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EFFECT OF MODE OF SILICA ADDITION ON THE TRANSFORMATION OF QUARTZ INTO CRISTOBALITE

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ABSTRACT

The effect of the different forms of active silica, namely, silica gel, silica glass, rice husk ash silica (RH-ash) and fine quartz on the transformation of quartz into cristobalite was followed at different temperatures ranging from 1350 to 1500°C. A mixture of 95% quartz and 5% of the different active forms of silica was studied.

The transformation reaction was followed by DSC and by X-ray analysis. SEM studies were carried out to throw light on the texture of the powders and the bodies produced. Results showed that the different additives acted in various ways on the transformation process and size of the cristobalite formed.

INTRODUCTION

The silica basis for the production of refractory silica bricks is quartzite. Orthoquartzite is the raw material preferred because it readily transforms into cristobalite when fired at 1450–1500°C. It is believed that the high content of bonding material favours its early conversion [1].

Different cations affect the transformation process in various ways. A mixture of iron oxide and calcium oxide is usually added to enhance the reaction [1]. Flint [2], South African silicrete, quartz glass from the waste of quartz glass industry [1], silica gel and diatomite [3] are also added for the same purpose.

According to Grimshaw et al. [4] the transformation of quartz into cristobalite starts at the surface of the grains. Therefore, the addition of a mineralizer or a surface-active material with a high surface area will enhance the reaction.

In this study different sources of active silica, namely, fine quartz less than 10 μm, silica gel, rice-husk ash silica (RH-ash) fired at 500°C and silica glass are added to quartz. The conversion reaction into cristobalite is followed by DSC and by X-ray analysis. The surface of the grains is studied by SEM.

TABLE 1

Chemical analysis of quartz and RH-ash silica

Main constituent elements	Quartz	RH-ash silica
SiO_2	99.65	93.66
Al_2O_3	0.18	1.69
Fe_2O_3	0.58	0.198
Na_2O	0.12	0.48
K_2O	–	1.67
CaO	–	0.71
MgO	–	0.78
Loss on ignition	0.15	0.98
Main grain size	**Quartz grain size**	
20–45 μm	30	
10–20 μm	35	
<10 μm	35	

EXPERIMENTAL

Raw material

Pure quartz (99.65%) from the quartz veins occurring in the Eastern Desert, rice husk ash silica (RH-ash) fired in an atmosphere of air [5], silica gel (Merck) and silica glass (Schott) were used. The chemical analysis and grain size of the raw material are represented in Table 1.

Processing

Mixtures of 95% quartz and 5% of the different forms of active silica were processed in the form of discs with a diameter of 2.5 cm and a thickness of 0.5 cm under a pressure of 30 kN. Specimens were fired between 1350 and 1500°C with a temperature interval of 50°C in a globar furnace for three days comprising heating, soaking at maximum firing temperature for one hour and cooling.

The transformation reaction was followed by DSC. The amount of cristobalite formed and the remaining quartz were quantitatively determined. Samples of 21 mg of the mixtures fired at the different temperatures were mounted in capsules and scanned against reference empty capsules in a DSC cell No. 900600902 DuPont. The run was carried out in an atmosphere of argon. The heating rate was 20°C min^{-1}, the sensitivities chosen were 0.5 mcal s^{-1} in^{-1} and for the temperature 1° in^{-1}. Standard samples for cristobalite and quartz were prepared and scanned under the same conditions. The area under the peaks was measured from the height of the respective peak (quartz at 573°C and cristobalite at 250°C) multiplied by the width at half height. The contents of quartz and cristobalite were obtained from the standard curves [6]. Results are presented in Figs. 1 and 2 and Table 2.

X-ray analysis was carried out for the four powders of the active silica forms fired at 1500°C for 1 h and the mixtures fired at 1350°C and 1500°C. Results obtained are shown in Figs. 3 and 4. The texture of the different powders and mixtures fired at 1500°C was examined by SEM. Mixtures were first polished and etched. Micrographs of the powders are shown in Fig. 5.

