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# Glass transition effect of amorphous borates[☆]

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**Abstract**

The glass transition effect of thermal amorphized borate minerals and glasses of the same composition obtained by the cooling of the melt was studied and the influence of the origin and structural differences of the vitreous materials on the glass transition effect was considered.

It has been found that thermally amorphized borates exhibit a reversible, endothermal glass transition effect which confirms their vitreous nature. The glass transition effect of amorphous borates occurs at somewhat higher temperatures and shows higher values of the apparent activation enthalpy in comparison with glasses of the same composition. It is accompanied by smaller changes of $\Delta c_p$ in comparison with borate-like glasses obtained by melting oxide mixtures. The above dependencies are due to the differences in the middle-range order in the structure inherited from different precursors, and the method of the preparation of the glassy substance.

*Keywords:* Amorphized and amorphous borates; Borate-like glasses; DSC; Endothermal glass transition effect; FTIR; Vitreous materials; X-ray diffraction

## 1. Introduction

During heating and cooling vitreous substances exhibit a structure-strains relaxation phenomenon termed the glass transition effect. These strains are the consequence of the disordered arrangement of elements in the glass structure. According to Ref. [1] the glass transition process distinguishes glass from other amorphous solids. For glasses of simple chemical composition the transformation temperature $T_g$ is approximately equal to 2/3 of the melting temperature [2].

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Relaxation of strains in the glass structure at the transition temperature is connected with a sudden change of 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 attains about $10^{13,3}$ dPas. Up to the transition temperature glass behaves like a brittle, rigid body but above this temperature it assumes viscoelastic properties.

During heating of the glass there takes place loosening of some of the chemical bonds in the glass structure which is manifested by an endothermal deflection on the DTA curves. This glass transition effect is reversible.

It has been shown that the glass transition effect occurs also in some amorphous substances for which a vitreous nature is not evident [3]. The present study discusses the glass transition effect occurring in amorphous borates which are formed as a result of thermal decomposition of their crystalline precursors. The structures of the thermal amorphized borates contain preserved elements of the primary mineral structures; this distinguishes them from the typical glass obtained by cooling of the melt. The influence of the origin and structural differences on the glass transition effect, using as an example thermal amorphized borate minerals and glasses of the same composition, is the subject of the paper.

## 2. Experimental

Several coarse-crystalline borate minerals have been examined. They were: colemanite—$Ca_2B_6O_8(OH)_6 \cdot 2H_2O$, pandermite—$Ca_2B_5O_8(OH)_3 \cdot 2H_2O$, kaliborite —$HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O$ and borax—$Na_2B_4O_5(OH)_4 \cdot 8H_2O$. Details of the thermal decomposition of the particular borates can be found elsewhere [4–9].

Glasses of borate-like composition were prepared by melting appropriate amounts of oxides at temperature between 700 and 1000°C and quenching the melts.

The amorphous nature of the borates and glasses was also examined by XRD, FTIR and RDF. The thermal measurements were made with a Perkin–Elmer DTA-7 apparatus which has both DTA and DSC modes of operation. In the DTA mode, the system monitors the signal representing the difference in temperature between the sample and an inert reference material as a function of temperature. In the DSC mode the normal signal is optimized and conditioned by the computer so that the output is calibrated in units of mW, facilitating peak area measurements. The temperature and heat calibrations of the instrument were performed using the melting temperature and melting enthalpy of high purity aluminium and gold supplied with the instrument. The samples, placed in platinum crucibles and dry nitrogen atmosphere, were first heated to a temperature ~ 50°C above the glass transition effect where they were in both structural and thermal equilibrium. The samples were then cooled through $T_g$ to room temperature at constant cooling rates of 5, 10, 15, 20 or 25°C $min^{-1}$ and then reheated at a constant rate of 10°C $min^{-1}$ through the glass transition region.

