

Ba₇[Si₇O₂₁].~10BaCl₂ – a compound with a new type of cyclic silicate anions

by

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ABSTRACT. — The compound 2BaO.2SiO₂.3BaCl₂ was investigated by the molybdate method, paper chromatography, solid-state high-resolution ²⁹Si NMR spectroscopy and the trimethylsilylation method, followed by gas chromatographic and mass spectroscopic characterization of the formed reaction products. The results received by these methods give evidence that there are cyclohepta silicate anions [Si₇O₂₁]¹⁴⁻ in the compound, so that it has to be formulated as Ba₇[Si₇O₂₁].~10BaCl₂. This type of silicate anions is a new one and hitherto unknown in natural or synthetic silicates.

RÉSUMÉ. — La constitution des anions silicates du composé 2BaO.2SiO₂.3BaCl₂ est étudié par la méthode molybdique, par chromatographie sur papier, par spectrographie RMN ²⁹Si de haute résolution à l'état solide, par la méthode de la substitution de cations par le radical triméthylsilyl suivie de la caractérisation des produits de la réaction par chromatographie en phase gazeuse et spectroscopie de masse. L'ensemble des résultats fournit la preuve de l'existence d'anions cycloheptasilicates [Si₇O₂₁]¹⁴⁻, d'où la formulation Ba₇[Si₇O₂₁].~10BaCl₂. Cette espèce d'anions silicates était inconnue jusqu'à présent dans les silicates naturels ou synthétiques.

INTRODUCTION

In a previous publication [1] some calcium-, strontium- and barium chloride silicates with a molar ratio MeO: SiO₂ = 1 were described. The

investigation of the constitution of the silicate anions in these compounds showed that they do not contain the same anion types which were detected in chloride free silicates of the same molar $\text{Me}^{\text{II}}\text{O} : \text{SiO}_2$ ratio. As an example it may be mentioned that both the calcium and the strontium compound of the composition $\text{MeSiO}_3 \cdot \text{MeCl}_2$ ($\text{Me} = \text{Ca}, \text{Sr}$) are built up by cyclo-tetra silicate anions $[\text{Si}_4\text{O}_{12}]^{8-}$ [1, 2]; whereas CaSiO_3 and SrSiO_3 depending on the respective modification contain cyclotri silicate anions $[\text{Si}_3\text{O}_9]^{6-}$ or high polymere single chain anions $[\text{SiO}_3]_n^{-2n}$. The formation of different types of anions is due to the fact that the geometrical arrangement of the $[\text{MeO}_x]$ -polyhedra plays an important role in the formation of condensed silicate anions, because they influence the anion formation by a matrix effect [3]. The observed facts may be explained therefore in the following way:

The cation polyhedra are modified by the incorporation of chloride ions so that silicate anions of another constitution are fitting this modified cation matrix much better than that in the chloride free system. In our investigations in the system $\text{BaO-SiO}_2\text{-BaCl}_2$ the compound $2\text{BaO} \cdot 2\text{SiO}_2 \cdot 3\text{BaCl}_2$ was synthesized, which was recognized already by Garcia and coworkers by its X-ray diffraction pattern to be a special phase. In our paper mentioned above [1] we did not deal with the anion constitution of this compound because the methods available at that time give only a hint at an anion type different to any silicate anion hitherto known.

The results of our further investigations by using additional methods are given in the following paper.

EXPERIMENTAL

For synthesizing the compound $2\text{BaO} \cdot 2\text{SiO}_2 \cdot 3\text{BaCl}_2$ a mixture of equivalent amounts of BaCO_3 and amorphous SiO_2 with an excess of anhydrous BaCl_2 ($\text{BaCO}_3 : \text{SiO}_2 : \text{BaCl}_2 = 1 : 1 : 2$) was heated at $1,020^\circ \text{C}$ for one hour in the same way as the chloride silicates of strontium and calcium had been prepared [1]. During heating the part of the furnace containing the sample was floated by a stream of dry nitrogen. After heating the product was treated by methanol for extracting unreacted BaCl_2 . The crystalline residue was analytically characterized by determining SiO_2 and BaO gravimetrically as SiO_2 and BaSO_4 respectively and chloride argentometrically according to the method of Vollhardt. From these results the composition of the substance is calculated to be $2\text{BaO} \cdot 2\text{SiO}_2 \cdot 3,2\text{BaCl}_2$. According to the relative low solubility of BaCl_2 in methanol it cannot be excluded that the compound is contaminated by a very small amount of residual BaCl_2 . The X-ray powder diffraction data are in accordance with those described by Garcia [4].