RESULTS AND DISCUSSION

Results for the mixtures

Results obtained by DSC (Figs. 1 and 2) for the different mixtures fired between 1350 and 1500°C give an idea of the degree of transformation and

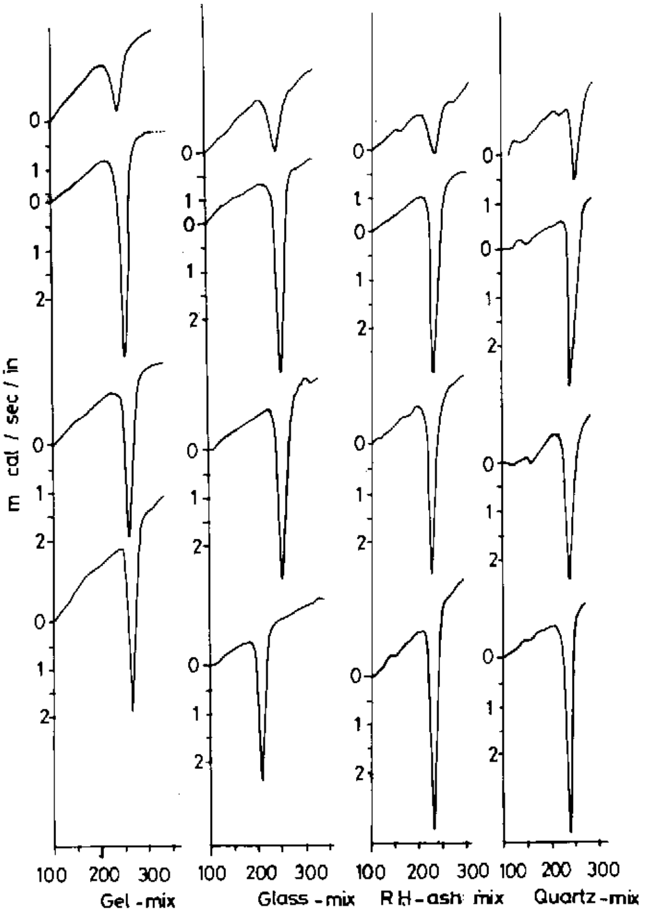

Fig. 1. Peak temperature of cristobalite as detected by DSC in the mixtures.

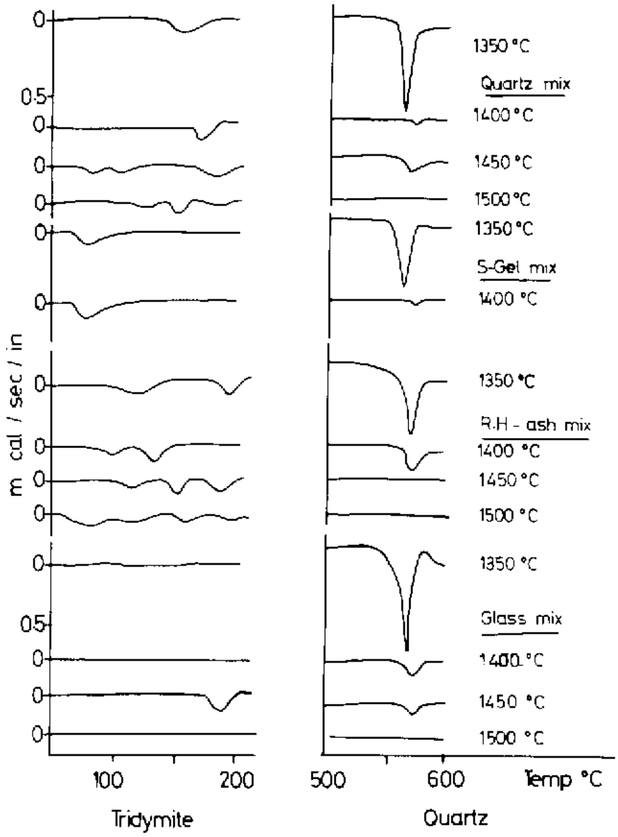

Fig. 2. Peak temperature of quartz and tridymite as detected by DSC in the mixtures.

