Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

SOLID-STATE THERMAL AMORPHIZATION OF INORGANIC POLYMERS

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Abstract

Inorganic polymers such as silicates, borates and phosphates can be transformed into amorphous solids by heating to an appropriate temperature. Thermal amorphization can be obtained by: 1. thermal dissociation of a crystalline compound, 2. distortion of the crystal structure of a solid during prolonged heat treatment, without change of its chemical composition. The specificity of the materials received, the crystallochemical conditions necessary for the amorphization which takes place, and the high-temperature processes of internal structure reconstitution and recrystallization in the amorphous products are considered.

Keywords: amorphization structural mechanism, amorphous solids, crystallization, glass transformation, phase transitions, thermal amorphization

Introduction

During the past decade, there has been increased interest in the solid-state crystalline to amorphous transformation process. Amorphous materials, and especially amorphous alloys, are often characterized by high hardness, corrosion and oxidation resistance, high magnetic permeability and electric resistivities, etc. The amorphization of alloys and many other materials and minerals is carried out by ion beam irradiation or by a high-pressure-induced process.

The products of thermal decomposition of some crystal solids are amorphous and they may retain this state in a wide range of temperature. Inorganic polymers such as silicates, borates and phosphates can be amorphized relatively easily by heating to an appropriate temperature. Such transformations belong among the less well-known solid-state processes. This paper presents the fundamentals of the formation of amorphous materials by heat treatment of crystalline, inorganic polymers. The amorphized substances considered here are substances in which the internal structure order is distorted or destroyed to a certain degree, thereby excluding the appearance of X-ray diffraction lines characteristic of them.

Thermally amorphized materials can be used as precursors for ceramic and glass-ceramic materials, such as those produced by micro-powder technology, as isolating materials, micro-porous absorbents for environment protection, etc. Thermal amorphization changes the physicochemical properties of zeolites. A knowledge of the mechanism of the solid-state crystalline to amorphous transformation process is required for a better understanding of the phase stability of crystalline materials, the crystallization and melting of solids and glass formation.

Thermal amorphization of solids can be attained by (1) thermal dissociation of crystalline compounds (dehydration of certain hydrous silicates, borates, phosphates, etc.), or (2) destruction or distortion of the crystal structure of solids during prolonged heat treatment (quartz).

The paper provides information on the thermal amorphization process and the stability of the amorphous substance obtained. It is based on the authors' experimental research on the decomposition of some borates [1-5]. The results are generalized and compared with information on similar processes in silicates, and the regularities governing all the considered phenomena are formulated.

Amorphization by thermal decomposition

Amorphous phase formation and stability

Amorphous phase formation by the thermal decomposition of a crystalline solid is a chemical process resulting in a change in composition of the precursor substance. The amorphous substance results from the breaking of bonds in the precursor structure due to the formation of gaseous products, followed by distortion of the preserved part of the precursor structure.

The products of thermal decomposition of the hydrated borates of Ca, Mg, Na and K are amorphous and maintain this form in a relatively wide range of temperature. Our earlier investigations [1-5] revealed that hydrated borates undergo several processes on heat treatment: 1. dehydration, 2. dehydroxylation, 3. rearrangement of the primary structure accompanied by the removal of the residual OH groups and water molecules preserved within the structure, 4. amorphization of the structure following dehydration and dehydroxylation, 5. rearrangement of the amorphous structure connected with the reconstruction

of boron-oxygen anions, displacement of the metal cations and crystallization of the anhydrous borates.

The amorphization ability and thermal stability of the amorphous decomposition products depend on the chemical composition of the borates. A few examples are discussed below.

The thermal decomposition of colemanite, $Ca_2B_6O_8(OH)_6 2H_2O$, proceeds violently in two stages, at 369 and 386°C. The solid product of the successive dehydroxylation and dehydration maintains some OH groups and free water molecules enclosed in the empty voids of the structure. They escape slowly during heating up to 650°C. This process is accompanied by the gradual destruction of the primary structure of the borate. A small endothermic DTA peak appears at 650°C, resembling the glass transition effect (T_g). At 741°C, the amorphous substance recrystallizes and crystalline 2CaO·3B₂O₃ is formed. It melts at 950°C [4].

