_2$, the stable phase, is never produced (no peak at the Ca(NO$_3$)$_2$ liquidus at ~300 °C is seen). Rather, the crystallization of the rapidly nucleating phase NaNO$_3$ is completed (at about 130 °C) and then these crystals remelt. The melting process finishes at ~160 °C (433 K), according to Figure 4, which is consistent with
the metastable liquidus temperature of \(170 ^\circ C\) (443 K) obtained by the extrapolation of contours in Figure 1b (thick dashed line) to the composition of our melt. The liquid obtained in this remelting process can be held at 180 \(^\circ C\) (453 K) for more than 8 h without any crystals of \(Ca(NO_3)_2\) appearing. This important observation is critical to fixing the minimum crystallization time (nose of the TTT curve) for the stable phase relative to the metastable but kinetically crystallizable \(NaNO_3\) phase. \(Ca(NO_3)_2\), which nucleated first during 5 K/min cooling at low \(K^+\) contents, is now evidently extremely slow to nucleate despite a supercooling of nearly 150 K, much greater than the (very small, \(\sim 25\) K) degree of supercooling that provokes the metastable crystallization of \(NaNO_3\). Indeed, \(Ca(NO_3)_2\) only crystallized if \(NaNO_3\) crystallization had occurred first, changing the composition (see Figure 4 caption). Metastables often nucleate first (see ref 28b).

The low temperature nucleation of \(NaNO_3\) must be thought of as being driven by supercooling below the projected \(NaNO_3\) liquidus temperature of 175 \(^\circ C\) (448 K; see extrapolations in Figure 1b), not as driven by supercooling below the much higher \(Ca(NO_3)_2\) liquidus temperature. Holding the liquid at 448 K (where \(NaNO_3\) is stable against crystallization) for long enough must, of course, eventually generate the stable \(Ca(NO_3)_2\), but it takes more than \(3 \times 10^4\) s. Escaping the anion coordinated complex structure to nucleate is evidently a very slow process. The minimum crystallization time for \(Ca(NO_3)_2\) must occur at temperatures very far above that for \(NaNO_3\) and, thus, will seem to be quite disconnected from the glass transition kinetics. Such a disconnection has been seen before for equilibrations in which long diffusion distances are involved, for instance, dyestuff dimetallizations in dilute solutions. 33 This is a point of primary importance to the present paper and will be elaborated upon further below.

In Figure 5, we summarize the cooling onset, and heating onset, crystallization temperatures, and show them in relation to the equilibrium liquidus temperatures \(T_l\) and the glass transition temperatures \(T_g\). The crystallization product of exotherms observed in downscans at 20 K/min is always \(Ca(NO_3)_2\). The primary crystal may be \(Ca(NO_3)_2\) but only in the binary system \(NaNO_3-Ca(NO_3)_2\). When \(KNO_3\) is present, \(Ca(NO_3)_2\) crystallization is repressed and, according to X-ray diffraction data, it is then only seen after its concentration has been increased by prior crystallization of \(NaNO_3\). If the cooling rate is reduced to
5 K/min, then in the absence of KNO₃, Ca(NO₃)₂ crystallization can be observed, see below.

Because Ca(NO₃)₂ primary crystallization in the ternary system is so rare, but is intrinsically so interesting (because of the more complex sort of ion shell fluctuations it requires) we provide, in Figure 6, additional data for the binary system, NaNO₃ + Ca(NO₃)₂, in which Ca(NO₃)₂ primary crystallization is indeed observed. The liquidus lines in Figure 6 are from ref 10. It is notable how closely these are reproduced by the cooling crystallization data, for NaNO₃-rich compositions. These are plotted for both 20 and 5 K/min coolings and it is seen that there is essentially no supercooling for NaNO₃. This contrasts with the Ca(NO₃)₂ side of the eutectic composition where supercooling is always observed. Indeed, primary crystallization at our isocom composition is only observed if the cooling rate is lowered to 5 K/min. As shown in ref 31, NaNO₃ crystallization occurs over the composition range 100−60 mol % NaNO₃ even though the eutectic composition is at 72% NaNO₃. Tg values for the crystal-free glassforming compositions are included in Figure 6.