TABLE 2

Degree of quartz transformation in the different mixtures

Mixture composition	Firing temp. (°C)	Cristobalite (%)	Remaining quartz (%)	Intermediate phase (%)
Quartz mixture	1350	26.3	26.01	47.7
RH-ash mixture	1350	31.05	16.17	52.78
Silica gel mixture	1350	29.04	29.53	41.43
Quartz mixture	1400	68.3	0.93	30.77
RH-ash mixture	1400	68.3	14.76	16.94
Silica gel mixture	1400	72.33	0.7	26.97
Silica glass mixture	1400	67.13	8.2	24.67
Quartz mixture	1450	50.63	5.62	43.75
RH-ash mixture	1450	77.59		22.41
Silica gel mixture	1450	57.17	–	42.83
Silica glass mixture	1450	62.83	1.75	35.42
Quartz mixture	1500	73.84	–	26.16
RH-ash mixture	1500	86.21	–	13.79
Silica gel-mixture	1500	62.83	–	37.17
Silica glass mixture	1500	39.46	–	60.54

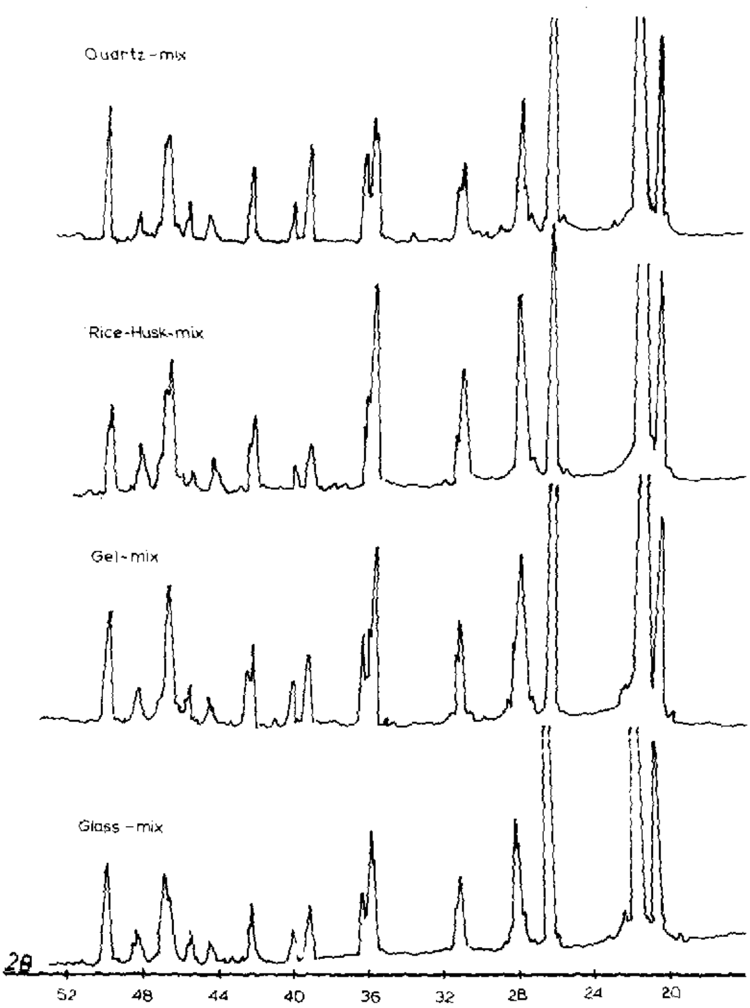

Fig. 3. X-Ray patterns of mixtures fired at 1350°C.

