Journal of the European Ceramic Society **8** (1991) 177–180

Phase Transformation in Al–Si–Mg Gels: Effect of Additions of Ti, Ce and Zr

A. V. Galakhov & V. Ya. Shevchenko

High-Tech Ceramics Scientific Research Centre, USSR Academy of Science, Ozernaya 48, Moscow, 119361, USSR

(Received 13 September 1990; revised version received 22 March 1991; accepted 15 April 1991)

Abstract

Phase transformations in polymeric Al–Si–Mg gels of cordierite composition with addition of 5 wt% TiO_2, ZrO_2 and CeO_2 have been investigated. An addition of TiO_2 and CeO_2 stimulates the formation of petalite phase ($Al_2O_3 . MgO . 3SiO_2$) instead of μ-cordierite in the range 700–1000°C. TiO_2 and CeO_2 reduce the crystallization temperature of μ-cordierite, whereas ZrO_2 produce no essential effect on the phase transformations in Al–Si–Mg gels.

An polymeren Al–Si–Mg–Gelen wurden im Bereich der Cordieritzusammensetzung und unter Zugabe von 5 Gew.% TiO_2, ZrO_2 und CeO_2 Phasenumwandlungsreaktionen untersucht. Im Temperaturbereich von 700–1000°C fördert eine TiO_2–bzw. CeO_2–Zugabe die Bildung von Petalit ($Al_2O_3 . MgO . 3SiO_2$) anstatt des μ-Cordierits. TiO_2 und CeO_2 reduzieren die Kristallisationstemperatur des μ-Cordierits. ZrO_2 hat dagegen keinen wesentlichen Einfluß auf die Phasenumwandlungen in Al–Si–Mg-Gelen.

On a étudié les transformations de phase dans des gels polymériques Al–Si–Mg de composition cordiérite avec des additions de 5% massiques de TiO_2, ZrO_2 et CeO_2. L'ajout de TiO_2 et de CeO_2 favorise la formation de phase pétalite ($Al_2O_3 . MgO . 3SiO_2$) à la place de la cordiérite μ dans la gamme de températures 700–1000°C. TiO_2 et CeO_2 abaissent la température de cristallisation de la cordiérite μ, tandis que ZrO_2 n'a pas d'effet notable sur les transformations de phase au sein des gels Al–Si–Mg.

1 Introduction

The temperature of sintering of cordierite ($2Al_2O_3 . 2MgO . 5SiO_2$) prepared from natural mineral raw materials is equal to 1300–1410°C.[1] The use of synthetic cordierite powders obtained by sol–gel technology makes it possible to reduce the sintering temperature of cordierite to 800–900°C.[2] In heat treatment of amorphous Al–Si–Mg gel of cordierite composition at 1000–1100°C, there is formed a phase which is known alternatively as μ-cordierite[3] (hexagonal, space group *P*622) or as quartz-like phase.[4] At a temperature of 1100–1250°C this phase transforms into β-cordierite (hexagonal, space group *P*6/*mcc*), which on a further increase of temperature gradually transforms into α-cordierite (orthorhombic, space groupe *Cccm*). As is known from work devoted to investigation of phase transformations in Al–Si–Mg glasses, the use of additions of TiO_2, ZrO_2 and CeO_2[5] leads to reduction of the crystallization temperature of cordierite. The present work presents the results of investigations of the effect of these additions on the phase transformations in powders of cordierite composition prepared by sol–gel technology.

2 Experimental

As the initial substances for preparation of Al–Si–Mg gels, tetraethoxysilane (TEOS) of extra-pure quality, $Al(NO_3)_3 . 9H_2O$ (chemically pure), $Mg(NO_3)_2 . 6H_2O$ (analytically pure), $Ce(NO_3)_3 . 6H_2O$ (analytically pure), $ZrOCl_2 . 8H_2O$ and $TiCl_3$ (pure, 20% alcohol solution) were used. Crystalline

