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*Influence of temperature on the hydration equilibria
and phase transitions. I. Polythermal crystallization
of $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$ from water*

Wpływ temperatury na równowagi i przemiany hydratacyjne.
I. Politermiczna krystalizacja $\text{La}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$

1. INTRODUCTION

The trivalent ions of the light lanthanides: Ce(III) – Nd(III) and La(III) – denoted as Ln(III), combine a high charge and a large ionic radius in one and form high coordination complexes in the solid phase as well as in the aqueous solutions [1,2]. The content and structure of these complexes are modified by various factors, among which temperature, concentration of water and type of anions in the complexing salts are of major importance. Crystallization of simple lanthanide salts from nonaqueous and mixed solvents creates new possibilities to obtain a lot of solvates with structural diversibility [3].

The influence of temperature is observed through change of the “classical” power of interactions between the molecules having a permanent dipole moment [4]. The increase of temperature leads to the decrease of the “orientation” energy between the molecules of water and next to loosening of the hydration sphere. The weakened competitive ability of water molecules is the origin of many hydration equilibria and transitions in the first and further coordination spheres of the cation [5]. The influence of temperature on the hydration equilib-

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ria can have a more “chemical” nature, expressed by the enhanced acid-base processes between the coordinated water molecules and anions [6,7]. The topology of the acid-base centers within the coordinated cation and the state of acid-base equilibria in these centers affect significantly manifestation of polycondensation type transformations [8].

In examination of equilibria and phase transformation registration as well as analysis of the curves: temperature vs time is a universal method of thermal analysis. Non-monotonical course of these curves indicates existence of phase transition in the system [9]. The study is an attempt to use polythermal crystallization to investigate the influence of temperature and different concentration of water on the hydration equilibria and transformation in the crystal phases and saturated (concentrated) solutions based on the cooling curves and their higher order derivatives. The knowledge of the influence of temperature on differentiation of physico-chemical properties of the treated material in dynamic conditions can have a very practical aspect in optimization of continuous and counter-current processes of crystallization [10], as well as in technology of substances of special purity, e.g. of lanthanum chloride with the content of $\text{Ca} \leq 5\text{ppm}$ [11], and of special properties, e.g. of double lanthanum and cerium nitrates which are used in optical systems for generation of the second harmonic [12]. The fractional crystallization of double nitrates is still of preparative importance [13] and can be useful, e.g. for utilization of industrial wastes of rare earth elements [14,15].

2. EXPERIMENTAL

The lanthanum-ammonium nitrate: $\text{LaNO}_3 \cdot 2\text{NH}_4\text{NO}_3 \cdot 4\text{H}_2\text{O}$, was obtained by means of polythermal crystallization from water of lanthanum nitrate (>99.9%) own production and ammonium nitrate p.a. (ZA. Tarnów) which was mixed in the mole ratio of 1 : 2. The samples of 80.0g crystals were put to a microreactor with the water jacket, with the addition of 5.0cm^3 solution containing 100ppm of Na, K, Mg, Ca, Mn, Fe, Co, Ni, Cu and Zn nitrates and then the increasing amounts of redistilled water were introduced. The resulting mixture was heated to 90°C by hot water from the thermostat. Changes of temperature during dissolution and crystallization of the solid phase were recorded with $\pm 0.01^\circ\text{C}$ accuracy, by means of the measuring instrument CX-721 (ELMETRON) with the temperature sensor PT-100. Crystallization took place due to mechanical and spontaneous cooling to 25°C in air after introduction of seeds of obtained salt

into the saturated solution. The crystals were filtered on the water and vacuum pump for 30 minutes and then dried at 30°C to constant weight.

The numerical differentiation and integration with the use of the natural spline functions (NSpline) were carried out using the PS-Plot program.

3. RESULTS AND DISCUSSION

The characteristics of the examined crystallization systems and the values of some parameters of polythermal crystallization are presented in Table 1.