types of silica formed. Thus, cristobalite formed at 1350°C is a disordered form with the peak temperature at 235°C. The content of cristobalite varies with the type of addition (Table 2). Silica gel gave the least amount of cristobalite, the minimum content of remaining quartz and, as a result, the highest percentage of the intermediate phase. The amount of disordered cristobalite formed at 1400°C ranged between 67–72% while the content of quartz left without conversion did not exceed 1% in all mixtures except the RH-ash mix. The difference represents the intermediate phase and the tridymite formed which was identified from the peaks found at 85, 135 and 165°C. The amount of this intermediate phase present was greatly reduced. The disordered cristobalite still exists in the mixtures fired at 1450°C, but in

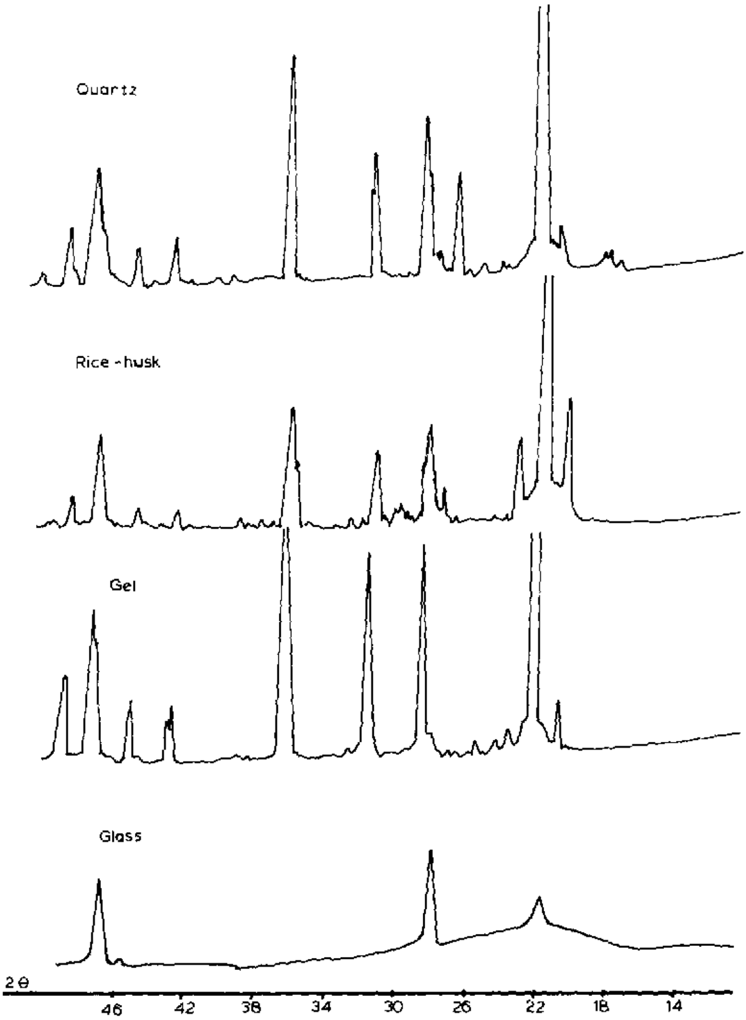

Fig. 4. X-Ray patterns of powders fired at 1500°C.

a smaller amount than in the mixtures fired at 1400°C, except that containing RH-ash silica. At 1500°C maximum transformation was obtained by this mixture (86%). The addition of silica gel and silica glass favoured the formation of one modification only which is disordered cristobalite with peak temperatures at 235 and 195°C, respectively. This was confirmed by the results of X-ray analysis. Mixtures fired at 1350°C show the presence of tridymite and cristobalite together with the remaining quartz (Fig. 3).

