

CHEMICAL COMPONENT EXCHANGE AND TRANSPORT PHENOMENA ACCOMPANYING PHASE TRANSFORMATIONS IN MINERALS AND MATERIALS

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Abstract

Chemical component exchange and transport phenomena accompanying the multistage phase transformations of several silicate and aluminosilicate-phosphate glasses and borates as model systems are considered. It is demonstrated that the component transport limitations modify the role of chemical affinity influence and determine the sequence of new compound formation.

Keywords: aluminosilicate-phosphate glass, borates, mass transport, multistage crystallization, phase transformations, silicate glass

Introduction

Solid medium processes

The creation of a new mineral by rebuilding of the internal structure of an earlier existing mineral precursor is a common natural process in the Earth's crust. In this way, crystalline solids accommodate themselves to changes in pressure, temperature or the surrounding composition. Rebuilding of the internal structure takes place continuously during the firing of ceramic bodies or the processing of glass-ceramic materials.

Polymorphic transformations are examples of internal structure rebuilding processes which do not involve change in the chemical composition of the final product. However, many internal structure rebuilding processes are accompanied by chemical component reassembly. New phases with different structures and/or chemical compositions then appear inside the primary mineral. The well-known process of the formation of (Si, Al)-spinel and later mullite and cristobalite formation during kaolinite firing is an example. They are accompanied by the exchange of chemical components between crystallizing phases and amorphous matrix.

Many of these processes have the character of chemical reactions, similar to the reactions in liquids, but proceeding within the rigid structure of the parent mineral, as the reaction medium. The chemical components of the primary mineral structure are the reaction substrates, and solid products are formed within the mineral precursor grain. The term intrinsic or internal reactions has been proposed for this kind of processes [1].

Examples of intrinsic reactions include the transformation of layer silicates at ambient and elevated temperatures, the crystallization of glasses and gels, and the thermal dehydroxylation and recrystallization of silicates, borates and phosphates.

The formation of a new mineral via parent mineral rebuilding is classified in mineralogy as a mineral transformation process. In material science, the term phase transition is used. When a close relationship exists between the crystal structures of precursor and product (structural inheritance), the term topotactic reaction is used. Processes with the same structural mechanism proceed in inorganic materials. The specificity of a solid body structure as reaction medium means that the functional relationships developed for reactions in ideal gases are of limited application to solids. The use of the Arrhenius equation to describe the kinetics of thermal dissociation of solids is an example. On the other hand, this exponential equation may be successfully used for transportation processes of individual ions or atoms (diffusion) or electric charge transfer (electrical conductivity of solids) in a uniform solid medium free of phase boundaries. Such mechanisms seem to display many similarities to those of reactions in a homogeneous system. In the case of reactions connected with the creation of phase boundaries, the use of Arrhenius kinetic parameters as indicators of the mechanism of the process has no merit.

Component transport phenomena

The specific features of the structure of a solid as reaction medium determine the peculiarities of internal structure rebuilding processes [2]. In solids, the atoms are firmly localized and occupy definite positions in the structure. In solid-state reactions, only those components may participate which at the given temperature possess sufficient freedom of displacement; this is expressed, among others, by their diffusion coefficient. The displacement freedom of the components of the given substance increases with temperature to various degrees. For this reason, some of them reach the displacement freedom earlier than the others, which allows them to take part in chemical reactions and to form a new phase, while the others, at the same temperature, behave as a neutral matrix [3].

This means that many internal structure rebuilding processes often exhibit a multistage course. The thermodynamic stable state of the system is then obtained by step-by-step rebuilding of the internal structure and intermediate, metastable phase formation. This is one of the peculiarities of these processes. Due to this, the transport of the components is the main factor determining the order and mechanism of new phase formation.

At low temperatures, when the possibility of the rearrangement of this structural elements is limited, those phases are formed most easily whose chemical composition and/or structure are closest to the structure of the parent phase or particular elements and domains in this structure.

Accordingly, mass transport is a factor exerting a considerable influence on the course of internal reactions, and modifying the decisive role of the thermodynamic factor, expressed by the tendency to obtain a minimum free enthalpy (ΔG) value and the law of mass action as the agent selecting the most probable process.

Study of the diffusion of components in glass [4] indicates that, in the low and intermediate temperature ranges, the most mobile components are cations, particu-

larly alkali metals and proton. They can be transported relatively easily for long distances by the simple diffusion process of individual atoms and substitute other cations at their sites in the oxygen anion skeleton.

