Kinetics of phase transitions in TEA$_2$ZnCl$_4$ crystal

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Abstract
The kinetics of thermal anomalies at the phase transitions in the tetraethylammonium zinc tetrachloride crystal [N(C$_2$H$_5$)$_4$]$_2$ZnCl$_4$ has been studied by the differential scanning calorimetry method over a wide range of rate of temperature change, from 1 to 100 K min^{-1}. The crystal is known to undergo structural phase transitions of first order at which the nucleus of the final phase characterized by a symmetry different to that of the initial phase appears and develops. The classical Johnson–Mehl–Avrami model cannot be applied to describe the two phase transitions taking place in the non-isothermal process. Making use of the isothermal process taking place below T_1^{C}, the intermediate phase has been shown to be metastable; the energy of the process is $E_{\mathrm{a}} = 146 \pm 7$ kJ mol^{-1}, while the Avrami exponent $n = 2.3 \pm 0.2$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The crystal structure of the substance with the general formula A$_2$BX$_4$ is composed of isolated almost ideal BX$_4^{2-}$ tetrahedra and monovalent A$^+$ ions localized in two inequivalent polyhedral cavities. With decreasing temperature, initially relatively significant movements of the tetrahedra become frozen and the tetrahedra undergo small deformations, which gives rise to interesting phase transitions. If the structure of the crystals is of the β-K$_2$SO$_4$ type, the phase transition sequence is as follows: normal phase of pseudohexagonal symmetry $\rightarrow$ incommensurate phase $\rightarrow$ commensurate ferroelectric phase with tripling of the elementary cell relative to the prototypic phase $\rightarrow$ commensurate ferroelectric–ferroelastic phase, in which the elementary cell size is further doubled. In the crystals in which the A$^+$ ions are tetraethylammonium ones (TEA$^+$), the high temperature phase has a tetragonal symmetry with the point group $4/mmm$. On decreasing temperature the crystals undergo two phase transitions to the centrosymmetric phase of the orthorhombic symmetry mmm [1, 2]. As follows from the symmetry changes, the low temperature phase should have ferroelastic properties and the characteristic domain structure which is, unfortunately, not observed under a polarization microscope. Only for the TEA$_2$CuCl$_4$ crystal has the presence of ferroelastic domains of the size of micrometers been suggested, by the splitting of the XRD peaks [3] and an increase in the intensity of the polarized light passing through the crystal [4].

In the crystal tetrachlorides (TEA$_2$MeCl$_4$—Me = Ni, Zn, Co, Mn, Hg) the two phase transitions are of first order and lead to rapid breaking of the samples along the cleavage planes. The phase transitions are induced by the two-stage ordering of the TEA$^+$ ions [5]. Particularly interesting in this group is the crystal TEA$_2$ZnCl$_4$, which undergoes two phase transitions on cooling but only one on heating. The crystal has been a subject of a number of studies; in particular the changes in its specific heat have been determined by adiabatic calorimetry and DSC methods [6, 7] and its thermal expansion has been measured [8]. The relatively great changes in the crystal size reaching 1% lead to sample damage. The permittivity of the crystal has been measured in the low frequency range [9, 10] and birefringence changes have been determined at the phase transitions, indicating a decrease in the symmetry from optically uniaxial to biaxial [4]. However, the kinetics of the phase transitions taking place in this crystal has remained unknown, which has prompted us to investigate it by the DSC method.

The standard method applied in investigation of the kinetics of chemical or physical processes in different materials is the Johnson–Mehl–Avrami (JMA) analysis proposed a few decades ago [11–15]. Many authors have studied the kinetics of thermal decomposition, recrystallization in the glassy phase, conformation changes in polymers and other cases. All these

processes are assumed to involve the appearance of a nucleus and development of a new phase in the prototype phase. Moreover, the JMA analysis is based on the assumption that the process studied is the only one taking place, is uniform and does not depend on the rate of temperature change. The TEA_2ZnCl_4 crystal undergoes phase transitions of the first order in which the nucleus leads to development of a final phase whose symmetry differs from that of the initial phase. Therefore, at first the possibility of application of JMA analysis to investigate the kinetics of phase transitions in the crystal studied must be checked.

2. Theoretical background

According to the JMA theory, the relative part of the substance volume subjected to isothermal transformation is the following function of time [16, 17]:

$$x(t) = 1 - \exp(-kt^n), \tag{1}$$

where n is the Avrami parameter depending on the type of the nucleation process, and k is the temperature function of the nucleus growth:

$$k = k_0 \exp(-E_a/k_B T), \tag{2}$$

E_a is the activation energy of a given process and k_B is the Boltzmann constant. The JMA model assumes a constant form and is independent of the temperature rate of nucleation and the spatial growth of the nucleus until complete transformation to a new phase has occurred. Taking the double logarithm of equation (1) gives

$$\ln[-\ln(1 - x(t))] = n \ln t + \ln k_0 - E_a/k_B T. \tag{3}$$

The fit of the experimental data to the linear dependence $\ln[-\ln(1 - x(t))]$ versus $\ln t$ for different temperatures T permits the calculation of n, k_0 and E_a. The value of n is known to strongly depend on the mechanism of nucleation and the morphology of nucleus growth and for the ideal case it should be a whole number. The JMA model does not take into account the anisotropy of the crystal lattice and internal stress appearing on first-order phase transitions.

