



# Crystallization of 45S5 during Isothermal Heat Treatment

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## Abstract

Bioglass 45S5 has been shown *inter alia* to enhance bone growth, making it an interesting material for implants and scaffolds. Scaffolds are sintered from powdered glasses, and are partially crystalline. Crystallization of powdered 45S5 is well reported in the literature. 45S5 easily crystallizes also during hot-working to various implants. Crystallization of 45S5 plates at isothermal treatments was studied systematically for up to six hours at ten different temperatures (600-1000°C). The samples were inserted into a preheated furnace, and after the treatment the samples were rapidly cooled in the nitrogen flow. XRD, SEM, and optical microscope were used to identify the phase changes. According to the optical microscope images, the phase separation commenced around 600°C. The phase separated regions became more apparent at 700°C, and above 800°C a uniform crystal structure was observed. According to SEM, the crystal aggregates in the bulk showed truncated cube-like morphology (10-40 µm). At higher temperatures two different crystal structures could be identified on the surface. The X-ray diffraction pattern evolution was followed as the functions of time and temperature. The first peaks were observed at 650°C and the best match was obtained with Na<sub>2</sub>CaSi<sub>2</sub>O<sub>6</sub>. An evident broadening of the main peak (at 2θ ≈ 34°), leading to a separation into two peaks, was observed around 700°C; the separation of the peaks increased linearly as the function of temperature. On plate surfaces the crystallization was similar to the reported results with powdered samples, while in the cross-sectional surface only one crystalline phase was observed.

**Keywords:** 45S5, Crystallization, XRD

## KRYSTALIZACJA BIOSZKŁA 45S5 W TRAKCIE IZOTERMICZNEGO WYGRZEWANIA

W przypadku bioszklą 45S5 *inter alia* pokazano, że sprzyja wzrostowi kości, co czyni go interesującym materiałem na wszczepy i rusztowania. Rusztowania szkieła się ze sproszkowanego szkła i są one częściowo krystaliczne. Krystalizacja sproszkowanego szkła 45S5 jest dobrze opisana w literaturze. Szkló 45S5 łatwo krystalizuje również podczas obróbki na gorąco prowadzącej do wykonania różnych wszczepów. Krystalizację płytek ze szkła 45S5 podczas izotermicznej obróbki badano systematycznie aż do sześciu godzin w dziesięciu różnych temperaturach (600-1000°C). Próbkę umieszczano we wcześniej nagrzanym piecu, a po obróbce, próbki szybko schładzano w strumieniu azotu. Metody XRD, SEM i mikroskopii optycznej wykorzystano do zidentyfikowania zmian fazowych. Zgodnie z obrazami mikroskopii optycznej, rozdzielenie fazowe rozpoczęło się w około 600°C. Obszary rozdzielenia faz stały się bardziej widoczne w 700°C, zaś powyżej 800°C zaobserwowano jednorodną strukturę krystaliczną. Zgodnie z obserwacjami SEM, agregaty krystaliczne w objętości materiału pokazały morfologię podobną do ściętego sześcianu (10-40 µm). W wyższych temperaturach dwie różniące się struktury krystaliczne można było zidentyfikować na powierzchni. Ewolucja dyfraktogramów rentgenowskich śledzona była w funkcji czasu i temperatury. Pierwsze piki zaobserwowano w 650°C i najlepsze dopasowanie uzyskano dla Na<sub>2</sub>CaSi<sub>2</sub>O<sub>6</sub>. Widoczne poszerzenie głównego pikę (przy 2θ ≈ 34°), prowadzące do rozdzielenia na dwa piki, zaobserwowano w 700°C; rozdzielenie pików zwiększało się liniowo w funkcji temperatury. Na powierzchniach płytkowych krystalizacja przebiegała podobnie do opisanej w próbkach proszkowych, podczas gdy na powierzchni przekroju zaobserwowano tylko jedną fazę krystaliczną.

**Słowa kluczowe:** 45S5, krystalizacja, XRD

## 1. Introduction

Bioglass 45S5 has been shown to enhance bone growth making it an interesting material for implants and scaffolds. Interconnected porosity of the scaffold allows good diffusion of nutrients throughout the entire structure, and thus the cell attachment, proliferation, and migration are enhanced. In the recent years partially crystalline scaffolds sintered of powdered 45S5 have been developed [1-3]. In order to control the physical properties and the crystallization mechanism

of the scaffolds the time and temperature windows for the crystallization need to be mastered.

