

THERMAL REACTIONS OF SOLID-STATE AMORPHIZED BORATES AND BORATE GLASSES

A comparative study

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Abstract

The properties and course of phase transition of amorphous borates obtained by solid-state thermal and mechanical treatment of hydrated borates and melt quenched glasses with the compositions of these borates were studied. Processes of structural relaxation and crystallization were considered.

It was found that different methods of preparation of amorphous borates and the differences in their structural ordering resulting from these methods affect the rate and the mechanism of transformations occurring during their heating.

Keywords: crystallization, glass transition, solid-state amorphization

Introduction

In consequence of their unconventional properties, glasses and other amorphous materials are finding increasing application and the study of these materials has become an important branch of science. The results of these studies justify investigations of the relation between the glasses and other amorphous materials, the properties of these materials and methods for their synthesis.

The traditional method of obtaining glasses consists in quenching a melt, but they may also be obtained by deposition from a vacuum system. Another way of obtaining noncrystalline materials is based on the possibility of forming a network of glass at low temperatures by reactions in solutions of suitable compounds (sol-gel method).

There has recently been increased interest in the solid-state crystalline to amorphous transformation process [1]. The formation of an amorphous substance by a solid-state amorphization reaction occurs through destruction of a crystalline structure under the influence of energy supplied from the outside in various forms, such as heat treatment (below the melting temperature), mechanical treatment or radiation.

Depending on the mode of formation of amorphous substances and their chemical compositions, the degree of randomness of the internal structure of a solid body may vary. It may be manifested by preserved middle-range structure order of thermally amorphized inorganic polymers. In some amorphous substances, there oc-

curs only short-range ordering, limited to the particular coordination polyhedra. Glasses of simple composition obtained by the traditional melting method are examples of this.

During the heating of amorphous materials, phase transitions of glass transition type and phase segregation in a vitreous matrix (phase separation and/or crystallization) take place. The state of randomness may change the nature of the interatomic reactions, and this affects the chemical and structural transformations occurring in the amorphous substance.

The aim of the present studies was to investigate the properties and course of transformations occurring in amorphous solids obtained by solid-state thermal and mechanical treatment and traditional melting of oxide mixtures. The model substances selected for the examinations were hydrated borates with low melting temperatures.

Experimental

Coarse, crystalline borate minerals from the collection of the Mineralogical Museum at Wrocław University were examined. They were: colemanite – $\text{Ca}_2\text{B}_6\text{O}_8(\text{OH})_6 \cdot 2\text{H}_2\text{O}$, pandermite – $\text{Ca}_2\text{B}_5\text{O}_8(\text{OH})_3 \cdot 2\text{H}_2\text{O}$, kaliborite – $\text{HKMg}_2\text{B}_{12}\text{O}_{16}(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$, borax – $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$, and kernite – $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$.

The amorphous materials were obtained by the thermal decomposition of these minerals (thermal amorphization). Dry grinding of the chosen mineral was carried out in a laboratory vibration mill (mechanical treatment). Borate glasses of the compositions corresponding to the chemical compositions of the borate minerals in their anhydrous form were obtained by conventional melting of the respective oxides in platinum crucibles at about 1000°C.

The amorphous state of the materials and the structural changes during their heating were followed by X-ray diffraction, FTIR spectroscopy and thermal examinations. The course of phase transitions in amorphous materials was studied by using the Perkin-Elmer DTA-7 system operating in heat flux DSC mode. Samples of 50 mg in platinum crucibles in dry nitrogen atmosphere were heated and cooled at a rate ranging from 1.0 to 25 K min⁻¹. The activation energy of the crystallization process was determined by using Kissinger's relation based upon measurement of peak temperatures at different heating rates.

Results and discussion

Solid-state amorphous phase formation in borates

During heat treatment, the hydrated borates undergo dehydration and dehydroxylation (Fig. 1) and the products of these processes are amorphous. The ability to undergo thermal amorphization depends on the chemical composition and primary structure of the borates.