The phase transitions in solid state are usually studied by non-isothermal methods at a constant rate of heating or cooling. The rate of transformation at the phase transition reaches a maximum when the majority of nuclei have already appeared and undergo spatial growth. The temperature corresponding to this maximum (T_p) is observed experimentally as a peak of the DSC anomaly. A popular method of analysis of non-isothermal processes developed by Kissinger [18] gives a final much simplified formula:

$$\ln(\Phi/T_p^2) = \text{const} - E_a/k_B T_p, \tag{4}$$

where Φ is the rate of heating or cooling.

The application of the Kissinger equation has been often criticized in the literature, for example [19], as it assumes that the reaction is of first order ($n = 1$) and the actual temperature dependence of the rate of growth of the new phase strongly deviates from the Arrhenius type curve near the phase transition. The deviation becomes more visible when the range of change in the rate of heating/cooling is greater than one order of magnitude.

For the non-isothermal transformation the JMA model gives

$$x(t) = 1 - \exp(-Kt^n), \tag{5}$$

where

$$K = K_0 \Phi^n \exp(-E_a/k_B T). \tag{6}$$

The fraction of the substance volume that has been transformed at T_p is $x(T_p) = 1 - e^{-1} \approx 0.63$ [20], so equations (4) and (5) can be written as

$$K_0(T_p^2/\Phi)^n \exp(-E_a/k_B T_p) = 1. \tag{7}$$

Taking logarithms of both sides gives

$$\ln(\Phi/T_p^2) = 1/nK_0 - E_a/nk_B T_p. \tag{8}$$

On the basis of measured $T_p(\Phi)$ a linear dependence of $\ln(\Phi/T_p^2)$ versus $1/T_p$ can be obtained and then from its slope the value of E_a/n can be found. On the other hand, taking double logarithms of equations (5) gives [20]

$$\ln[-\ln(1 - x)] = 2n \ln T + \ln(K_0/\Phi^n) - E_a/k_B T$$
$$\approx -E_a/k_B T. \tag{9}$$

A combination of the above obtained slope and the results of equations (2) leads to the Avrami parameter n and the activation energy E_a.

3. Experimental results and discussion

The zinc chloride was dissolved in redistilled water into which tetraethylammonium chloride was added at the stoichiometric ratio. The monocrystals of TEA_2ZnCl_4 were obtained by slow evaporation of the solution at 300 K. The process of recrystallization was repeated three times. The crystals grew in the form of ditetragonal pyramids. The crystals have five easy cleavage planes: the four unit planes and the plane perpendicular to the tetragonal axis.

Thermal anomalies accompanying the phase transitions in the crystal were determined by differential scanning calorimetry (DSC), using an instrument DSC-7 made by Perkin-Elmer. Using the exact calibration procedure [21] based on the melting points and enthalpies of transition established for two extra pure substances: indium and mercury, the precision of the calorimeter was achieved as ±0.05 K. The non-isothermal measurements were performed on linear heating and cooling for a wide range of rate of temperature change: 1, 2, 5, 10, 20, 50 and 100 K min^{-1}. The isothermal DSC measurements were made for temperatures ranging from T_1^C to T_2^C. The measurements were performed for monocrystals of a few mg sealed in aluminium capsules.
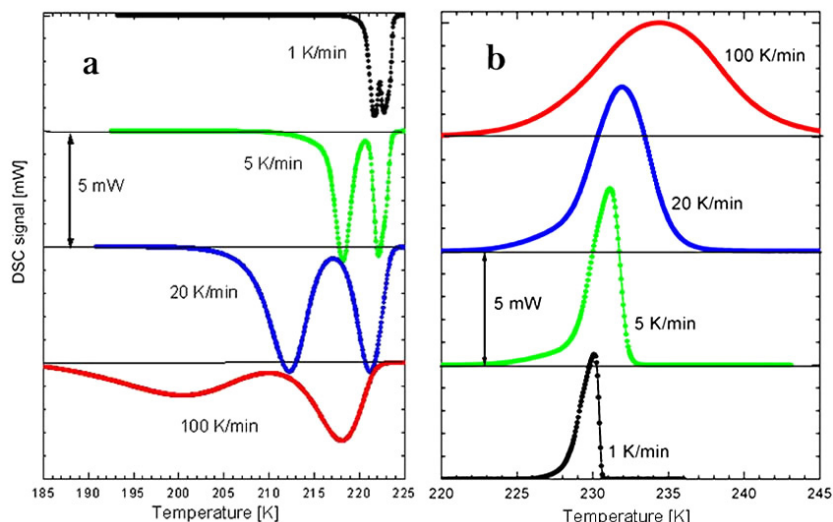
Figure 1. DSC anomalies (baseline subtracted) in the region of the phase transitions in the TEA$_2$ZnCl$_4$ crystal: (a) cooling, (b) heating.
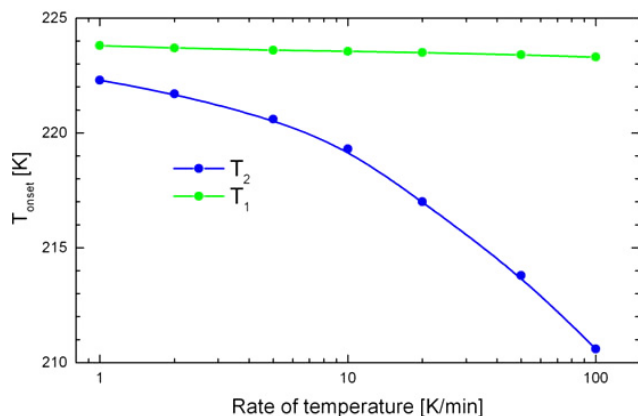