Journal of the European Ceramic Society 0955-2219/91/$3.50

hydrates of aluminium and magnesium nitrates were dissolved in absolute ethyl alcohol in a proportion $Al^{3+}:Mg^{2+}=2:1$. TEOS was added to the salt solution to make the composition $2Al_2O_3.2MgO.5SiO_2$. Additions in the form of crystalline hydrates of Ce and Zr salts or $TiCl_3$ solution in the amount of 5 wt% (in terms of oxide) were introduced at the stage of preparation of the alcohol solution of aluminium and magnesium salts. After adding TEOS and stirring for 0·5 h, the solutions were placed into a thermostat preheated to 60°C. The time of gelation for all compositions was roughly the same and equal to around 4 h. The gels were transparent and glass-like. They were dried at 100°C and then subjected to thermal treatment at a temperature of 700, 900, 1000, 1100, 1200 and 1300°C. The heating rate till a given temperature was equal to 400°C/h. The aging time at a given temperature was equal to 3 h. The gel without additions will be further designated as K, that with an addition of TiO_2 as KT, that with addition of ZrO_2 as KZ, and that with CeO_2 as KC.

3 Results

Differential thermal analysis of gels was carried out in a Paulic–Paulic system thermoanalyser model Q-1500. The temperature was raised at a rate of 7·5°C/min. The mass of specimens was kept at the same level of 600 mg. DTA curves for the gels are given in Fig. 1. The gel without additions (K) exhibited two exothermic signals at 1050 and 1270°C. A similar behaviour was found for KZ gel. KC gel was characterized by the appearance of a slight additional exo-effect in the low-temperature region: 870°C. For KT gel a substantial drop in the temperature of the exopeak was observed in the region 1000°C (from 1050 to 940°C as compared to K gel without additions). For KC gel, this reduction was less substantial.

X-Ray patterns of gels subjected to 3-h thermal treatment at different temperature were taken in a DRON-3M diffractometer in CuK_α emission. They are shown in Fig. 2. The results of phase analysis are summarized in Table 1. Except for the gel with CeO_2 at 700°C, all other gels were amorphous. In KC gel, the broad diffraction lines corresponding to CeO_2 were observed together with the amorphous phase. In K gel without additions, the phase transformations under rising temperature occur generally in accordance with the common scheme observed in crystallization of glasses of cordierite composition,[5] but with a slight difference. After thermal treatment at 900 and

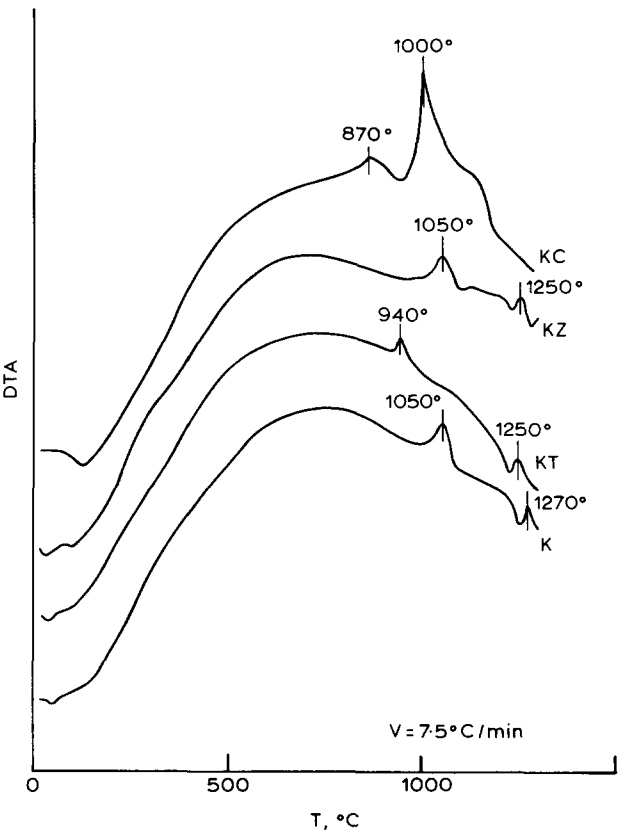

Fig. 1. DTA curves for Al–Si–Mg gels.

