Phase Transformations in Amorphous Solids

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ABSTRACT

This paper presents the results of investigations of amorphous substances formed as a result of thermal decomposition of inorganic crystalline solid bodies by way of their structural rearrangement in a solid phase as an order-disorder transformation. The investigations were conducted on model substances represented by hydrated borates of alkalis and alkaline earths as well as silica-rich zeolites. We examined the glass transition phenomenon as a mode of cancellation of internal stresses induced by the state of structure randomness, and next the recrystallization process of thermally amorphized substances. Recrystallization processes proceed usually in several stages with their structural mechanism changing with temperature.

The formation of the amorphous states and their recrystallization represent a cycle of phase transition realised by means of continuous rearrangement of the internal structure.

These processes may be utilized as an alternate method of obtaining vitreous and glass-ceramic materials of various relations between the crystalline phase and the glassy matrix.

1. INTRODUCTION

Solid bodies may occur in two forms differing in their internal structure, i.e. as crystalline substances of ordered internal structure, and as amorphous bodies of random structure. The amorphous state has not yet been exactly defined, and it comprises substances of different ordering degree of internal structure, varying micro- and macrohomogeneity and varying origin.

Amorphous substances are formed as a result of different processes. Gels are obtained through precipitation from solutions in which the parent compound is in a state of molecular dispersion. Glasses are most often obtained by supercooling a liquid, but also by means of the deposition from a vapour and by sputtering in a vacuum system.

The amorphous state can also be formed through destruction of a crystalline structure under the influence of energy supplied from the outside in various forms, such as heat, pressure or radiation.

The degree of the randomness and inhomogeneity of the internal structure of amorphous substances depends to a high extent on the degree of the dispersion of the primary substance. The highest homogeneity is demonstrated, for example, by glass obtained by condensation of vapours or from solutions (in the sol-gel method) when the parent substance was in the state of molecular dispersion.

Amorphous substances formed through destruction of the crystalline structure of the precursor in a solid state, at low temperature, preserve to a considerable degree the elements of the primary structure. An example here are the metamictic minerals rendered amorphous by radiation.

Depending on the mode of their formation and chemical composition, the degree of randomness of the internal structure of a solid body may vary. It may overcome only the long range ordering, manifested by

the geometry of the crystal lattice of the given substance, i.e. long range order with preserved medium range order, for example, such as the assemblage of coordination polyhedra. Examples are the amorphous substances formed by thermal decomposition of inorganic polymers (silicates, borates, phosphates) and certain glasses of complex composition.

In some amorphous substances there occurs only short-range ordering limited to the particular coordination polyhedra. Glasses of simple composition are examples of this.

The randomness may also extend to a first coordination zone, i.e. the nearest surroundings of atoms forming the amorphous structure. This takes place in the case of elements in a glassy form or certain glassy metals.

It has been assumed in this paper that the internal structure order in the amorphous substances has been distorted or destroyed to a degree excluding the appearance of the X-ray diffraction lines characteristic of their crystalline forms. This means that the disappearance of long-range ordering in the structure is a sufficient reason to regard the substance as an amorphous one; the state of randomness in X-ray amorphous substances may, obviously, have a wider range of occurrence and include even the first coordination sphere.

The state of randomness in the area of the first coordination sphere may change the nature of the interatomic interactions and thus affect the electrical and magnetic properties of the substance. These states are the subject of investigations in solid state physics.

To investigate the amorphous substances, especially those in which the short- and medium-range ordering has been retained, attempts are being made to apply methods used in structural chemistry and crystallochemistry. With respect to their chemical and physical properties, these substances show considerable similarity to the affinated crystalline substances. They contain the same type of coordination polyhedra as the corresponding crystalline substances. Occasionally, the transition into the amorphous state cancels the deformations of coordination polyhedra to which they are subjected in a crystal structure. This takes place, for example, in the case of SiO_4 tetrahedra in vitrified framework silicates /1/. The transition into the amorphous state, on the other hand, does not introduce any essential changes in the nature of chemical bonds, or such changes are relatively small. The coordination number of some cations, however, is occasionally changed. These factors, together with the degree of randomness of the internal structure, determine the differences in the properties of the amorphous and crystalline substances.

The subject of the present study is the chemical and structural transformations occurring in amorphous inorganic polymers obtained by heat treatment of crystalline substances.

As already shown earlier /2/, it is possible to obtain an amorphous substance by heat treatment in cases where the destruction rate of the primary crystalline structure is greater than the recrystallization rate of the amorphous matrix which is then formed.

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

The investigations were carried out on a few selected borates and zeolites rich in silica. The occurring phase transitions, consisting in rearrangement of the internal structure under the influence of temperature, were determined and the observed phenomena compared with those occurring in other substances rendered amorphous by heat treatment and in glasses.

The aim of the investigations was to recognize the regularities controlling the phase transformations by the structural rearrangement of amorphous solids.

An attempt has also been made to define the mutual relations between substances rendered amorphous by heat treatment and glasses.

Thermal amorphization appears to be a promising method of obtaining some glasses and glass-ceramic materials, as well as ceramic powders, especially those that cannot be obtained by the sol-gel method.

Moreover, the examined processes correspond to those occurring during vitrification and crystallization of xero-gels in the sol-gel method of obtaining glasses and glass-ceramic materials.

2. MATERIALS

The model substances selected for the examinations were the borates of alkalis and metals of alkaline earths which have different complex borate anions. They have their equivalents among the borate glasses. Moreover, these borates belong to substances of low melting temperature. Coarse-crystalline, pure borate minerals from the collection of the Mineralogical Museum of the Wroclaw University were examined. They included:

colemanite $Ca_2B_6O_8(OH)_6 \cdot 2H_2O$,
pandermite $Ca_2B_5O_8(OH)_3 \cdot 2H_2O$,
kaliborite $HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$),
ulexite $NaCaB_5O_6(OH)_6 \cdot 5H_2O$,
tincalconite $Na_2B_4O_5(OH)_4 \cdot 3H_2O$, and
kernite $Na_2B_4O_6(OH)_2 \cdot 3H_2O$.

Synthetic borax was also examined.

Synthetic zeolites: ZSM-5 zeolite of high SiO_2 content and NaA zeolite containing aluminium in its structure were examined too. They belong to framework silicates and are built of SiO_4 and AlO_4 tetrahedra. They may be regarded as substances corresponding to minerals of the SiO_2 groups and aluminium-doped quartz glass on account of their chemical composition and the kind of short-range order of internal structure. They differ from the above materials in the medium- and long-range order. The zeolites were in their Na-form.

3. METHODS

To investigate the processes occurring during heating of the examined substances, the DTA method as well as the conventional and constant-rate TG and DTG methods were used. The measurements were performed on a Q-1500D derivatograph and a computer-controlled C-derivatograph (MOM Budapest).

In order to examine the structural changes taking place during heating, the samples were heated at a rate of 2.5°C min^{-1} up to the characteristic temperatures, cooled and next subjected to X-ray diffraction and IR spectroscopic examinations. X-ray powder patterns were made with a DRON-3 diffractometer using CuK_α radiation. Absorption IR spectra were obtained with a Zeiss Ur-10 spectrometer and with a Digilab FTS-60V Fourier Transform Infrared Spectrometer. Samples were prepared as KBr pellets.

In the case of some substances, of which there were sufficiently large amounts available, the changes in density and microporosity induced by phase transitions were also determined.

Measurements of the specific surface (BET), pore volume and size were conducted, taking advantage of the phenomena of adsorption and desorption of pure nitrogen at the temperature of liquid nitrogen by means of a computer-controlled ASAP 2000 apparatus (Micromeritics). Density measurements were performed in an Accu-Pyc 1330 helium pycnometer (Micromeritics).

4. RESULTS

A. Phase Transformations in Amorphous Borates

Results of the thermal analysis (Fig. 1), X-ray patterns (Fig. 2) as well as IR spectra (Figs. 3, 4, 5) indicate the range of amorphous structure stability and the course of its recrystallization. They depend on the chemical composition and primary structure of borates (Tables 1 and 2).

Thermal decomposition of chain borate colemanite $Ca_2B_6O_8(OH)_6 \cdot 2H_2O$ proceeds in two stages at 369°C and 386°C /3/. This process is accompanied by the gradual destruction of the primary structure of the borate. At 650°C a small endothermic DTA peak appears resembling the glass transition effect (T_g). At 741°C amorphous substance recrystallizes and crystalline $2CaO \cdot 3B_2O_3$ is formed. It melts at 950°C.

Dehydration and dehydroxylation of layer borate pandermite $Ca_2B_5O_8(OH)_3 \cdot 2H_2O$ 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 $CaO \cdot B_2O_3$ starts followed by $CaO \cdot 2B_2O_3$ formation according to the stoichiometry of composition of the amorphous substances. They melt at 1100°C (solidus temperature) /4/.