Figure 2. The phase transition temperatures on cooling as a function of the rate of temperature change.

Figure 3. Kissinger dependence for the non-isothermal experiment.

3.1. Non-isothermal measurements

Figure 1(a) presents the results of non-isothermal DSC measurements made on cooling at a few rates of temperature change after subtraction of the baseline. The second phase transition begins before completion of the thermal process related to the first phase transition. Figure 2 presents the temperatures of the two phase transitions, at the onset of the changes, as a function of the rate of temperature change. The extrapolation of the rate of heating/cooling gives $T_1^C = 224.0$ K and $T_2^C = 222.8$ K. Integration of the dependences presented in figure 1(a), and taken after precise calibration of the instrument permitted a determination of the changes in enthalpy taking place in both transitions as $\Delta H_1 + \Delta H_2 = 8.4 \pm 0.2$ kJ mol^{-1} and this value is in agreement with earlier literature values of 8.87 [6], 8.4 kJ mol^{-1} [7], and ΔH_1 is close to 3.2 kJ mol^{-1}. On heating, the low temperature phase III is transformed directly to phase I. Figure 1(b) presents the DSC results for the same rates of temperature change. It should be noted that the sum of the enthalpy changes on cooling is equal to that on heating.
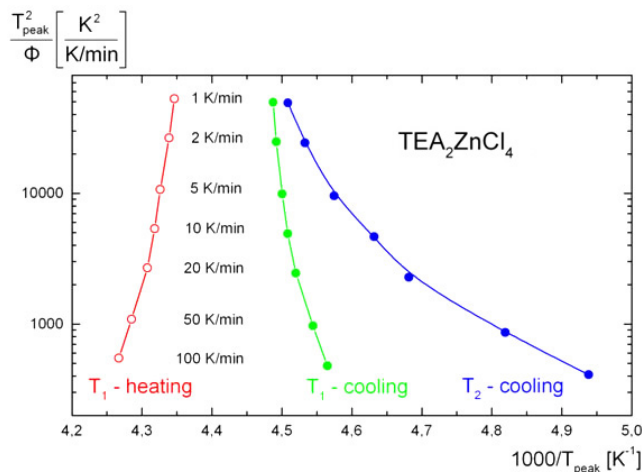
According to the above relations, equations (4), the dependence of T_p^2/Φ on $1/T_p$ should be linear; T_p is the temperature of the maximum rate of the process. The slope of this dependence gives the activation energy. Figure 3 presents this dependence and the deviation from linearity for higher rates of temperature change of 50 and 100 K min^{-1}. The activation energies calculated by the Kissinger method for the first phase transition are similar: 770 (on cooling) and 680 kJ mol^{-1} (on heating). It should be emphasized that for the second phase transition the dependence of T_p^2/Φ on $1/T_p$ deviate greatly from the linear function assumed by Kissinger.