The thermal decomposition of chain borate-colemanite $\text{Ca}_2\text{B}_6\text{O}_8(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ proceeds in two stages up to 400°C. This process is accompanied by gradual destruction of the primary structure of the borate [2].

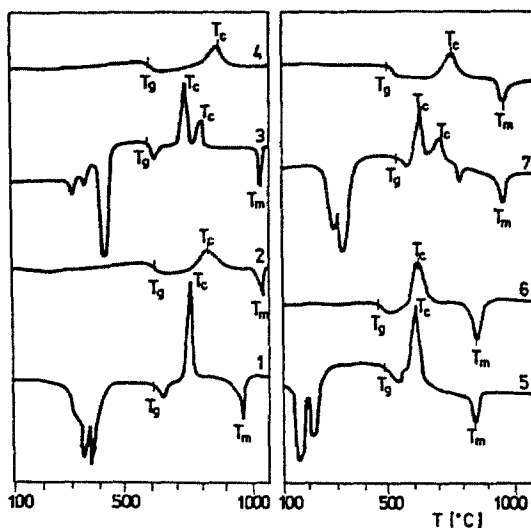


Fig. 1 DTA curves of 1 - colemanite, 2 - $2\text{CaO}\cdot 3\text{B}_2\text{O}_3$ glass, 3 - pandermite, 4 - $4\text{CaO}\cdot 5\text{B}_2\text{O}_3$ glass, 5 - kernite, 6 - $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ glass, 7 - kaliborite, 8 - $\text{K}_2\text{O}\cdot 2\text{MgO}\cdot 6\text{B}_2\text{O}_3$ glass

The two-stage dehydration and dehydroxylation of layer borate-pandermite $\text{Ca}_2\text{B}_5\text{O}_8(\text{OH})_3\cdot 2\text{H}_2\text{O}$ results in the formation of an X-ray amorphous substance at about 580°C [3].

The thermal decomposition of chain borate-kaliborite $\text{HKMg}_2\text{B}_{12}\text{O}_{16}(\text{OH})_{10}\cdot 4\text{H}_2\text{O}$ proceeds up to 400°C . As a result of the dehydration and dehydroxylation process, the borate chains of kaliborite structure are destroyed [4].

A solid product of dehydration (200°C) of the island structure borate-borax $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4\cdot 8\text{H}_2\text{O}$ is the amorphous matrix containing OH groups, which are gradually removed up to about 500°C [5].

The amorphous form of chain borate-kernite $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2\cdot 3\text{H}_2\text{O}$ exists only at 300°C and contains OH groups which are removed up to about 500°C .

The amorphous structures formed through thermal decomposition of the borates preserve some kind of middle-range structure order, inherited from the structure of the primary borate [6].

The mechanical treatment of hydrated borates causes solid-state amorphization of these minerals, manifested by the disappearance of long-range ordering, characteristic of crystalline structures. With increasing grinding time for colemanite, the thermal bonds linking the water molecules with the borate structure diminish and finally disappear. Accordingly, the decreasing value of the dehydration enthalpy can be a quantitative measure of the degree of colemanite amorphization [7].

It follows that amorphous phase formation by thermal decomposition and by mechanical treatment of crystalline borates is a process accompanied by a change in composition of the precursor substance. Amorphous borate appears as a result of the breaking of bonds in the precursor structure.

Structure reconstitution processes of solid-state amorphized borates and borate glasses

Structural relaxation phenomenon

Structural relaxation, which is responsible for the glass transition, is a consequence of the disordered arrangement of elements in the glass structure. Since liquid-like degrees of freedom are involved in the structural relaxation process, the glass transition region may also be thought of as the temperature range above which an amorphous material assumes viscoelastic properties and below which it behaves as a rigid solid. The location of the glass transition region is specified in terms of the glass transition temperature T_g , which is 'the approximate midpoint of the temperature range over which the glass transition takes place' (ASTM D 4092 terminology relating to Thermophysical Properties).