Table 1. Characteristics of crystallization systems and the conditions of polythermal crystallization of lanthanum-ammonium nitrate from water

Charakterystyka układów krystalizacyjnych i warunki politermicznej krystalizacji azotanu lantanowo-amonowego z wody

No. system	R_0	T_0 in [°C]	Rlt. yield (k)	End temp. in [°C]	Cool. rate [deg·min ⁻¹]
I	5.9326	73.2366	0.9338	25.03	0.3881
II	6.7057	69.5952	0.8475	25.01	0.4643
III	7.2855	68.4915	0.8075	25.00	0.4108
IV	7.8652	62.0928	0.7756	25.03	0.5069
V	8.2518	60.0246	0.7025	25.05	0.4744
VI	9.0248	58.2182	0.5822	25.09	0.4444
VII	9.7979	55.1812	0.5700	24.65	0.3514
VIII	10.5709	48.8899	0.5038	25.02	0.3847
IX	11.3440	42.1365	0.3825	25.06	0.4674
X	12.1170	37.4327	0.3088	25.01	0.5240
XI	12.5035	35.3354	0.2662	24.95	0.4600
XII	12.8901	34.1114	0.2212	25.01	0.4391
XIII	13.2766	31.6808	0.1850	24.92	0.4275
XIV	13.6631	29.6716	0.1400	25.04	0.4446
XV	12.8901	33.2019	n.d.	23.93	0.4730
XVI	12.5035	20.9359	n.d.	20.37	0.5150
XVII	7.8652	66.8103	0.7350	25.01	0.1679
XVIII	7.8652	66.2280	0.7588	25.01	0.3263
XIX	7.8652	63.0990	0.7450	24.85	0.4003
XX.	7.8652	59.0569	0.7562	25.01	0.4897
XXI	11.7305	40.5692	0.3512	25.00	0.3761

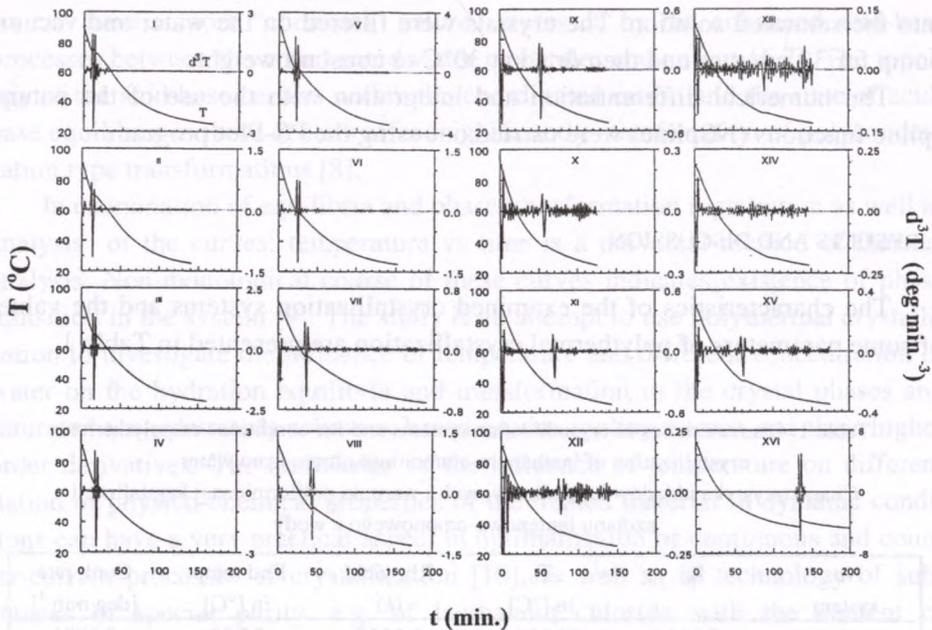


Fig. 1. Cooling curves (T) of the examined crystallization systems against the background of their third derivatives (d^3T)
 Krzywe ochładzania (T) badanych układów krystalizacyjnych na tle ich trzecich (d^3T) pochodnych

Figure 1 shows the changes of temperature in the time function (cooling curve) during the crystallization processes with different relative concentrations (R_0) of water; R_0 is the mole ratio of water and lanthanum nitrate in the system. Their third derivatives are put on the individual cooling curves. Each of the cooling curves has a characteristic bend (break) which is connected with formation of crystalline phase. That bend becomes less sharp and moves to lower temperature when the water concentration in crystallization system increased.