The two-stage dehydration of pandermite, $Ca_2B_5O_8(OH)_3\cdot 2H_2O$, causes rebuilding of the crystal structure of this compound, which maintains its crystalline character. Gradual dehydroxylation in the range 438 to 580°C results in the formation of an X-ray amorphous substance. At 650°C, a small endothermic peak of transformation appears. At 745°C; the crystallization of CaO·B₂O₃ starts, followed by CaO·2B₂O₃ according to the stoichiometry of composition of the amorphous substance [1].

The thermal decomposition of kaliborite, $HKMg_2B_{12}O_{16}(OH)_{10}\cdot 4H_2O$, proceeds in two steps (at 258 and 272°C). Water molecules and OH groups are gradually released up to 400°C. The thermal amorphization of anhydrous kaliborite proceeds in a step by step mode as all the OH groups are released. As a result of the dehydration process, the borate chains of the kaliborite structure are destroyed. During further heating, the endothermic effect of transformation appears at 640°C. At 679°C, the amorphous substance becomes crystalline [2].

The solid product of dehydration of ulexite, $NaCaB_5O_6(OH)_6.5H_2O$, is the amorphous matrix containing OH groups, in which calcium borates crystallize at once. Above 550°C, the OH groups are gradually removed and new compounds crystallize [5]. The processes of reconstitution of the solid product of dehydration proceed step by step, overlapping one another, and in the DTA curve only an exothermic peak of crystallization accompanied by the removal of OH groups is detected.

Dioctahedral layer silicates are transformed into X-ray amorphous substances after dehydroxylation, with the original structure preserved to a considerable degree. The structure of these minerals contains layers, which consist of sheets of silicon-oxygen tetrahedra and aluminium-oxygen-hydroxyl octahedra. The mechanism of thermal transformation of most of these minerals is well known.

Kaolinite, $Al_4Si_4O_{10}(OH)_8$, and its polymorphs (1:1 layer silicates) are built up of pairs of tetrahedral and octahedral sheets. They dehydroxylate at 400–700°C and the dehydroxylation products preserve about 10% of the OH group content. Their structure includes a distorted silicon-oxygen tetrahedral sheet. The octahedral sheet is reconstituted and transformed in the regions of the distorted Al–O tetrahedra, containing randomly distributed isolated residual OH groups associated with Al–O coordination polyhedra of octahedral and tetrahedral symmetry [6]. At 970°C, the OH groups are removed and simultaneously the amorphous structure is transformed into defective Al-rich (Al,Si)-spinel and mullite in an amorphous SiO₂ matrix [7].

The thermal transformation of 2:1 layer silicates built up of layers consisting of two tetrahedral and one octahedral sheet inside is more complicated. Dehydroxylation starts at a higher temperature. This is well explained by 'the sealed box' model of thermal decomposition [8]. The 2:1 structure is less permeable for water molecules than the 1:1 structure. The internal pressure of water vapour necessary to disrupt it must be higher and a high temperature is therefore required for this reaction. Consequently, the range of existence of the X-ray amorphous structure is much narrower.

The major dehydroxylation of pyrophyllite takes place in the range 500-800°C. Pyrophyllite can tolerate the loss of up to 30% of its OH group water without destruction of its crystal structure. The loss of more water results in the formation of an X-ray amorphous structure with 5-coordinated aluminium. It contains about 10% of the OH groups; removal of the OH groups causes the gradual crystallization of mullite in an amorphous silica matrix [9]. Dehydroxylation of muscovite, $KAl_2[AlSi_3O_{10}](OH)_8$, begins at 700°C (a more dense structure less permeable for H₂O molecules). On the completion of dehydroxylation, a (Si, Al)-spinel crystallizes and the interlayer K⁺ with a tetrahedral sheet form a feldspar-like phase related to leucite; next, highly aluminous mullite is formed at the expense of the spinel [10]. The temperature of completion of dehydroxylation is too high for a real X-ray amorphous structure to exist.

Montmorillonite (Cheto modification) starts to dehydroxylate at 450°C. The interlayer spaces are a convenient route of escape for the water molecules. Due to this, the dehydroxylation process is completed at about 650°C. Residual OH groups are removed slowly up to 840°C (endothermic peak). At this temperature, the structure is completely amorphized. OH group removal results in the formation of 5-coordinated aluminium with smaller amounts of 4- and 6-coordinated aluminium. The degree of dehydroxylation necessary for the amorphous

structure to be formed is obtained at a lower temperature than in the case of pyrophyllite, in spite of the similarity in structure of these minerals. The open interlayer spaces of the montmorillonite structure, the small particle size and the crystal defects make it possible for the water molecules obtained from the clay by dehydroxylation to be permeable enough to escape at a relatively low temperature.