To ascertain the constitution of its silicate anions the substance was investigated by the molybdate method, the paper chromatography, the solid-state high-resolution ^{29}Si NMR-spectroscopy and the trimethylsilylation method followed by gas chromatographic and mass spectroscopic characterization of the formed trimethylsilyl ester.

RESULTS AND DISCUSSION

As a first step the compound $2\text{BaO} \cdot 2\text{SiO}_3 \cdot 3\text{BaCl}_2$ was investigated by means of the molybdate method [6]. In this method there is used the reaction rate of the formation of the silicomolybdic acid from an acidic solution of the silicate to be investigated and molybdic acid as an indicator for the degree of condensation or the medium molecular weight of the silicate anions respectively. The results of these measurements are given in figure 1. It shows that the molybdate reaction is finished after nine minutes and that the reaction curve does not correspond to those of the well known cyclohexa silicate anions $[\text{Si}_6\text{O}_{18}]^{12-}$ or the double four-ring silicate anions $[\text{Si}_8\text{O}_{20}]^{8-}$ which show similar reaction curves (see fig. 1). From the fact that the reaction curve of the barium chloride silicate is situated between those of the hexameric and the octameric anions it is only possible to assume that the degree of condensation or the medium molecular weight respectively of the silicate anions in the barium chloride silicate has to be in the limits of these two values.

A further confirmation for this assumption comes from the paper chromatographic separation [7] of the anions of the chloride silicate which results in a spot with the highest intensity in a position between those of the cyclohexa and the double four ring silicate anions, so that a cyclic type of silicate anions formed by 7 SiO_4 tetrahedra is to be assumed.

To get more evidence for this supposition the barium chloride silicate was also investigated by the high-resolution solid state ^{29}Si NMR spectroscopy using magic angle spinning of sample. This method gives the possibility by the ^{29}Si chemical shift value do differentiate the five possibilities of variously bridged Si atoms according to the number ($n = 0, 1, 2, 3, 4$) of Si-O-Si bridges in which they are involved. In the literature [8] the following regions of chemical shifts are published for the mentioned five types Q^n of SiO_4 tetrahedra

Q^0	— 60 to — 80 ppm	Q^3	— 92 to — 98 ppm
Q^1	— 68 to — 82 ppm	Q^4	— 107 to — 120 ppm
Q^2	— 75 to — 95 ppm		

The high-resolution solid state ^{29}Si -NMR spectrum of the compound $2\text{BaO} \cdot 2\text{SiO}_2 \cdot 3\text{BaCl}_2$ shows only one signal at $-92,5$ ppm with a line width smaller than 100 Hz (fig. 2). According to this spectrum the silicate anions in this compound are formed by one type of SiO_4 tetrahedra only. Because of the overlapping of the chemical shift values for the Q^2 and Q^3 groups

it is unfortunately not possible to decide if there are single ring silicates in the case of Q^2 groups or double ring silicates in the case of Q^3 groups. In the latter case the anions would have to be built up by an even number of SiO_4 tetrahedra but this would be in contradiction to the results of the molybdate method and the paper chromatographic investigations mentioned above.