Results for powders

Fine quartz, silica gel, RH-ash silica and silica glass powders heated at 1500°C for 1 h gave the X-ray patterns shown in Fig. 4. It is evident that quartz is nearly transformed into cristobalite, RH-ash silica gave mainly tridymite, while cristobalite prevailed in silica gel. Silica glass melted completely but the main peak of cristobalite was readily identified at $2\theta = 22°$, $d = 4.05$ Å. X-Ray analysis was also carried out for silica gel samples fired at low temperatures (800 and 900°C) for 24 h. Cristobalite was the silica form identified.

SEM of the powders fired at 1500°C are shown in Fig. 5. Fine quartz showed sintered agglomerates that have lost their original shape. The surface of the quartz grains is totally covered with small crystals of cristobalite. Grains of silica glass powder melted and cristobalite crystals are found mainly along the cracks and fissures (Fig. 5b). RH-ash silica preserved its shape even when fired at 1500°C. The skeleton showed a melted phase with the predomination of rounded grains less than 1 μm embedded in it (Fig. 5c). Grains of silica gel powder were fused together giving clusters and showing no distinct shape but the presence of a liquid phase is quite evident. The cristobalite crystallites could not be identified (Fig. 5d).

DISCUSSION

The transformation of quartz into cristobalite does not take place with the formation of an equivalent amount of cristobalite. It passes through an intermediate phase with unknown structure that varies with the temperature of treatment. Thus, it can be quartz melt or quartz with a thermally defective structure which readily transforms into disordered cristobalite [7]. This view has already been proposed and confirmed by Schwiete and Stollenwerk [8]. They stated that the transformation of quartz into cristobalite is accompanied by the existence of about 20–45% X-ray amorphous substance, which is highly active and leads to the formation of disordered cristobalite.

It is evident from the results for the mixtures under investigation that this intermediate phase is affected by the type of active silica added too. Thus the presence of silica gel raised the amount of this intermediate phase to 54.26% at 1350°C. The possible existence of either a liquid phase or thermally defective quartz is dependent on the temperature of treatment, content of foreign ions present and fineness of the material.

From the above results it is evident that the small additions of active silica to quartz favoured its early transformation to both tridymite and cristobalite at low temperatures of 1350–1400°C. Two phenomena may have occurred simultaneously. The high specific surface area of silica gel (600 $m^2 g^{-1}$) [9] and RH-ash silica (200 $m^2 g^{-1}$) [10] causes a change in the surface energy of the quartz grains and enhances the self-diffusion of the ions that lead to the early transformation, first, to the intermediate amorphous phase state and then to the disordered form of cristobalite. Second, the presence of foreign ions in RH-ash silica and silica glass contributes to the early formation of a