The apparent activation energy for structural relaxation $E$, of amorphous borates and glasses of borate-like composition was obtained from the dependence of the transformation temperature $T_g$ on the cooling rate [10]. The transformation temperature $T_g$ decreases with decreasing cooling rate. The above dependence is related to the activation energy by the equation:

$$\frac{\mathrm{d}\ln\beta}{\mathrm{d}(1/T_g)} = \frac{-E}{R}$$

where $\beta$—cooling rate in °C $\mathrm{min}^{-1}$, $T_g$—transformation temperature in °C, $E$—activation energy in kJ $\mathrm{mol}^{-1}$, $R$—gas constant in J °C $\mathrm{mol}^{-1}$

## 3. Results and discussion

The products of the thermal decomposition of borates are amorphous and retain their amorphous form over a relatively wide range of temperature. Amorphization causes most of the X-ray diffraction lines to disappear, but some are transformed into diffuse bands (Fig. 1). They are evidence of the occurrence of some kind of middle range order in the structure. They frequently occur within the same range of angles in which the strongest lines of the primary crystalline phases are found [3].

As the temperature increases the IR spectra of amorphized borates obtained by thermal decomposition of their crystalline forms become similar to those for glass of the same chemical composition (Fig. 2, 3). Amorphization cancels the splitting of the infrared absorption bands 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.

X-ray-determined radial distribution functions (RDF) of amorphized borates heated to temperatures close to $T_g$ confirmed the similarity between the structure of amor-

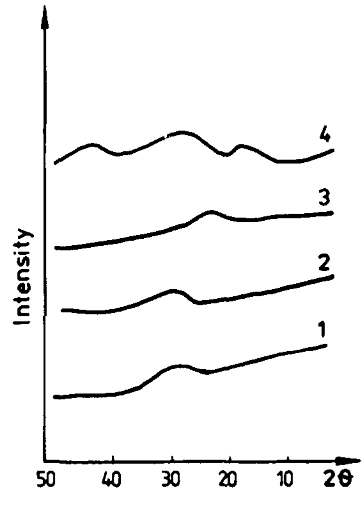

Fig. 1. X-ray patterns of borates: (1) amorphized colemanite, (2) amorphized pandermite, (3) amorphized kaliborite, (4) amorphized borax.

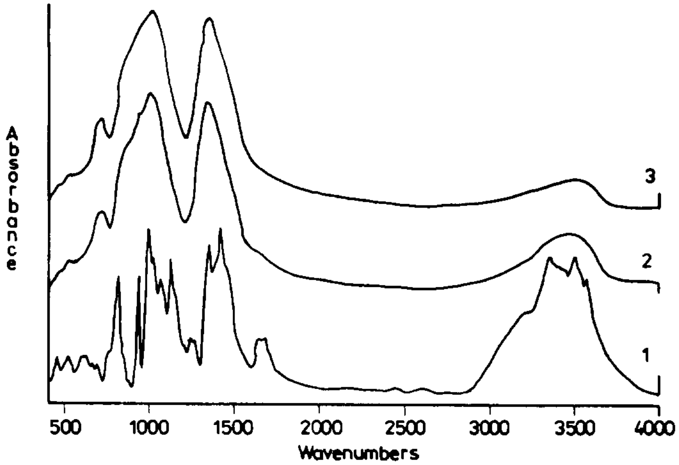

Fig. 2. IR spectra of borax heated at various temperatures: (1) room temperature, (2) 220°C, (3) 300°C.

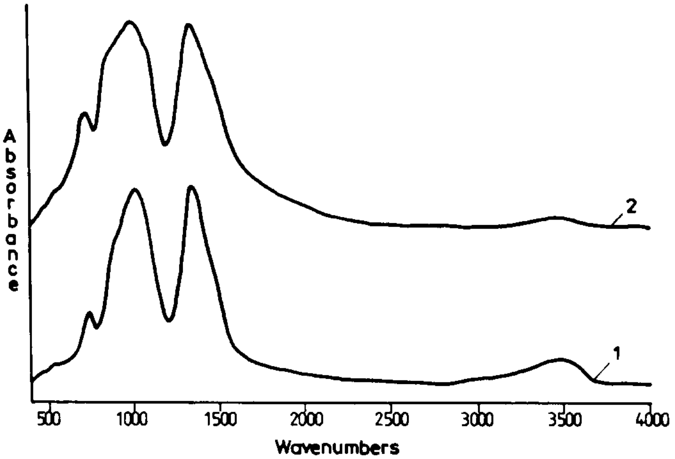

Fig. 3. IR spectra of (1) amorphized colemanite, (2) $2CaO{\cdot}3B_2O_3$ glass.