On cooling, the phase transitions taking place in the TEA$_2$ZnCl$_4$ crystal cannot be separated and the JMA model cannot be applied, so determination of the Avrami parameter n is impossible. Also the dependences predicted from other models of kinetics of phase transitions in the solid state like the Ozawa–Chen model [22] or the Mo model [23] do not agree with the experimental results. The JMA model predicts
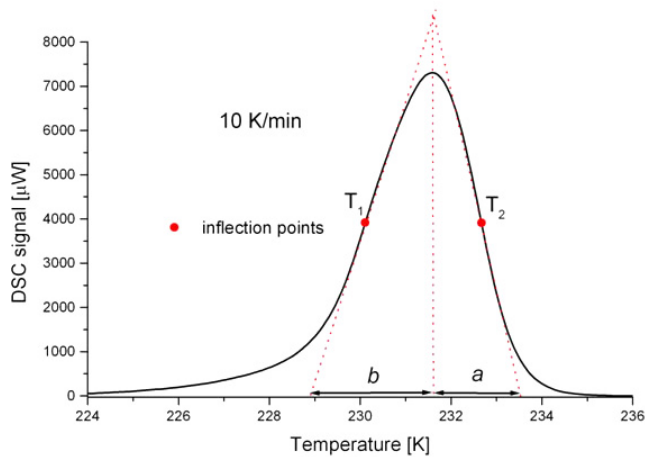
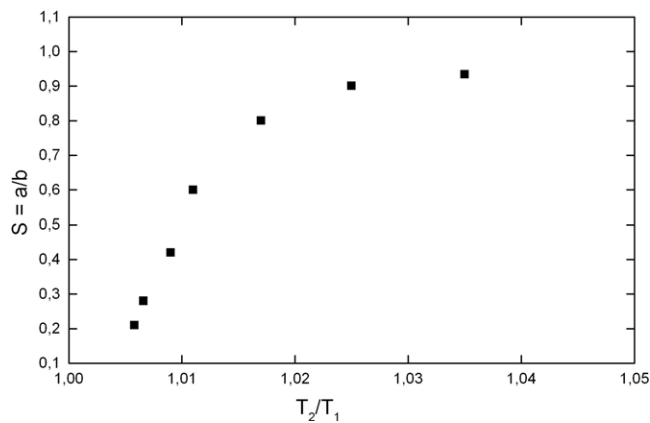**Figure 4.** The method of the shape index determination, **S = a/b**.

Figure 5. The shape index versus the ratio of temperatures of the inflection points.

linear dependences of $\ln[-\ln(1-x)]$ on $1/T$, as parallel lines for different heating rates; however, the experimental dependences obtained for TEA_2ZnCl_4 are not linear, which means that the simple model assuming uniform growth of the high temperature phase cannot be applied. The reason could be the fusion of the two phase transitions on heating.

On the other hand, with increasing rate of heating the shape of the DSC curves changes and they become increasingly symmetrical; see figure 1(b). The index of the shape of the

DSC curves is defined as in figure 4 [24] for an exemplary DSC curve recorded on heating at the rate of 10 K min^{-1}.

Malek [25] has proved a linear relationship between the shape index S and the ratio of temperatures of the inflection points:

$$S = S^{\infty} + K(T_2/T_1), \qquad (10)$$

where S^{∞} and K are constants. This relationship may be used as a simple test of the applicability of the JMA model. Figure 5 presents the above relation for a wide range of rate of temperature change of two orders of magnitude. The relation proves that the JMA model cannot be used to interpret the transition to the high temperature phase. In order to obtain a good fit between the theoretical and experimental data we could use the Šesták–Berggren model [26], in which the function describing the kinetics of the phase transition has two independent exponents m and n; unfortunately they have no clear physical sense [27].

The zero value of $d(DSCsignal)/dT$ corresponds to the temperature at which the process of transition from the tetragonal phase is the fastest. A close inspection of the DSC curves, in particular at low rates of temperature change, reveals an additional anomaly manifested as a change in the slope. For better illustration the DSC curves have been differentiated and, as shown in figures 6(b) and 7(b), the anomaly appears both on heating and on cooling. In these figures the zero value of $d(DSCsignal)/dT$ corresponds to the maximum rate of the transition from the tetragonal high temperature phase. For low rates of temperature change (to 5 K min^{-1}) this additional anomaly is at $\sim$0.7 K below T_1. This phenomenon has not been earlier reported in literature and its nature can be related to the thermoelastic effect—we studied monocrystalline samples and not powdered ones. At this phase transition the crystal size changes significantly, which leads to its cleavage [8] starting at a temperature a little below T_1 [4].

3.2. Inconsistency with the JMA theory

The results for DSC anomalies found at the first-order phase transitions in the TEA_2ZnCl_4 crystal by the non-isothermal method for a wide range of rate of temperature change have shown that the transition anomalies cannot be described by the JMA model. Our results support the opinion expressed in [28] that the JMA model is unsuitable for analysis of kinetics of phase transitions in solid phase, in particular in crystals. In the non-isothermal experiments:
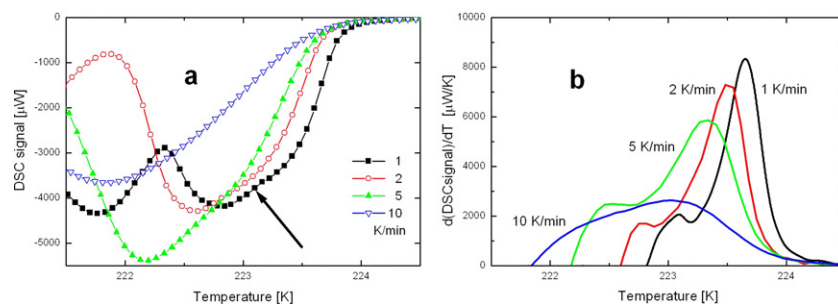

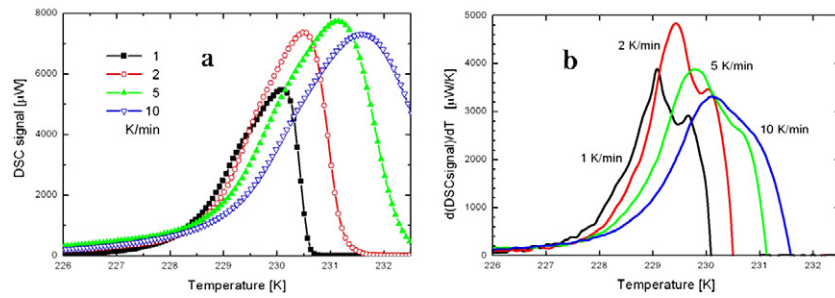**Figure 6.** Cooling near T_1: (a) DSC plots, (b) DSC derivative.

