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F. Pancrazi, J. Phalippou, F. Sorrentino, J. Zarzycki. GELS IN THE SYSTEM CaO-Al₂O₃-SiO₂ PREPARATION AND STRUCTURAL EVOLUTION. Journal de Physique Colloques, 1982, 43 (C9), pp.C9-279-C9-283. 10.1051/jphyscol:1982952 . jpa-00222481

HAL Id: jpa-00222481

<https://hal.science/jpa-00222481>

Submitted on 4 Feb 2008

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GELS IN THE SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ PREPARATION AND STRUCTURAL EVOLUTION

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Résumé.—Les gels du système $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ ont été élaborés par la méthode de destabilisation d'un sol. Les ions aluminium et calcium sont ajoutés sous forme de solutions aqueuses de nitrates à une solution colloïdale de silice. Afin d'éviter toute précipitation sélective d'hydroxydes de calcium et d'aluminium, la gélification est effectuée à des pH bien définis. Les domaines de formation des gels des binaires $\text{Al}_2\text{O}_3\text{-SiO}_2$ et CaO-SiO_2 ont été établis et s'étendent respectivement de la silice pure à 75 % molaire en SiO_2 et de 100 % à 25 % molaire en SiO_2 . Le domaine de formation des gels du système ternaire $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ s'étend du côté de l'oxyde de calcium et des gels contenant jusqu'à 75 % molaire en CaO ont été synthétisés. L'ion calcium diminue le temps de prise alors que l'ion aluminium l'augmente. L'évolution structurale des gels a été suivie en fonction de la température par diffraction des rayons X. Des nitrates de calcium cristallisés apparaissent à basse température et se décomposent avec un accroissement de température. Cette décomposition s'effectue d'autant plus facilement que la composition du gel est riche en alumine.

Abstract. - Gels in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ were prepared by the sol destabilization method. Aqueous solutions of calcium and aluminium nitrate were added to a colloidal silica solution. In order to avoid a selective precipitation of calcium and aluminium hydroxide, the gelation was done at definite pH. The ranges of gel formation in the binary systems $\text{Al}_2\text{O}_3\text{-SiO}_2$ and CaO-SiO_2 have been established. They lie from 100 to 75 mole % SiO_2 and from 100 to 25 mole % SiO_2 respectively. The range of formation in the ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was displaced towards the compositions rich in calcium and gels containing up to 75 mole % CaO were prepared. The gelation time was reduced by calcium ions while the aluminium ions increased it. The structural evolution of these gels were followed as a function of temperature by X-ray diffraction. Calcium nitrate crystals occurred at low temperature and decomposed as the temperature increased. This decomposition was facilitated in the composition domain rich in aluminium.

1. **Introduction.** - The ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ is very interesting for ceramists (refractories, cements) as well as for glass scientists. The absence of alkali ions gives to the glasses of this system interesting dielectric properties on the one hand a good resistance to devitrification on the other. When other oxides like MgO , TiO_2 , ZrO_2 and P_2O_5 are added in small quantities, they form a class of glass ceramic

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materials having remarkable refractory and mechanical properties. Additionally, all the glasses based on this ternary system have an excellent chemical durability. In recent years a new technique for preparing amorphous materials from gels has received a great deal of attention (1). The present work was undertaken to investigate the potential of the gel method in this ternary system and in this first paper a colloidal solution of silica was used for the preparation of the gels.