For better recognition of temperature and water concentration influence on polythermal crystallization mechanisms and quality of compounds, the cooling curves were subjected to threefold differentiation and NSpline interpolation and then the process of formation of crystalline phase was discussed based on (I) crystallization systems.

In Figure 2 nine vertical lines derived from four zero points, two maxima and three minima of the third derivative (d^3T) determine two cycles of polythermal crystallization and each cycle includes four phases.

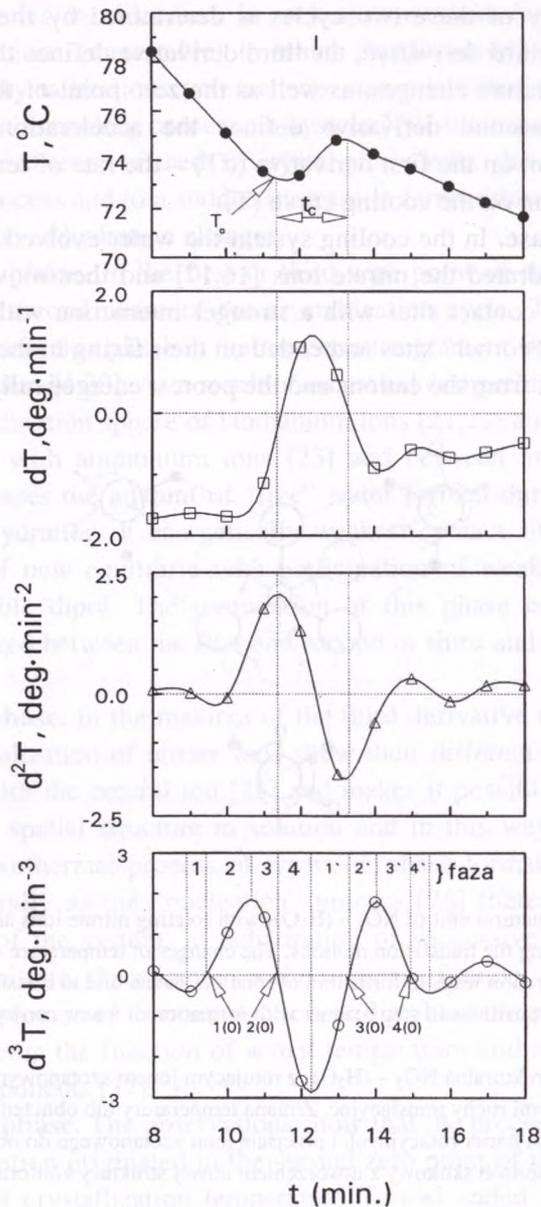


Fig. 2. Cooling curve (T) with two first crystallization cycles determined for first (I) system against the background of its first (dT), second (d^2T) and third (d^3T) derivative

Krzywa ochładzania (T) z pierwszymi dwoma cyklami krystalizacyjnymi w przypadku układu I na tle jej pierwszej (dT), drugiej (d^2T) i trzeciej (d^3T) pochodnej

The boundary of these two cycles is determined by the central, deepest minimum on the third derivative; the third derivative defines the acceleration of the rate of temperature changes, as well as the zero point of the second derivative (d^2T); the second derivative defines the acceleration of temperature changes, maximum on the first derivative (dT) – the rate of temperature change and inflection point on the cooling curve (T).

The first phase. In the cooling system the water evolved during the dissolution process hydrated the nitrate ions [16,17] and then moved [18], (Fig. 3) from the “crook” contact sites with a stronger interaction with cations through the “roll-on” and “corner” sites and ended on their fixing in the “top” site which is the most distant from the cations and the poorest energetically [19].