Thermal decomposition of chain borate kaliborite $HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$ proceeds in two steps

Table 1

Phase transformations of alkaline earth borates

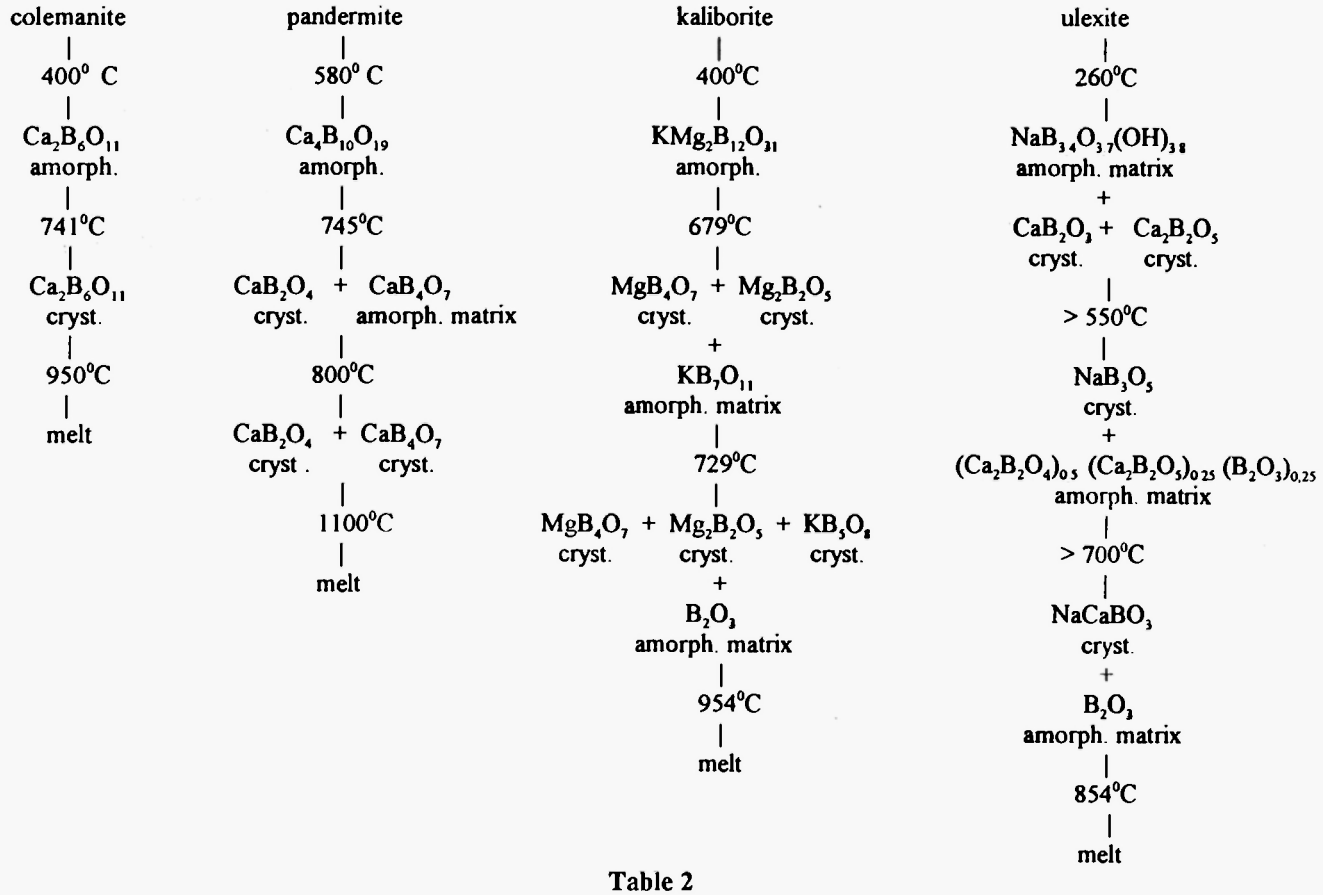
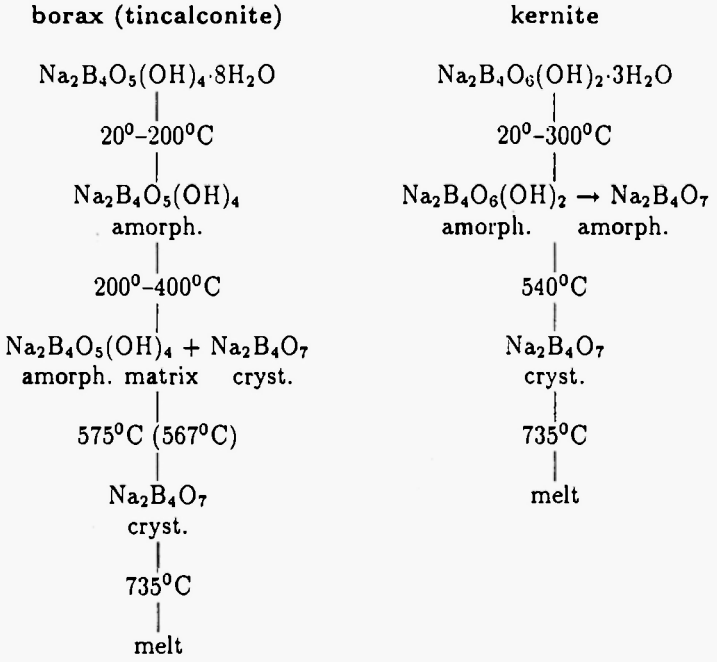


Table 2

Phase transformations of sodium borates



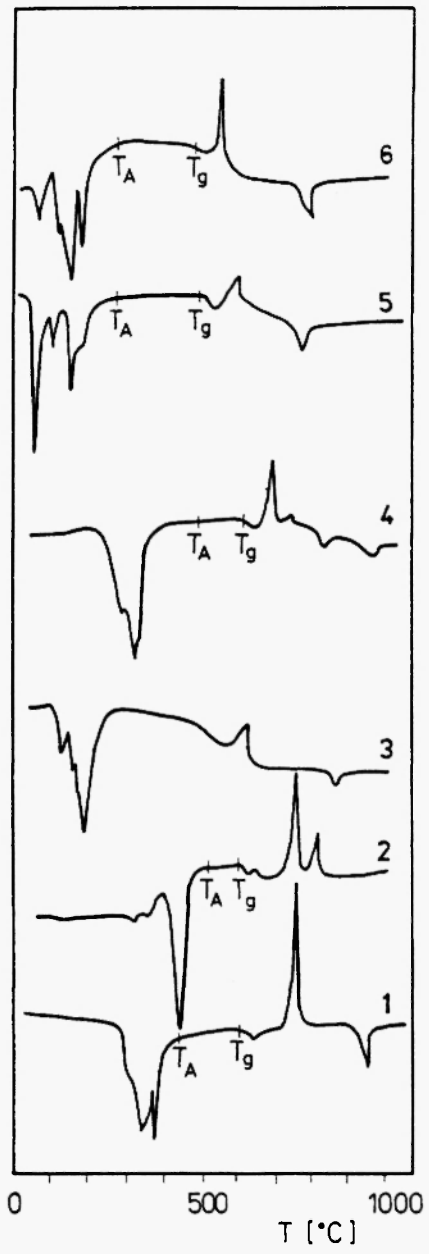


Fig. 1: DTA curves of borates
1) colemanite; 2) pandermite; 3) ulexite; 4) kaliborite; 5) borax; 6) kernite; T_A - temperature of amorphization; T_g - glass transition

(258°C and 272°C). Water molecules and OH groups are gradually released up to 400°C. 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 kaliborite structure are destroyed. During the further heating at 640°C, the endothermic effect of transformation appears. At 679°C amorphous substance becomes crystalline /5/. Excess of B_2O_3 forms amorphous matrix. Newly formed compounds melt at 954°C.

A solid product of dehydration of the island-structure borate ulexite $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ is the amorphous matrix containing OH groups in which calcium borates crystallize at once /6/. Above 550°C the OH groups are gradually removed and new compounds crystallize. They melt at 854°C.

Borax gradually loses its molecular water up to the temperature 200°C. Dehydration is associated with amorphization of the crystalline structure. The newly formed amorphous substance, on the other hand, preserves all OH groups /7/. Further increase in temperature causes their gradual removal. At the temperature 400°C, when the number of OH groups decreases to 20%, the crystallization of $Na_2B_4O_7$ begins. When all the OH groups are removed, at the temperature 520°C, there appears the reversible endothermal DTA peak, corresponding to the glassy state transition. It is followed by complete recrystallization of the amorphous matrix.

Borax belongs to the island borates. In its structure there occur the $B_4O_5(OH)_4^{2-}$ polyions consisting of two BO_2 (OH) triangles and two BO_3(OH) tetrahedra. In between the polyions there are sodium cations surrounded by water molecules.

X-ray determined radial distribution functions (RDF) allowed it to be established that in the structure of a dehydrated, thermally amorphized borax the distances B–O and O–O are 1.48 Å and 2.42 Å, respectively. According to /8/, such values are characteristic of the BO_4 tetrahedra. It means that in the amorphous structure, free from the OH groups, all the boron atoms change their coordination numbers to 4, and that a tetrahedric configuration is adopted.

Tincalconite behaves similarly during heating in spite of its slightly different structure in the hydrated state. Its structure is more compact on account of a smaller number of water molecules. Moreover, the OH groups of the polyions combine with the Na^+ cations.