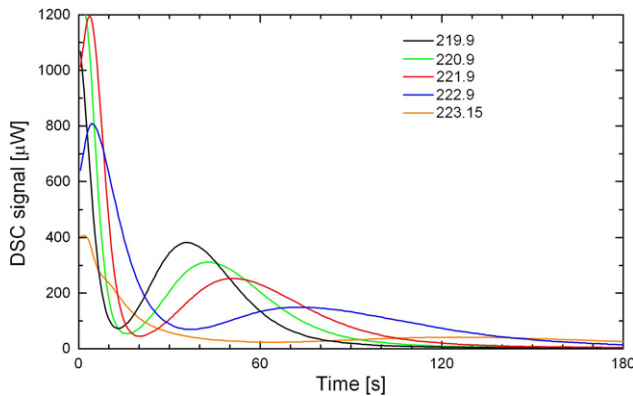**Figure 7.** Heating near T_1: (a) DSC plots, (b) DSC derivative.

Figure 8. Isothermal DSC changes for selected temperatures below T_1.
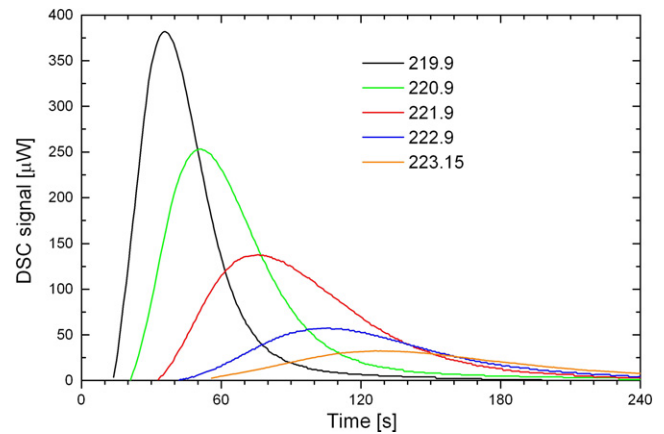

Figure 9. Isothermal DSC changes corresponding to the second phase transition.

- the thermal gradients are significant, especially in the regions of first-order phase transitions as the heat transfer affects the activation energy [29];
- in the equation for the reaction rate the partial derivative of the volume fraction of the material that has already been transformed over temperature must be taken into account;
- the rate of nucleation is not constant but depends on temperature and the rate of nuclei growth deviates from the Arrhenius dependence [30];
- in general, the solid state transitions are heterogeneous and not homogeneous.

Moreover, the JMA model takes into account neither the anisotropy of physical properties in crystals of symmetries lower than the regular one nor the internal mechanical stress accompanying the first-order phase transitions. The influence of the nucleus shape and the elastic effects on the kinetics of the phase transition has been theoretically studied by Brener *et al* [31]. The cleavages and kinks formed on phase transitions in the TEA_2ZnCl_4 crystal are active centres of nucleation and are able to change the kinetics of growth of the new phase. Therefore, if the phase transition takes place over a narrow temperature range, the actual kinetics of the phase transition can be substantially different from that predicted from the isokinetic model assuming that the rate of the phase growth obeys the Arrhenius dependence [30]. The poor agreement of the experimental data with the JMA equations may correspond to a more complex nonlinear nucleation and the kinetics of growth can be described using nonlinear functions of the nucleus radius [32, 33] and should take into account the anisotropic growth possibility [34].

3.3. Isothermal measurements

As on cooling of TEA_2ZnCl_4 it is impossible to separate the two phase transitions, we have decided to use isothermal measurements. Initially the crystalline sample of 15 mg was cooled at the rate 10 K min^{-1} to a temperature below $T_1^C = 224.0$ K. Then in the range 223.15–219.9 K the temperature was stabilized at a constant value every 0.25 K and the DSC anomalies were observed. The results for a few selected temperatures and after the baseline subtraction are presented in figure 8.