45S5 crystallizes easily during hot-working, and is not of suitable composition, e.g. for the continuous fiber drawing [4]. However, as crystallization is reported to only retard the hydroxyapatite layer formation, 45S5 has been used as a scaffold material [5]. Furthermore, the crystallization degree allows the way to tailor the bioactivity of the scaffold.

The structural transformations of 45S5 are well reported in the literature [6]. Most of the studies concentrate on pow-

dered samples. The crystallization of 45S5 is reported to commence around 600°C, and as a primary crystal phase most often the so called 1N2C3S, *i.e.*  $\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 3\text{SiO}_2$ , is suggested [1, 7, 8]. Another type of sodium calcium silicate considered in the literature is  $\text{Na}_2\text{CaSi}_2\text{O}_6$  [6, 9, 10]. Also silicorheanite ( $\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4$ ) has been suggested to form around 800-950°C [6]. As a secondary phase, apatite-like structures have also been suggested to crystallize at higher temperatures [11]. Furthermore,  $\text{Ca}_{10}(\text{PO}_4)_6$  has been identified in the partially crystallized glass-ceramics consisting of 48  $\text{SiO}_2$ , 9.5  $\text{P}_2\text{O}_5$ , 20  $\text{Na}_2\text{O}$  and 22.5  $\text{CaO}$  (wt%) [12].

In this work the crystallization of 45S5 plates at isothermal treatments for up to six hours at ten different temperatures (600-1000°C) was studied. The aim was to shed light on the crystallization characteristics of glass 45S5. A more comprehensive understanding of the crystallization is essential, *e.g.* in choosing sintering parameters in manufacturing of partially crystallized scaffolds of parent glass 45S5.

## 2. Experimental

Glass 45S5 (45 wt%  $\text{SiO}_2$ , 6 wt% of  $\text{P}_2\text{O}_5$ , 24.5 wt% of both  $\text{Na}_2\text{O}$  and  $\text{CaO}$ ) was prepared of analytical grade reagents by using the same melting procedure and reagents as described by Arstila *et al.* [13]. The glass was cut to monolithic samples (20×10×5 mm), and then subjected to isothermal heat treatments (30 min, 20 h). The experiments were carried out over the temperature range 600-1000°C. A preheated electrical furnace equipped with a nitrogen atmosphere was used in this study; the heat treatment procedure and the sample preparation have been described before [4]. After the heat treatment the samples were cooled in the nitrogen flow to room temperature. The samples were cut with a low speed diamond saw, and the cross-sectional surface of one half was polished. The cross-section was first imaged with the optical microscope (LEICA), and then with the scanning electron microscope, equipped with the electron dispersive X-ray analysis (FEG-SEM/EDXA, LEO 1530 by Zeiss and Vantage by Thermo Electron Corporation).

The other halves of the cut samples were ground to powder with an agate mortar and a pestle, and the crystalline phases were analyzed with X-ray diffraction (X'pert by Philips,  $\text{CuK}\alpha$  radiation, 40 kV, 30 mA, 5-60° 2 $\theta$ , 0.8°/min). Some samples were also analyzed as plates on the top surfaces. To more closely follow the peak separation taking place around 34° 2 $\theta$ , a slower scan rate was used (30-40° 2 $\theta$ , 0.12°/min.) for some of the samples. No signs of crystallization were observed in the glass before the heat treatments. The powder of the size fraction 25-45  $\mu\text{m}$  was also heat treated at 600, 700, 800, and 900°C for one hour in order to establish whether bulk and powdered samples have different crystallization characteristics.

## 3. Results and discussion

According to the optical microscope images the phase separation commenced around 600°C. The phase separated regions became more apparent at 700°C, and with the increasing duration of the heat treatment the phase separation was clear. Fig. 1 shows the surface of a plate after one hour at 750°C. A clear separation into two regions has occurred. The same structure was also seen in the cross-sectional im-

ages. The surface appearance changed clearly at 800°C to a uniform white structure indicating that the entire bulk had undergone crystallization. With the optical microscope no additional visual changes were found to occur after a heat treatment at higher temperatures or longer times.