Fig. 1 DTA curves of amorphised colemanite and glass of colemanite composition

XRD and IR studies of amorphous borates and data on the structural transformations of layer silicates indicate that the thermally amorphized solid structure contains preserved elements of the precursor structure. At the beginning, the polymeric anions are distorted but still preserved, and the distribution of the cations is nearly the same as the precursor structure. This chemical microheterogeneity changes when the temperature is increased. The polymeric elements are burst into pieces and all chemical components are redistributed. A new compound can be formed inside the amorphous matrix.

When the chemical heterogeneity of an amorphous solid formed by thermal dissociation is not high and its structure is flexible, it becomes similar to glass. Internal structural strains can be relaxed without crystallization, giving rise to an endothermic effect of glass transition (T_{e}) . This effect is reversible and it differs from other peaks in the DTA curve of the decomposing substance. Anhydrous colemanite and pandermite are examples (Figs 1 and 2). When the chemical composition of the amorphous product is complex, at elevated temperature more than one compound can crystallize, and the glass transition effect is followed by an endothermic peak, which seems to be connected with the redistribution and regregation of chemical components preceding the crystallization of the new phases (Fig. 2). When several different processes overlap during the heating of amorphous solids, this endothermic effect will not be visible. Ulexite and kaliborite are examples. These amorphous solids are similar to glass, and the term 'para-glasses' is proposed for them and for other amorphous, glass-like substances whose distinct microheterogeneity distinguishes them from a real glass.

According to the definition of Zarzycki, a glass is a noncrystalline solid capable of exhibiting a temperature of reversible change of some properties, i.e. a glass transition effect [11]. The glass transition effect is taken here too as the feature distinguishing amorphous substances of a vitreous nature from other amorphous solids.

The structures of amorphous anhydrous layer silicates are heterogeneous, and more stable due to the chemical bonds being stronger than those in the borate structure, and they remain rigid up to high temperature; this is why their reconstruction is connected with immediate crystallization. Due to this difference from the glass structure, the glass transition effect does not appear.

It is also evident that some amorphous structures are stabilized by the residual OH groups entrapped inside them. They are bound to one of the chemical components (Al in layer silicates, Na or B in borates) according to the chemical affinity and base-acid interaction. Amorphous SiO_2 (silica gel) retains a small quantity of OH groups up to high temperatures [12].



Fig. 2 DTA curves of amorphized pandermite and glass of pandermite composition

The anhydrous amorphous products of thermal dissociation are microporous. Escaping water vapour exfoliates and destroys crystals of the parent substance. As the temperature is increased, the porosity diminishes and the mechanical properties change in a manner resembling nano-ceramic sintering. Our measurements of the porosity and specific surface area of colemanite (Table 1) indicate rapid increase in microporosity and specific surface area at the

Temp. / °C	Total cumulative pore volume / mm ³ ·g ⁻¹	Specific surface area / m ² ·g ⁻¹	Average pore radius / nm	Internal change
20	73.49	0.82	394.3	starting material
360	76.40	1.07	249.1	thermal decomposition
440	145.67	8.39	31.6	internal water repelling
700	124.15	3.08	125.4	sintering

Table 1 Porosity of colemanite heated at various temperatures

temperature of violent water escape. They diminish as the temperature is increased, due to sintering.

Amorphous structure reconstitution

The processes considered above indicate that, during the heating of the amorphous decomposition products, their internal structure progressively changes. The radical rebuilding of the structure and the segregation of its components are sometimes accompanied by an endothermic DTA peak, preceding the exothermic peak of crystallization. In glasses, it appears above the transition temperature (T_g) . The endothermic effect of internal structure rebuilding is irreversible, which makes it different from the reversible effect of the glass transition. The internal reconstitution of the crystal lattice caused by amorphization leads to the formation of domains having a chemical composition and structure close to those of the structural units of the precursor. Formation of the first crystal phase inside the amorphous matrix may be achieved by rearrangement and ordering of these domains.