$Na_2B_4O_6(OH)_2 \cdot 3H_2O$ kernite, a member of the borax family, contains in its structure the same polyions as borax or tincalconite, but the polyions are

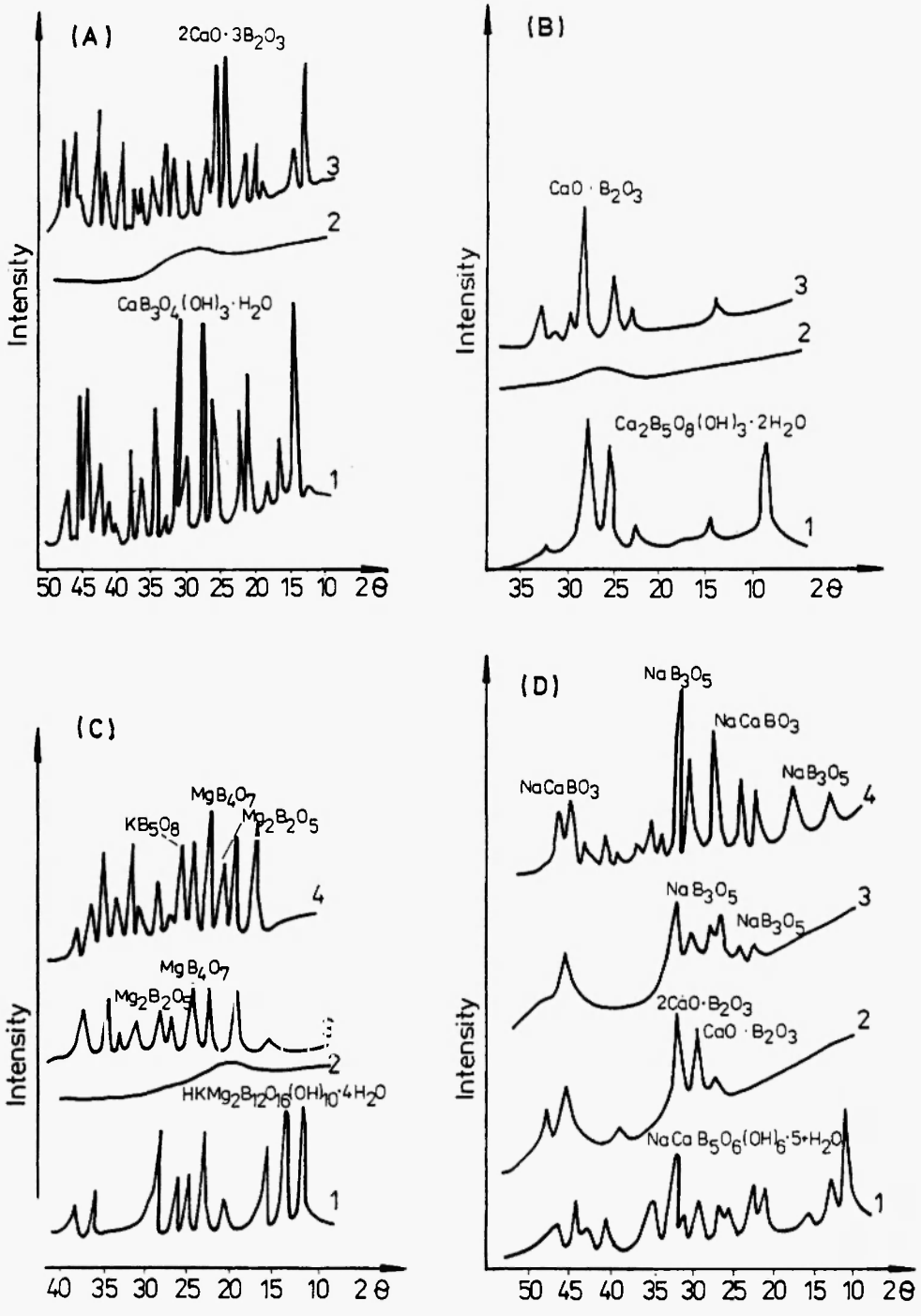


Fig. 2a: X-ray patterns of borates
(A) colemanite: 1) mineral, 2) amorphous form, 3) recrystallized
(B) pandermite: 1) mineral, 2) amorphous form, 3) recrystallized
(C) kaliborite: 1) mineral, 2) amorphous form, 3) and 4) recrystallized
(D) ulexite: 1) mineral, 2), 3) and 4) recrystallized.

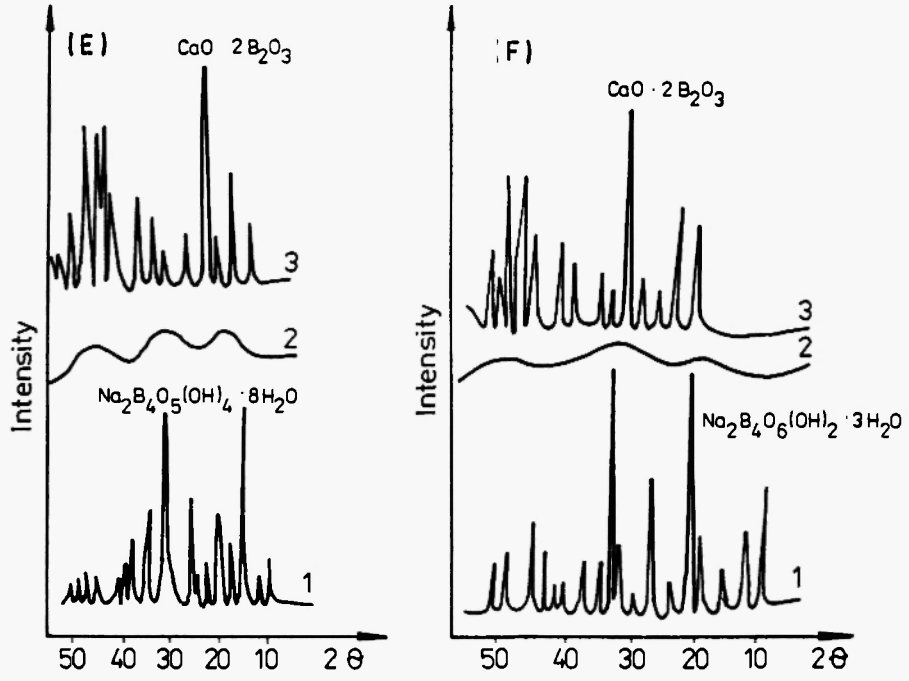


Fig. 2b: X-ray patterns of borates:
(E) borax: 1) mineral, 2) amorphous form, 3) recrystallized
(F) kernite: 1) mineral, 2) amorphous form, 3) recrystallized

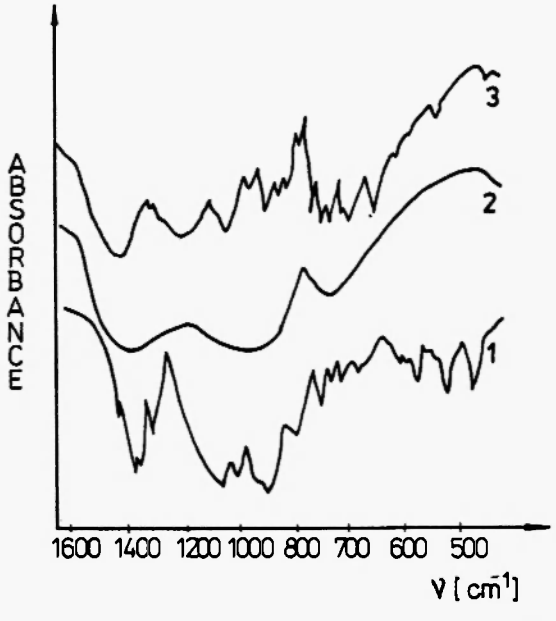


Fig. 3: IR spectra of pandermite: 1) mineral, 2) amorphous form, 3) recrystallized

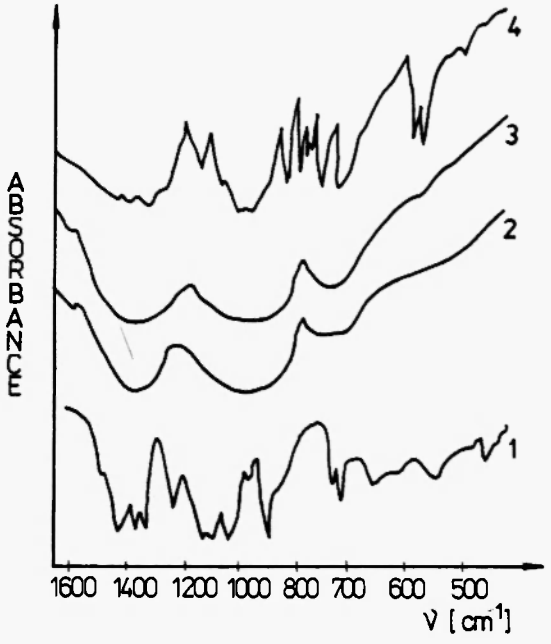


Fig. 4: IR spectra of ulexite:
1) mineral 2) and 3) amorphous form (260° and 550°C), 4) recrystallized

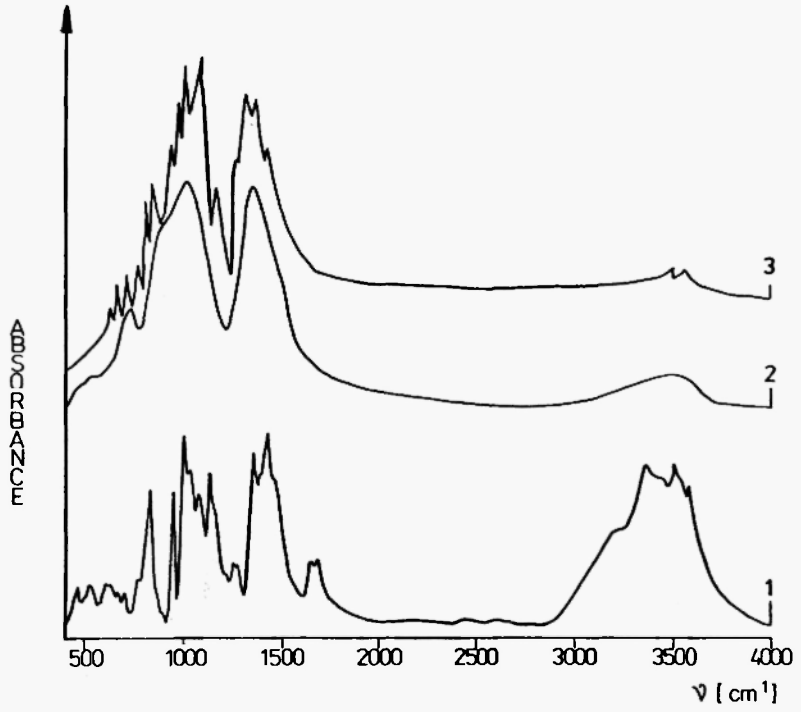


Fig. 5: IR spectra of borax (tincalconite): 1) mineral, 2) amorphous form, 3) recrystallized

polymerized infinite chains.