With decreasing temperature the intensity of the DSC thermal anomaly corresponding to the first phase transition (T_1) grew and the rate of the process increased; the FWHM values were 12 s at 223.15 K and 4.2 s at 219.9 K. Changes in the anomaly corresponding to the second phase transition were similar. To investigate the kinetics of this second transition the two anomalies were separated. The isothermal changes in the second anomaly at a few selected temperatures are shown in figure 9, and the corresponding changes in its enthalpy are given in figure 10. It should be noted that if the isothermal measurements were performed at 1 K below T_1^C, the change in enthalpy would reach only one third of its value of 5.2 kJ mol^{-1} measured far from T_1^C.
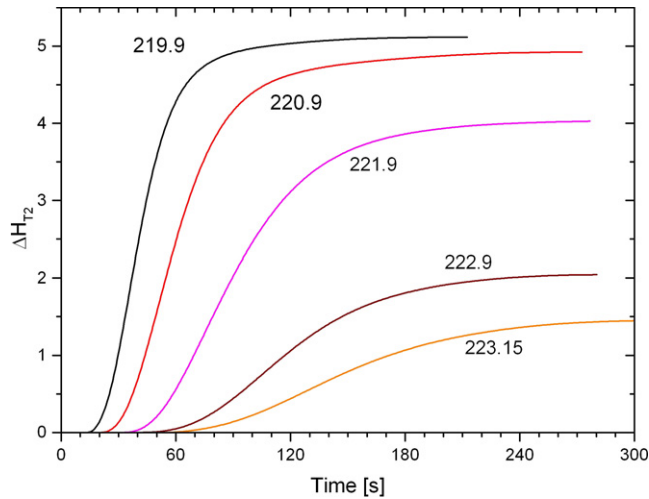
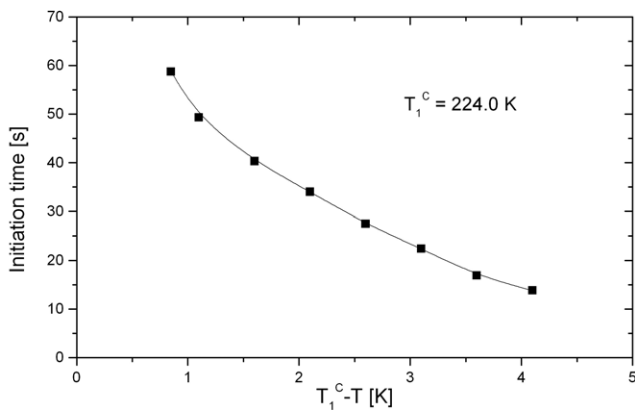**Figure 10.** Isothermal changes in enthalpy at the second phase transition.

Figure 11. The time needed for initiation of the second phase transition.

Figure 12. Isothermal contributions to enthalpy at the two phase transitions and the time needed to reach a maximum rate of transition to phase III.

Figure 13. Changes in enthalpy on the isothermal process at a temperature below T_1^C; ΔH_1 and ΔH_2 correspond to the enthalpy changes at the first and second phase transition, respectively.

With increasing distance from T_1^C towards lower temperatures, the time needed for initiation of the second phase transition shortens; figure 11. The temperature dependence of the initiation time can be described as the activation process with the activation energy close to that of the phase transition, which is often encountered in investigation of the crystallization process [35].

The time needed for initiation of the second transition changes similarly to the time of reaching the maximum rate of transition to phase III (t_{max}). The enthalpy of the transition to phase III increases with decreasing temperature at which the cooling was stopped, reaching the value of 5.2 kJ mol^{-1}. The isothermal contributions to the enthalpies of the two phase transitions are shown in figure 12, while figure 13 presents the results for both processes.

In order to calculate the Avrami parameter and the activation energy of the phase transition to the low temperature phase III, the relation $\ln[-\ln(1 - x(t))]$ versus $t - t_0$ was drawn (figure 14), where t_0 is the initiation time, along with $\ln K$ versus $1/T$ obtained assuming the Arrhenius dependence (figure 15). By combination of equations (1), and (2) with
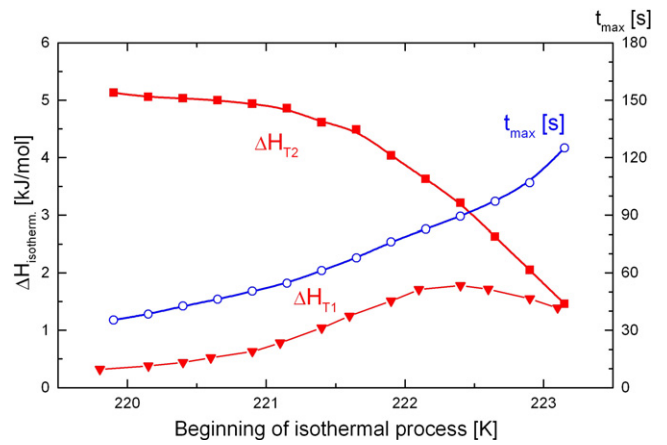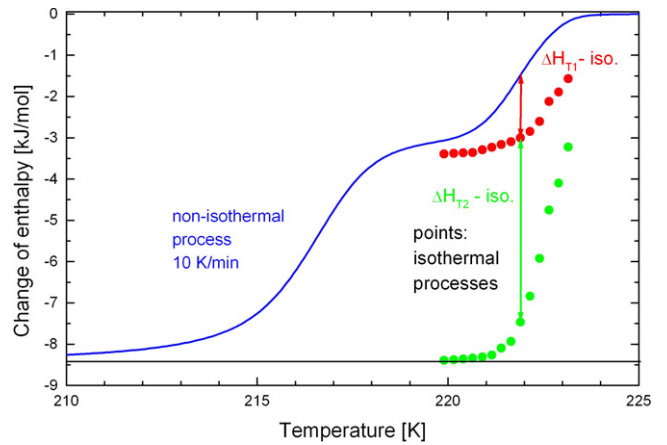
the slopes of the experimental lines, the final values of $E_a = 146 \pm 7$ kJ mol^{-1} and $n = 2.3 \pm 0.2$ were calculated.