In Figure 7, we show the results of isothermal crystallization studies like those described in refs 17 and 26. Part (a) shows the crystallization exotherms and part (b) displays the crystallization onset, also crystallization peak times, in relation to observation temperature, using a log scale. Here we can compare the time for the exotherm onset at a given temperature, with the temperature of onset during upscan at 20 K/min from Figure 4 (not expecting a correspondence) and with the onset temperature during cooling at 20 K/min from Figure 5 (where a correspondence might be expected). This is taken up at the beginning of the Discussion section.

In Figure 8 we show data obtained for fictive temperatures of glasses obtained at different downscan rates, using the modified

\[ T_f \frac{1}{Q} \]

Moyihian method of ref 34 for selected compositions across the whole pseudobinary. These are needed for the subsequent construction of Figure 9.

These fictive temperatures, which are temperatures at which structure became frozen during cooling at rate Q K/s, are

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**Figure 7.** (a) Isothermal crystallization exotherms for the sample \( x = 0.35 \), held at different temperatures after quenching from above the liquidus. (b) Peak and onset temperatures for the isothermal crystallizations of Figure 7a Filled circle indicates relative location of the minimum nucleation time for Ca(NO₃)₂ at \( T = 370 \) K and the solid curve gives the shape that is then implied for the TTT curve for Ca(NO₃)₂ lower section. The temperature of onset of crystallization during cooling at 20 K/min is noted for comparison with the isothermal crystallization onset temperature which occurs a little earlier than 100 s.

**Figure 8.** \( T_f \)-scaled Arrhenius plot of reduced cooling rates vs inverse fictive temperatures to obtain the m fragilities of compositions along the 40% alkali nitrate tie line in the NaNO₃−KNO₃−Ca(NO₃)₂ system. With \( T_f = T_g \) this plot is seen to be an alternate form of \( T_g \)-scaled Arrhenius plot of (inverse) relaxation times. An unexpected finding is the systematic variation of the fragility with KNO₃ content, (a sort of “mixed alkali effect" that implies intermediate range ordering of the alkali cations).
DISCUSSION

The first point to be discussed is the relation between \( T_g \) on heating, \( T_c \) on cooling, and the isothermal crystallization time, referring to Figures 2 and 7.

Since the isothermal crystallization protocol we have used does not expose the sample to a fast nucleation zone \([20]\), it should be more closely connected to the cooling crystallization temperature than to that observed on heating up from an initially quenched glass. Thus, we compare the results of cooling samples at 20 K/min (Figure 2) with those of the isothermal crystallization studies (Figure 7). It is notable that the onset of isothermal crystallization occurs after \(10^{-1.5}\) s, that is, 30 s at 410 K and 10 s at the nose, whereas for this composition no crystallization at all was seen in Figure 2 during cooling at 20 K/min. The latter is therefore close to the critical cooling rate \(^1\) for this composition.

It is implied from the above that when the onset of crystallization is observed during cooling, the characteristic onset time for the process is less than 30 s. This time scale is shown as a horizontal line in Figure 9, (the key diagram of this paper, taken up below). This crystallization onset time is a little smaller than, but of the same order as, the 100 s relaxation time attributed to the onset glass transition observed during 20 K/min upscans, and the difference could be attributable to the “dead” time of the experiment needed to reach the temperature of the isotherm of observation. To observe the onset of crystallization during cooling at this composition, then, the cooling rate must be reduced to 10 K/min.

The second point to be emphasized in this discussion is the fact that the crystallization of \( \text{Ca(NO}_3\text{)}_2 \) is seen as the first crystallization process only under conditions of high temperature, slow cooling, and low KNO\(_3\) content, even though it is always the thermodynamically stable phase, that is, the one that should form first. This points to some important principles controlling crystallization kinetics in complex systems that have not been properly discussed in previous studies. To understand these more fully, we first construct a time/temperature diagram, evolved from Figure 7, in which we compare the internal relaxation time of the liquid (100 s at \( T_g \)), with the different crystallization times.

