Since such a glide plane does not exist in Fm3m, to which the crystal structure of $M_{23}C_6$ belongs, the above restrictions do not exist in this case. Furthermore, by calculating the structure factors for electron scattering of these two carbides it was shown that the reflections such as 4 2 0, 5 3 1, 6 0 0, etc., are of much higher intensities in $M_{23}C_6$ than in M_6C; on the other hand, reflections such as 4 0 0, 3 3 1, 5 5 1, etc., are of much higher intensities in M_6C than in $M_{23}C_6$. In spite of the effects of multiple diffraction which always exist in the case of selected area electron diffraction, one can still differentiate M_6C from $M_{23}C_6$ by means of these reflections. This may be a better criterion for the identification of M_6C than the condition of $h^2 + k^2 + l^2 = 4(2n + 1)$ given by Ohmori [3] because the latter is not generally valid. According to the latter criterion, 6 2 2 should be a weak reflection but in fact it appears as a medium one.

References

1. A. TAYLOR and K. SACHS, *Nature* **169** (1952) 411.
2. G. PREIS and G. LENNARTZ, *Arch. Eisenhuttenw.* **46** (1975) 509.
3. Y. OHMORI, *Trans. Iron Steel Inst. Japan* **11** (1974) 341.

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TiO_2–SiO_2 glasses prepared from metal alkoxides

One of the advantages of preparing oxide glasses from metal alkoxides through hydrolysis and gelling rather than by the conventional melting method is that only relatively low temperatures are required [1, 2]. This technique, therefore, can be applied to the preparation of glasses which are difficult to obtain by a melting method because of their high melting temperatures.

The nature and properties of a gel, precursor for an oxide glass obtained from metal alkoxides through hydrolysis, has been shown to be affected by the added water and catalyst contents, the hydrolysis temperature and the solution pH [3, 4]. Fibres could be drawn from alkoxide solutions in the course of hydrolysis, when water was added in an amount insufficient for the completion of the hydrolysis, which made it possible to prepare glass fibres of the TiO_2–SiO_2, Al_2O_3–SiO_2 and ZrO_2–SiO_2 systems [5, 6]. On the other hand, homogeneous hydrolysis of metal alkoxides with excess water gave jelly-like masses suitable for obtaining non-particulate glasses. This indicated that excess water for the hydrolysis of metal alkoxides is an important requirement for making monolithic glasses from alkoxides, even though the rate of heating the gels and the porosity of the gels should also be controlled. The monolithic SiO_2 [7], Al_2O_3–SiO_2 [8] and B_2O_3–SiO_2 [9] glasses, so far, have been prepared from metal alkoxides.

In the present note, the metal alkoxide method for glass preparation was applied to the monolithic glasses of the TiO_2–SiO_2 systems on the basis of above considerations. The TiO_2–SiO_2 glasses containing TiO_2 up to about 10 wt% are known to show ultra-low thermal expansions [10]. With a

TABLE I Composition of the oxide glasses formed through the hydrolysis and gelling method

Specimen	Amounts of raw materials					Calculated composition of the oxide glass (wt%)
	$Ti(OC_3H_7)_4$ (g)	$Si(OC_2H_5)_4$ (g)	H_2O (g)	CH_3COOH (g)	C_2H_5OH (ml)	
1	0.65	20.42	90.0	0.06	80	3.0% TiO_2–97.0% SiO_2
2	1.08	20.02	90.0	0.06	80	5.0% TiO_2–95.0% SiO_2
3	1.73	19.37	90.0	0.06	80	7.9% TiO_2–92.1% SiO_2

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melting temperature as high as 1700° C, specially designed apparatus would be required for making these glasses by the melting method.

