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Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze application

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The effect of crystallization produced by addition of TiO_2, ZrO_2 and P_2O_5 oxides to glass-ceramic of the system $CaO-MgO-SiO_2$ was studied using structural and thermal techniques. The devitrification process was independent of thermal treatment. X-ray diffraction studies performed on the glass-ceramic system indicated that diopside crystalline phase was more thermodynamically favourable than other phases. The effect of the nucleating agent depends on its nature: TiO_2 decreased the activation energy while P_2O_5 and ZrO_2 did not. SEM analysis of the doped glass-ceramics showed randomly distributed crystals with significant dimensional variations from those of the undoped system. All these formulations, showing a high crystallization rate, and a fast heating rate, can be used as tile glazes and/or tile-glaze components.

1. Introduction

Glass-ceramics are microcrystalline materials obtained from a parent glass by almost complete devitrification, that generally have low coefficients of linear thermal expansion together with high chemical and thermal shock resistance, and have a wide variety of applications [1–4]. Recently, some formulations have found practical application as tile glazes, resulting in finished ceramic floor-tile products that have enhanced abrasion and wear resistance and improved mechanical properties [5, 6].

Glass-ceramics obtained from the crystallization of glassy compositions belonging to the ternary $CaO-MgO-SiO_2$ system can be separated into several crystalline phases (forsterite, diopside, protoenstatite, and akermanite) [7]. Owing to the peculiar durability and mechanical properties of the silicate phases which can be present in the glass-ceramic materials, these products are suitable for many applications, such as in the production of chemical-resistant fibres [8].

In this work, studies were performed on low-cost glass-ceramics of the ternary $CaO-MgO-SiO_2$ system that, despite having a composition within the forsterite stability field, devitrified to the diopside crystalline form during a one-step heat treatment [9]. Because of particular interest in determining the physico-chemical properties which would be a useful reference and guideline for selecting a candidate as a tile-glaze component, the effects of (a) 0–10 wt % of the common nucleating agents TiO_2, ZrO_2 and P_2O_5 on the crystallization process, and (b) fast one-step heating cycles, were investigated. The values of the activation energies for the crystallization processes were evaluated by a DDTA method.

2. Experimental procedure

2.1. Sample preparation

The glassy compositions studied are shown in Table I [8]. Well-mixed dried powders containing appropriate amounts of industrial grade $MgCO_3$, $CaCO_3$ and SiO_2, were melted in platinum crucibles for 2 h in an electric furnace at 1420 °C and immediately quenched in water to obtain amorphous materials.

In order to prepare glass-ceramic samples, different heating cycles in a muffle kiln were used:

(a) cycle one, performed to investigate both nucleation mechanism and thermodynamically favourable forms. Heating rate = $10\,^{\circ}C\,min^{-1}$ with four holds for 1 h each at 800, 900, 1000 and 1100 °C and a room-temperature cooling in 60 min;

(b) cycle two, to study the kinetically favoured crystals and to realize fully their potential in industrial applications as tile glazes or coating films on a clay support. Heating rate = $25\,^{\circ}C\,min^{-1}$, one hold at 1100 °C for 10 min, and a room-temperature cooling in 20 min.

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TABLE I Compositions (wt %) of the various glasses

Name	SiO_2	CaO	MgO	TiO_2	ZrO_2	P_2O_5
Un-glass	50	25	25			
Ti-glass	45	22.5	22.5	10		
Zr-glass	45	22.5	22.5		10	
P-glass	45	22.5	22.5			10

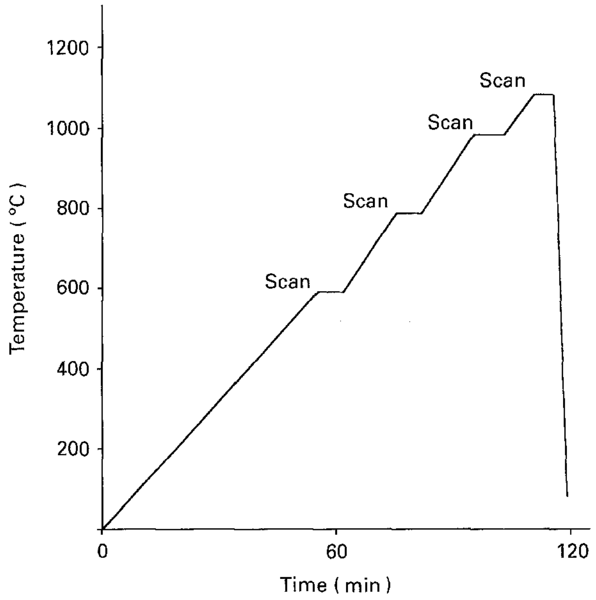

Figure 1 Heat-treatment cycle XRD scans during holding at particular temperatures.