phous borates and that of glass of the same chemical composition. They have shown that the mean distances of the B–O and O–O bonds in amorphous colemanite and borax and in glasses of $2CaO{\cdot}3B_2O_3$ and $Na_2O{\cdot}2B_2O_3$ composition are similar (Fig. 4.).

On the DSC curves of amorphized borates and glasses of corresponding chemical composition the endothermal deflection is well visible and it is reversible. The glass transition in amorphized borates is accompanied by a certain value of excess enthalpy, which does not disappear on reheating (Fig. 5).

The values of characteristic temperatures for the transformation range of examined substances determined from DSC curves (the so-called "onset temperature" and $T_g$) and

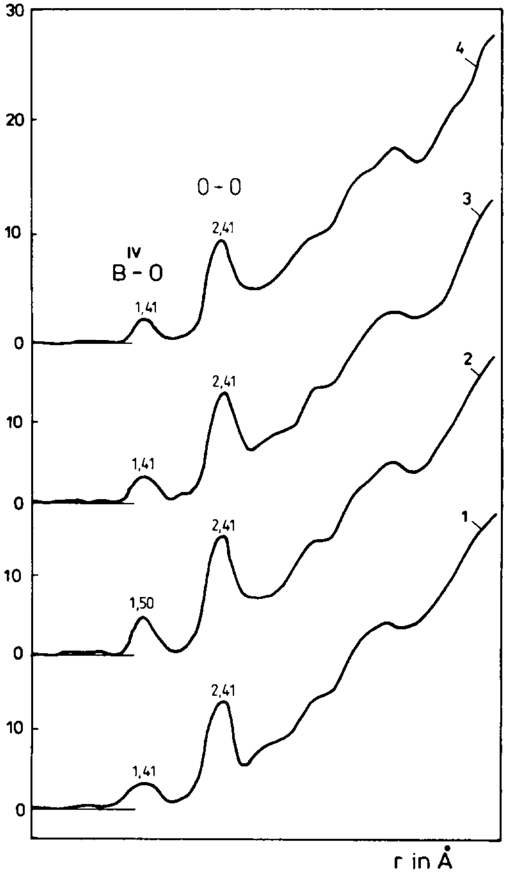

Fig. 4. Radial distribution functions for (1) amorphous colemanite, (2) glass colemanite, (3) amorphous borax, (4) glass borax.

the jump-like changes of the specific heat, excess enthalpy accompanying the glass transition ($\Delta H$) and values of the apparent activation energy for structural relaxation ($E$) are shown in Table 1. The determination of $T_g$ from the inflection point in the rapidly rising part of the enthalpy curve (Fig. 5) and enthalpy values accompanying the glass transition were performed using the DEC Personal Workstation with 7 Series/Unix Thermal Analysis Software Library.

From the presented data it follows that the values of both the "onset temperature" and $T_g$ of amorphized borates are higher than the temperatures of the respective points for glasses obtained by melting and cooling the melt. Only amorphous borax shows a lower transition temperature in comparison with the respective glass.

The structural relaxation of amorphous borates and glasses of the same composition is accompanied by changes of the specific heat $\Delta c_p$, the values of which are somewhat smaller for amorphous borates obtained by thermal decomposition of crystalline substances when compared with the respective borate glasses.