2. Experimental procedure. -

2.1. - Solutions preparation : A colloidal solution (Ludox AS40) was used as a source of silica. The calcium and aluminium ions were introduced in form of aqueous solutions of calcium nitrates (3M) and aluminium nitrates (2M) prepared by dissolving $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water. The solutions whose compositions are situated inside this ternary system were prepared from mixed solutions of calcium and aluminium nitrates having different $\text{Ca}^{2+}/2\text{Al}^{3+} = R$ ratios. This ratios are 9,3,1.5,0.66 and 0.25 respectively. The gels of the two binary systems and the ternary system were prepared in such a way that the final pH of the solution was equal to 3.0. For the binary $\text{Al}_2\text{O}_3\text{-SiO}_2$ and CaO-SiO_2 systems, the starting solutions are homogeneous if they are prepared at $\text{pH} < 4$ and $\text{pH} < 8$ respectively. The colloidal solutions of silica were made acidic by nitric acid (1N). The nitrate solutions were added dropwise to the stirred silica sol. If necessary the final solution was adjusted to a pH equal to 3.0 with ammonia (1N). The mixture was stirred for some minutes to complete the homogenization. The solution was then poured into a closed polyethylene container in order to avoid the possible reaction with CO_2 present in air and was left until gelation occurred. The gel is considered to have formed when the top surface of the solution no longer flows under stresses as weak as the inclination of the container.

2.2. - Heat treatment and structural evolution : After their formation, the gels were at first dehydrated in an oven at 60°C for 48 hours. A time of 1 hour was selected for all the heat treatments which were performed from 100 to 1100°C . All the heat treatments were carried out on the same gel for a given composition. The structural evolution was followed as a function of temperature by X-ray diffraction.

3. Results and Discussion. -

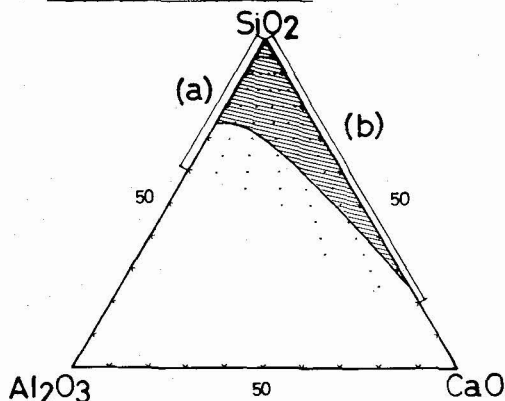


Fig. 1

3.1. - The range of gel formation : The domain of studied compositions is shown as (a) and (b) respectively in Fig. 1 for the binaries $\text{Al}_2\text{O}_3\text{-SiO}_2$ and CaO-SiO_2 .

The ternary compositions are denoted by points in this figure. The range of gel formation attains up to 75 mole % SiO_2 for the first binary system and between 100 and 25 mole % SiO_2 for the second system. The range of gel formation in the ternary system is displaced towards the compositions rich in calcium oxide (hatched range). The starting solutions whose composi-

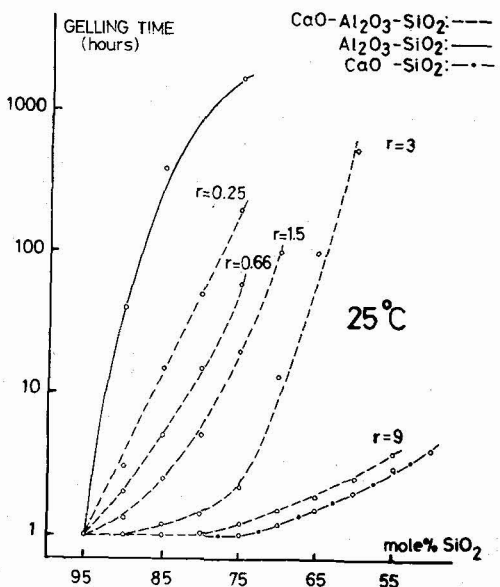


Fig. 2

tions are outside this range have shown the phenomenon of flocculation. The temperature of gelation has no effect on the formation range.