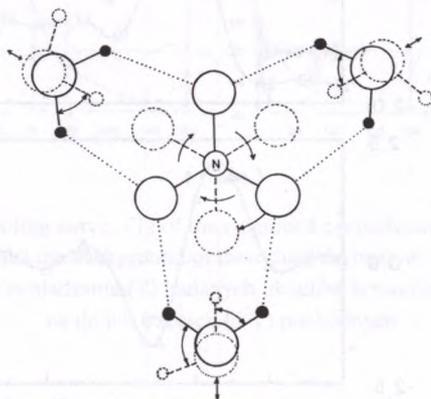


Fig. 3. Flat structural unit of $\text{NO}_3 - (\text{H}_2\text{O})_3$ with rotating nitrate ions and with water molecules making the translation motions. The changes of temperature or the decrease in water concentration leads to formation of rotation barrier and to transfer of nitrate ion to new contact positions in step manner with formation of a new conformal structure

Płaska jednostka strukturalna $\text{NO}_3 - (\text{H}_2\text{O})_3$ z rotującym jonem azotanowym i z cząsteczkami wody wykonującymi ruchy translacyjne. Zmiana temperatury lub obniżenie stężenia wody prowadzi do powstania barier rotacyjnych i przejścia jonu azotanowego do nowej pozycji kontaktowej w sposób skokowy z utworzeniem nowej struktury konformerowej

The picture of the equilibrium and transitions is more distinct at higher temperatures because that process takes place in the region of increased cooling rate and high-energetical transformations with participation of ion-ion and ion-dipol interactions. With the increase of the water concentration the pictures of

crystallization cycles are disturbed. In such systems there form readily the supersaturated solutions (metastable) in which “undissolved” structures from a given (present) crystallization cycle undergo non-controlled transformations in further stages of the cooling process. In system XVI the increased cooling rate and first of all the absence of seeds of crystal phase led to the non-controlled crystallization process and to a sudden increase in temperature, even in the low-temperature region of hydration changes.

The second phase. In the first or third zero point of the third derivative there begins the second phase of the crystallization cycle. The main “driving force” of changes in this phase is the temperature gradient between the system and the environment [4,20]. As a result of increased competitive ability of water for the first coordination sphere of lanthanum ions [21,22] and strengthening of hydrogen bonds with ammonium ions [23] and between molecules of water [24], there decreases the amount of “free” water formed during crystallization and there is dehydration of energetically weakest contact sites of nitrate ions and formation of new equilibria with participation of weak interactions, e.g. aqueous ion–stable dipole. The termination of this phase corresponds to the maximum localized between the first and second or third and fourth zero points of d^3T function.

The third phase. In the maxima of the third derivative the exposed structure-forming localization of nitrate ions show their different modes of binding (coordination) with the central ion [25] and makes it possible to form the first “nuclei” of new spatial structure in solution and in this way there begins the third phase of exothermal process of crystalline phase formation. In this phase considered generally as the “nucleation” process [26] there comes, owing to further cooling of the system, to dehydration of successive structure-forming localizations of nitrate, there increases the number of nuclei in the system. and there begins the process of formation of crystalline phase characterized by a new spatial system being the function of actual temperature and steric properties of the solution components [27].

The fourth phase. The observations show that the process of intensive and visible crystallization originated in the second zero point of the third derivative and at the initial crystallization temperature T_0 and ended in second or succeeding minima of this derivative and it stakes out the area of the fourth phase of crystallization cycles. The initial crystallization temperature (T_0) as shown in Table 1, is determined by the concentration of water in the system (R_0) at the moment of crystal phase formation.

The dependence T_0 on R_0 is shown in Figure 4 together with the solubility of ammonium-lanthanum nitrate at different temperatures [28]; the solubility was expressed as a mole ratio of water and lanthanum nitrate in the saturated solution (R). A good agreement of this function with literature data indicates that utilization of the function: T_0 on R_0 can be a rapid and comfortable way of determination of solubility of the crystalline phase at the moment of its formation (*in statu nascendi*).

