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BEHAVIOUR OF GERMANIUM IN PHASE SEPARABLE GLASSES OF THE SYSTEM

 $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$

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Résumé - Le rôle de GeO_2 dans le quaternaire $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ qui présente un domaine de séparation de phases spinodale est abordé. Les propriétés physiques de ce système sont comparées à celles des borosilicates de sodium. Les conditions de lessivabilité des verres sont examinées. La coordinance du germanium a été étudiée dans un verre brut et dans le verre lixivié correspondant.

Abstract - The rôle of GeO_2 in the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ quaternary system which presents a spinodal decomposition domain is studied. The physical properties of this system are compared to those of the system without GeO_2 . The leaching conditions of these glasses and the coordination of Ge are studied.

I. INTRODUCTION

The mechanism of phase separation by spinodal decomposition is used in the Vycor^R process to obtain 96 % silica rich glasses from base glass of the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system. In order to prepare $\text{GeO}_2 - \text{SiO}_2$ glasses, phase separation by spinodal decomposition has been studied in the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ system. This paper reviews some physical and chemical properties of these glasses. Interpreting the leaching mechanism, and EXAFS studies of the germanium coordination, the rôle of GeO_2 is shown.

II. PROPERTIES OF GLASSES OF THE QUATERNARY SYSTEM

Base glass preparation : The glasses were melted in a platinum 10 % rhodium crucible in oxidizing atmosphere. The starting raw materials were "ultrapure" grade quality silica, germanium oxide, borax and boric oxide or boric acid. Melting temperature ranged between 1100 and 1350°C depending on the silica content.

Phase - separated leachable glass compositions : Fig. 1 (1) represents the domain of immiscibility in the quaternary system. The leachable glass compositions in the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system lie in the Vycor^R optimum line. In the vicinity of the line the densities of the glasses show an unusual behaviour Fig. 2a (2-3). In the quaternary composition plane with $\text{SiO}_2 = 54\%$ (mole) - Fig. 2b - densities show identical properties (4). The $\text{Na}_2\text{O}/\text{Na}_2\text{O} + \text{B}_2\text{O}_3$ ratio for leachable glasses in the quaternary system $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ is identical to the corresponding one in the Vycor^R optimum line - Fig. 3 - The presence up to 20 mole % of GeO_2 does not drastically modify the leaching behaviour of the corresponding borosilicate.

FIG. 1 : IMMISCIBILITY REGION IN THE $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{GeO}_2 - \text{SiO}_2$ SYSTEM

FIG.2: GLASS DENSITY (a) $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ (2-3)(b) $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{GeO}_2-\text{SiO}_2 = 54\%$

FIG.3: CORRESPONDING OPTIMUM LINE IN THE QUATERNARY SYSTEM

FIG.4: TYPICAL D.S.C CURVE

Microstructure and heat treatment : A calorimetric study was conducted with a 1090 Dupont DSC equipment. Three parameters can be deduced from the DSC curves - Fig. 4 -

- T_{g1} : correlated to the T_g measured by dilatometric method
- T_{g2} : assigned to the T_g of the silica rich phase
- T_{coex} : coexistence temperature.

As shown in Table I a variation of T_{g1} and T_{coex} cannot be seen distinctly with the heat treatment, whereas T_{g2} displays the same behaviour as the mean pore radius (1) - Fig. 5 -

FIG.5: EVOLUTION OF MICROSTRUCTURE (a) AND T_{g2} (b) VS HEAT TREATMENT

Température °C	Temps h.	T _{g1} °C	T _{g2} °C	T _{coex} °C
525	3	486	542	691
	5	489	541	691
	17	488	544	691
	41	488	547	691
540	3	490	549	690
	5	489	549	691
	17	487	550	690
	41	486	554	691
560	3	488	552	695
	5	489	555	695
	17	484	558	693
570	3	489	560	693
	5	489	564	691
	17	484	565	696
	41	488	573	697
580	3	491	567	692
	5	489	568	695
	17	-	575	700
600	0,5	489	567	693
	3	489	579	696
	5	489	584	695
620	0,5	493	584	695
	1	491	589	696
	3	492	-	702
640	0,25	492	592	697
	0,5	490	600	698
	1	492	603	700
	3	491	606	702
	5	492	615	704
	17	493	619	-
	41	493	628	-

TABLE 1: T_{g1}, T_{g2}, T_{coex} VALUES VS HEAT TREATMENT

Up to 23 %, GeO₂ does not fundamentally change the rôle of Na₂O and B₂O₃ in the phase separation by spinodal decomposition as in the case of Vycor^R.

Leaching of the glass : A germanium radial concentration profile appears during the acid attack of the phase separated glass - Fig. 6 - due to diffusion (4). The concentration difference Δc between the center Cc and the border of rod Cb tends to zero when the time increases to infinity, whereas Cb tends to a finite value - Fig. 7 - Some part of germanium always remains in the silica phase. Cb and Cc values depend upon the leaching conditions - Fig. 7 -

FIG. 6 : RADIAL CONCENTRATION PROFIL AFTER LEACHING.

GLASS	COMPOSITION MOL %				LONGUEUR Ge-O	OBSERVATIONS
	SiO ₂	GeO ₂	B ₂ O ₃	Na ₂ O		
1	0	100	0	0	1.73	GLASS COMPOSITION AFTER LEACHING A
2	36.5	63.5	0	0	1.73	
3	87.5	12.5	0	0	1.73	
4	54	10	28	8	1.725	

TABLE II : Ge-O BOND LENGTH FOUR GLASSES

III. GERMANIUM COORDINATION

EXAFS studies were made to determine the germanium coordination (5). The Ge-O bond lengths in different glasses are shown in Table II. The Ge-O bond length in glass A is the same as for vitreous GeO₂. The addition of silica to germania does not change the germanium coordination (Table II, glasses 2 and 3). Ge in glass A remains four-fold coordinated in the base glass and in the final glass after acid leaching. Experiments on heat-treated glass are being carried out to determine the Ge coordination in the leachable phase.

FIG.7: GeO₂ CONCENTRATION WITH LEACHING DURATION

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