2.2. Physical characterization and microstructural analysis

The characteristic glass transition temperatures, T_g, and crystallization temperatures, T_c, were determined using a Netzsch STA 409 differential thermal analysis (DTA) using glass samples ground to < 20 μm grain size. The heat treatment was carried out on about 100 mg of sample in a platinum crucible in the apparatus and compared with the same amount of Al_2O_3 as reference. Static non-isothermal experiments were performed by heating the glass sample from 20 °C to 1400 °C at the rate of 20 °C min^{-1}. Data for the run were collected directly from the DTA.

To confirm the non-crystalline structure of the parent glasses and to detect and identify the crystalline phases formed during the heat treatments, X-ray diffraction (XRD) was performed. Appropriate powders of quenched glasses and of glass-ceramics were analysed by a Philips PW 1050 X-ray powder diffractometer using nickel-filtered CuK_α radiation in the 2θ range from 20°–45° at a scanning speed of 1° min^{-1} and a powder diffractometer with a high-temperature Anton Paar HTK stage attachment, model Philips PW 3710. The heat-treatment cycle is shown in Fig. 1, and the scans were performed in the 2θ range from 25°–38°.

A Philips PSEM XL40 scanning electron microscope (SEM) with an energy dispersive spectrometry (EDS) attachment was used for morphological observations on freshly fractured glasses and glass-ceramics surfaces.

2.3. Industrial tests

To verify the devitrification capability of these systems at the very fast heating rates currently used in the modern tile industries, thin (~ 1 mm) films of quenched and finely powdered (particle size < 63 μm) parent glass formulations on a clay support of 10 cm × 5 cm, were heated as indicated in cycle two. XRD measurements and SEM observations were directly performed on the obtained coating films.

3. Results and discussion

3.1. Thermal results

In order to design a glass-ceramic material with the desired properties, it is necessary to achieve a thorough knowledge of the thermal behaviour of the parent glass and of the devitrification kinetics of the system, including a thorough understanding of the role played by the addition of nucleating oxides that enable optimization of the heat treatment (heating cycles, and temperatures) to be achieved.

The complete DTA thermograms of the four glass formulations investigated are shown in Fig. 2. Similar features in each thermogram are apparent:

(a) an endothermic event, corresponding to an increase in specific heat, signifying the glass transition, T_g. It is worth noting that for all the compositions investigated, different T_g values were observed. Because it is known that at the glass transition temperature all the glassy systems present very similar viscosity values (10^{13}–$10^{13.5}$), it can be hypothesized that, for the investigated systems, the changes in the bulk atomic structure due to the presence of the nucleating oxides are not similar [10];

(b) an exothermic event indicating crystallization with a maximum T_c at a temperature of about 900,

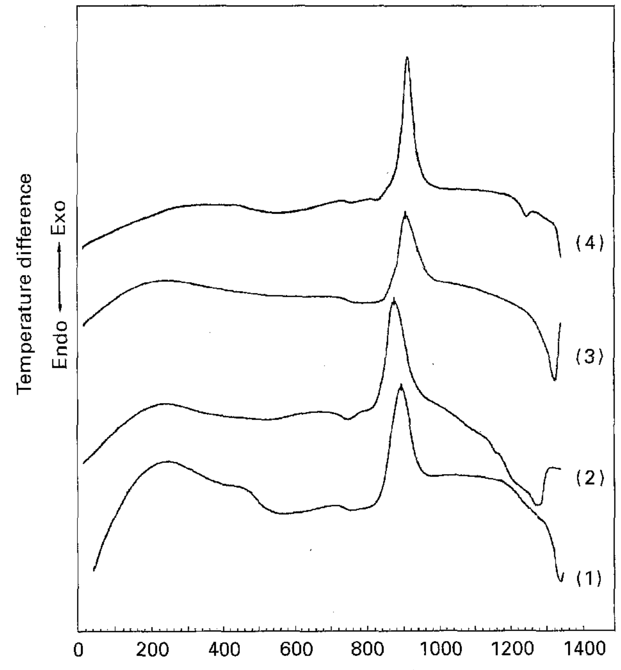

Figure 2 DTA curves of the studied glasses: (1) Un-glass; (2) Ti-glass; (3) Zr-glass; (4) P-glass.

