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HEAT CAPACITY OF NEUTRON-IRRADIATED SILICA GLASS

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The heat capacities of unirradiated silica glass and three samples of fast neutron-irradiated silica glass were measured between 6 and 340 K. For the glass samples irradiated with fast neutrons, a decrease in heat capacity was observed in comparison with the starting silica glass. This agrees with the assumption that at higher doses the silica glass is converted into the metamict phase, which has a different local structure.

The best-known form of amorphous silicon dioxide is silica glass resulting from the solidification of molten SiO_2. Another amorphous state of SiO_2 (a metamict phase) can be obtained by the irradiation of silica glass or crystalline quartz with fast neutrons ($2.0 \cdot 10^{20}$ cm^{-2}). The metamict phase differs from silica glass in some properties (density and refraction index), and when it is heated to about 1000 K it is transformed into ordinary silica glass with an endothermic effect of ~ 15 kJ mol^{-1} [1]. In [2], the supposition has been made that this discrepancy in properties is caused by differences in the local structures of this state and silica glass. As we have no direct data about their structures, study of the physical and thermal properties of amorphous phases of silicon dioxide is especially important. Only for ordinary silica glass have the thermodynamic properties been studied in detail in a wide temperature range [3–8]. Data on the influence of neutron irradiation on the heat capacity of silica glass are scarce [9, 10]. The heat capacity of glass after irradiation ($5 \cdot 10^{19}$ cm^{-2}) has been shown to be smaller than that of the unirradiated material.

The aim of this work was to investigate the temperature-dependence of the heat capacities in the temperature range 6–340 K of several modifications of amorphous silicon dioxide: ordinary silica glass and three samples of silica glass irradiated with fast neutrons. These data can be used for a revision of the nature of the amorphous SiO_2 state. Sample 1 was the stating silica glass with incidental impurities (Ca, Al, Ba, Sb, Pb, Mn, B, N and Zn) in the range $1 \cdot 10^{-3}$–$1 \cdot 10^{-1}$ mass%. Samples 2, 3 and 4 were silica glass of the same brand irradiated with fast neutrons ($2.0 \cdot 10^{19}$, $9.3 \cdot 10^{19}$ and $2.2 \cdot 10^{20}$ cm^{-2}, respectively).

For measurement of the isobaric heat capacity in the range 5–340 K, a vacuum adiabatic calorimeter with pulse heating was used. The calorimetric vessel, made

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Table 1 Experimental heat capacities of unirradiated SiO_2 glass, in $J \cdot K^{-1} \cdot mol^{-1}$. $M(SiO_2) = 60.0843\ g \cdot mol^{-1}$

T, K	C_p	T, K	C_p	T, K	C_p	T, K	C_p
Series 1		129.28	21.62	271.69	41.48	21.56	1.802
135.76	22.71	132.34	22.19	276.32	41.96	23.55	2.143
140.10	23.45	Series 3		280.91	42.41	25.01	2.386
144.59	24.23	169.03	28.27	Series 5		26.43	2.635
148.97	24.95	172.87	28.91	289.01	43.24	27.81	2.866
152.99	25.66	176.65	29.42	292.67	43.64	31.55	3.517
156.94	26.32	180.37	29.99	296.30	44.01	Series 7	
160.82	26.97	184.04	30.46	299.96	44.40	32.97	3.759
164.67	27.54	187.65	31.02	303.55	44.74	34.12	3.968
165.11	27.59	191.22	31.52	307.11	45.02	35.19	4.147
168.37	28.17	195.02	32.08	310.64	45.39	37.63	4.590
Series 2		199.17	32.64	314.15	45.73	39.76	4.974
80.05	12.37	203.26	33.18	317.64	46.07	46.32	6.062
83.63	13.04	207.29	33.71	321.09	46.35	48.67	6.532
87.01	13.66	211.29	34.32	324.54	46.61	52.51	7.206
90.22	14.28	Series 4		327.94	46.99	55.33	7.738
93.50	14.91	213.67	34.51	331.34	47.24	58.27	8.267
96.86	15.59	217.72	35.08	334.75	47.71	60.96	8.758
100.08	16.24	222.48	35.69	338.14	47.94	63.45	9.218
103.00	16.72	227.67	36.35	Series 6		66.46	9.769
105.82	17.31	232.80	36.98	11.63	0.4172	71.51	10.70
108.75	17.86	237.86	37.63	12.72	0.5191	75.02	11.34
111.59	18.37	242.85	38.23	13.82	0.6559	Series 8	
114.37	18.84	247.79	38.77	14.88	0.8081	6.46	0.0634
117.08	19.36	252.67	39.33	15.98	0.9517	7.53	0.1109
119.73	19.85	257.50	39.93	17.15	1.114	8.59	0.1962
122.32	20.35	262.28	40.44	18.49	1.316	10.52	0.3143
125.72	20.98	267.00	40.99	20.05	1.559	11.08	0.3612