In spite of this, the oxygen anion skeleton is a stable structure, especially in the polymeric structure of silicates, phosphates and borates, containing a number of oxygens bridging individual tetrahedra. Rebuilding of the oxygen anion sublattice requires appreciable energy to break some of the chemical bonds, and convert the given oxygen atom assembly into a new one. However, small changes in the distribution of the oxygen polyhedra are easy and possible without their links being broken, due to the flexibility of the oxygen bridging bonds. In spite of this, in molten silicates, where the silicate skeleton is depolymerized, oxygen is one of the most mobile components.

To explain the role of component transport in internal structure rebuilding processes, we have undertaken studies of the multistage phase transformations in model systems. Multicomponent glasses and thermally amorphized borate minerals were used as models. These materials possess high reactivity, and the chemical composition of the glass can easily be changed. The latest results of these investigations and some generalizing comments are presented in this paper.

Experimental

A temperature gradient furnace was used for the crystallization of glass in a bulk study. Pieces of glass were heated for 2 to 24 h and their crystallization was studied as a temperature-dependent process.

Samples were investigated by XRD, optical microscopy and SEM. The distribution of the chemical components in the crystallized glass was examined by means of EDX. Crystallization of powdered glass (0.1–0.3 mm fraction) was studied by DTA and DSC (Perkin-Elmer DTA-7 apparatus). FTIR (Digilab equipment) was used for glass structure control.

The procedure for the preparation of the amorphous borates and the methods of their study were described earlier [4].

Results and discussion

Component transport in crystallizing glass

The crystallization of multicomponent glass often starts with the formation of a crystal phase whose chemical composition and structure are close to those of the parent glass. In glasses in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems, the first crystallizing phase is often a quartz-like solid solution of chemical composition similar to the parent glass composition. At higher temperatures, its structure is rebuilt, with the formation of crystal phases whose chemical compositions are increasingly closer to those of the stable thermodynamic phases (spodumene or cordierite).

Our investigations of glasses from the K_2O (10 wt%) – CaO (20 wt%) – MgO x – SiO_2 y – P_2O_5 (15–20 wt%) system in a powdered form (surface nucleated crys-

tallization) revealed that these glasses start to crystallize above the glass transition temperature (T_g) and Ca phosphate (apatite) is formed first. Forsterite (Mg_2SiO_4) crystallized next. After that, kaliophilite ($KAlSiO_4$) crystallizes in the remaining glassy matrix.

Bulk, homogeneous crystallization experiments involving the 24 h heating of glass rods in a temperature gradient furnace indicated that the crystallization of glasses in the Na_2O (10 mol%) – MgO (20 mol%) – $AlPO_4$ – SiO_2 system is a specific process. It starts near the glass transition temperature (T_g) and aggregates of small, rounded grains of $AlPO_4$ – cristobalite modification are formed. At a slightly higher temperature, needles of $Mg_3(PO_4)_2$ crystallize, together with $AlPO_4$. Above the glass softening temperature, only well-shaped dendrites of $AlPO_4$ appear.

The crystallization of glass containing more Al_2O_3 than corresponds to the formula $AlPO_4$ takes a different course. Corundum and $Mg_3(PO_4)_2$ crystallize as the main phases. Corundum has the form of thin, fibrous, curved crystals. Above the softening temperature, lath-like and platy corundum crystallize.

The nature of the crystallizing phases formed in the course of glass heating in this system indicates that the chemical affinity of phosphorus pentoxide for magnesium oxide is higher than that for aluminium oxide. This is manifested by the formation of $Mg_3(PO_4)_2$ in all glasses and corundum as the main crystal phase in glass with a reduced P_2O_5 content. It is also indicated by thermodynamic calculations. The ΔG value of $AlPO_4$ formation from the oxides is $-72.8 \text{ kcal mol}^{-1}$, where ΔG for the reaction of magnesium phosphate formation is $-117.74 \text{ kcal mol}^{-1}$. This means that chemical affinity is not the deciding factor here. The formation of $AlPO_4$ in the glass with $Al_2O_3:P_2O_5$ close to 1:1 is presumably determined by a structural factor: the structural similarity of silica and aluminium phosphate.

Chemical component exchange in internal processes

Compounds crystallizing at the beginning of the internal synthesis process exchange chemical components with the surrounding matrix as the temperature is increased, and compounds with new compositions appear. Exchange of components between crystallizing phases and subsequent compound formation are also observed (crystallization of quartz-like solid solutions, indialite and cordierite).