In the amorphous solids of materials with a complex chemical composition, a temperature increase leads to the redistribution of chemical elements and new different phases are formed. The segregation and redistribution of the chemical elements occur according to their chemical affinity principles. Recrystallization of this solid is usually a multistage process. The thermal reactions of Ca, Na and K borates illustrate the regularities mentioned above (Tables 2 and 3).

The amorphous product of the thermal decomposition of colemanite has exactly the chemical composition of the compound $2CaO\cdot 3B_2O_3$, which crystallizes at 740°C. This crystallization is the process of internal structure rearrangement, which occurs much below the melting temperature of the compound (950°C). Glass with the composition $2CaO\cdot 3B_2O_3$ crystallizes in the same manner, but the temperature of crystallization is a little higher (Fig. 1).

A point representing the chemical composition of anhydrous pandermite in the two-component CaO-B₂O₃ phase diagram lies in the area of coexistence of the compounds CaO·B₂O₃ and CaO·2B₂O₃. Both are formed during the crystallization of the amorphous anhydrous pandermite, but they are not created simultaneously. The state of equilibrium of the solid is attained gradually and the compound CaO·B₂O₃ crystallizes first (Table 2). The sequence of crystallization of the artificial glass of pandermite composition, obtained by melting of the mixture of the oxides, is the reverse and the temperatures of the corresponding DTA peaks are higher (Fig. 2).

Stages of the internal feedistrue	tion of the amorphous ca bolate.	
$Ca_2B_6O_8(OH)_6 H_2O$	$Ca_2B_5O_8(OH)_3 \cdot 2H_2O$	
colemanite	pandermite	
1		
400°C	580°C	
$Ca_2B_6O_{11}$	$Ca_4B_{10}O_{19}$	
amorph.	amorph.	
	1	
741°C	745°C	
$Ca_2B_6O_{11}$	$CaB_2O_4 + CaB_4O_7$	
cryst.	cryst. amorph.	
	matrix	
	i	
	800°C	
	$CaB_2O_4 + CaB_4O_7$	
	cryst. cryst.	

Table 2

According to the principle of structural similarity [13], the first to crystallize from the amorphous phase are compounds with chemical compositions and structures close to those of some microregions (domains) inside the precursor structure. The crystals of CaO·B₂O₃, are formed inside an anhydrous matrix with a composition close to that of the compound CaO·2B₂O₃, at 800°C. The higher temperature of this crystallization may be accounted for by the difficulties in the formation of more complex boron-oxygen anions, which requires greater displacements of the pieces of the matrix structure over longer distances. Both processes take place below the solidus temperature (823°C) (Table 2).

Within the amorphous anhydrous kaliborite framework, crystallization of Mg borates begins. The matrix with a composition close to KB_7O_{11} is retained in an amorphous form. Later, $K_2O.5B_2O_3$ crystallizes in it. Formation of this compound requires a considerable displacement of the K⁺ ions, which are localized in the parent structure between the magnesium-oxygen coordination polyhedra. Complex pentaborate anions are also formed. The excess of B_2O_3 remains amorphous (Table 3).

Table 3

Stages of the internal reconstitution of the amorphous K, Mg and Na, Ca borates				
HKMg2B12O16(OH)10·4H2O	NaCaB5O6(OH)6.5H2O			
kaliborite	ulexite			
400°C	260°C			
	1			
$KMg_2B_{12}O_{21}$	NaB _{3.4} O _{3.7} (OH) _{3.8}			
amorph.	amorph. matrix			
	+			
679°C	$CaB_2O_4 + Ca_2B_2O_5$			
	cryst. cryst.			
$MgB_4O_7 + Mg_2B_2O_5$				
cryst. cryst.	> 550°C			
+	1			
KB ₇ O ₁₁	NaB ₃ O ₅			
amorph. matrix	cryst.			
ļ	+			
729°C	$[(Ca_2B_2O_4)_{0.5}(Ca_2B_2O_5)_{0.25}(B_2O_3)_{0.25}]$			
ļ	amorph. matrix			
$MgB_4O_7 + Mg_2B_2O_5 + KB_5O_8$				
cryst. cryst. cryst.	> 700°C			
+				
B ₂ O ₃	NaCaBO ₃			
amorph. matrix	cryst.			
	+			
	B ₂ O ₃			
	amorph. matrix			

The reconstitution of the anhydrous ulexite structure is especially complex. The crystallization of Ca borates immediately follows the removal of the molecules of water coordinating the metal cations. They are formed in the amorphous sodium-borate matrix containing OH groups. Removal of the OH groups destabilizes the amorphous structure. On the reaction of the components, exchange between the matrix and crystalline Ca borates takes place and the system becomes homogenized. Above 700°C, the equilibrium compound NaCaBO₃ is formed, while the excess of B₂O₃ is left amorphous (Table 3).