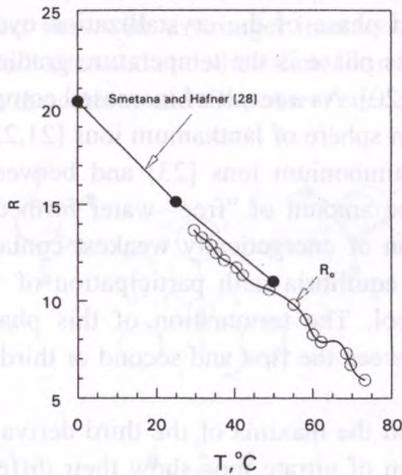


Fig. 4. Relative concentration of water (R_0) as a function of initial crystallization temperature as compared to the solubility of lanthanum-ammonium nitrate in water (R) presented also as a function of temperature [28]

Stężenie względne wody (R_0) w funkcji początkowej temperatury krystalizacji (T_0) w porównaniu z rozpuszczalnością azotanu lantanowo-amonowego w wodzie (R) w funkcji temperatury

The results presented in Table 1 show that relative concentration of water (R_0) and initial crystallization temperature (T_0) has a significant effect on crystallization yield and can be very useful for analysis and control of macrocomponent crystallization degree (k) in the continuous, especially counter-current fractional crystallization methods.

The functional dependence of T_0 on R_0 may be used for analyzing temperature effects on the mechanism of hydration transitions in the crystallization processes. For this purpose in Figure 5 there were plotted this dependence and the third derivatives for the crystallization systems with a constant water concentration ($R_0 = 7.8652$) not containing microcomponents (system XVII–XX).

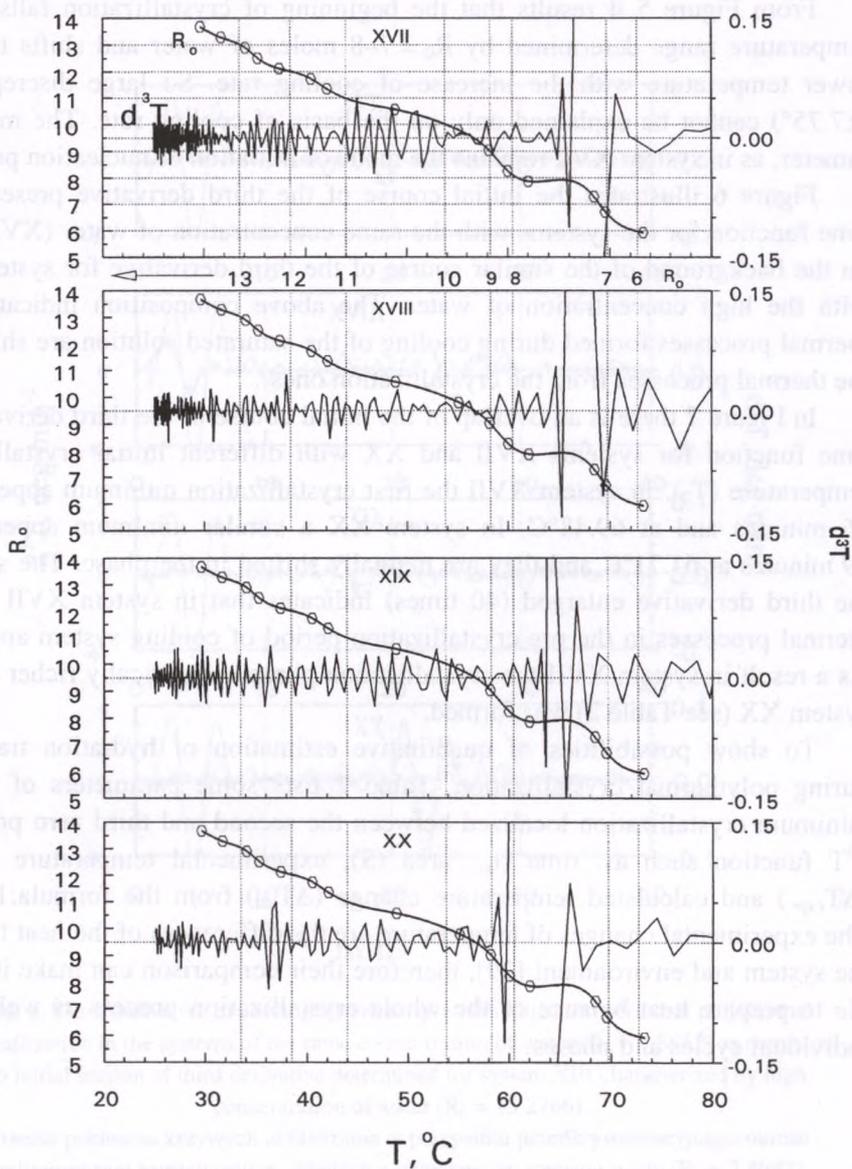


Fig. 5. Third derivative of cooling curves (d^3T) and relative concentration of water (R_0) as a function of temperature for the systems of the same concentration of water ($R_0 = 7.8652$)
 Trzecia pochodna krzywych ochładzania (d^3T) i stężenie względne wody (R_0)
 w funkcji temperatury w przypadku układów o jednakowym stężeniu wody