In spite of small structural differences between borax and kernite, with similar chemical composition after dehydration, the thermal reactions in both minerals proceed in a different way. The amorphous form of kernite exists just at the temperature 300°C. It crystallizes rapidly, which is indicated by the sharp DTA peak, while the crystallization of amorphous borax extends over a wide temperature range. Crystallization of kernite occurs at a lower temperature (540°C) in comparison with that of borax (575°C) and tincalconite (567°C).

A comparison of the behaviour of these two minerals at elevated temperatures reveals the undoubted effect of structure on the thermal reactions in solid bodies.

Dehydration and dehydroxylation of borates causes an increase in porosity. A colemanite sample increases its total pore volume from73.5 mm^3/g up to 145.7 mm^3/g at 440°C. The appearing pores have a diameter of 31.6 nm. With increasing temperature the volume of the pores gradually decreases, but their diameters increase. they attain the values of 124 mm/g and 125.4 nm, respectively.

Amorphized borax has pores of a total volume of 4.5 mm^3/g, and their diameters amount to 3.8 nm. Its apparent density is only 1.7655 g/cm^3, while glass of the same composition has a density of 2.3697 g/cm^3. This means that it contains a great number of fine, closed pores, not measurable by the BET method.

B. Phase Transformations in Silica-Rich Zeolites

NaA zeolite loses water up to 600°C, yet it still retains its crystalline structure up to the temperature 800°C (Fig. 6). Starting from this temperature, the zeolite lines on an X-ray pattern gradually disappear (Fig. 7), which is an indication of amorphization of the structure. The amorphization process is accompanied by a characteristic deflection on the DTA curve at 800°C.

At 860°C there takes place the crystallization of cristobalite (SiO_2) inside the amorphous aluminosilicate matrix. This is a slow process, marked by a weak DTA peak.

At a somewhat higher temperature cristobalite reacts with the amorphous matrix and there crystallizes the framework silicate nepheline.

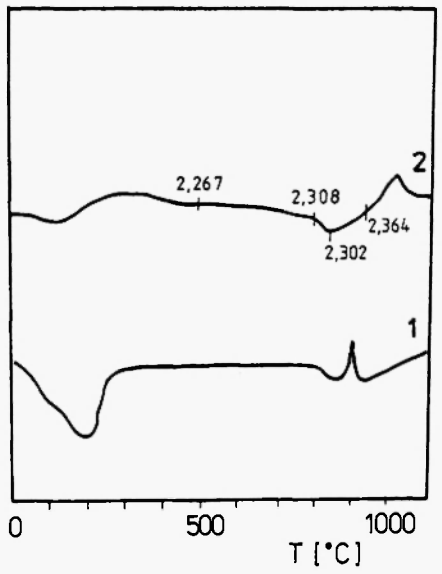


Fig. 6: DTA curves of zeolites
1) NaA zeolite, 2) ZSM-5 zeolite. The numbers denote the density of zeolite [g/cm^3] at various temperatures

ZSM-5 zeolite retains an unchanged crystalline structure up to about 840°C. At this temperature the DTA curve shows a weak, irreversible endothermic effect. From that temperature upwards there begins a gradual rearrangement of the open structure of zeolite into a compact structure of cristobalite. This process is completed by the time the temperature reaches 1000°C.

It is worth noticing that in both zeolites the reconstruction of the open skeleton framework of zeolite into the compact structure of nepheline or cristobalite proceeds step by step and is not accompanied by any greater thermal effect. As it seems, this rearrangement consists of a change in the orientation of the tetrahedra in the loose structure of the zeolite, without breaking any greater number of bonds.

Unlike the transformation of the zeolites, the transition of the compact structure of quartz into that of cristobalite, which is included in their constructive polymorphous transformations, consists of the initial formation of an intermediate amorphous phase, within

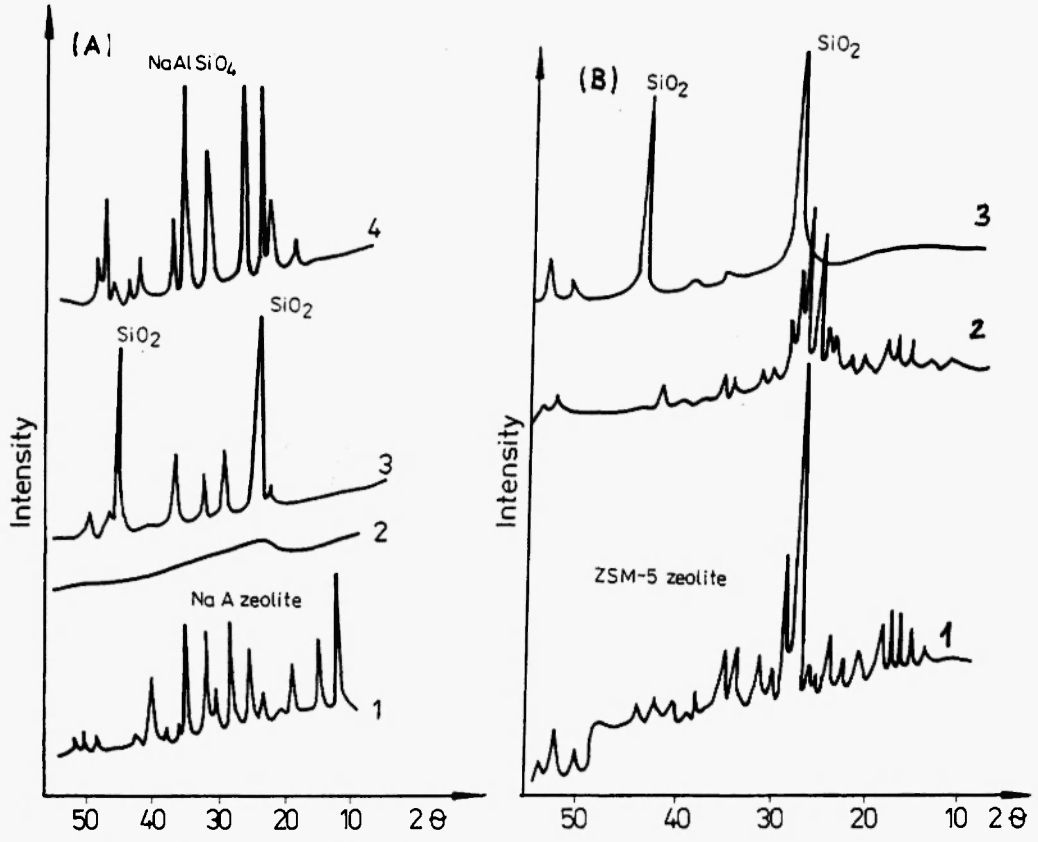


Fig. 7: X-ray patterns of zeolites
(A) NaA zeolite: 1) crystals, 2) amorphous forms, 3) and 4) recrystallized
(B) ZSM-5 zeolite: 1) crystals, 2) reconstructed, 3) recrystallized

which cristobalite crystallizes afterwards. In view of an almost identical composition of the ZSM-5 zeolite and of quartz, it is clearly seen that the primary structure has a decisive influence on the mechanism of phase transition.

Amorphization of NaA zeolite is connected with structure condensation. Dehydrated zeolite has a specific surface BET of 4.07 m^2/g, pore volume of 15.5 mm^3/g, the diameter of which equals 111.7 Å. When the irreversible endothermal process has been completed at 800°C, these values are as follows: 2.04 m^2/g, 6.80 mm^3/g and 133.07 Å. This means a twofold reduction of the volume of pores available for N_2, which points to a radical condensation of the material.

5. DISCUSSION

A. Multi-Stage Crystallization of Amorphous Solids

Crystallization of the majority of the considered amorphous substances proceeds in several stages. One-stage crystallization takes place when the chemical composition of the amorphous precursor is similar to that of the crystalline phase formed from it.

In all the examined cases, crystallization of amorphous substances begins at temperatures considerably lower than their melting temperature.

Colemanite and silica-rich zeolite are examples of a single-stage crystallization. In the first case, crystallization is a rapid process and the accompanying exothermal DTA peak is exceptionally sharp, similarly to the peak of the Al-silicate metakaolinite crystallization. In the opinion of the authors, this is an indication of the diffusionless mechanism of this phase transition. The crystalline phase is formed through the reorientation and topological adjustment of the elements of the amorphous structure like in displacive polymorphic transformations /9/. This is possible due to structural similarity between the structure of the precursor and that of the crystalline phase being formed. In the first case ring borate, like its crystalline precursor, and in the other case, (Si, Al)-spinel, are built of the same tetrahedra which form an amorphous structure.