3.2. - Gelling time determination : The gelling time depends on the compositions as shown in fig.2. The calcium ion accelerates the gel formation of silica gel considerably. In the binary system CaO-SiO_2 , the gelation time shows only a slight

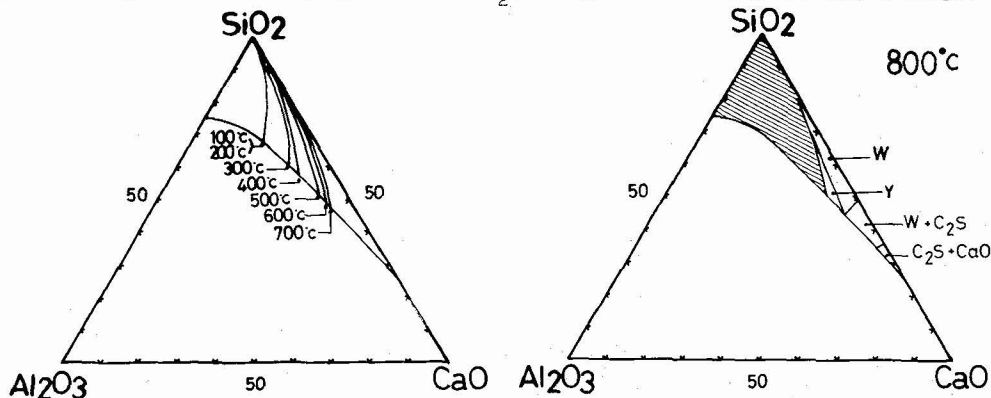


Fig. 3

Fig. 4

increase with increasing concentration of calcium in the solution. The role of aluminium is much less marked as far as silica gel is concerned. However, the gelation time increases in a more important manner with increasing concentration of aluminium in the binary system Al_2O_3 - SiO_2 . The gelation time of the ternary system is situated between the limits of the above two binary systems. The rigidity of the gel depends on the composition, with the gels rich in aluminium being more fragile than those rich in calcium.

3.3. - Structural evolution : At room temperature all the gels freshly prepared are amorphous and remain so even after the drying treatment at 60°C. In the binary system CaO-SiO_2 two formed calcium nitrates $\text{Ca}(\text{NO}_3)_2\cdot n\text{H}_2\text{O}$ ($n = 0$ or 2) crystallize at 80°C. These nitrates decompose at a temperature higher than 560°C. For the concentrations higher than 20 mole % CaO , a heat treatment at $T > 560^\circ\text{C}$ promotes the appearance of cristobalite, calcium silicate (pseudo-wollastonite, dicalcium-silicate $(2\text{CaO}\cdot\text{SiO}_2)_\beta$) or lime depending on the composition. For the composition below 20 mole % CaO , the materials remain amorphous between 560°C and 900°C. At about 900°C cristobalite, quartz or pseudo-wollastonite start appearing. The crystallization of the nitrates at lower temperatures influences the structure of these materials at higher temperatures. The presence of water is thought to be responsible for the appearance of the crystals of the nitrates. A gelation at 80°C and at very low pH allowed the elimination of the maximum quantity of water consequently a lower rate of nitrate formation was observed (2). For the sake of comparison, the gels of composition lying between 20 and 30 mole% CaO prepared at 80°C and pH=1 could be obtained as amorphous materials in a temperature interval : 560-800°C, while for the gels prepared at lower temperature (25°C) the crystals of cristobalite appeared from 560°C. For the ternary compositions the range of formation of amorphous materials is displaced progressively towards the binary CaO-SiO_2 side with the increase of temperature from 100 to 700°C (Fig.3). The crystalline nitrates decompose at much lower temperature as the composition is more richer in aluminium. It is to be noted that the precipitation of aluminium nitrates has never been observed. The range of formation of amorphous materials decreases for temperatures higher than 700°C. The crystalline phases present at various temperatures are also shown in figures 4,5,6 and 7. Two crystalline phases X and Y could not be identified. The phase Y appearing at 800°C and in a relatively small compositions range shows only few peaks ($d = 2.96, 2.75, 1.82$) poorly resolved emerging from a diffuse pattern. The intensities of the two X-ray peaks of the phase X ($d = 2.03, 1.62$) increase when the composition is richer in alumina. The gels' compositions are near to the ternary eutectic point (65 % SiO_2 , 26 % CaO , 9 % Al_2O_3) show two particular types of behaviour. They sinter