From Figure 5 it results that the beginning of crystallization falls in the temperature range determined by $R_0 = 7-8$ moles of water and shifts towards lower temperature with the increase of cooling rate. So large discrepancies ($\pm 7.75^\circ$) cannot be explained only on the basis of cooling rate. The main parameter, as in system XVI, remains the mode of initiation of nucleation process.

Figure 6 illustrates the initial course of the third derivative presented in time function for the systems with the same concentration of water (XVII–XX) on the background of the similar course of the third derivative for system XIII with the high concentration of water. The above composition indicates that thermal processes formed during cooling of the saturated solution are shifted to the thermal processes from the crystallization ones.

In Figure 7 there is an overlap of the initial course of the third derivative in time function for systems XVII and XX with different initial crystallization temperature (T_0). In system XVII the first crystallization minimum appeared in 16 minutes and at 69.48°C . In system XX a similar minimum appeared in 19 minutes at 61.71°C and they are mutually shifted in the phase. The scale of the third derivative enlarged (40 times) indicates that in system XVII not all thermal processes in the pre-crystallization period of cooling system appeared. As a result in system XVII the crystallization phase energetically richer than in system XX (see Table 2) was formed.

To show possibilities of quantitative estimation of hydration transition during polythermal crystallization, Table 2 lists some parameters of “deep” minimum crystallization localized between the second and third zero points of d^3T function such as: time (t_c), area (S), experimental temperature change ($\Delta T_{\text{expr.}}$) and calculated temperature change (ΔT_{cal}) from the formula: $1/2S \cdot t_c^2$. The experimental changes of temperature are the differences of the heat force of the system and environment [29], therefore their comparison can make it possible to prepare heat balance of the whole crystallization process as well as its individual cycles and phases.