In the DSC curves of thermally amorphized borates and glasses of corresponding chemical composition, the glass transition effect is well visible (Fig. 1); it is reversible. The values of characteristic parameters for the transformation range, measured from DSC heating curves at a rate of $10^\circ\text{C min}^{-1}$, after prior cooling at the same rate through the glass transition, are shown in Table 1. They are T_1 and T_2 , identified as the intersections of the tangent at T_g with the extrapolated glass and liquid heat capacities, the temperature of half-vitrification T_g and step-like changes in specific heat Δc_p (Fig. 2).

Table 1 Thermal data of the glass transition of thermal amorphized borates and glasses

	$T_1/$	$T_2/$	$\Delta T = T_2 - T_1/$	$T_g/$	$\Delta c_p/$	$\Delta H/$
	°C				$\text{kJ mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	kJ mol^{-1}
Amorphous colemanite	644	664	20	659	0.19	1.66
2CaO·3B ₂ O ₃ glass	643	670	27	654	0.51	–
Amorphous pandermite	649	659	10	656	0.19	5.36
4CaO·5B ₂ O ₃ glass	638	658	20	650	0.92	–
Amorphous kaliborite	545	564	19	560	0.07	1.86
K ₂ O·2MgO·6B ₂ O ₃ glass	496	532	36	527	0.34	–
Amorphous borax	403	425	22	422	0.06	1.15
Na ₂ O·2B ₂ O ₃ glass	457	472	15	464	0.16	–

For thermally amorphized borates, the glass transition is accompanied by a certain value of enthalpy ΔH which does not disappear on reheating.

The presented data indicate that the characteristic temperatures for the transformation range of thermally amorphized borates are higher than the temperatures of the respective points for glasses obtained by melting and cooling of the melt. The structural relaxation of amorphous borates and glasses of the same compositions is accompanied by changes in specific heat Δc_p , the values of which are somewhat smaller for amorphous borates obtained by thermal decomposition of crystalline substances as compared with the respective borate glasses.

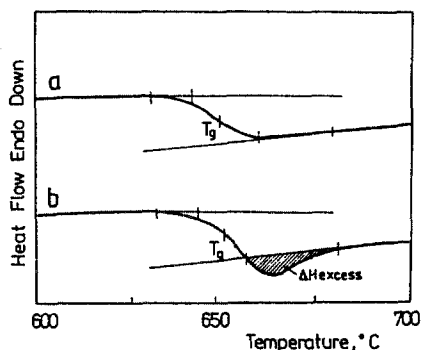


Fig. 2 DSC curve of structural relaxation of: a) $2\text{CaO}\cdot 3\text{B}_2\text{O}_3$ glass, b) colemanite

The structure of melted glasses is homogeneous, whereas the amorphous structures of borates formed by the thermal decomposition of crystalline forms preserve elements of the primary structure. This may be the reason why a substance whose structure contains larger elements requires a higher temperature to attain the viscosity specific for the glass transition. Less wide glass intervals ΔT and smaller changes in the specific heat accompanying the glass transition in amorphous borates as compared with glasses of the same compositions may indicate that the degree of structural rearrangement in amorphous borates is smaller than that which takes place in glasses. The preserved elements of the primary structure of borates are sufficiently strong and do not undergo such deep rearrangement as in glasses formed by cooling the melt. This explanation finds confirmation in the fact that, unlike the borate glasses melted by traditional methods, the structural relaxation in amorphized borate minerals is accompanied by certain values of enthalpy, probably associated with loosening of some of the chemical bonds in the preserved elements of the structure.