1000°C, the presence of petalite phase[6] was found in the material. The formation of this phase was earlier noted in crystallization of Li-containing Al–Si–Mg glasses.[7] In gels with additions of Ti and Ce, the petalite phase forms instead of μ-cordierite at the initial stage of crystallization. In KT gel, no titanium-base phases were found. In KZ gel in the temperature region 900–1200°C, ZrO_2 is present in monoclinic and tetragonal forms and at temperatures above 1200°C, zircon ($ZrSiO_4$) is present. In KC gel, cerium dioxide, which is formed at 700°C, forms no phases with other elements at all temperatures of thermal treatment.

In order to determine the nature of the thermal effects corresponding to the exopeaks of the DTA

Table 1. Phase composition of Al–Si–Mg gels after 3 h thermal treatment

T(°C)	*K*	*KT*	*KZ*	*KC*
700	Am	Am	Am	Am, C
900	μ, P	P	μ, Zt, Zm	P, C
1 000	μ, P	P	μ, P, Zt, Zm	P, C
1 100	μ	μ, P	μ, Zt, Zm	μ, C
1 200	β	β	β, ZS	β, C
1 300	β	β	β, ZS	β, C

Am = Amorphous phase; μ = μ-cordierite; β = B-cordierite; P = petalite phase; Zt = zirconium oxide (tetragonal); Zm = zirconium oxide (monoclinic); ZS = zircon; C = cerium oxide.