Crystallization of amorphized zeolite is associated with a complete change in the medium-range ordering and a transition from an open zeolite structure to a more dense cristobalite structure. Hence this process is slower and the accompanying thermal effect broadened (Fig. 6).

In the case of substances of a complex chemical composition, recrystallization proceeds in several stages. The following general regularity can be observed.

In the borates the first to crystallize are the borates of bivalent cations of simple composition and a low ratio of the number of boron atoms to the number of cations in the formula, which means that their structure contains the borate anions with a low degree of polymerization of BO_4 tetrahedra (orthoborates, ring borates, less frequently chain borates) /10/.

They are formed in the amorphous matrix enriched with B_2O_3. An example here is pandermite. If the compound contains alkalis, they are retained in the amorphous matrix (kaliborite, ulexite).

The next crystallization step occurring at a higher temperature comprises the crystallization of the borates of alkalis (kaliborite) or the calcium borates formed in the first stage are dissolved, and next the double borates of alkalis and alkaline earth metals crystallize, according to the chemical composition of the given substance (ulexite).

When an amorphous substance contains alkali cations besides those of alkaline earth, crystallization causes their segregation. The cations of alkalis, as the more basis ones, remain in the amorphous matrix, being strongly bound to the borate anions which have an acidic character. Segregation is thus controlled by chemical affinity. The cations of the alkaline earths, having greater field strength, form with the borate anions relatively stable elements which, it is assumed, may even be inheritance from the primary structure of the crystalline substance. The segregation of the components makes the amorphous matrix rich in B_2O_3, thus its cross-linking increases accordingly.

High-temperature phase transformations of layer silicates are very well known processes /11/.

Dioctahedral layer silicates transform 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 Al-silicates) are built up of pairs of tetrahedral and octahedral sheets. They dehydroxylate at 400-700°C and dehydroxylation products contain about 10% of preserved OH. Their structure has a distorted silicon-oxygen tetrahedral sheet. An octahedral sheet is reconstituted and transformed in regions of distorted Al–O tetrahedra, containing randomly distributed isolated residual hydroxyls associated with Al–O coordination polyhedra of octahedral and tetrahedral symmetry /12/. At 970°C hydroxyl groups are removed and at the same moment the amorphous structure is transformed into defective Al rich (Al, Si)-spinel and mullite in amorphous SiO_2 matrix /11/.

Thermal transformation of 2:1 layer silicates, made up of layers consisting of two tetrahedral and one octahedral sheet inside, is more complicated. Dehydroxylation starts at a higher temperature. It explains well the "sealed box" model of thermal decomposition /13/. The 2:1 structure is less permeable to water molecules than the 1:1 structure. The internal pressure of water vapour necessary to disrupt it must be higher, thus a high temperature is required for this reaction. Consequently, the range of existence of X-ray amorphous structure is much narrower.

The major dehydroxylation of pyrophyllite takes place in the range of 500–800°C. Pyrophyllite can tolerate the loss of at least 30% of hydroxyl water without destruction of its crystal structure. The loss of more water results in the formation of an X-ray amorphous structure with five coordinated aluminium. It contains about 10% of OH groups; removal of the hydroxyls causes the gradual crystallization of mullite in amorphous silica matrix /14/. Dehydroxylation of muscovite $KAl_2[AlSi_3O_{10}](OH)_8$ begins at 700°C (more dense structure, less permeable to H_2O molecules). On the completion of dehydroxylation, (Si, Al)-spinel crystallizes and interlayer K^+ with tetrahedral sheet form a feldspar-like phase related to leucite, next highly aluminous mullite at the expense of spinel is formed /15/. The temperature of dehydroxylation completion is too high for a real X-ray amorphous structure to exist.

Montmorillonite (Cheto modification) starts to dehydroxylate at 450°C. Interlayer spaces are a convenient way of escape of water molecules. Due to this, the dehydroxylation process is completed at about 650°C. Residual OH groups are slowly removed up to 840°C (endothermal peak). At this temperature, the structure is completely amorphized. Hydroxyl removal results in the formation of 5-coordinated aluminium with smaller amounts of 4- and 6-coordinated aluminium. The dehydroxylation degree necessary for the amorphous structure to be formed is reached at a lower temperature than in pyrophyllite, in spite of the similarity in structure of these minerals. Open interlayer spaces of montmorillonite structure, small particle size and crystal defects make it permeable to the water molecules, which are obtained from the clay dehydroxylation, to escape at a relatively low temperature /16/.

Substances which are the dehydroxylation products of layered silicates retain pieces of the structure of the primary material up to about 1000°C. Afterwards they undergo internal rearrangement which consists of the formation of new crystalline phases. This process proceeds in several stages.

In kaolinite the first transition at the temperature 980°C is very rapid (extremely sharp DTA peak) and it consists of a small, diffusionless reorientation of AlO_4 and SiO_4 tetrahedra with the formation of (Al, Si)-spinel and mullite in amorphous silica matrix. At about 1200°C there follows an exchange of components between the matrix and the earlier crystallized phases, and mullite $Al_8O_{3.5}(AlSi_3O_{16})$ and cristobalite SiO_2 are formed. It is a thermodynamically stable phase composition.

In the first-stage crystallization of internal character, ribbon-like crystals of spinel and mullite are formed within the kaolinite plates, and their orientation remains in a topological relation to the primary structure. During the second stage, mullite of prismatic habit, typical of this mineral, is formed. Its crystals are variously oriented and they reach far beyond the plate area /11,12/.

The dehydroxylated pyrophyllite structure contains 10% of the residual OH groups combined with Al five-coordinated aluminium. Above 900°C, when they are

removed, there begins the step-like crystallization of mullite which occurs at about 1100°C, and next the silicate matrix recrystallizes into cristobalite /14/.

On account of its chemical composition, dehydroxylated muscovite recrystallizes with the formation first of (Al, Si)-spinel which later recrystallizes into mullite, and from the amorphous matrix a leucite-like phase is crystallized /15/.

Magnesium-rich montmorillonite, Cheto-type, after a loss of 10% of the residual OH groups, recrystallizes with the formation first of a solid solution of a quartz structure and enstatite $MgSiO_3$. Aluminium is initially included in a high-cordierite phase ($Mg_2Al_4Si_5O_{18}$), which at higher temperatures is replaced by sapphirine $(Mg,Fe)_4Al_8Si_2O_8$. At 1200°C the quartz-like component is completely transformed into cristobalite /16/.

The course of phase transition of layered silicate shows many similar features to that of phase transitions in borates. In either case the first new compounds crystallize in the amorphous matrix in two stages. In the case of silicates, the matrix is rich with SiO_2. The type of the first phase being formed is determined by the cations. In silicates, the groups of cations, forming the preserved fragments of the octahedral layer, are the starting material for new compounds (crystallization of Al,Si-spinel or high cordierite and quartz solid solution).

At higher temperatures the second stage of crystallization takes place; this is connected with an exchange of chemical components between the previously formed compounds and the matrix. New compounds are then formed which, with respect to composition and structure, correspond to the state of the thermodynamic equilibrium of the system.

The dehydroxylation products of layer silicates are porous. Their dehydroxylation, similarly to that of borates, is an internal process of crystals and water vapour is formed in their entire volume /17/. As a result the products of dehydroxylation have a microporous structure. Dehydroxylation of kaolinite causes a decrease of density from 2.55 to 2.34 g/cm^3 /18/. Crystallization of spinel and that of mullite is accompanied by a rapid diminution of the specific volume and densification of the structure. In a similar way, dehydroxylation of muscovite brings about an increase in the specific volume /17/. It subsequently diminishes as crystallization proceeds. The densification processes of the amorphous structures of borates and silicates of microporous structure, on account of the pore dimensions and the character of the internal structure of the substance, resemble the sintering of ceramic powders of nanometric dimensions.

B. Components Mobility Control

Multistage recrystallization of the amorphous solids considered here belongs to the internal structure reconstitution processes. The mechanism of these processes is specific, according to the particular properties of the primary structure as a medium of these reactions.

Internal structure reconstitution processes or internal processes occur through the displacement of the parent structure components which rate changes in a different manner with temperature. The result is the formation of intermediate metastable phases and a multistage course of many internal processes and step-by-step mode of the thermodynamic stability state reached /19/.

The crystallization of many glasses takes a multistage course and may be an example.

In silicate glasses the first crystallizing phase is often a quartz-like solid solution or another compound of the structure and chemical composition close to the parent glass. At higher temperatures their structure becomes rebuilt with the formation of crystalline phases whose chemical composition is increasingly closer to the stable thermodynamic phase (cordierite, spodumene, mullite, etc.). Many examples of multistage crystallization of glasses can be found in recent scientific literature /20-22/. Complex reaction series in amorphous borates and silicates, considered here, can be included among them.

Multistage recrystallization can be explained as the consequence of limited mobility of the components-reagents which changes with temperature. In the formation of new phases the participation is permitted only of those chemical components which at the given temperature have a possibility of rearrangement or displacement determined by their diffusion coefficient.

The diffusion coefficient of the components of solid structure increases with increasing temperature, but

this increase is different for different chemical components. It may happen that at various temperatures different components become capable of forming new compounds. Then, compounds differing in their chemical composition successively crystallize.