TABLE II Values obtained by DTA analysis

Name	T_g (± 5 °C)	T_c (± 2 °C)	Melting point (± 2 °C)	Activation energy (kcal mol^{-1})
Un-glass	719	899	1340	80
Ti-glass	687	885	1282	77
Zr-glass	730	920	1328	130
P-glass	739	921	1250, > 1350	103

885, 920 and 921 °C for the unnucleated (Un), TiO_2 (T), ZrO_2 (Z), and P_2O_5 (P) glasses respectively;

(c) an endothermic event at different temperatures indicating the melting of the crystal phases formed during heating.

The DTA curves show a decrease in the maximum peak temperature, T_c, when TiO_2 was added, while for the other two nucleating agents, a slight increase was noted. The glass transition temperature, T_g, and the maximum crystallization temperature, T_c, values for all formulations, are shown in Table II.

From phase diagram studies, it is possible to predict the thermodynamic stability of each phase. However in glass-ceramics preparation, kinetics play a fundamental role and thus predictability is difficult. Many methods can be used to determine the kinetic parameters (activation energy, reaction order, pre-exponential factor) [11–14] of the devitrification processes. When DTA and DDTA data can be simultaneously recorded, the method of the derivative [15] is applicable. This easy method gives good indications of the range of values of activation energies [16].

In the preparation of glass-ceramic materials based on this system, crystallization is most often ensured using TiO_2 and ZrO_2 nucleating agents or mixtures thereof [17]. The presence of the nucleating agents increases the tendency to phase separation, but the mode of operation of these oxides is more problematic than for the metallic nucleating agents. The values of the activation energies for the crystallization processes in our glasses are shown in Table II. A slight decrease in the activation energy, when TiO_2 was added, and a slight increase for the addition of the other two nucleating agents, were observed. As reported in the literature, the effect of nucleating agent oxides depends on their nature; while TiO_2 decreases the activation energy, P_2O_5 and ZrO_2 do not [17]. This can be explained by considering that the viscosity increases dramatically with increasing ZrO_2 content and to a much greater extent than with the other elements of the same series (titanium and thorium) both in plastic glass melts and in the transformation interval of glass [18]. ZrO_2 increases the viscosity particularly in the absence of alkali metal oxides, while P_2O_5 was observed to be an effective nucleating agent in low Al_2O_3 content glass, in some cases alone, but in the very low expansion glass ceramics in combination with other nucleants, such as ZrO_2.

3.2. Microstructural determination

After the two thermal treatments, all the glass-ceramic samples contained diopside crystals [19] with the only exception of composition P-glass which also indicated small amounts of wollastonite [20]. Figs 3 and 4 show the XRD patterns of glass-ceramic powders obtained after the two different cycles (as indicated above). The development of the individual crystalline phase is independent of the heat treatment and of the presence of the nucleating agents. Nucleating agents did not modify the crystalline phases present in the glass-ceramic samples after the devitrification process and this effect was independent of the

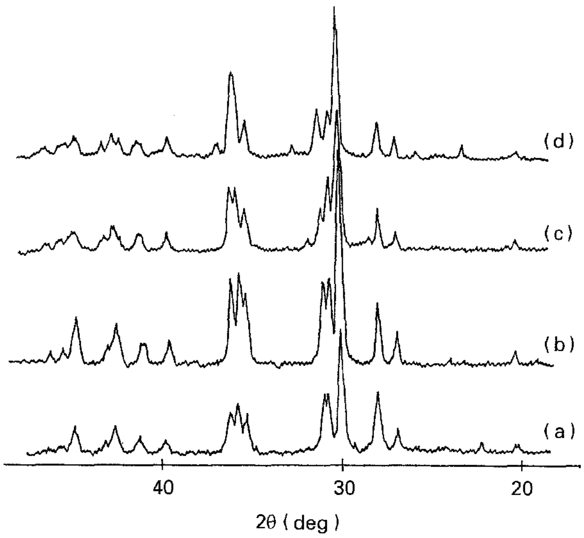

Figure 3 XRD patterns of glasses after thermal treatment with cycle 1: (a) Un-glass; (b) Ti-glass; (c) Zr-glass; (d) P-glass.