In anhydrous dioctahedral layer silicates, the sheet of silicon-oxygen tetrahedra is disturbed but is still preserved, and pieces of the deformed octahedral sheet composed of 5- and 4- coordinated aluminium exist. Their rebuilding starts with the formation of pairs of Al-rich mullite and the (Al,Si)-spinel or γ -Al₂O₃ in the aluminium-oxygen polyhedra islands. Rebuilding of these intermediate compounds into real mullite and the crystallization of crystobalite can proceed in minerals with a high aluminium content. In muscovite, due to the high concentration of potassium, in the interlayer space leucite-like feldspar is formed between the tetrahedral sheets [6, 9, 10].

From these data, it is obvious that the internal synthesis of new compounds in amorphous decomposition products, and their crystallization, start with the formation of compounds having structures and chemical compositions close to those of elements or domains of the primary structure (crystallization of Ca and Mg borates, formation of Al-rich spinel and γ -Al₂O₃ in layer silicates). It may occur by the small displacement of pieces of the polymeric anion and diffusional displacement of the cations to small distances: translative diffusionless rebuilding stage [14].

At higher temperatures, when the diffusion becomes intensive, redistribution of the chemical components, decomposition of the previously formed metastable phases and the formation of the equilibrium crystal phases take place. At this stage of recrystallization, the chemical elements bind together according to their affinity [14]. The formation of Na-borates and NaOH in the amorphous matrix of some borates is an example.

Amorphization by crystal structure distortion

During the heating of crystals of quartz in the range $1100-1600^{\circ}$ C, amorphous phase formation preceding the crystallization of crystobalite is observed [15]. This is an example of thermal amorphization which is not involved in a chemical composition change. In this range of temperatures, the thermodynamic instability of the α -quartz structure causes the thermally activated breaking of some of the chemical bonds, and significant quantities of the amorphous

phase appear inside the transforming crystal. However, at these temperatures, the atomic vibrations are still not able to destroy at once the 5-membered rings of the SiO₄ tetrahedra (which contain a strong, but relatively flexible tectosilicate network of quartz) and to build the crystobalite structure (containing 6-membered rings of tetrahedra). As a consequence, a metastable, intermediate amorphous phase appears. When the duration of heating is prolonged or the temperature is increased, α -crystobalite crystallizes inside the amorphous matrix. This crystal formation is accompanied by the redistribution of Al admixtures and other impurities. They can not be incorporated in the crystobalite structure, and concentrate in the amorphous matrix.

Even so, the polymorphous transformation:

 α -quartz $\rightarrow \alpha$ -crystobalite

is in fact a multistage process:

 α -quartz \rightarrow amorphous phase $\rightarrow \alpha$ -crystobalite

The second stages involve a solid-state, heterogeneous process of crystallization of a new crystal phase in an amorphous matrix. This explains the irreversible character of the α -quartz – α -crystobalite transition.

Conditions of formation of inorganic amorphous solids

Solid-state amorphization by thermal decomposition is a structure disordering process.

Amorphous phase formation is possible when the rate of primary crystal structure destruction (V_d) is higher than the amorphous matrix recrystallization rate (V_c) , and the activation energy of destruction is lower than that of crystallization (heterogeneous process with new interface formation). This is a general kinetic criterion of solid-state amorphization.

The study of mixed network glasses revealed a structural similarity of these glasses and inorganic amorphous solids [16]. The crystallochemical criterial for their formation are:

1. Flexibility of the structure, allowing the random arrangement of structural elements.

2. The presence of components stabilizing the random distribution of structural elements and preventing their ordering. Polymeric pieces inside the structure and OH groups may play this role.

They may be extended to other inorganic amorphous solids. The main difference between glass and many thermally amorphized solids lies in the greater micro- and macroheterogeneity of the latter. When the heterogeneity and the number of broken chemical bonds in the structure of the amorphized solid resemble those of the cluster structure in glass, its properties become similar to the properties of glass. It shows a transition effect (T_g) , viscous flow and sintering ability at temperatures far below the melting point. The borates discussed above are an example.