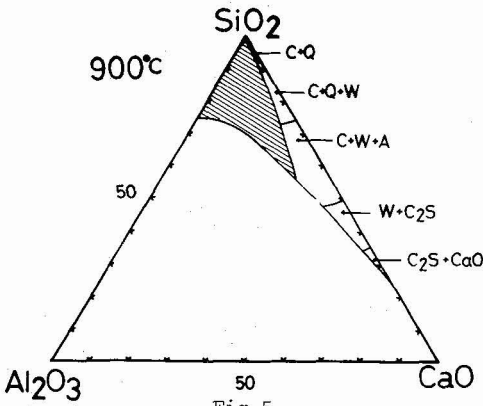


Fig. 5

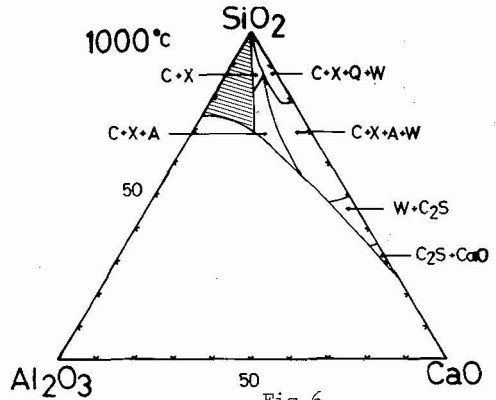


Fig. 6

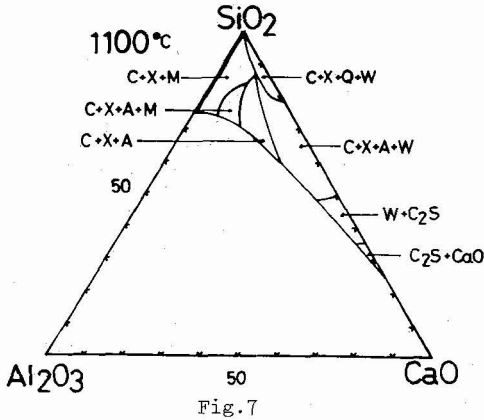


Fig. 7

- C : Cristobalite
- Q : Quartz
- W : Pseudo-wollastonite
- A : Anorthite
- M : Mullite
- C₂S : (2CaO-SiO₂)_β
- X : see the texte
- Y : see the texte

at 800°C and the grains then agglomerate and thus giving rise to a compact material. However these same gels treated at 900°C transform to a foaming material. These two phenomena do not seem to affect the amorphous nature of the material. A dehydration treatment under vacuum at 700°C for 5 hours was sufficient to eliminate the foaming phenomenon. The gels of the binary system Al₂O₃-SiO₂ crystallize only at temperatures higher than 1150°C. For concentrations lower than 5 mole % Al₂O₃ the cristobalite is the only crystalline phase which appears. For the concentration higher than 20 mole % Al₂O₃ the crystalline phase is mullite. In the intermediate composition range both these crystalline phases appear together. In this case the aluminium plays a rôle of inhibiting crystallization since the silica gels obtained by destabilization of a colloidal silica solution crystallize at temperatures lower than 950°C (3).

4. Conclusion. - The gels of CaO-Al₂O₃-SiO₂ system may be obtained in a narrow range of composition much smaller than those of the glasses. It is only at temperature higher than 1150°C where the gels of the binary system Al₂O₃-SiO₂ crystallize.

Thus, alumina like B₂O₃ (4) plays a rôle of inhibiting crystallization of gels containing silica. Another composition range which is interesting is the ternary eutectic point. In this case, the gels can undergo a sintering treatment or a heat treatment going rise to a foaming material. These two phenomena occur without altering the amorphous nature of the materials and can be controlled following the heat treatments.

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