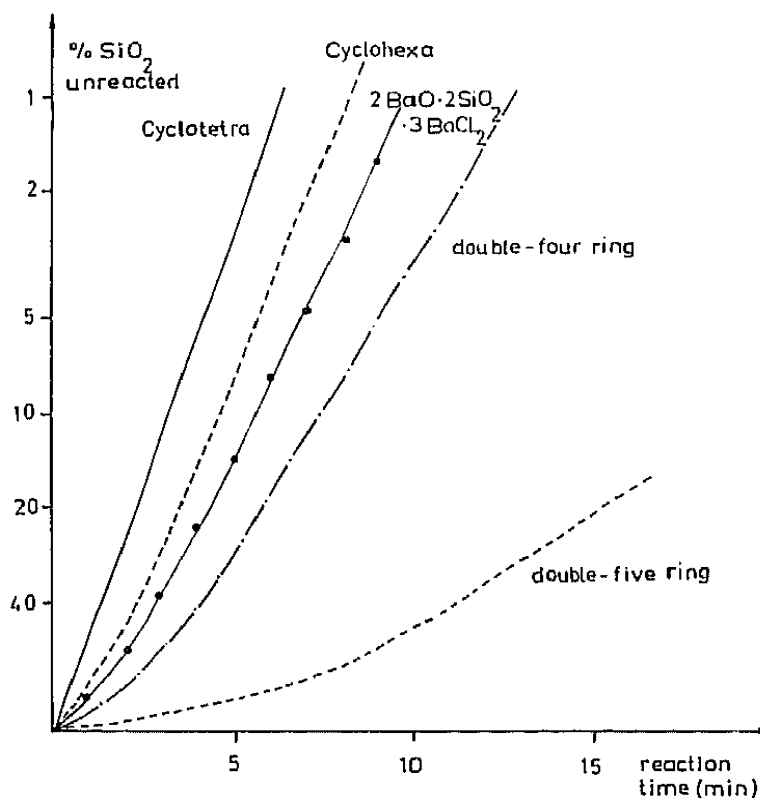


Fig. 1. — Molybdate reaction curve of $2BaO \cdot 2SiO_2 \cdot 3BaCl_2$.

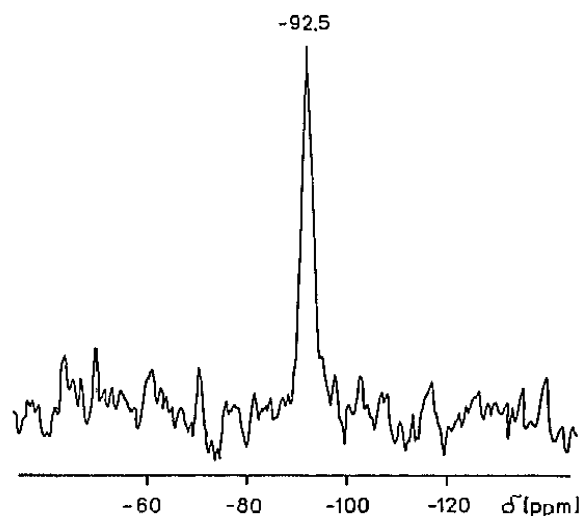


Fig. 2. — ^{29}Si NMR spectrum of $2BaO \cdot 2SiO_2 \cdot 3BaCl_2$.

Therefore the silicate anions of the barium chloride silicate were transformed to the corresponding trimethylsilyl ester according to the procedure of Tamas, Sarkar and Roy [9] but without using a cation exchanger treatment. The reaction products were separated by gas chromatographic analysis [10]. The gas chromatogram shows essentially 3 peaks with relatively long retention times of 21,4 min (18 % of total peak area), 28 min (24 %) and 41,5 min (50 %) (see fig. 3). The ester corresponding to peak 1 was identified as penta chain silicic acid ester $[(CH_3)_3Si]_{12} \cdot Si_5O_{16}$ by comparing it with test materials and by determining the mole mass by the means of mass spectroscopy. On the basis of the dependence of gas chromatographic retention data on the number of $(CH_3)_3Si$ -groups per ester molecule [11] it is possible to conclude from the retention times of peak 2 and 3 that both