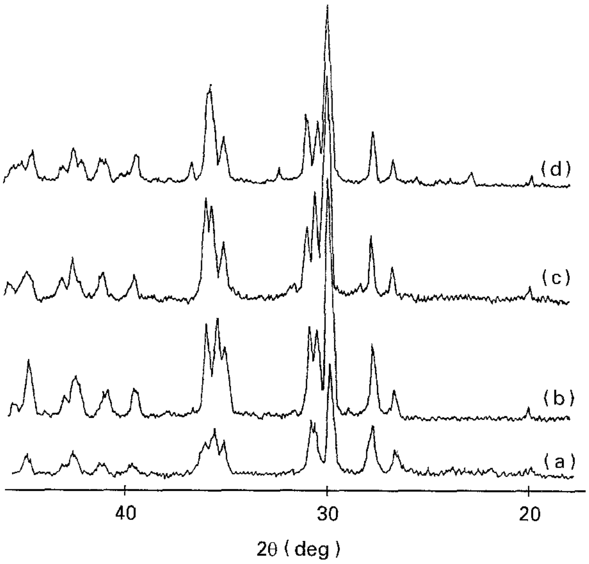

Figure 4 XRD patterns of glasses after thermal treatment with cycle 2: (a) Un-glass; (b) Ti-glass; (c) Zr-glass; (d) P-glass.

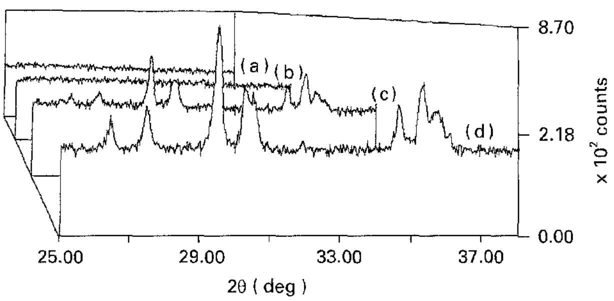

Figure 5 XRD patterns during scans of Fig. 4: (a) 600 °C; (b) 800 °C; (c) 1000 °C; (d) 1100 °C.

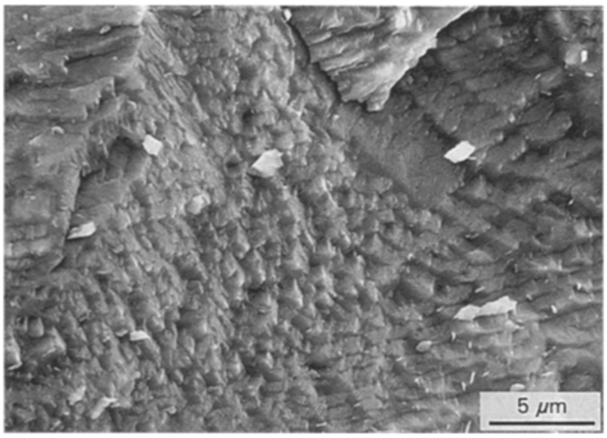

Figure 6 Scanning electron micrograph of Un-glass after thermal treatment.

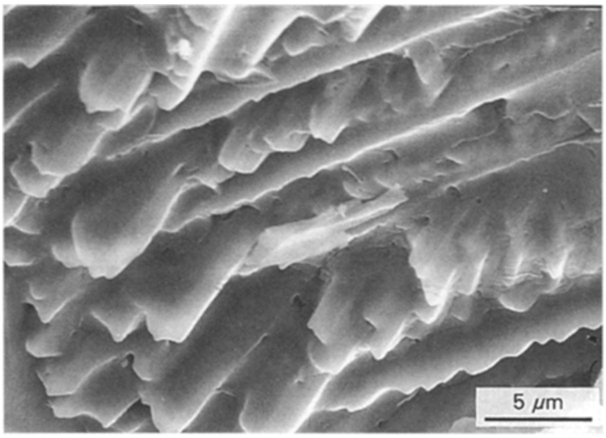

Figure 7 Scanning electron micrograph of P-glass after thermal treatment.

thermal treatment, indicating that the diopside crystalline phase was kinetically and thermodynamically more favourable than all other possible crystals in this area of the phase diagram.