3.4. Metastability of phase II

Phase II of TEA$_2$ZnCl$_4$, occurring only on cooling in the range 222.8–224.0 K, has been found metastable. When on cooling the temperature was stabilized below T_1^C, there appeared a thermal DSC anomaly corresponding to formation of the third phase. The time needed for its initiation and the time of reaching the maximum rate of phase growth became longer as the temperature became closer to T_1^C. For $T_1^C - T = 0.85$ K they were $t_{ini} = 59$ s and $t_{max} = 125$ s, while the time needed for completion of the phase transition was 4 min. These data are in agreement with our earlier optical studies whose results have shown that the breaking of the crystal related to the second phase transition at a temperature of 0.2 K below T_1^C ended after 8 min. On the other hand, the enthalpy changes taking place at the isothermal transition also depend on the temperature of the process: the closer to T_1^C, the lower ΔH_{T2}; and the value of 5.2 kJ mol^{-1} is reached only at 220 K. The facts
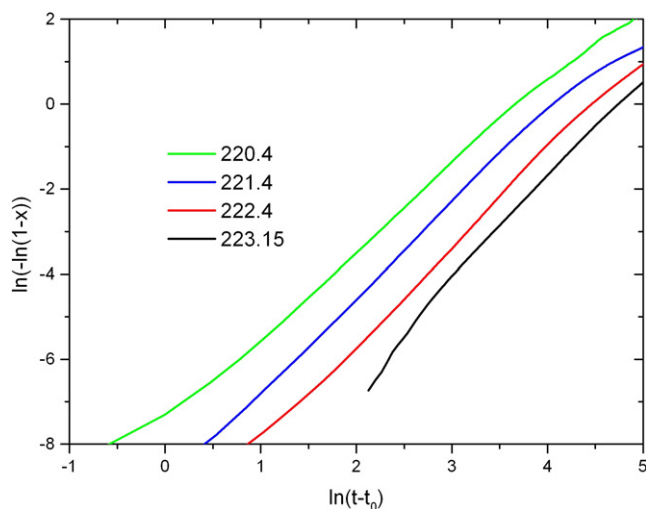
Figure 14. The Avrami plot for the isothermal transition to phase III.
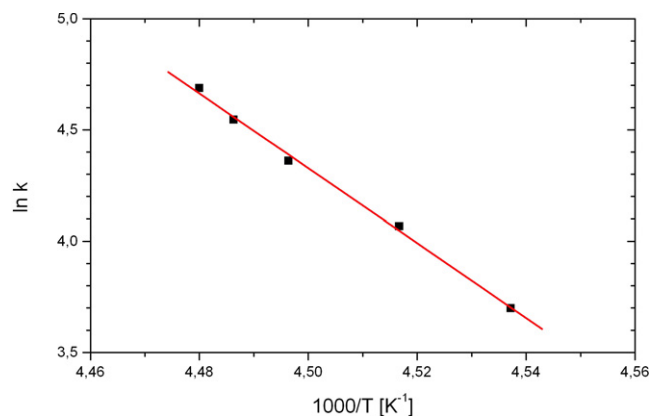

Figure 15. The Arrhenius dependence for the isothermal transition to phase III.

imply that the transition does not take place over the whole volume of the crystal and that the low temperature phase II is mixed and metastable. The long-lived metastable phases appearing at the phase transitions and producing contributions to thermal anomalies have been analysed by Renth *et al* [36] and Iwamatsu [37].

The low temperature phase (III) is formed at two first-order phase transitions, while on heating only one DSC anomaly is observed. This means that thanks to a great hysteresis, the stability of phase III is lost at a temperature at which phase II is already unstable and that is why phase III does not appear on heating. If the process of cooling is stopped at a temperature T_0 between T_1^{peak} and T_2^{peak}, and subsequently the crystal is heated, a new DSC anomaly appears at about 6 K below the main DSC peak. This effect was already observed by Caetano *et al* [7]. Taking into account the results of our study of isothermal DSC changes, showing that the nucleation and growth of phase III are very slow, we can suppose that at T_0 these processes are stopped and the new DSC anomaly is a result of the disappearance of the already formed nuclei of phase III.