peaks correspond to esters containing more than 12 $(\text{CH}_3)_3\text{Si}$ groups per molecule, and that the ester with the longest retention time (peak 3) contains at least one $(\text{CH}_3)_3\text{Si}$ -group more than that one of peak 2. The M-15 masses of the esters corresponding to the peaks 2 and 3 were found by mass spectroscopy to $\frac{m}{e} = 1467$ and 1539 respectively from which the mole masses of the esters are calculated to 1482 and 1554. The mole mass 1554 fits exactly the mass of the trimethylsilyl cyclohepta silicic acid ester of the formula $((\text{CH}_3)_3\text{Si})_{14}[\text{Si}_7\text{O}_{21}]$ ($M = 1554$). The mole mass 72 units lower corresponds to an ester of the same silicic acid which contains only 13 $(\text{CH}_3)_3\text{Si}$ groups because one hydrogen atom was not substituted by a trimethylsilyl group $((\text{CH}_3)_3\text{Si})_{13}\text{H}[\text{Si}_7\text{O}_{21}]$ ($M = 1482$). The detected penta silicate anions amounting to 18 area % are probably due to a contamination by another silicate phase. It is less probably that these anions are a product of a side reaction of the trimethylsilylation procedure. The constitution of a cyclohepta silicate proved by the trimethylsilylation method agrees well with the results of the molybdate method, the paper chromatography and the ^{29}Si NMR spectroscopy described above. The existence of isomeric cyclohepta silicate anion structures, which may be discussed too according to the measured mole masses of the silicic acid esters formed, must be excluded by reason of the ^{29}Si NMR results, because in those isomeric structures there has to be more than one type of SiO_4 tetrahedra. Thus the formula $\text{Ba}_7[\text{Si}_7\text{O}_{21}] \cdot \sim 10\text{BaCl}_2$ with cyclohepta silicate anions results very clearly from our investigation on the constitution of the barium chloride silicate $2\text{BaO} \cdot 2\text{SiO}_2 \cdot 3\text{BaCl}_2$.

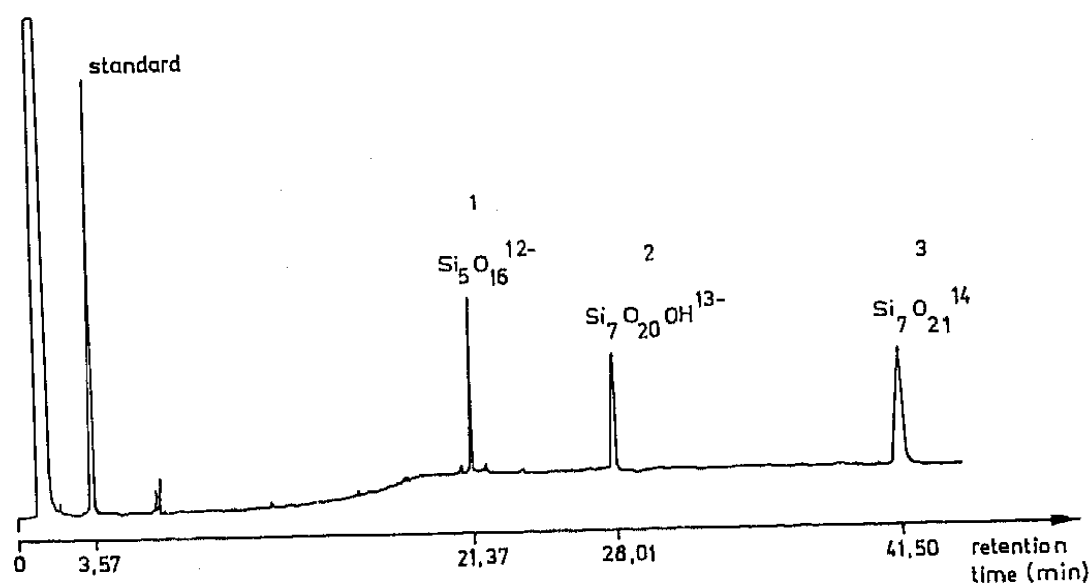


Fig. 3. — Gas chromatogram of the trimethylsilylated barium chloride silicate.

With respect to the chloride free compound $\text{BaO} \cdot \text{SiO}_2$ which is constructed either of high-molecular chain silicate anions with the formula $[\text{SiO}_3]_n^{2n-}$ or of cyclotri silicate anions with the formula $[\text{Si}_3\text{O}_9]^{6-}$ the system being investigated is a further example for changing the type of silicate anions by introducing chloride. Comparing the barium chloride silicate with the adequate chloride silicates of calcium and strontium it gets evident that the larger radius of the Ba^{2+} cation connected with its higher coordination number by O^{2-} and Cl^- and the higher chloride content of the barium compound gives obviously such a modification of the $[\text{Ba}(\text{O}, \text{Cl})_x]$ polyhedra that the formation of the bigger cyclohepta silicate anions, hitherto unknown, becomes possible.

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