Our earlier studies [4] revealed the existence of internal reaction series in the Ca, Mg and alkali metal borates. We have now confirmed that, during their heating, their reconstruction takes place, which results first in the formation of Ca or Mg borate in an amorphous matrix of alkali metal borates. At higher temperature, reactions of component exchange between the matrix and the crystalline borate formed earlier, occur. Complex borates containing Ca or Mg and alkali metals, corresponding to the chemical composition of the parent mineral, are then formed. They can be models of component exchange processes. The mineral ulexite in its dehydrated form is an amorphous, glass-like substance. At higher temperatures, calcium borates (CaB_2O_4 and $Ca_4B_2O_5$) crystallize into it. Next, NaB_3O_5 crystallizes. Later, the calcium borates exchange components with the amorphous matrix, and $NaCaBO_3$ (as final equilibrium phase) plus B_2O_3 are formed.

A similar sequence of reactions is observed when kaliborite (K, Mg borate) is heated. Magnesium borates are first formed, and next KB_5O_8 crystallizes in the B_2O_3 matrix.

These examples indicate that the sequence of formation of new phases is dependent to a considerable degree on the position of the components in the primary structure and the strengths of their chemical bonds. As the mobility of the components increases, their exchange between earlier formed phases becomes possible, and finally compounds corresponding to the composition of the equilibrium phase crystallize.

Polymorphic transformations as a model of internal structural element reassembly

The structural element rearrangement accompanying polymorphic transformations of minerals can be taken as a model of mass transport phenomena which determine the progress of reactions in a solid body medium.

Depending on the mechanism of structural element displacement and rearrangement, the following types of polymorphic transformations can be distinguished:

I. Diffusional long-distance rearrangements: a. connected with the displacement of coordination polyhedra over long distances and/or anion sublattice rebuilding, including a) change in the first coordination sphere – reconstructive transformations; b) redistribution of isomorphic substitutions by the migration of cations and exchange of their positions in the anion sublattice – substitutional, disorder–order transformations.

II. Diffusionless transformations: by displacement for a short distance or by rotation of atoms or their assemblages – displacive transformations.

The long-distance rearrangement of structural elements is characteristic in slow, reconstructive polymorphic transformations connected with the deep rebuilding of structure and the far-range redistribution of the coordination polyhedra (SiO_4 tetrahedra displacement during the high-quartz–high-cristobalite transition or the anatase–rutile transition, $\text{Al}_2\text{Si}_2\text{O}_5$ polymorphism connected with a change in the coordination number of Al. Most of these belong in the transformations of order I in Ehrenfest's thermodynamic classification [5].

The disorder–order change of distribution of Al in plagioclase and K – feldspars, or Mg and Fe isomorphic substitutions in pyroxenes and amphiboles, are examples of substitutional transformation by long-distance cation redistribution.

Diffusionless mechanism is typical for rapidly progressing, displacive polymorphic transformations according to Buerger's classification. This is the mechanism of martensitic transformations of metals and alloys [6]. The transformations tetragonal–monoclinic ZrO_2 , and low-quartz–high-quartz or low–high cristobalite are examples. They belong among the order II or higher order transitions.

The mechanisms described above can not occur in the pure form. In oxide systems, the sublattice formed by the less mobile oxygen anions can undergo a minor correlated redistribution, as in diffusionless process, whereas the mobile cations are displaced for longer distances to occupy new sites by diffusion.

For many substances, the changes in several extensive properties as a function of the intensive thermodynamic parameters of state (pressure and temperature) accompanying the phase transition are as for processes of order I, whereas others are as for processes of order II ('mixed order process' [5]). This may indicate that they belong among mixed, diffusionless-diffusional processes and the shape of the characteristic thermodynamic function depends on the contributions of the diffusional and diffusionless displacements in the whole process.

The principle of the unity of the phenomena allows the postulation that mass transport mechanisms similar to those described above are operating, when internal chemical reaction or other structure rebuilding processes occur in the solid medium.

The formation of structure similar to the parent structures is possible by small rearrangements in the anion network, similar to those which occur in the displacive polymorphic transformations or martensitic transitions. The formation of other intermediate phases requires a more complex mechanism, when a change in the anion network has a diffusionless character, but the mobile cations are displaced in a diffusional mode. This is an analogy to the disorder-order transformations.

In parallel with a temperature increase and the increasing mobility of the primary structure components, the proportion of diffusive displacements may increase, with a corresponding change in the compositions of the new compounds formed.

At the diffusional stage of the process, when all the chemical components have sufficient mobility, the formation of new compounds is determined by their chemical affinities. Accordingly, the compounds corresponding to the thermodynamic equilibrium state of the system are formed at that stage. In the low-temperature stage of internal structure rebuilding, due to the selectively limited mobility of the components, the action of chemical affinity as a factor determining the course of the reaction is strongly modified by the mobilities of the components.

Phase transitions in glass can be regarded as solid-state processes, if they take place below the glass transition temperature (T_g) and the glass is a rigid body. This can be extended, with some limitations, to the range of the higher temperature in which the glass preserves its visco-elastic properties, which indicates that its network is not very disturbed.