The increase in the mobility of the structural elements with temperature can be easily observed in glasses. Up to the temperature of the glass transition, which corresponds to the viscosity $10^{13.3}$dPa·s, glass behaves like a rigid and brittle body. A little above this temperature it demonstrates viscoelastic properties with rearrangement of large fragments of the network and/or structural units. When the temperature increases, causing a reduction of viscosity to 10^6-10^3 dPa·s, the glass shows the ability of viscous deformation connected with the orientable flow of the structural unit with a geometry of chains, spheroids and disc-like particles. With further increase in the temperature, the dimensions of these units diminish and accordingly the viscosity of the glass decreases /23/.

This scheme of change of mobility of the structural elements with temperature can be extended to the amorphous borates and other glass-like amorphous substances.

At low temperatures, when the mobility and possibility of rearrangement of structural elements is limited, only those phases may be formed whose chemical composition and structure are close to the primary structure. Recrystallization of amorphized colemanite or the first stage of amorphized layer silicate crystallization are suitable examples.

In that case, the formation of new structure is possible, as it seems, through short distance rearrangements of structural elements, similar to those occurring in the so-called displacive or distortional polymorphic transitions according to Buerger's classification /9/. The formation of another intermediate phase requires a more complex mechanism, when a change in the anion subnetwork, usually less mobile, has also a diffusionless character, but the mobile cations become displaced at considerable distances in a diffusional mode. Crystallization of calcium and magnesium borates in amorphized borates of the complex composition are an example.

This is an analogy to the disorder-order transformations in pyroxenes and feldspars /24/.

With increasing temperature and mobility of the primary structure components, the proportion of long-distance diffusive displacements may increase, causing a corresponding change in the mechanism of formation of new phases.

It changes into the diffusional mechanism, which enables exchange of the components between the grains of phases formed earlier, as well as between the amorphous matrix. This permits the decomposition of the metastable phases and crystallization of new thermodynamic stable ones. This takes place in alkalis and alkaline earth borates.

At this stage, due to sufficient mobility of all chemical components, the formation of new compounds is determined by their chemical affinity. According to Prigogine /25/, the free energy of the proper reaction is a measure of this affinity. Accordingly, the compounds corresponding to the thermodynamic equilibrium state of the system are formed at that stage of the phase transitions.

In the first, low temperature stage of the phase transitions, due to the selectively limited mobility of components, this mobility becomes a governing factor. Compounds containing the most mobile components are then formed or diffusionless transformations take place.

C. OH Groups in Amorphous Solids

Amorphous solid bodies retain a number of OH groups. They remain in their structures to very high temperatures. The data collected here indicate that the OH groups have an essential influence on the stability of the amorphous structure, although they occasionally occur in a small number.

The OH groups retain the amorphized island borates, containing Na, in the structure of which there occur isolated polyions made up of triangles and coordination polyhedra in which the OH groups exist, i.e., ulexite, borax, tincalconite and kernite.

The borate-sodium matrix with the OH groups retains its amorphous state up to above 500°C. Calcium borates (ulexite) crystallize in it. It becomes fully recrystallized, forming sodium borates, not until the OH groups have been completely removed (Table 1).

The amorphized dioctahedral layer silicates also

retain part of the OH groups (10%) which are associated with the Al-O polyhedra. Removal of the residual OH groups from kaolinite is connected with rapid crystallization of (Al, Si)-spinel. Pyrophyllite also retains about 10% of the OH groups which are released at a temperature of about 1000°C followed by the crystallization of mullite /14/. In dehydroxylated montmorillonite, removal of the residual 10% OH groups starts crystallization /16/.

These examples indicate that the OH groups stabilize the existence of the amorphous forms of some substances. When these groups are removed, there is a rapid rearrangement of the amorphous structure and crystallization.

D. Structure Inheritance

X-ray patterns of amorphized borates and silicates do not show sharp diffraction lines of the crystal lattice. Instead, there appear broad, diffused bands of amorphous structure (Fig. 2). They are evidence of the occurrence of some kind of middle-range order in the structure. Similar bands can be observed in X-ray patterns of glasses.

They frequently occur within the same range of angles in which the strongest lines of the primary crystalline phase are found. Examples are colemanite and pandermite, as well as ulexite. In the latter case, the X-ray pattern of an amorphized sample shows two bands, about 30° and 45° 2Θ, with superimposed lines of calcium borates which have started to crystallize.

In the case of kaliborite, the diffused band appears at about 20° 2Θ, i.e. beyond the range of the diffraction lines of the primary structure. This may be attributed to the formation, in the course of amorphization, of a middle-range order other than the primary one. This band is transformed next into diffraction lines of magnesium borates.

The sodium borates, borax and kernite, in the amorphous state, show three bands in the range of angles, 45° or 50°, and 30° and 18°. Two of them correspond to the most intensive lines of the primary phase. All three become transformed into an intensive line of the crystalline phases formed from the amorphous phase.

Amorphized zeolite NaA yields a band at about 25° 2Θ, i.e. within the range of angles in which the strongest line of cristobalite appears. Amorphization brings about total collapse of the open structure of zeolite, as already mentioned.

The phenomena described above indicate the existence of some relations between the structure of the amorphous phase and the crystalline phases derived from it. On the other hand, the middle-range ordering of the amorphous phase appears also be inherited, at least in part, from the primary structure.

The existence of such structural dependences is also indicated by the course of the crystallization of amorphous phases, as discussed in detail earlier in this paper.

Amorphization cancels the splitting of the absorption bands in infrared, induced by the influence of the crystal field. It is for this reason that the amorphized substances exhibit broad, smooth bands of the IR spectrum (Figs. 3, 4, 5, 8). Positions of the bands do not change, which is an indication that the transition into the amorphous state does not change the chemical bonds and does not disturb the near order of the elements of the anion framework. It is not changed by the subsequent recrystallization, either.

E. Structure Relaxation Phenomena

Inorganic as well as organic glasses exhibit a structure strain relaxation phenomenon termed the glass transition effect. According to /26/, the glass transition process distinguishes glass from other solid bodies.

Glass transition is defined as that phenomenon in which a substance exhibits a sudden change in its properties, such as heat capacity, expansion coefficient and viscosity, from crystal-like to liquid-like values.

At the transition temperature, the viscosity of glass decreases to about $10^{13.3}$dPas. This means that the relaxation of stresses is connected with loosening part of the chemical bonds in the glass structure. Up to the transition temperature glass behaves like a brittle body of rigid structure. A little above this temperature it has viscoelastic properties.

The transformation effect is induced by the relaxation of internal stresses occurring in the glass structure at temperatures lower than the glass transition

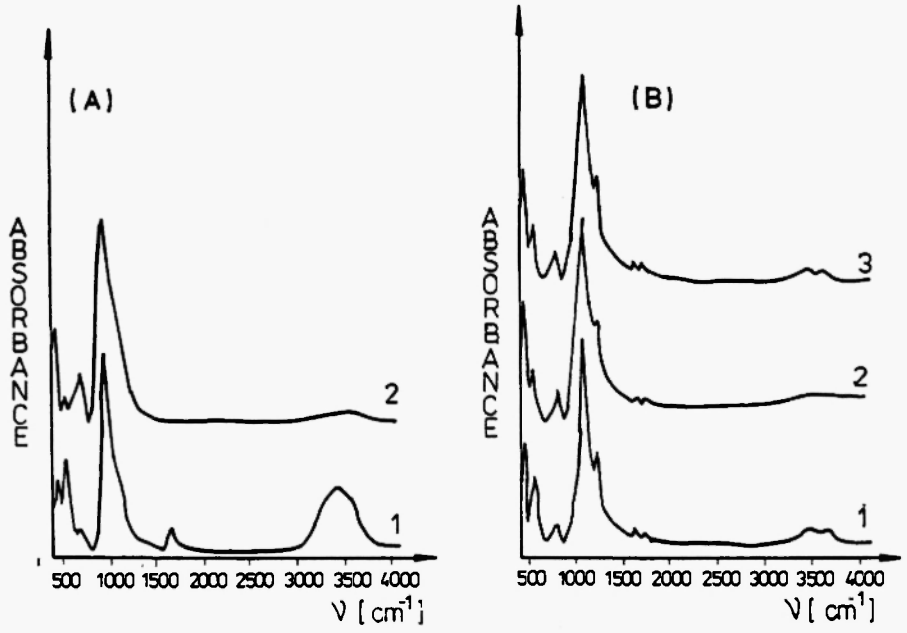


Fig. 8: IR spectra of zeolites:
(A) NaA zeolite: 1) crystals, 2) amorphous form
(B) ZSM-5 zeolite: 1) crystals, 2) and 3) reconstructed (890° and 950°C)

point, i.e. when it has the properties of a brittle body. These stresses are, among other things, the consequence of the disordered arrangement of elements forming the glass structure.

Relaxation of stresses in the structure at the glass transition temperature is coupled with a change in its properties as mentioned above. For glasses of simple chemical composition the transformation temperature is approximately equal to 2/3 of the melting temperature /27/.

As demonstrated by Suga *et al.* /28,29/, the phenomena of structure relaxation occur in some crystalline substances. They are also manifested by the anomaly of the curve of heat capacity as a function of temperature, which is reversible and depends on the thermal history of the substance in the same way as the transition of glass. Suga has termed the substances exhibiting this phenomenon "glassy crystals".

These are crystalline substances in which at elevated temperatures the molecules forming them show orientational disorder (orientationally disordered crystals). The disorder generally disappears discontinuously through a solid–solid phase transition to achieve a fully ordered state. There are certain crystals for which the remaining disorder is frozen which becomes the reason for the above phenomenon.

This transformation has been observed i.a. in $B(OH)_3$, (290K), in some hydrates and it may be attributed to the randomness of the proton arrangement. It is exhibited by $SnCl_2 \cdot 2H_2O$ (150K), hexagonal ice (105 K) and a number of organic compounds /29/.