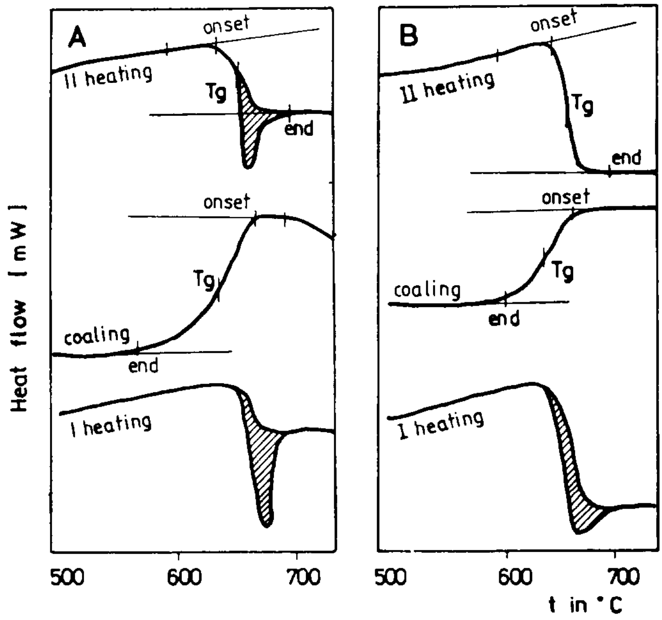

Fig. 5. DSC curves of glass transition effect of (A) amorphous colemanite, (B) glass colemanite.

Plots of the logarithm of the cooling rate $\beta$ versus the inverse of the transition temperature are shown in Fig. 6.

The apparent activation energy for structural relaxation equals 178.5 kJ $mol^{-1}$ for amorphous colemanite and 164.2 kJ $mol^{-1}$ for glass of $2CaO \cdot 3B_2O_3$ composition. A higher activation energy relative to glass of the composition $Na_2O \cdot 2B_2O_3$ is also characteristic of amorphous borax (Table 1). Because of lack of a sufficient amount of monocrystalline minerals the activation energy for amorphous pandermite and kaliborite was not determined.

It follows from the above results that thermally amorphized borates exhibit a reversible, endothermal effect of glass transition. This means that near $T_g$ the structure of amorphous borates becomes flexible enough and can be transformed into a liquid-like structure of glass. The temperature of this transformation is lower than the temperature of their crystallization. This makes possible the transformation of the borates into the glassy state through structural rearrangement of their primary crystalline structure, without melting them.

In structures in which the temperature increase brought about sufficient loosening of some of the chemical bonds, there may take place a reversible relaxation transition such as the glass transition. This is possible especially in amorphous substances of relatively low melting temperature. The amorphized borates discussed here belong to this group.

As has been shown above, the glass transition effect of amorphous borates occurs at somewhat higher temperatures and exhibits higher values of the apparent activation energy for structural relaxation relative to glasses of the same composition. The

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

| Substance | Onset temp./°C | $T_g$/°C | $\Delta c_p$/(kJ mol$^{-1}$ °C$^{-1}$) | $\Delta H$/(kJ mol$^{-1}$) | $\Delta E$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| Amorphous colemanite | 644 | 659 | 0.19 | 1.66 | 178,5 |
| $2CaO \cdot 3B_2O_3$ glass | 643 | 654 | 0.51 | – | 164,2 |
| Amorphous pandermite | 649 | 656 | 0.19 | 5.36 | |
| $4CaO \cdot 5B_2O_3$ glass | 638 | 650 | 0.92 | – | |
| Amorphous kaliborite | 545 | 560 | 0.07 | 1.86 | |
| $K_2O \cdot 2MgO \cdot 6B_2O_3$ glass | 496 | 527 | 0.34 | – | |
| Amorphous borax | 403 | 422 | 0.06 | 1.15 | 135,1 |
| $Na_2O \cdot 2B_2O_3$ glass | 457 | 464 | 0.16 | – | 123,2 |