The products of thermal decomposition of many substances of complex chemical composition are X-ray amorphous; decomposition of basic aluminium ammonium sulfate is an example [17]. Rearrangement of large molecules or structural units to form a new crystal structure is difficult and slow.

Thermal amorphization is a characteristic feature of substances whose structures contain large units composed of polymerized coordination polyhedra. These probably make the amorphous structure more stable. Flexibility of the polymeric structure seems to be a necessary condition for many amorphous structures to exist. This is why dehydroxylated Al-layer silicates are amorphous, whereas their Mg-containing analogues crystallize at once. Flexibility is expressed here as the ability of aluminium to change its coordination number. The affinity of aluminium for OH is probably another reason for the amorphous structure stability. Small quantities of OH groups inside the structure, or other trace admixtures, function as amorphous structure stabilizers.

The amorphous structures considered here appear as intermediates of internal reactions of solids which proceed according to the scheme:

order -- disorder -- order

When the mobility of the components of the solid structure is low, as in polymeric structures, amorphous substances may be formed and exist in a wide range of temperature.

The formation of an amorphous substance on the heat treatment of a crystalline solid is a frequently observed phenomenon in inorganic compounds of polymeric structure. Thermal decomposition accompanied by internal structure rearrangement creates very convenient conditions for intermediate amorphous decomposition products to be formed.

Transformation from the disordered amorphous structure to the ordered crystalline form is achieved by the crystallization of a new compound inside the amorphous matrix, which appropriately changes its chemical composition and gradually disappears.

References

- 1 L. Stoch and I. Waclawska, Thermochim. Acta 215 (1993) 255.
- 2 L. Stoch and I. Waclawska, Thermochim. Acta 215 (1993) 265.
- 3 L. Stoch and I. Waclawska, Thermochim. Acta 215 (1993) 273.

- 4 I. Waclawska, L. Stoch, J. Paulik and F. Paulik, Thermochim. Acta 126 (1988) 307.
- 5 L. Stoch and I. Waclawska, J. Thermal Anal., 36 (1990) 2045.
- 6 K. J. MacKenzie, I. W. M., R. H. Meinhold and M. E. Bowen, J. Amer. Ceram. Soc., 68 (1985) 293.
- 7 G. W. Brindley and J. Lemaitre, Chemistry of Clays and Clay Minerals A. C. D. Newman Ed., Mineralogical Soc. Monograph, London 1987 p. 319.
- 8 L. Stoch, J. Thermal Anal., 37 (1991) 1415.
- 9 K. J. MacKenzie, I. W. M. Brown, R. H. Meinhold and M. E. Bowen, J. Amer. Ceram. Soc., 68 (1985) 266.
- 10 K. J. MacKenzie, I. W. M. Brown, C. M. Cardile and R. H. Meinhold, J. Mat. Sci. 22 (1987) 2645.
- 11 J. Zarzycki, Glass and Vitreous State, Univ. Press, Cambridge 1991.
- 12 J. Rouquerol, Proc. 10th ICTA Congress Hatfield 1992, J. Thermal Anal., 40 (1993) 107.
- 13 L. Stoch, Thermochim. Acta, 148 (1989) 149.
- 14 L. Stoch, J. Thermal Anal., 38 (1992) 131.
- 15 L. Stoch, M. Laczka and I. Waclawska, Mineralogia Polonica, 16 (1985) 43.
- 16 L. Stoch, High Temp. Materials and Processes, 10 (1992) 245.
- 17 B. Pacewska, J. Pysiak, J. Thermal Anal., 37 (1991) 1665.

Zusammenfassung — Durch Erhitzen auf eine entsprechende Temperatur können anorganische Polymere, wie zum Beispiel Silikate, Borate und Phosphate in amorphe Feststoffe überführt werden. Eine thermische Amorphisierung kann erreicht werden durch: 1. thermische Disso- ziierung einer kristallinen Verbindung, 2. Verzerrung der Kristallstruktur eines Feststoffes durch hinausgezögertes Erhitzen ohne Veränderung der chemischen Zusammensetzung. Es wurden die Spezifität der erhaltenen Substanzen, die für die stattfindende Amorphisierung erforderlichen kristallchemischen Bedingungen und die Hochtemperaturprozesse für interne Umstrukturierung und Rekristallisierung in den amorphen Produkten betrachtet.