Titanium tetraisopropoxide $Ti(OC_3H_7)_4$ and silicon tetraethoxide $Si(OC_2H_5)_4$, supplied by Wako Chemicals Co., Japan, were used as raw materials. The alkoxide mixtures consisting of the alkoxides corresponding to 0.1 mole of the oxide and 40 ml ethanol for dilution were prepared as shown in Table I. The mixture of 90 g water and 0.06 g glacial acetic acid as catalyst, diluted with another 40 ml of ethanol, was added under stirring to the alkoxide mixtures for hydrolysis. The molar ratios of the water and acetic acid were 50.0 and 0.01, respectively. The resultant clear solutions were transferred to 500 ml polypropylene beakers (of bore diameter about 8 cm) lined with paraffin, covered with thin plastic films having several pinholes and kept at 40° C. The solutions gelled into jelly-like masses of about 150 ml (about 8 cm in diameter and 3 cm in thickness) in 5 days. The gels were kept standing in the room for about 4 months for drying. Finally, the non-particulate gels of about 5 ml (about 4 cm in diameter and 0.5 cm thick) were obtained. They were then heated slowly up to a temperature of 90° C, kept there for 1 day, and then heated up to 900° C with a heating rate of 6° C h^{-1} to remove the remaining organic matters and water. Fig. 1 shows photographs of the resultant plates about 0.4 cm thick for the compositions of 5.0 wt % TiO_2–95.0 wt % SiO_2 and 7.9 wt % TiO_2–92.1 wt % SiO_2. The X-ray diffraction pattern, observed after heating, showed no crystalline phase and no appreciable small angle scattering, indicating that the plates are substantially oxide glasses.

The densities of the glasses were measured by Archimedes' method at 19° C using water as the replacing liquid. The thermal expansion measurements were made using a bar of length, L, where L = 1.5 cm. Relative changes in length, ΔL, between 25° C and 700° C were measured with a dilatometer manufactured by the Rigaku Denki Co. using a fused silica rod as a reference, and the data are shown in Fig. 2. Thermal expansion coefficients, $\alpha_{25-700°\,C}$, of the glasses were derived from the slopes of the curves in Fig. 2, and corrected for the expansion of the fused silica rod used as a reference by adding its expansion coefficient over this temperature range which is equal to $\alpha_{Si} = 5.5 \times 10^{-7}$. Densities and thermal expansion coefficients of the glasses obtained in the present study are given in Table II, together with those obtained by the melting method for comparison (taken from [10]). The TiO_2 contents of the present alkoxy-derived glasses in Table II are those calculated from the compositions of alkoxides. It has been found previously that essentially no differential loss of particular metal atom occurred during the processes and the calculated compo-

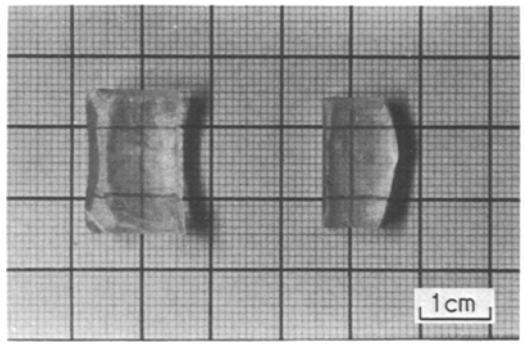

Figure 1 Photographs of the compositions 5.0 wt % TiO_2–95.0 wt % SiO_2 (left) and 7.9 wt % TiO_2–92.1 wt % SiO_2 (right) heated to 900° C.

TABLE II Densities and thermal expansion coefficients, α, of TiO_2–SiO_2 glasses prepared from metal alkoxides and prepared by melting.

Prepared from metal alkoxides			Prepared by melting (values from [10])		
TiO_2 content (wt %)	Density (g cm^{-3})	α ($\times 10^{-7}$) (25–700° C)	TiO_2 content (wt %)	Density (g cm^{-3})	α ($\times 10^{-7}$) (25–700° C)
3.0	2.197	+ 1.3	3.42	2.201	+ 2.312
5.0	2.157	− 1.6	6.00	2.199	+ 0.133
7.9	2.166	− 0.7	7.20	2.200	− 0.741
			7.40	2.199	− 0.326
			8.36	2.197	− 1.156
			9.45	2.198	− 1.926