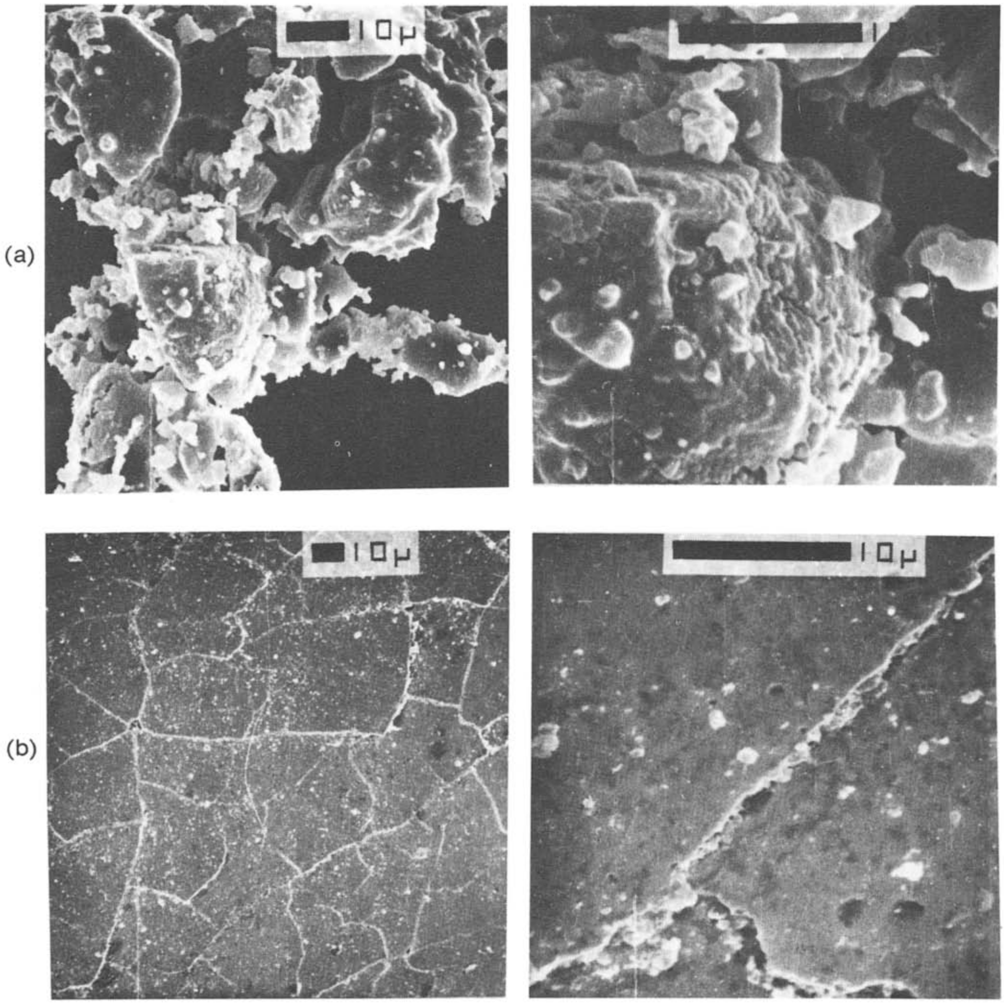

Fig. 5. SEM of powders fired at 1500°C. (a) Quartz, (b) glass.

mixture of disordered cristobalite and tridymite due to the presence of a liquid phase.

The action of the fineness of the material is better seen in the mixture containing silica gel. It was expected that the presence of silica gel would lead to the complete transformation into well ordered cristobalite at low temperature. Instead disordered cristobalite was formed and prevailed even at a high temperature of 1500°C.

The relative stability of cristobalite and tridymite is a matter of controversy in the literature. According to Fenner [1] quartz is transformed into tridymite at 870°C which readily converts into cristobalite at 1470°C. Flörke [11], on the other hand, postulated that tridymite exists only in the presence of a liquid phase. Tridymite crystals that give a DTA peak at 200°C are