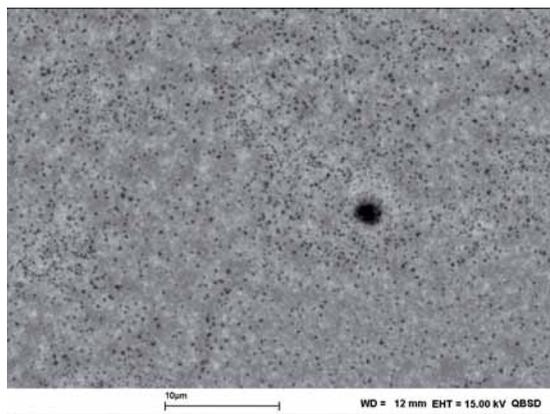
Fig. 1. Optical microscope image of the surface of 45S5 plate after one hour at 750°C.

Fig. 2 shows the SEM images taken from the top surface and the cross-section after one hour at 800°C. Smaller crystals can be detected on the surface of the plates (A) and a crystalline network (B) can be detected on the cross-section. A similar crystal structure for heat treated 45S5 has also been reported by Arstila *et al.* [4, 13]. Crystal aggregates in the surface of a void seen in the bulk sample showed a truncated cube-like morphology. The aggregate size grew with the increasing temperature from 10 (700°C) to 40  $\mu\text{m}$  (900°C). A similar crystal shape and size have been reported for isolated crystals in the surface of a plate of 45S5 after the heat-treatment at 715°C for 15 min. Only one crystalline phase was identified [9, 10]. In the same study after the prolonged heat treatment time (60 min) the crystals were found to be impinged with each other.

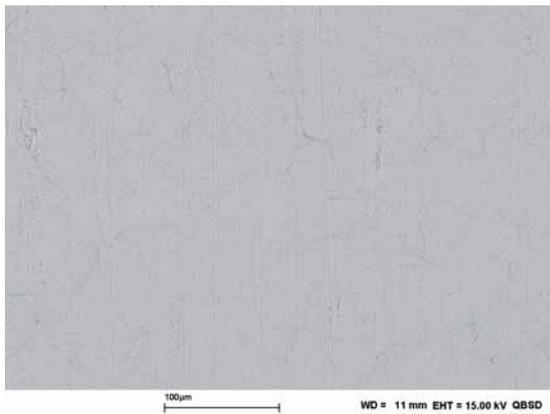
According to the results in this work, the heat treatment temperature showed a greater effect than time on the crystallization. This implies that the growth of individual crystals was prevented by the neighboring crystals already after one hour of heat treatment. Thus, the crystal growth rate decreased with a prolonged heat treatment. The SEM image showing a higher magnification suggests that the aggregates consisted of a network of smaller crystals (Fig. 2d). At higher temperatures the small crystals seemed to become more arranged, and the interface between the crystals was not clear.

After six hours at 1000°C two different crystal structures were identified on the surface of 45S5; one consisting of sodium calcium silicate and the other containing also phosphorus [4]. The SEM image shows indications of separation into two different phases on the plate surface already after 30 minutes at 900°C (Fig. 3). However, no reliable EDX analysis was achieved because of the small size of the crystals. The phase separation into two crystalline phases became clearer after four hours at the same temperature.

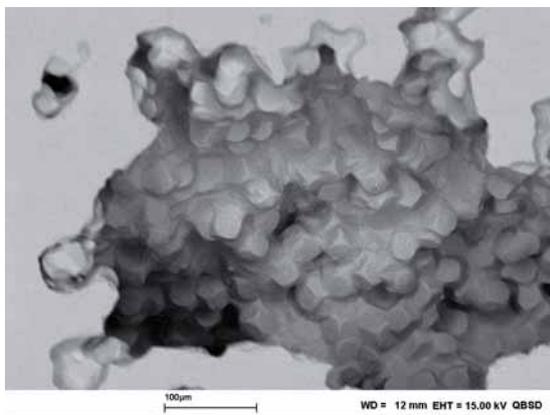
The XRD diffractograms of plates heat treated for one hour at different temperatures are shown in Fig. 4. The plates were powdered prior the analysis. The two different polymeric sample holders used in the XRD experiment series