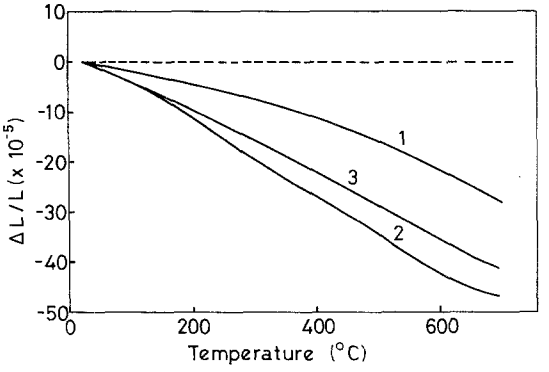

Figure 2 Thermal expansion of the TiO_2–SiO_2 glasses prepared from metal alkoxides. Fused silica is used as a reference.

sitions of the glasses agreed with the analysed ones for the TiO_2–SiO_2 system [11]. The densities of the present glasses are slightly lower than those prepared by melting method, which may be partly attributed to the inclusion of some small pores giving the foggy appearance seen in Fig. 1. The thermal expansion coefficients of the present glasses are as low as those prepared by melting method. In summary, the monolithic TiO_2–SiO_2 glasses of the ultra-low thermal expansion were made from metal alkoxides through hydrolysis and gelling processes.

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References

1. H. DISLICH, *Glastech. Ber.* 44 (1971) 1.
2. K. KAMIYA, S. SAKKA and I. YAMANAKA, Proceedings of the 10th International Conference on Glass, Kyoto July, 1974 (The Ceramic Society of Japan, Tokyo, 1974) pp. 13–44.
3. S. SAKKA and K. KAMIYA, Proceedings of the International Symposium of Factors in Densification and Sintering of Oxide and Non-Oxide Ceramics, Hakone, Japan, 1978, edited by S. Somiya and S. Saito (Tokyo Institute of Technology, Tokyo, 1978) p. 101.
4. M. YAMANE and S. OKANO, *J. Ceram. Soc. Japan* 87 (1979) 434.
5. K. KAMIYA, S. SAKKA and N. TASHIRO, *ibid.* 84 (1976) 614.
6. K. KAMIYA, S. SAKKA and Y. TATEMICHI, *J. Mater. Sci.* 1187.
7. M. YAMANE, S. ASO, S. OKANO and T. SAKAINO, *ibid.* 14 (1979) 607.
8. B. E. YOLDAS, *ibid.* 12 (1977) 1203.
9. *Idem, ibid.* 14 (1979) 1843.
10. P. C. SCHULTZ and H. T. SMYTH, "Amorphous Materials", edited by R. W. Douglas and Bryan Ellis, (John Wiley and Sons, New York and London, 1972) pp. 453.
11. K. KAMIYA and S. SAKKA, Research Report of the Faculty of Engineering, Mie University 2 (1977) 87.

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Ni–Si–B metallic glasses with high metalloid contents

The compositions of metal–metalloid glassy alloys prepared from the melt in thicknesses $\gtrsim 20\,\mu m$ have generally been limited to fairly narrow ranges centred around deep metal-rich eutectics, typically at ~ 20 at% metalloid [1, 2]. Over these composition ranges glass formation is kinetically favoured because the reduced glass temperature, T_g/T_{liq}, (where T_g and T_{liq} are the glass transition and liquidus temperatures, respectively) is usually $\gtrsim 0.5$ [3]. The structure of the metal–metalloid glasses has been described [4] as a dense random-packed metal network into which the generally smaller metalloid atoms are packed interstitially and it has also been proposed that this would promote glass formation specifically in the range of 15 to 25 at% metalloid. Recently, however, work on ternary systems based on Fe, Ni or Co with Si and B [5–7] has demonstrated that the glass-forming ranges can be extended well beyond 25 at% metalloid, up to ~ 35 at%. In this paper the results of a comprehensive investigation into the formation and properties of Ni–Si–B metallic

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