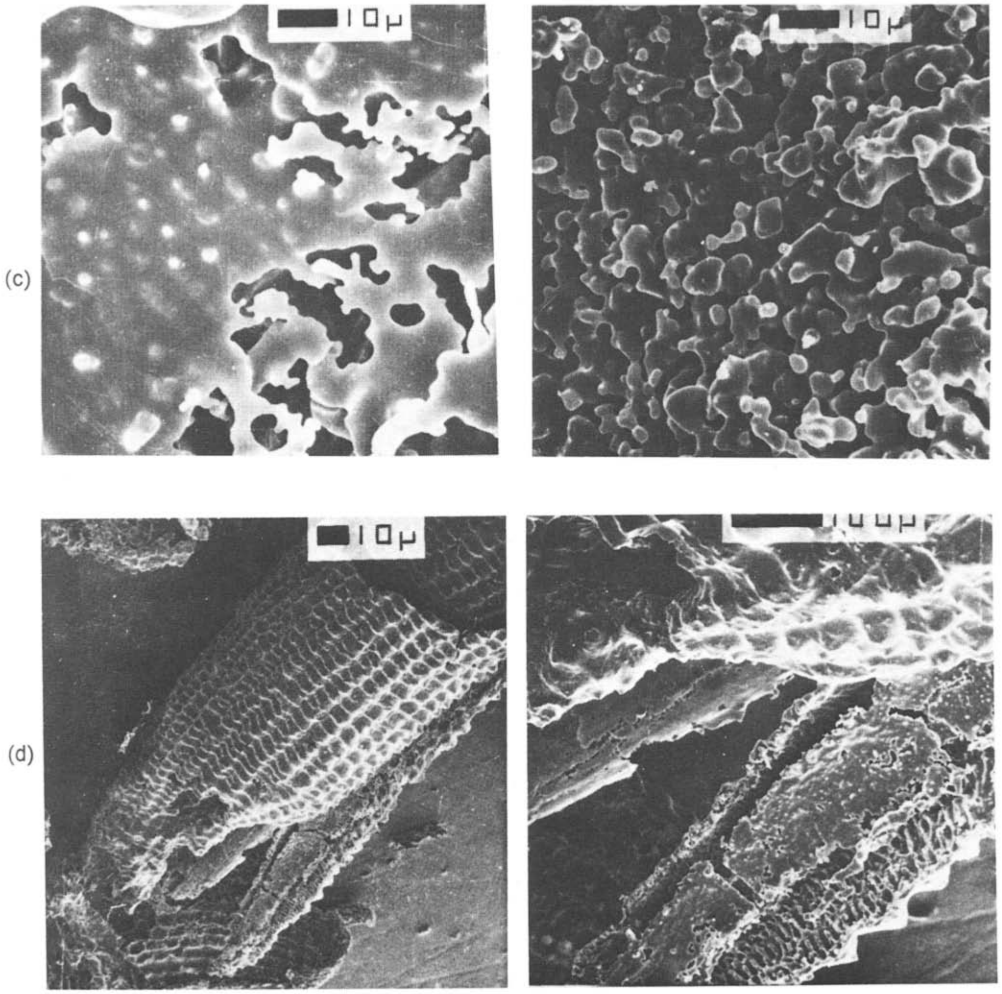

Fig. 5. (c) RH-ash, (d) gel.

nearer to the structure of cristobalite and have three-layer stacking. Not only is it the structure and the degree of disorder that governs the conversion but also the way and amount of foreign ions incorporated in the lattice. He added that the presence of 0.1% Na_2O is sufficient for the stabilization of tridymite. Also cristobalite does not require the presence of foreign ions for its formation but these ions favour the formation of disordered cristobalite even at high temperature [12]. This agrees with the results obtained by silica gel heated at 900°C giving only cristobalite and the presence of disordered cristobalite with the peak temperature at 195°C found in the silica glass mixture.

According to Sosman [13] the relative stability of cristobalite and tridymite can change sign with increasing size of the crystalline unit. It is believed that the cubic close-packing arrangement characteristic of cristobalite is the more stable as long as the crystalline nucleus is small. As it grows to larger dimensions the tridymite structure becomes the more stable, but is produced slowly and only with difficulty because of the necessity of breaking bonds in the cristobalite structure. These deductions are in good agreement with the fact that for the devitrification of vitreous silica, cristobalite is the phase that most readily appears (Figs. 4 and 5b). Also, the results of the mixtures fired at 1400°C show a higher content of cristobalite than the mixtures fired at 1450°C. The content of the intermediate phase and tridymite is higher at 1450°C.

CONCLUSIONS

The amount of amorphous intermediate phase is affected by the type of active silica added, fineness of the material and the temperature of treatment. Silica gel favoured the formation of cristobalite at the low temperature of 1400°C while RH-ash silica enhances its formation at the higher temperature of 1500°C. Finally, addition of silica glass to quartz leads to the formation of disordered cristobalite with the peak temperature at 195°C.

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