The described phenomena occur at low temperatures and the anomalous change of the heat capacity is associated with the freezing of the orientational freedom or other relatively small displacements of the elements of the crystalline structure which as a whole exhibits a high degree of ordering. For this reason a change in the heat capacity accompanying the transition is very small and can be measured only by means of extremely sensitive calorimeters.

Suga's findings essentially modify our views on the glass transition phenomenon as a feature distinguishing glasses from other solid bodies. It has been visualised that a glass transition effect occurs in solid bodies, both in amorphous and crystalline ones, when a certain state of disordered structure has become frozen in.

Thermally amorphized borates show a reversible endothermic effect which corresponds to that of a glass transition (Fig. 9). The temperatures of this effect are listed in Table 4. They are higher for calcium borates (650°C) than for sodium borates (520°C).

Applying the 2/3 rule to the examined borates and calculating their transformation temperatures from their melting temperatures indicated by DTA curves, we will obtain temperature values very close to the measured ones. For calcium borates the calculated T_g value amounts to 640°C, and for sodium borates – 534°C. This may be interpreted as a confirmation of the hypothesis that the reversible endothermic effect of amorphous borates is produced by a heat change, that is induced by the glass transition effect. This effect has not been recorded on the DTA curve of ulexite, since at the temperature at which it should occur there is a crystallization of the amorphous matrix, which cancels the frozen randomness. In the case of kernite, the effect of glass transition coincides with the beginning of crystallization.

Unlike borates, the zeolites do not demonstrate the glass transition effect. Their melting temperature is so high that this effect should appear at 1020°C in the

Table 3
Phase transformations of zeolites

NaA zeolite	ZSM-5 zeolite
$NaAlSiO_4 \cdot 2{,}25H_2O$	$Na_{0,03}Al_{0,03}Si_{0,97}O_4 \cdot 0{,}3H_2O$
20°–600°C	20°–400°C
$NaAlSiO_4$ zeolite	$Na_{0,03}Al_{0,03}Si_{0,97}O_4$ zeolite
600°–800°C	840°C
$NaAlSiO_4$ zeolite → $NaAlSiO_4$ amorph.	$Na_{0,03}Al_{0,03}Si_{0,97}O_4$ zeolite → SiO_2 cristobalite
800°–860°C	1000°C
$NaAlSiO_4$ amorph.	SiO_2 cristobalite
860°–960°C	
$xSiO_2$ + $NaAlSi_{1-x}O_4$ cristobalite amorph. matrix	
960°C	
$NaAlSiO_4$ nepheline	

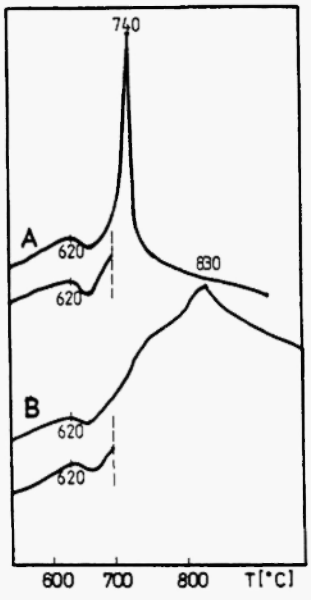


Fig. 9: DTA curve of (A) colemanite and (B) glass of colemanite composition

Table 4
Glass transition temperature (T_g) of amorphized borates

Mineral	Amorphous Substance	T_g	T_m
Colemanite	$Ca_2B_6O_{11}$	650°C	950°C
Pandermite	$Ca_4B_{10}O_{19}$	650°C	1100°C
Kaliborite	$KMg_2B_{12}O_{21}$	640°C	954°C
Ulexite	$NaB_{3,4}O_{3,7}(OH)_{3,8}$	-	854°C
Borax (tincalconite)	$Na_2B_4O_5(OH)_4$	520°C	755°C
Kernite	$Na_2B_4O_6(OH)_2$	520°C	735°C

case of NaA zeolite and at 1150°C in the case of ZSM-5 zeolite, i.e., when they have already undergone complete recrystallization.

The DTA curves for zeolites record small irreversible endothermic peaks or deflections at the temperature 810°C for NaA zeolite and at 820°C for ZSM-5 zeolite.

These transitions are accompanied by evident condensation of the structure, manifested by a change in microporosity or density. This fact allows us to assume that the considered effect is induced by collapse or reorganisation of the amorphous structure, which precedes the crystallization process. Collapse of zeolite structure causes an increase in its density above the small endothermic temperature (Fig. 6). It is worth pointing out that this rebuilt structure obtains a density proper for cristobalite structure (2,364 g/cm^3) before the beginning of the exothermic peak of its crystallization. In the case of crystallization processes occurring in the solid phase and consisting in the rearrangement of the primary structure, it may be assumed that the formation of a new crystal structure consists in fitting in the elements of the amorphous structure.

A similar endothermic effect, not definitely explained as yet, is demonstrated by the montmorillonite Cheto modification. This is a relatively intensive effect occurring at a temperature of about 840°C, when the residual OH groups are being removed. It precedes the crystallization of mullite and of spinel (exothermal DTA peak). This is an indication that the irreversible processes of the rearrangement of amorphous structures preceding crystallization are more frequent. They occur, most probably, when the structure of the amorphous phase is rigid and the release from stresses in the structure proceeds through its continuous rearrangement.

From the above data it follows that the occurrence of the so-called glass transition effect is not restricted to glasses. This alone cannot be regarded as an immanent feature of the glassy state. Randomness of structure is an indispensable parallel criterion. It appears in various types of amorphous substances as well as in crystalline ones when a certain state of disordered structure has been frozen in. Certain amorphous substances do not exhibit this effect, since in the given temperature range the amorphous structure is too rigid for stress relaxation to occur without disturbing it. In this case the disturbance of the amorphous structure induces crystallization.

As demonstrated here, it may also occur that further destruction of the amorphous structure takes place, but the crystallization process is slow and it attains a measurable rate at a higher temperature than this transition. It is marked by a small DTA peak, thus it is accompanied by a change of the molar heat or enthalpy. This is an irreversible transition contrary to the glass transition. Montmorillonite and zeolites examined here supply the appropriate examples.

In elastic structures, where the temperature increase brought about sufficient loosening of a part of the chemical bonds, a reversible relaxation transition, such as the glass transition, may take place. This is possible especially in glasses and amorphous substances of relatively low melting temperature.

Even so, the glass transition effect indicates that the amorphous solid obtained flexibility and uniformity of its structure corresponding to the glass.

F. Thermal Amorphized Solids and Glass Relation

A complete definition of glass which would characterize all types of glass known so far has not been formulated until now. Neither have the criteria indispensable for the formation of the glassy state been defined. Hence, a very general definition of glass formulated by the U.S. National Research Council /30/ is frequently used, according to which glass is an X-ray amorphous material exhibiting the glass transition effect.

The glass structure is usually described by a "random network" model, and considering the existence of microinhomogeneities in the glass structure resulting from the existence of the elements of medium-range order and/or non-uniform distribution of the components – the "random array" picture of glass structure is viewed as being more adequate. According to this model, in glass no unit of structure is repeated at regular intervals in three dimensions.

These models are derived from the traditional Zachariasen's model of silicate glass as a three-dimensional, continuous, but geometrically disordered

network in which part of the oxygen bridges combining the SiO_2 tetrahedra is broken by cations of uni- or bivalent metals (modifiers).

It is known now that besides glasses of polymeric homogeneous continuous network as mentioned above, one can distinguish glasses of a polymeric, continuous but inhomogeneous framework. Among these are glasses of mixed network, built of coordination polyhedra of various kinds (alumino-silicate, boro-silicate, alumino-silicate-phosphate glasses, etc.). The structure of a polymeric, discontinuous framework is made up of chains or rings of tetrahedra linked by surrounding cations (phosphate and borate glasses). A number of glasses have non-polymeric structure. Some of them are made up of oxides or halides with small interspersed islands of coordination polyhedra of other components.

The structural diversity of glasses known so far, in which different coordination polyhedra assemble and all kinds of chemical bonds are encountered, allows one to conclude that factors regarded so far as indispensable to the formation of the glassy state of matter have proved not to be essential or to play a limited role.

The following factors can be indicated as essential for glass formation /31/:

1. The glass structure must possess enough elasticity to enable its elements to occupy varying positions with respect to each other and to adjust each other to a degree sufficient to give their arrangement the character of a random array.
2. Agents must operate to stabilize the random arrangement and counteract their ordering. These are, among others, strong bonds in the polymeric structure or admixtures and inhomogeneities in non-polymeric glasses.

According to this glass is a solid body with a flexible random structure. The construction and uniformity of the structure depend on the chemical composition and the origin as well as the history of the glass (flexible framework model of glass /31/).

The criterion of the structure flexibility and the factors preventing ordering of the structure as indispensable to the existence of glasses and other inorganic amorphous substances comprise all the particular criteria which have so far been considered as indispensable for the existence of this state.

This refers, among other things, to Goldschmidt and Zachariasen's crystallochemical criterion of the necessary existence of a three-dimensional network built of tetrahedra or triangles joined with each other in the corners, which in fact is indispensable if the network is to be flexible. Of equal importance is Smekal's criterion of the necessary existence of mixed chemical bonds, i.e. the directed (covalent bonds) but also misoriented ones (ion and Van der Waals bonds), i.e. those that permit the necessary displacement of the structural elements. In Sun's criterion the requirement that the glass forming substances possess high bond energy (90 kcal/mole) corresponds to the strong spatial network in polymeric glasses as a factor inhibiting the ordering of the glass structure.