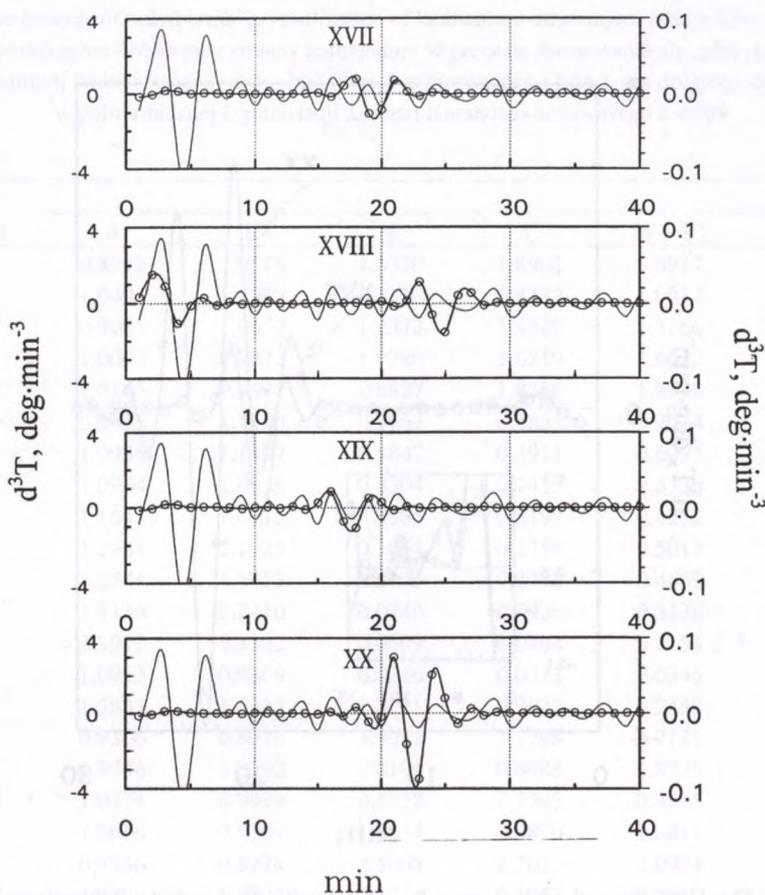


Fig. 6. Third derivative of cooling curves for pre-crystallization period of polythermal crystallization in the systems of the same concentration of water ($R_0 = 7.8652$) as compared to initial section of third derivative determined for system XIII characterized by high concentration of water ($R_0 = 13.2766$)

Trzecia pochodna krzywych ochładzania w przypadku przedkryształizacyjnego okresu politermicznej krystalizacji w układach o jednakowym stężeniu wody ($R_0 = 7.8652$) w porównaniu z początkowym odcinkiem trzeciej pochodnej odnoszącej się do układu XIII o dużym stężeniu wody ($R_0 = 13.2766$)

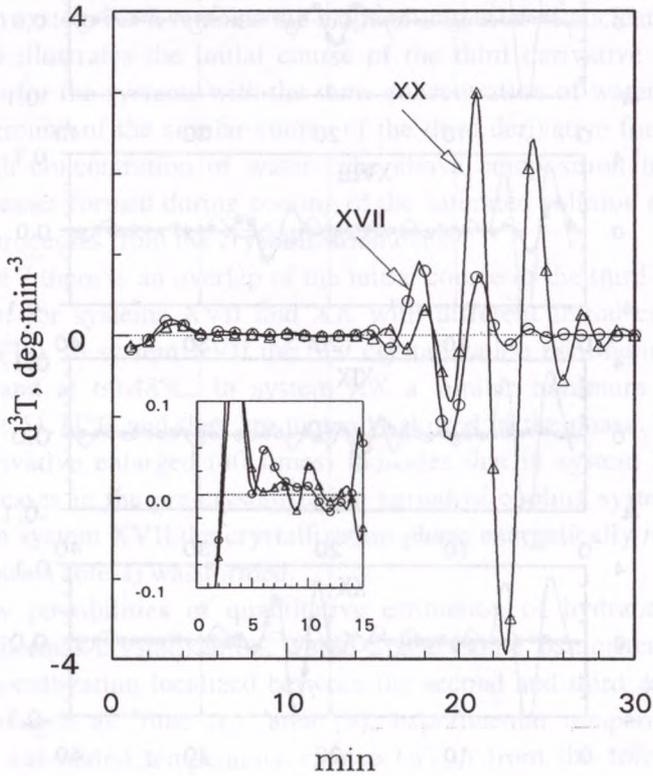


Fig. 7. Third derivative of cooling curve for pre-crystallization period as a function of time obtained for systems XVII and XX characterized by the same concentration of water, but different initial temperature of crystallization

Trzecia pochodna krzywej ochładzania z okresu przedkryształizacyjnego w funkcji czasu w przypadku układów XVII i XX o jednakowym stężeniu wody, lecz innej początkowej temperaturze kryształizacji

Table 2. Experimental and calculated changes of temperature during formation of "deep" minimum of third derivative (4^{th} phase of first, and 1^{st} phase of second cycle) obtained in the process of polythermal crystallization of lanthanum-ammonium nitrate from water
 Doświadczalne i obliczone zmiany temperatury w procesie formowania się „głębokiego” minimum funkcji trzeciej pochodnej (faza 4-ta pierwszego i faza 1-sza drugiego cyklu) w politermicznej krystalizacji azotanu lantanowo-amonowego z wody