In situ high-temperature XRD patterns performed on the powdered samples confirmed the above results. Fig. 5 reports, as an indicative example, the XRD patterns recorded on the undoped glass samples heated as indicated in Fig. 1. At the indicated heating cycle the glass powders are completely amorphous up to about 800 °C, and crystallization occurs starting from about 1000 °C. The doped formulations show similar behaviour: at 1100 °C all the glasses are completely crystallized, and only crystalline diopside was observed, confirming:

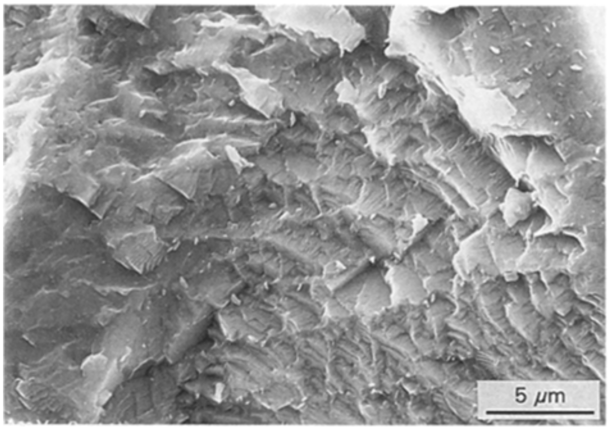

Figure 8 Scanning electron micrograph of Zr-glass after thermal treatment.

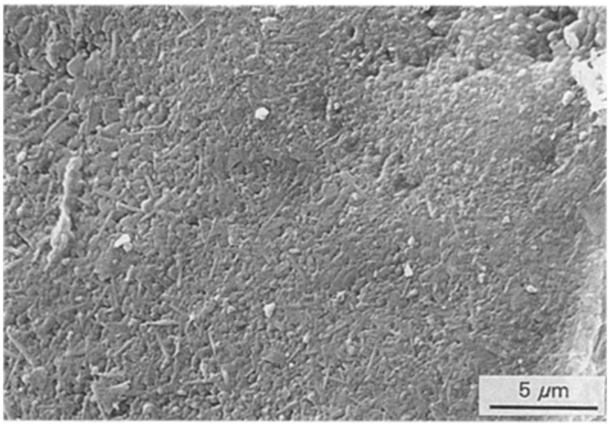

Figure 9 Scanning electron micrograph of Ti-glass after thermal treatment.

(a) the high stability of the diopside, as previously shown on samples obtained by the traditional two-step nucleation and crystallization method;

(b) their potential applications as glass-ceramic glazes for ceramic tiles in which high heating rates are used during manufacture.

Figs 6–9 show scanning electron micrographs of the glass-ceramic fracture surfaces. Observations revealed the presence of a very close network of crystals of diopside having different sizes and shapes. P_2O_5- and ZrO_2-doped glass-ceramics resulted in randomly distributed crystals when compared to undoped samples and the crystal sizes (Figs 7 and 8) were larger than those of the undoped system, from 1–5 μm (Fig. 6). The presence of TiO_2 produced a less-compact microstructure with very fine grain size, < 0.5 μm (Fig. 9).

3.3. Industrial results

SEM analyses of the coating films obtained by the fast firing process, show a dense microstructure very similar to that observed in the samples crystallized using cycle 1. XRD patterns confirmed only the presence of diopside crystals. The possibility of obtaining crystallized samples (nucleation + crystallization) using fast cycles, demonstrates that the $MgO-CaO-SiO_2$ system is appropriate in the formulation of tile glazes.