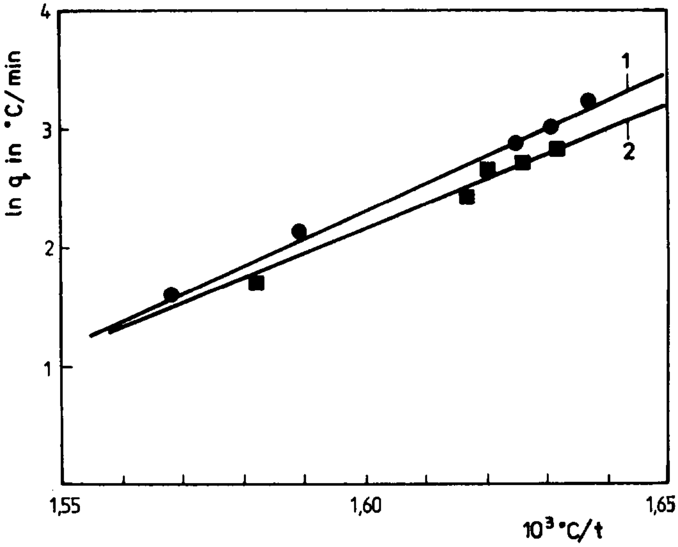

Fig. 6. Logarithm of the cooling rate versus the inverse of $T_g$ for (1) amorphous colemanite and (2) $2CaO \cdot 3B_2O_3$ glass.

structure of melted glasses is homogeneous, whereas the amorphous structures of borates formed by thermal decomposition of crystalline forms preserve a middle-range structure ordering inherited from the structure of the primary substance [3]. This may be the reason that the substance the structure of which contains larger elements requires a higher temperature and more activation energy to attain the viscosity specific for the glass transition effect. Smaller changes of the specific heat ($\Delta c_p$) accompany the glass transition in amorphous borates when compared with glasses of the same composition. This may indicate that the degree of the structural rearrangement accompanying the transition of amorphous borates is smaller than that which takes place in glasses of the same composition. It is probable that the preserved elements of the primary structure of borates are sufficiently strong and they do not undergo such deep rearrangement as takes place in glasses formed by cooling the melt, thereby making the structural rearrangement accompanying the transition effect difficult. As a result this rearrangement cannot be as far reaching as for a glass. This hypothesis finds confirmation in the fact that, unlike the borate glasses melted by traditional methods, the glass transition in amorphized minerals is accompanied by a certain values of excess enthalpy, diminishing, but not disappearing after several heating and cooling cycles. This enthalpy is probably associated with loosening of some of the chemical bonds in the preserved elements of the structure.

## 4. Conclusions

1. Thermally amorphized borates attain a state of structural elasticity allowing the relaxation of internal strains which is manifested by the reversible endothermal glass transition effect.
2. The glass transition effect of amorphous borates occurs at somewhat higher temperatures and shows higher values of the apparent activation energy in comparison with glasses of the same composition.
3. The glass transition effect of amorphous borates is accompanied by smaller changes of $\Delta c_p$ in comparison with glasses of the same composition.
4. The above dependencies are due to the differences in the middle-range order in the structure inherited from different precursors and method of the preparation of the glassy substance.

## References

[1] J. Zarzycki, Glass and Vitreous State, Pergamon Press, Oxford, 1991.
[2] S. Sakka and J.D. MacKenzie, J. Non-cryst. Solids, 6 (1971), 145.
[3] L. stoch and I. Wacławska, High Temp. Mater., 13 (3) (1994) 181.
[4] I. Wacławska, L. Stoch, F. Paulik and J. Paulik, Thermochim. Acta, 126 (1988) 307.
[5] L. Stoch and I. Wacławska, J. Therm. Anal. 36 (1990) 2045.
[6] L. Stoch and I. Wacławska, Thermochim. Acta, 215 (1993) 255.
[7] L. Stoch and I. Wacławska, Thermochim. Acta, 215 (1993) 265.
[8] L. Stoch and I. Wacławska, Thermochim. Acta, 215 (1993) 273.
[9] I. Waclawska, J. Therm. Anal. 43 (1995) 261.
[10] C.T. Moynihan, A.J. Easteal and J. Wilder, J. Phys. Chem., 78 (1974) 2673.