The Avrami parameter obeys the following relation [38]:

$$n = a + dm \qquad (a > 1), \qquad (11)$$

where d is the dimension of growth (i.e. 1, 2, 3 for the 1D, 2D or 3D growth), m is the index of growth ($m = 1$ when the growth rate is constant, interface-controlled growth; $m = 1/2$ when the position of the front depends on the square root of time, diffusion-controlled growth), a is the nucleation index describing the time dependence of the number of nuclei per unit volume of the crystal.

The Avrami parameter for the isothermal transition to phase III of the crystal TEA_2ZnCl_4, $n = 2.3 \pm 0.2$, implies that the nuclei of the new phase undergo interface-controlled growth in a 2D space, so they develop along the planes in which the crystal bonds are the weakest. The value of n is lower than that following from the classical JMA model $n = 3$, which can be related to the inhomogeneous distribution of the pre-existing nuclei in the anisotropic crystal lattice [39].

References

[1] Mahoui A, Lapasset J and Moret J 1994 *Acta Crystallogr.* C **50** 358
[2] Mahoui A, Lapasset J, Moret J and Sain-Gregoire P 1996 *Acta Crystallogr.* C **52** 2671
[3] Mahoui A, Lapasset J, Sannikov D G, Moret J and Sain-Gregoire P 1996 *Z. Phys.* **99** 543
[4] Biskupski P, Słaboszewska M and Tylczyński Z 2005 *Physica* B **370** 6
[5] Woithuis A J, Huiskamp W J, De Jongh L J and Carlin R L 1986 *Physica* B **142** 301
[6] Melia T P and Merrifield R 1971 *J. Chem. Soc.* A 1258
[7] Caetano O, Lopez M, Mahoui A, Lapasset J, Moret J, Assih T and Saint-Gregoire P 1995 *Ferroelectr. Lett.* **19** 69
[8] Kahrizi M and Steinitz M O 1990 *Solid State Commun.* **74** 333
[9] Iwata M and Ishibashi Y 1991 *J. Phys. Soc. Japan* **60** 3245
[10] Biskupski P, Tylczyński Z and Słaboszewska M 2001 *Ferroelectr. Lett.* **28** 55
[11] Kolmogorov A N 1937 *Izv. Akad. Nauk SSSR Ser. Mater.* **3** 355
[12] Johnson W A and Mehl R F 1939 *Trans. AIME* **135** 416
[13] Avrami M 1939 *J. Chem. Phys.* **7** 1103
[14] Avrami M 1940 *J. Chem. Phys.* **8** 212
[15] Avrami M 1941 *J. Chem. Phys.* **9** 177
[16] Denisov E T, Sarkisov O M and Likhtenshtein G I 2003 *Chemical Kinetics: Fundamentals New Developments* (Amsterdam: Elsevier)
[17] Jackson K A 2004 *Kinetic Processes* (New York: Wiley–VCH)
[18] Kissinger H E 1957 *Anal. Chem.* **29** 1702
[19] Mittemeijer E J 1992 *J. Mater. Sci.* **27** 3977
[20] Ruitenberg G, Woldt E and Petford-Long A K 2001 *Thermochim. Acta* **378** 97
[21] Drebushchak V A 2005 *J. Therm. Anal. Cal.* **79** 213
[22] Ozawa T 1965 *Bull. Chem. Soc. Japan* **38** 1881
[23] Liu T, Mo Z, Wang S and Hang H 1997 *Polym. Eng. Sci.* **37** 568
[24] Malek J 1993 *Thermochim. Acta* **222** 105
[25] Malek J 1995 *Thermochim. Acta* **267** 64
[26] Šestak J and Berggren G 1971 *Thermochim. Acta* **3** 1
[27] Holubova J, Černosek Z and Černoskova E 2000 *J. Therm. Anal. Cal.* **62** 715
[28] Henderson D W 1979 *J. Non-Cryst. Solids* **30** 301

[29] Galway A K 2003 *Thermochim. Acta* **397** 249
[30] Frade J R, Kharton V V, Marrero-Lopez D, Nunez P and Abrantes J C C 2005 *Thermochim. Acta* **435** 85
[31] Brener E A, Jordanskii S V and Marchenko V I 1999 *Phys. Rev. Lett.* **82** 1506
[32] Van Siclan C DeW 1996 *Phys. Rev.* B **54** 11845
[33] Weinberg M C, Birnie P P III and Shneidman V A 1997 *J. Non-Cryst. Solids* **219** 89
[34] Pusztai T and Granasy L 1998 *Phys. Rev.* B **57** 14110
[35] Altounian Z, Guo-hua T, Strom-Olsen J and Muir W B 1981 *Phys. Rev.* B **24** 505
[36] Renth F, Poon W C K and Evans R M L 2001 *Phys. Rev.* E **64** 031402
[37] Iwamatsu M 2005 *Phys. Rev.* E **71** 061604
[38] Kooi B J 2004 *Phys. Rev.* B **70** 224108
[39] Sun N X, Liu X D and Lu K 1996 *Scr. Mater.* **34** 1201