The effects of the grinding time on the thermal parameters characteristic of structural relaxation derived from DSC experiments for colemanite samples are shown in Table 2. In the early stage of colemanite grinding, the temperatures and the accompanying values of Δc_p remain practically unchanged. With increasing

Table 2 Effect of grinding time on structural relaxation of amorphized colemanite derived from DSC

Grinding time/h	$T_g/^\circ\text{C}$	$\Delta c_p/\text{kJ mol}^{-1} \text{ } ^\circ\text{C}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$
0	653.4	0.453	2.301
1	653.2	0.456	1.997
4	655.7	0.446	1.706
8	655.0	0.496	1.723
40	651.5	0.574	1.328
75	651.7	0.570	1.318
90	650.4	0.550	1.021

grinding time, the amount of preserved elements of the primary structure decreases, while the bonds of the remaining elements become weaker and weaker and during heating they undergo deeper rearrangement (higher Δc_p values), which facilitates the effect of structural relaxation and it occurs at lower temperatures. Simultaneously, the values of enthalpy accompanying the glass transition, which are responsible for the loosening of chemical bonds in the preserved structural elements, decrease.

The presented data demonstrate that the increasing randomness of the primary structure of colemanite causes an increase in its elasticity and homogeneity, which permits easier relaxation of the internal stresses. After a long grinding time, the rearrangement of the colemanite structure and the resulting type of disordering are similar to the disorder specific for glass obtained by the traditional melting method (similar values of Δc_p for mechanically amorphized colemanite and $2\text{CaO}\cdot 3\text{B}_2\text{O}_3$ glass).

Crystallization

At higher temperatures, thermally amorphized borates undergo recrystallization; this occurs through rearrangement of the amorphous structure and subsequent reconstitution of the successive intermediate crystalline phases.

Amorphous colemanite and kernite are examples of single-stage crystallization. The crystallization of glasses of simple chemical composition corresponding to the composition of vitrified colemanite and kernite is a one-stage process too (Table 3).

The crystallization of borates of complex chemical composition proceeds in several stages. The state of equilibrium of pandermite is attained gradually and the compounds $\text{CaO}\cdot\text{B}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ crystallize. The sequence of crystallization of the glass of pandermite composition, obtained by melting of the mixture of the oxides, is the reverse (Table 3).

Inside the amorphous matrix of kaliborite, the crystallization of magnesium borates takes place first, and next potassium borate appears (Table 3). The crystallization of glass of kaliborite composition also proceeds in two stages. At the beginning, the crystallization of $2\text{MgO}\cdot\text{B}_2\text{O}_3$ takes place; on further heating, new crystalline phases appear; $\text{MgO}\cdot 2\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}\cdot 5\text{B}_2\text{O}_3$. The first stage of glass crystallization is accompanied by a very weak exothermic effect, visible only in the course of rapid heating.

From the crystallization parameters presented in Table 3, it follows that the existence of the middle-range ordering in thermally amorphized borates favours the crystallization process. This is indicated by the lower values of crystallization temperatures and the thermal stability parameters K_{gl} [8] of vitrified minerals in comparison with those of glasses melted by the traditional method. The crystallization enthalpies of vitrified borates are larger than those of melted glasses, which means that the degree of crystallization of amorphous borates is somewhat higher. On the other hand, the activation energies of the crystallization of thermally amorphized borates are higher. This may be an indication that the larger energy is needed to initiate the displacements of preserved elements of middle-range structural ordering.

Table 3 Thermal and X-ray data for crystallization of borate glasses and their mineral analogues

Substance	$T_c/$ °C	K_{gt}	$E/$ kJ mol ⁻¹	$\Delta H/$ kJ mol ⁻¹	Phase crystallizing
2CaO·3B ₂ O ₃ glass	853	0.724	362.9	42.6	2CaO·3B ₂ O ₃
			$r=0.9995$		
2CaO·3B ₂ O ₃ vitrified colemanite	737	0.342	592.8	93.8	2CaO·3B ₂ O ₃
			$r=0.9940$		
4CaO·5B ₂ O ₃ glass	868	0.940	275.8	94.6	CaO·B ₂ O ₃ CaO·2B ₂ O ₃
			$r=0.9879$		
4CaO·5B ₂ O ₃ vitrified pandermite	738	0.320	478.8	130.6	CaO·B ₂ O ₃
	758	-	545.6		CaO·2B ₂ O ₃
			$r=0.9958$		
			$r=0.9995$		
Na ₂ O·2B ₂ O ₃ glass	554	0.476	552.6	27.1	Na ₂ O·2B ₂ O ₃
			$r=0.9718$		
Na ₂ O·2B ₂ O ₃ vitrified kernite	553	0.181	489.2	30.9	Na ₂ O·2B ₂ O ₃
			$r=0.9902$		
K ₂ O·2MgO·6B ₂ O ₃ glass	665		-		2MgO·B ₂ O ₃
	704	0.787	228.9	105.7	MgO·2B ₂ O ₃ K ₂ O·5B ₂ O ₃
			$r=0.9899$		
K ₂ O·2MgO·6B ₂ O ₃ vitrified kaliborite	675	0.412	346.2		2MgO·B ₂ O ₃ MgO·2B ₂ O ₃
	708	-	222.4	154.2	K ₂ O·5B ₂ O ₃
			$r=0.9932$		
			$r=0.9892$		