No. system	4	1'	4	1'	(4 + 1')	expr.
I	0.8912	1.0518	1.6320	1.8902	1.6937	1.6041
II	1.0492	1.1999	0.7376	0.8332	1.0057	0.2853
III	0.9085	1.0652	1.2373	1.4382	1.3266	1.0940
IV	1.0090	0.9272	1.7780	1.6219	1.6022	1.8419
V	1.0165	0.8891	2.0827	1.8386	1.8028	2.3682
VI	0.9615	1.1180	0.7667	0.8833	0.9064	0.5573
VII	1.0936	1.1407	0.4847	0.4911	0.6095	0.2689
VIII	1.0964	1.0038	0.8304	0.7433	0.8736	1.0858
IX	1.1645	1.0615	0.3585	0.3197	0.4232	0.2662
X	1.2981	2.1623	0.1064	0.1759	0.5012	-0.0609
XI	1.2744	1.5958	0.2125	0.2312	0.4669	0.4045
XII	1.5136	2.2210	0.0746	0.0926	0.3138	-0.1042
XIII	2.3912	1.3342	0.0609	0.0464	0.2154	-0.0592
XIV	1.0953	0.9369	0.0246	0.0223	0.0246	-0.0955
XV	1.5833	1.6335	0.0921	0.0972	0.2452	-0.1161
XVI	0.9306	0.8976	3.9012	3.7798	3.2121	6.4970
XVII	0.9546	1.0592	0.8194	0.8988	0.8775	0.3818
XVIII	1.0474	0.9999	0.8422	0.7993	0.8615	0.1729
XIX	1.0666	0.9709	1.0834	0.9870	1.0814	1.2008
XX	0.9956	0.8774	2.5005	2.2023	2.0924	3.0401
XXI	1.8209	1.2502	0.1711	0.1257	0.3819	-0.0335

4. CONCLUSIONS

1. From the analysis it results that the process of polythermal crystallization of lanthanum-ammonium nitrate consists of the series of the cycles with four phases in the cycle. Each cycle is determined by two successive minima on the function of the third derivative (d^3T) of the cooling curve.
2. Higher order derivatives of the cooling curves may be useful in the analysis of the effect of temperature and water concentration on hydration equilibria and

transitions during cooling of the concentrated solution of readily crystallized salts, either in spontaneous or controlled conditions.

3. The use of the third derivative makes possible precise determination of the initial crystallization temperature (T_0) and its presentation as a function of relative concentration of water (R_0) may be useful for determination of crystalline phase solubility at the moment of its formation.

4. Hydration equilibria and transition which exist during cooling of the readily soluble salt solutions can be characterized thermodynamically and one can make the thermal balance and direct calculation of the heat of crystallization.

5. The picture of the third derivative for the pre-crystallization period can make easier the discussion of the influence of the nucleation process on the quality of the product obtained in the polythermal crystallization.

6. The great complexity of crystallization of lanthanum-ammonium nitrate in the water is a result of not only the presence of highly coordinated lanthanum cation, ammonium cation forming numerous hydrogen bonds and nitrate ions with their numerous contact sites and also the solid-solution equilibria with the recrystallization process. To understand better equilibria and mechanisms of hydration transitions in the systems: $\text{Ln}(\text{NO}_3)_3 - \text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$, where Ln denotes La(III), Ce(III) – Nd(III) it is necessary to study the two-component systems: $\text{Ln}(\text{NO}_3)_3 - \text{H}_2\text{O}$ and $\text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$ and some physico-chemical properties of double nitrates from the narrow temperature intervals estimated from the third derivative of cooling curves, which will be the subject of further investigations.

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STRESZCZENIE

Zarejestrowano zmiany temperatury w funkcji czasu (krzywe oziębiania) podczas politermicznej krystalizacji azotanu lantanowo-amonowego w różnych ilościach wody i wyznaczono trzy kolejne pochodne. Stwierdzono dużą użyteczność trzeciej pochodnej w wyznaczaniu procesów termicznych w roztworze i fazie stałej. Szczegółowo omówiono proces powstawania fazy krystalicznej, wyróżniono w nim cztery fazy. Całkowanie numeryczne trzeciej pochodnej i stosowanie stężenia względnego wody (R) ułatwia wgląd w mechanizm przemian hydratacyjnych i ich bilansowanie. Wskazano na możliwość zastosowania trzeciej pochodnej do określania początkowej temperatury krystalizacji (T_0) i rozpuszczalności fazy krystalicznej w chwili jej tworzenia się (R_0) oraz ich użycia do kontroli stopnia krystalizacji (k).