4. Conclusions

All the glassy systems investigated show a high tendency for devitrification giving only one crystalline phase identified as diopside ($MgCa(SiO_3)_2$) even at very high heating rates. In industrial tile manufacturing, the currently used heating cycles are very similar to the one-step heat treatment used in this study, thus the undoped and doped formulations are suitable for use as tile glazes, tile-glaze components, and components of ceramic bodies. Nucleating oxides can change the morphology and the microstructure of the obtained glass-ceramic materials.

TiO_2 acts as nucleant for the diopsidic phase, favouring the crystallization process, because both the crystallization peak and the activation energy present values lower than the undoped system. ZrO_2 and P_2O_5 retard the crystallization process with respect to the undoped sample, but P-glass also forms a small amount of wollastonite phase. This last effect can explain the high activation energy value of P-glass in comparison with Zr-glass, because the diopside and wollastonite crystallization processes are simultaneous. Moreover, it is possible that the wollastonite phase inhibits the nucleation of the diopsidic phase, thus few nuclei are produced and the diopside crystals that do form have a larger size, as shown by the scanning electron micrograph. Ti-glass-ceramic crystallized giving smaller crystals than P-glass-ceramic, because the nucleating agent produces a larger number of crystalline seeds. The effect of ZrO_2 is midway between the undoped and P-glass systems. These glass-ceramic systems show a great crystallinity and appear compatible with the clay support. This suggests that these nucleated and unnucleated systems can be considered appropriate for use as tile glazes.

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References

1. S. R. LEVITT, *J. Mater. Sci.* **8** (1973) 793.
2. R. H. DOREMUS, "Glass science" (Wiley, New York, 1973) p. 75.
3. G. H. BEALL and D. A. DUKE, in "Glass-ceramic technology-glass science and technology", Vol 1, edited by D. R. Uhlmann and N. J. Kreidl (Academic Press, New York, 1983) pp. 403–45.
4. J. J. BRENNAN and K. M. PREWO, *J. Mater. Sci.* **17** (1982) 2371.
5. C. LEONELLI, T. MANFREDINI, M. PAGANELLI, G. C. PELLACANI, J. L. AMOROS ALBARO, J. E. E. NAVARRO, M. J. ORTS, S. BRUNI and F. CARIATI, *J. Am. Ceram. Soc.* **74** (1991) 983.
6. C. LEONELLI, T. MANFREDINI, M. PAGANELLI, G. C. PELLACANI, J. L. AMOROS ALBARO, J. E. E. NAVARRO, M. J. ORTS, and L. PENNISI, *Ind. Ceram.* **11** (1991) 7.
7. E. F. OSBORNE, *Am. J. Sci.* **240** (1942) 751.
8. M. SOPICKA-LIZER and S. PAWLOWSKI, *Ceram. Acta* **3** (1991) 39.
9. P. S. ROGERS, J. WILLIAMSON and P. E. JOHNSON, (SILCERAM) UK Pat. 1462 035 (1974) and US Pat. 3901 716 (1975).
10. D. N. COON and R. M. NEILSON JR, *J. Mater. Sci. Lett.* **7** (1988) 33.
11. H. E. KISSINGER, *J. Nat. Bur. Stand.* (US) **57** (1956) 217.
12. *Idem*, *Anal. Chem.* **29** (1957) 1702.
13. T. OZAWA, *Polymer* **12** (1971) 150.
14. J. SESTAK, *Phys. Chem. Glasses* **6** (1974) 137.
15. A. MAROTTA, S. SAIELLO, F. BRANDA and A. BURI, *J. Mater. Sci.* **17** (1982) 105.
16. L. BARBIERI, C. LEONELLI, T. MANFREDINI, M. ROMAGNOLI, G. C. PELLACANI and C. SILIGARDI, *Thermochim.* Acta, in press.
17. C LEONELLI, T. MANFREDINI, M. PAGANELLI, P. POZZI and G. C. PELLACANI, *J.Mater. Sci.* **26** (1991) 5041, and references quoted therein.
18. M. B. VOLF, "Chemical approach to glass" (Elsevier, New York, 1984) pp. 306–14.
19. Powder Diffraction File, Card no. 11-654a. Joint Committee on Powder Diffraction Standards, Swarthmore, PA, USA.
20. Powder Diffraction File, Card no. 19-249. Joint Committee on Powder Diffraction Standards, Swarthmore, PA, USA.

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