To explain this construction we note that the time scale for formation of any crystal must be infinite right at its thermodynamic liquidus temperature (or melting point in the case of a pure phase) because of the absence of any driving force to crystallize. The time scale then (obviously) decreases as supercooling occurs. A factor that determines whether glasses will form, at a given cooling rate, is the shortest crystallization time that is achieved before crystallization rate reverses at the “nose” of the TTT curve of ref 1 and ref 17. When there are competing crystals, there will need to be more than one TTT curve, one for each of the crystal phases in contention.

To discuss this further we rotate the TTT curve of Figure 7 by \(90^\circ\) (to vertical) to obtain a plot of relaxation time versus temperature, as is normal in consideration of relaxation processes. This gives us Figure 9 in which we can include the internal relaxation time, \( \tau_{int} \) for the system (as in ref 17 where the shear relaxation time from viscosity was used). Any of the various techniques mentioned in the introduction could be used to establish this internal relaxation time. Here, we use data from Figure 7.

Figure 9 then becomes a relaxation map for the various kinetic processes, nucleation + growth and relaxation, that are possible in this interesting system. We can use it for discussion of the complex interplay of competing crystallizations and meltings that we have documented earlier in the paper. In particular, we emphasize the metastable melting point of the first crystals that form during reheating of the ternary glasses (see Figure 4). This is marked as a vertical thick dashed line at 445 K. Because Figure 8 shows that the internal relaxation times do not change much with changing KNO\(_3\) replacement of NaNO\(_3\) (\( T_g \) is nearly invariant in Figure 5), we can see the consequence of the steadily decreasing liquidus temperatures (as NaNO\(_3\) is substituted by KNO\(_3\)) on the crystallization temperature for the fastest process (NaNO\(_3\) crystallization). This must “squeeze” the high temperature part of the TTT curve to lower temperatures, but because its movement is blocked by the constant internal relaxation time, the nose of the TTT curve is squeezed out to longer times, and so the glassforming propensity must increase. The “ideal glassformer” is obtained when the liquidus temperature has been pushed down below the \( T_g \) as was observed by Vuillard,\(^8\) for the \( \text{H}_2\text{Cr}_2\text{O}_7-\text{H}_2\text{O} \) eutectic (the likely existence of many such cases is discussed in a current report to Nature.)

The limited time range of the calorimetric crystallization measurements seriously restricts what can be said about the long
The coordinate shell rearrangement process is quite similar to the process needed to nucleate a Ca(NO$_3$)$_2$ crystal in the present multicomponent system. The lower “activation energy” for the process requiring the chemical order fluctuation is common to each case, and is associated with a more physical pre-exponent. Consistent with being a true activated process, and in contrast to the viscous relaxation process, it appears to be an exponential relaxation$^{37}$ like other chemical relaxation processes. These have, in common, the feature that their environment relaxes many times during the time necessary for the “target process”, that is, the chemical order relaxation or the nucleation process, to occur. Accordingly, such processes would not be expected to exhibit the TTT curves typical of simple glassformers, though their crystal growth rates might still exhibit the “dynamical heterogeneity” signatures common to simple relaxation processes in glass-forming liquids or the crystallization growth rates of single component systems$^{38}$ and stoichiometric glassformers.$^{39}$

**CONCLUDING REMARKS**

The majority of glassforming systems of practical importance are multicomponent in character, and the phenomenology described in this paper must be quite a common occurrence during the crystallization process. To the extent that it is an example of the Ostwald “law of stages”$^{40}$ the initial crystallization of a less stable phase should be the most common observation. It is certainly common in posteutectic aqueous solutions, where ice is the fast nucleating phase. Whether or not the detailed crystallization kinetics of the more slowly crystallizing phase follow the pattern we have described here is, however, less certain and must await further investigation. The phenomenon of a crystal phase (here NaNO$_3$) melting to give a supercooled liquid state, is unusual. However it is likely to be shared by aqueous solutions that have precipitated ice during cooling of post-eutectic solutions. Ice is the first crystal to nucleate from solutions in which the extrapolated ice liquidus curve remains above the glass temperature. The idea of ice melting into a metastable state would have been found appealing by Victoria Buch, to whom this work is dedicated.

**ASSOCIATED CONTENT**

Supporting Information. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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