Depending on the glass structure state and the displacement of atoms and the freedom of their assemblages, different structural mechanisms of glass crystallization can be considered.

At low temperature, diffusionless (anion sublattice) and diffusional (cations) transformation are possible: diffusionless-diffusional mechanism. Component transport and exchange is then limited and phases whose chemical composition and structure are close to those of the parent glass are formed (crystallization of quartz-like solid solutions in silicate glasses). This mechanism ensures the coherence of the interface of the crystal nucleus and the surrounding glass, at least in the initial stage of its formation. This permits low-temperature crystallization.

Near the softening temperature, the diffusional mechanism is operating and the liquid crystallization rules are valid.

In the low-temperature stage of the phase transformations, the selectively limited mobilities of the components lead to the rate of reactant transportation becoming a governing factor. In the stage of the diffusional mechanism of the process, in consequence of the sufficient mobility of all components, the formation of new compounds is determined by the chemical affinities of the reactants.

The change in AlPO_4 and corundum morphology during the crystallization of the glasses described above suggests a change in the crystallization micromechanism, due to the increasing mobilities of the components with temperature increase. Free diffusion favours well-shaped crystals; small, rounded grains result from short-distance rearrangements. In the molten glass, the primary network is broken into small pieces, which are mobile. This makes possible the formation of coarse, well-shaped crystals by a simple diffusional mechanism. Near the glass transition temperature, crystallization is probably achieved by the rearrangement of the nearest parts of the glass network, the exchange of Si, Al, and P atoms occupying tetrahedral positions in the network and the diffusional redistribution of cation modifiers (diffusionless-diffusional process). Preserved pieces of the parent glass network hamper perfect crystal growth and curved fibres of corundum are formed.

Thermoanalytical response

The micromechanism of the phase transitions should be reflected in the DTA peak shape and/or temperature.

The crystallization of (Al, Si) spinel in metakaolinite, which can be regarded as a diffusionless process, is rapid and gives a very sharp exothermic DTA peak. A peak of the same shape is afforded by the crystallization of thermally amorphized

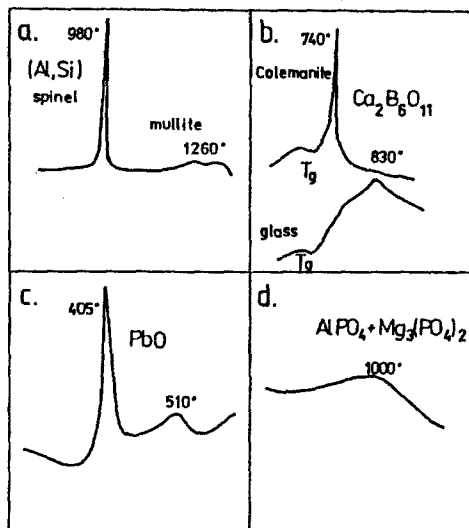


Fig. 1 DTA curves of amorphous materials crystallization: a. metakaolinite, b. colemanite, c. glass of non-polymeric structure PbO 90 mol%, SiO_2 10 mol%, d. polymeric structure glass $8\text{Na}_2\text{O}\cdot 20\text{MgO}\cdot 21\text{Al}_2\text{O}_3\cdot 18\text{P}_2\text{O}_5\cdot 33\text{SiO}_2$ (mol %)

Ca borates (colemanite, pandermite) or even the mineral borax [5]. When they are recrystallizing, the new crystal phase is formed in their structure by redistribution of the preserved elements of the parent mineral structure (middle-range ordering). This makes a diffusionless–diffusional mechanism possible. However, glasses with the composition of colemanite, pandermite or borax, but obtained by cooling of the melt, crystallize at higher temperature and the process is much more diffuse [7, 8]. The kinetic parameters of the process, calculated from the DTA data, are also quite different. This points to diffusion as a dominating factor, as in high-temperature mullite crystallization (Fig. 1). The change in mechanism is demonstrated by the change in DTA peak shape. The kinetic parameters are also different. The E value of colemanite crystallization, determined by the Kissinger procedure, is higher (593 kJ mol^{-1}) than that for the glass of colemanite composition (393 kJ mol^{-1}), but the peak temperature is lower [9]. This means that a lack of middle-range ordering changes the crystallization mechanism.

The crystallization of non-polymeric glasses is usually fast, as it involves only a simple reconstruction of the structure. It gives a sharp DTA peak. A PbO-rich (90 mol% PbO and 10 mol% SiO_2) glass is an example (Fig. 1).

This demonstrates the significance of structural factors in the initial stage of phase transitions in multicomponent substances.

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The work was supported by grant P040703406 from the National Committee of Scientific Research of Poland.

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