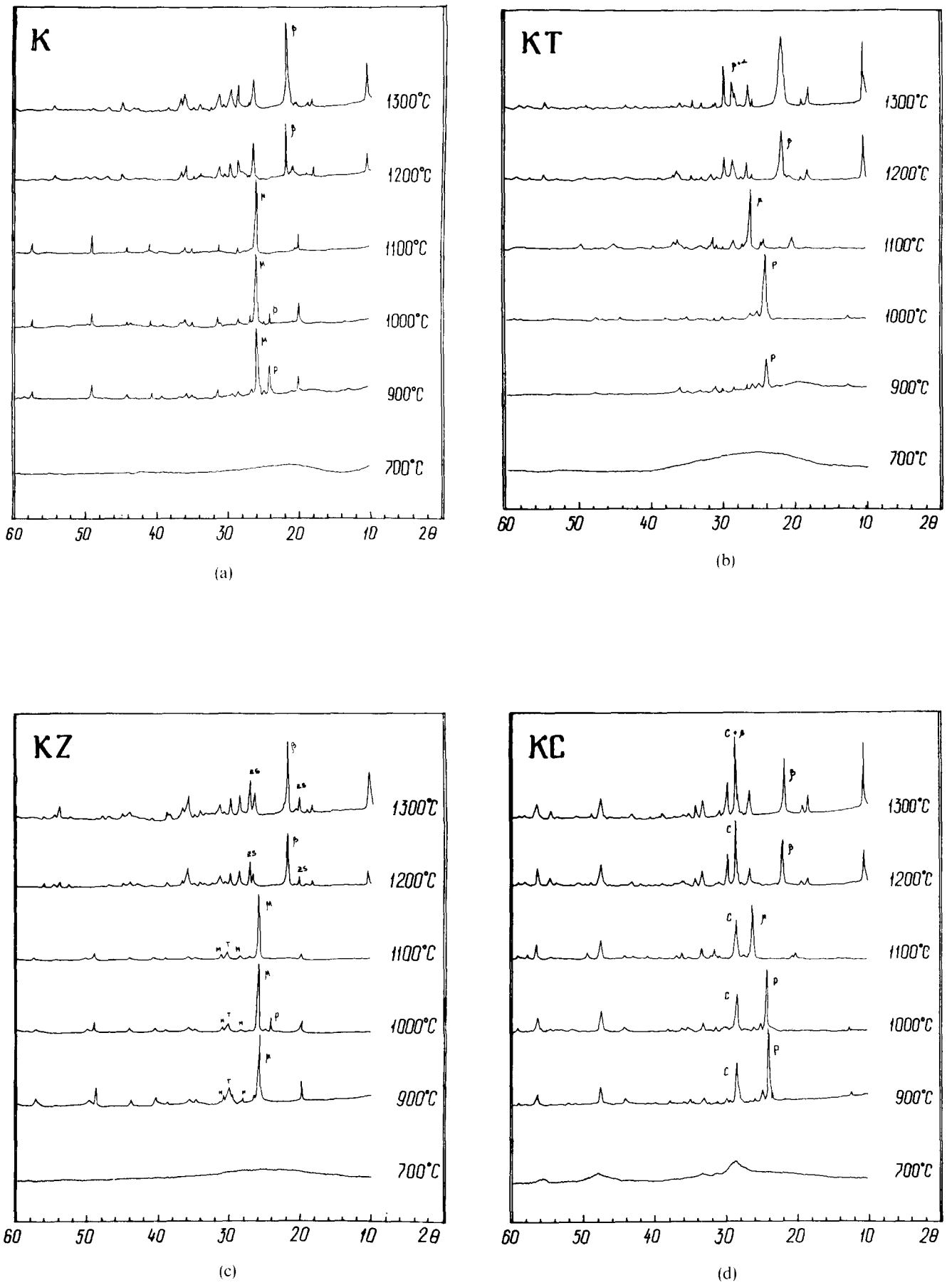

Fig. 2. X-Ray patterns of Al–Si–Mg gels after 3 h thermal treatment. Designations: μ = μ-Cordierite; β = β-cordierite; P = petalite phase; T = zirconium oxide (tetr.); M = zirconium oxide (monocl.); ZS = zircon; C = cerium oxide. (a) K; (b) KT; (c) KZ; (d) KC.

curves, phase analysis of gel specimens extracted from the thermoanalyser was carried out immediately before and after the exopeak. It has been established in this way that the cause of the appearance of the exo-effect in KC gel at 870°C is the thermal effect of crystallization of cerium dioxide. The temperatures of 1000°C for KC gel, 1050°C for K and KZ gels, and 940°C for KT gel correspond to the formation of μ-cordierite. It should also be noted that, in contrast to gels subjected to 3-h thermal treatment, in all cases considered, no petalite phase was detected before and after a peak. At temperatures of 1250–1270°C, μ-cordierite transforms into the β-form.

4 Conclusions

Upon analysis of the results obtained, it may be concluded that the process of formation of μ- and β-cordierite may occur gradually by diffusion at lower temperatures than those required for polymorphous transformations during fast heating. In the latter case, at the initial stage of crystallization of gels of cordierite composition, a petalite phase may form instead of μ-cordierite. This phase is richer in magnesium and aluminium ($MgO.Al_2O_3.3SiO_2$[6] than stoichiometric cordierite. Addition of zirconium has no effect on the temperature of formation of μ-cordierite in Al–Si–Mg gels, but this temperature is decreased substantially by an addition of titanium. Cerium produces a weaker effect. The indicated additions have no essential effect on the temperature of polymorphous $\mu \rightarrow \beta$-cordierite transformation.

References

1. Balkevich, V. L., *Technical Ceramics*. Stroyizdat, Moskow, 1984, in Russian.
2. Bernier, J. C., Rehspringer, J. L., Vilminot, S. & Poix, P., Synthesis and sintering comparison of cordierite powders. *Mat. Res. Soc. Symp. Proc.*, **73** (1986) 129–34.
3. Schreyer, W. & Schairer, J. F., Compositions and structural state of anhydrous Mg-cordierites: a re-investigation of the central part of the system $MgO–Al_2O_3–SiO_2$. *J. Petrol.*, **2** (1961) 324–406.
4. Syrajiddinov, N. A., Stable and metastable phases in crystallization of cordierite glasses. *J. Phys. Chim.*, **XLII** (1968) 101–4 (in Russian).
5. Gregory, A. G. & Veasey, T. J., Review: The crystallization of cordierite glass. *J. Mat. Sci.*, **6** (1971) 1312–21.
6. Schreyer, W. & Schairer, J. F., Metastable osumilite and petalite-type phases in the system $MgO–Al_2O_3–SiO_2$. *Am. Mineral.*, **47** (1962) 90–4.
7. Höland, W., Plumat, E. R. & Duvigueand, P. H., Crystallization of $SiO_2–Al_2O_3–MgO$ gel glasses. *J. Non-Cryst. Solids*, **48** (1982) 205–17.