These are displacements at a short distance, similar to those that occur in the diffusionless polymorphic transformations, the result of which is the formation of a substance whose composition and structure are close to the primary structure. In glasses whose structures are more homogeneous, however, the displacements consist in the diffusion of single cations and displacements of individual coordination polyhedra. The multistage crystallization of thermally amorphized borates of complex composition is a result of the limited mobility of the component in the amorphous structure of minerals [9]. With increasing temperature, different cations become displaced at greater distances, determined by their diffusion coefficients. As a result, at the beginning, the formation of intermediate phases takes place; this is followed finally by the formation of stable phases appropriate for the equilibrium state of the system. In this case, the differences in activation energy of crystallization between the vitrified minerals and their melted equivalents are smaller.

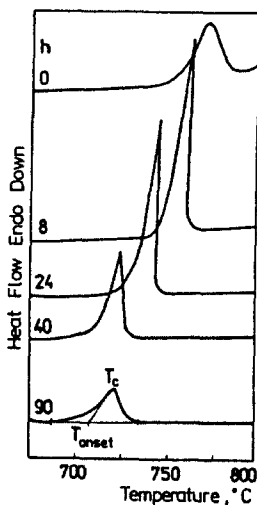


Fig. 3 DSC curves of crystallization of coarse and ground colemanite

The decreasing particle size and the increasing structural disorder of mechanically amorphized colemanite affect the crystallization occurring during heating of this amorphous material [10]. In the early stages of colemanite grinding, its crystallization temperature is decreased and the rate of this process is much greater (higher values of crystallization enthalpy). Such behaviour of the ground mineral is probably due to its rapidly increasing specific surface area, which nucleates the crystallization process. After a long period of grinding, crystallization of calcium triborate takes place at lower temperatures, but its rate is lower. This is evidenced by the shape of the crystallization peak, which becomes less sharp (Fig. 3). Simultaneously, the values of the crystallization enthalpy diminish, indicating a decrease in the recrystallization degree of the ground material.

It follows that the increase in the degree of structural disorder of the mineral that accompanies long grinding decreases its thermal stability, but makes difficult the process of its crystallization. The degree of randomness of the structure is probably so high that the crystallization proceeds by way of diffusional displacement of single atoms at longer distances, as in glasses obtained by melting.

Conclusions

Amorphous borates formed through destruction of the crystalline structure of the precursor by heat treatment at low temperatures preserve some kind of middle-range ordering, inherited from the primary structure. The structure of amorphous borates formed through destruction of their crystalline structure by mechanical treatment becomes similar to that of glass; thus, short-range ordering takes place in it, being limited to single coordination polyhedra.

Crystalline borates can be transformed into the glassy state through structural rearrangement of their primary structure without their undergoing melting, because

the chemical heterogeneity of their amorphous state is not high and the structure is flexible enough. Structural elasticity permits relaxation of the internal stresses during heating or cooling, this being manifested as the glass transition effect.

The different methods of preparation of non-crystalline borates and the differences in their range structural ordering resulting from these methods affect the thermal stability and kinetic parameters of their crystallization. In some cases, they also affect the succession and nature of the crystallizing phases.

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