It follows from considerations presented here that the flexible structure as a characteristic feature of the glassy state and a criterion of its existence are valid also with reference to other amorphous bodies.

It may be assumed that all amorphous substances differ from each other in the degree of elasticity of their structure and its micro- and macrohomogeneity.

The amorphous borates discussed here are distinguished by the elasticity of their structure which is as high as that of glass, and accordingly they exhibit a glass transition effect similar to that of glass. Thus with respect to the structure they represent an equivalent of glass of polymeric structure, but of low polymerization degree (rings, chains), hence an inhomogeneous structure.

On account of the degree of randomness of structure and its homogeneity, their state may be defined as a glassy one. They differ from glasses in the lack of uniformity, being microporous, whereas glasses should be uniform. However, by means of a sufficiently long thermal treatment, above the transformation temperature, they may be transformed into a homogeneous body.

On the other hand, layered silicates in an amorphous state exhibit a structure with a high degree of inhomogeneity manifested by the preservation of large elements of their primary layered structure. Thus the long-range ordering becomes retained to a great extent. This structure is not elastic enough for stress relaxation in the form of glass transition to occur prior to crystallization. Stresses may induce, on the other

hand, further destruction of the primary structure, which is an irreversible process preceding crystallization. Zeolites examined here behave in a similar way. Amorphized NaA zeolite structure resembles the mixed network alumino-silicate glass.

As we can see, the elasticity of structure is a criterion determining the properties and behaviour of many amorphous substances at different temperatures. The structural similarity between the given amorphous substance and glass of the same composition exists according to this feature.

6. FINAL REMARKS

Many crystalline substances, the inorganic polymers in particular, can be directly converted into the amorphous state by way of heat treatment. Some of them will retain the amorphous state within a temperature interval long enough for the phenomenon of thermal amorphization in a solid state to find practical application in the production of new materials.

At high temperatures these substances undergo recrystallization which often proceeds in several stages. It occurs through rearrangement of the amorphous structure and next through reconstitution of the successive metastable intermediate crystalline phases. Some of these stages are accompanied by an exchange of chemical compositions between the coexisting phases.

The amorphous state formation by thermal decomposition of a crystalline precursor represents one of the many stages of changes on the way from the state specific to the precursor substance at low temperatures to a state characteristic of it at high temperatures. This process is realized through permanent reconstruction of the internal structure.

The amorphous structures formed through thermal decomposition of solid bodies preserve to a greater or smaller extent the medium-range ordering inherited from the structure of the primary substance. This affects their properties as well as their thermal stability and changes which occur in these structures at higher temperatures.

Similarly to the glassy state, the amorphous state may come into existence when its structure exhibits sufficiently high elasticity, indispensable for the randomly oriented components to fit each other.

Some of the amorphous substances reach the state of structural elasticity which permits relaxation of the internal stresses induced by the state of randomness below their crystallization temperature. This is manifested as the effect of glass transition. The temperature of this effect equals about 2/3 of the melting temperature of these substances, similarly to glasses. This means that as regards the state of their structure they have the nature of glass. They differ occasionally from glasses in their microporosity which is a remainder of these gaseous components removed during decomposition. The porosity disappears quickly near the temperature of glass transition. Vitreous substances of this kind are formed as a result of thermal amorphization of borates. Some data suggest that they may be formed also by phosphates. This is an instance of the formation of a glassy state from a crystalline one by way of internal structure rearrangement of the order-disorder type under the influence of thermal vibrations.

Perspectives exist to utilize this process for the production of glassy materials including those of mixed network, as well as non-polymeric glasses such as the halide-oxide ones. Through appropriate crystallization it is also possible to obtain from them materials with different ratios between the crystalline phase and the glassy matrix. The number of possible variants of this type of materials seems to be very high.

Another type of amorphous substance is formed as a result of thermal amorphization of aluminosilicates. These substances are formed due to a certain elasticity of the aluminosilicate structure which results, on the one hand, from the possibility of the relation and a change of the angle between the tetrahedra in their framework, and, on the other hand, from the possibility that aluminium will form various coordination polyhedra (Al coordination number with respect to oxygen may be 4, 5 and 6). Magnesium does not exhibit such a property, and, consequently, magnesium silicates do not form amorphous intermediate structures.

The elasticity of their structure, however, is not high enough, and the stresses induced by the state of randomness are canceled through crystallization connected with segregation of the components. This

process takes place at a temperature considerably lower than the temperature at which the glass transition effect would appear. The structures of this group of substances preserve to a great extent fragments of the primary structure. This stabilizes the amorphous state but, at the same time, makes the structure more rigid.

In spite of distinct differences in structure and behaviour with increasing temperature, the groups of amorphous substances have many features in common.

One of them is the presence of the OH groups (about 10% of their initial number) performing the role of a factor that stabilizes the amorphous state.

Another phenomenon common to both groups of substances is the segregation of the chemical substances, accompanying crystallization, the effect of which is the formation of amorphous matrix in which the first crystallization stages take place. The structural mechanism of this crystallization changes in the same way with increasing temperature. It is manifested by an increasing number of components participating in the diffusive displacements at long distances, leading to a transition from diffusionless to diffusive transformations.

The phenomena and regularities described here appear to have a sufficiently general character to include vitrification and, subsequently, crystallization of xerogels formed in the sol-gel method. This suggestion will be the subject of examination in further studies.

REFERENCES

1. M. Handke and W. Mozgawa, *Ceramics*, Papers of the Commission on Ceramic Science, Polish Academy of Science, Cracow, 42, 49 (1993).
2. L. Stoch and I. Waclawska, *J. Thermal Anal.*, **40** (1993) in press.
3. I. Waclawska, L. Stoch, J. Paulik and F. Paulik, *Thermochim. Acta*, **126**, 307 (1988).
4. L. Stoch and I. Waclawska, *Thermochim. Acta*, **215**, 255 (1993).
5. L. Stoch and I. Waclawska, *Thermochim. Acta*, **215**, 265 (1993).
6. L. Stoch and I. Waclawska, *J. Thermal Anal.*, **36**, 2045 (1990).
7. I. Waclawska, *J. Thermal Anal.*, in press.
8. P. Medda, A. Musinn, G. Paschins and G. Piccaluga, *J. of Non-Cryst. Solids*, **150**, 76 (1992).
9. M.J. Buerger, *Fortschr. Mineral.*, 29, 9 (1961).
10. H.E. Patch, K.S. Pennington and J.D. Cuthbert, *Amer. Min.*, 47 (1962).
11. G.W. Brindlay and J. Lamaitre, in: *Chemistry, Clays and Clay Minerals*, A.C.D. Newman (ed.), Mineralogical Soc. Monograph, London, p. 319 (1987).
12. K.J.D. MacKenzie, I.W.M. Brown, R.H. Meinhold and M.E. Bowden, *J. Amer. Ceram. Soc.*, **68**, 293 (1985).
13. L. Stoch, *Thermochim. Acta*, **203**, 259 (1992).
14. K.J.D. MacKenzie, I.W.M. Brown, R.H. Meinhold and M.E. Bowden, *J. Amer. Ceram. Soc.*, **68**, 266 (1985).
15. K.J. MacKenzie, I.W.M. Brown, C.M. Cardis and R.H. Meinhold, *J. Mat. Sci.*, **22**, 2645 (1987).
16. W.M. Brown, K.J.D. MacKenzie and R.H.J. Meinhold, *J. Mat. Sci.*, **22**, 3265 (1987).
17. L. Stoch, *J. Thermal Anal.*, **37**, 1415 (1991).
18. F. Freund, *Proc. 1972 Int. Clay Conference*, Pergamon Press, London, 13 (1973).
19. L. Stoch, *J. Thermal Anal.*, **40**, 107 (1993).
20. S.M. Salman and S.N. Salmana, *Ceramic Int.*, **12**, 221 (1986).
21. Z. Strnad, *Glass-Ceramic Materials*, Elsevier, Amsterdam (1989).
22. A. Marotta, P. Pernice, A. Aronne and M. Catauro, *J. Thermal Anal.*, **40**, 181 (1993).
23. A.H. Babeck and R. Brückner, in: *Fundamentals of Glass Science and Technology, Proceedings of the Second Conference of the European Society of Glass and Technology*, Stazione Sperimentale del Vetro (publisher), Venice, Italy, 1993, p. 169.
24. A.B. Thompson and E.H. Perkins, in: *Thermodynamics in Minerals and Melts*, R.C. Newton, A. Navrotsky and B.J. Wood (eds.), Springer Verlag, New York, Heidelberg, Paris, 57 (1977).
25. I. Prigogine and R. Defay, *Chemical Thermodynamics*, Longmans Green and Co., London (1954).
26. J. Zarzycki, *Glass and Vitreous State*, Pergamon Press, Oxford (1991).

27. S. Sakka and J.D. MacKenzie, *J. Non-Crystalline Solids,* **6**, 145 (1971).
28. M. Oguni, T. Matuso, H. Suga and S. Seki, *Bull. Chem. Soc. Jpn.,* **50**, 825 (1977).
29. H. Suga, *J. Chem. Thermodynamics,* **25**, 463 (1993).
30. J. Wong and C.A. Angell, *Glass Structure by Spectroscopy,* Dekker, New York (1976).
31. L. Stoch, *High Temp. Materials and Processes,* **10**, 245 (1992).