from nickel, weighed 22.4 g and had a useful volume of $\approx 6\ cm^3$. The sample under study was placed into the vessel, which was then hermetically closed with a screw cover. The seal was made of teflon film. The temperature was measured with a platinum resistance thermometer ($R_0 = 50$ Ohm). The average deviation of the experimental values of the heat capacity of the empty cavity from the smoothed $C_{empty}(T)$ curve was 0.3% from 5 to 30 K, and less than 0.05% from 30 to 340 K. In order to check the technique, the heat capacity of 3.2240 g of benzoic acid was measured at 48 temperature points in the range 8–278 K. The agreement with the standard values [11] was quite satisfactory: the average deviation was about 0.2% in the range 50–278 K, and ~1.0% from 5 to 30 K. Measurements of the heat capacity of silicon dioxide were carried out under the same experimental conditions as those under which the $C(T)$ dependence was obtained for the empty cavity and benzoic acid. For each sample, 90–100 calorimetric measurements were made in the temperature range 6–340 K. Experimental values for the starting silica glass are shown in Table 1. The average deviation of these values from the smoothed $C_p(T)$ curve is 1% in the range 6–20 K, and 0.1% at higher temperatures. Such variations were observed for the irradiated glass samples too. For each sample, the enthalpy and entropy were calculated from 0 to 298.15 K (Table 2). The entropy in the range 0–6 K for the first sample was calculated using the data from [5, 6], while for the other samples the entropy was evaluated under the assumption that $C_p = A \cdot T^3$. For all samples, this addition did not exceed 0.03% of the entropy at 298 K. The residual entropy $S(O)$ for the silica glass was 4.71 ± 0.5 $J \cdot deg^{-1} \cdot mol^{-1}$ [12]. For the irradiated samples, it is unknown, but it probably differs from zero too.

For the glass samples irradiated with fast neutrons, a decrease in heat capacity was observed as compared to that for the starting silica glass. The deviation became

Table 2 Thermodynamic functions of SiO_2 glasses

	$C_p(298.15\ K)$, $J \cdot K^{-1} \cdot mol^{-1}$	$S(298.15\ K) - S(O)$, $J \cdot K^{-1} \cdot mol^{-1}$	$H(298.15\ K) - H(O)$, $J \cdot mol^{-1}$
Sample 1	44.22±0.05	43.51±0.10	7000±10
Sample 2	44.40±0.05	42.52±0.10	6940±10
Sample 3	43.61±0.05	41.27±0.10	6790±10
Sample 4	42.84±0.10	40.70±0.40	6700±20

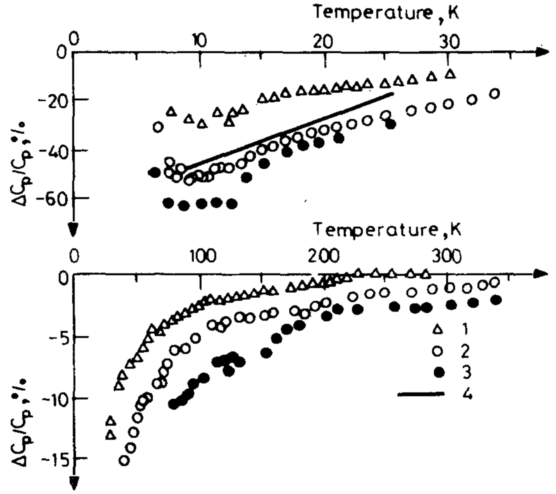

Fig. 1 Deviation plot of the heat capacity of irradiated silica glass from unirradiated SiO_2 glass (sample 1): (1) – sample 2, (2) – sample 3, (3) – sample 4, (4) – Clark and Strakna [10]

larger as the dose of radiation increased (Fig. 1). The deviation maximum was observed near 10 K, which agrees qualitatively with [10]. At low temperatures, the heat capacity of ordinary silica glass is known to be higher than that of quartz, i.e. the amorphization or the disappearance of long-range order results in an increase in heat capacity. From this point of view, the heat capacity decrease can be regarded as evidence of some ordering of the glass following the irradiation.

The relative deviation of the heat capacity at 10 K and the relative entropy change from 0 to 20 K for the glasses are shown in Fig. 2, as functions of the irradiation dose. It may be concluded that, at doses higher than $1 \cdot 10^{20}$ cm^{-2}, the dependence of the heat capacity on the irradiation is weak. This agrees with the assumption that the glass is converted by such an irradiation dose into the metamict phase, which has a different local structure [2]. Smaller irradiation doses probably yield mixtures of the starting glass and the metamict phase.

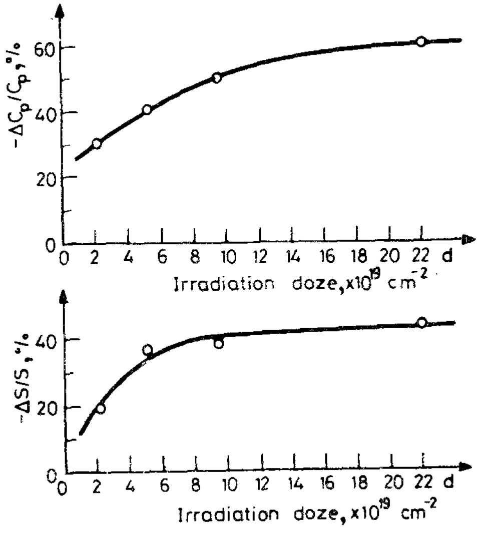

Fig. 2 (a) Relative deviation of C_p (10 K) and (b) – relative entropy change S(2OK)–S(OK) for glasses as function of the irradiation dose

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Zusammenfassung — Die Wärmekapazität von unbestrahltem Kieselglas und drei mit schnellen Neutronen bestrahlten Kieselgläsern wurde zwischen 6 und 340 K gemessen. Die bestrahlten Glasproben zeigen eine geringere Wärmekapazität als das Ausgangslas. Das Stimmt überein mit der Annahme, dass bei höheren Bestrahlungsdosen das Kieselglas in eine metamikte Phase mit abweichender lokaler Struktur umgewandelt wird.

Резюме — В температурном интервале 6–340 К измерены теплоемкости необлученного кварцевого стекла и трех образцов кварцевого стекла, облученного быстрыми нейтронами. В случае облученных образцов наблюдалось уменьшение теплоемкости по сравнению с необлученным кварцевым стеклом. Установленный факт согласуется с предположением, что кварцевое стекло при более высоких дозах облучения превращается до метамиктной фазы, обладающей другой локальной структурой.