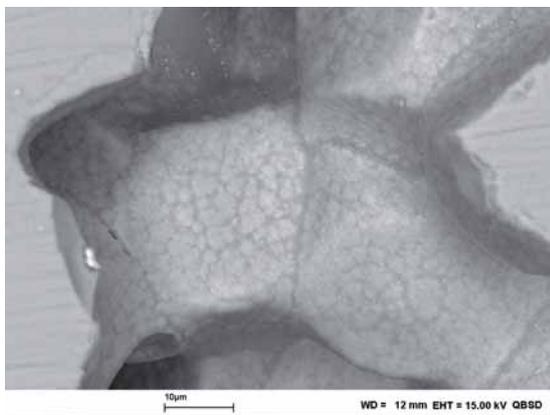
a)



b)

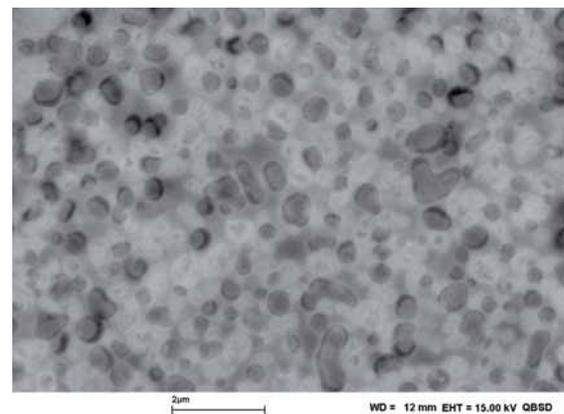


c)

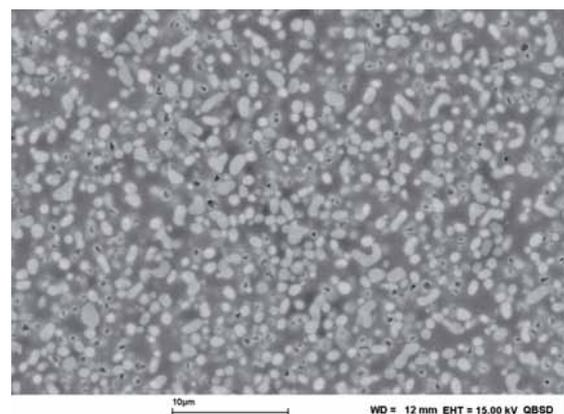


d)

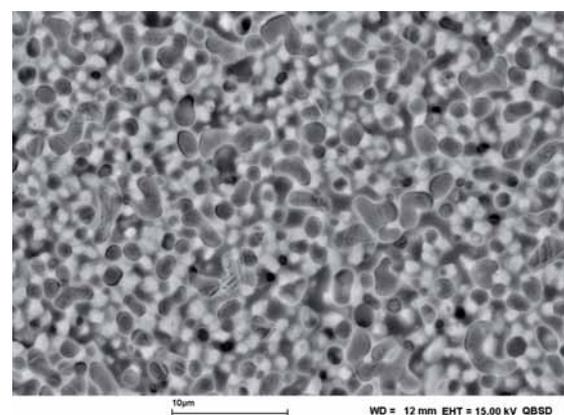
Fig. 2. SEM-image of the top surface (a) and cross-section of 45S5 plate after one hour at 800°C : b) 250x, c) 200x, and d) 1.5kx.



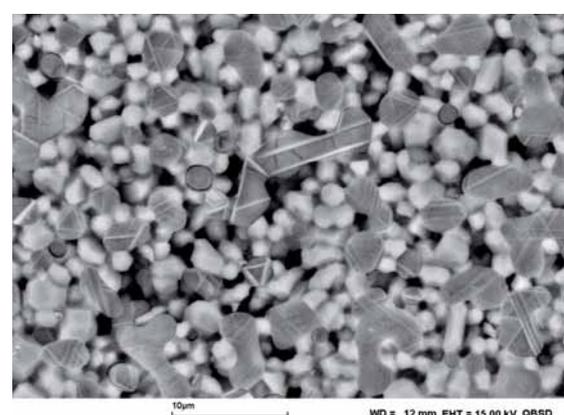
a)



b)



c)



d)

Fig. 3. SEM-image of the top surface of 45S5 plate: a) 30 min and b) 4 h at 900°C, c) 1 h [4] and d) 6 h at 1000°C [4].

caused relatively large variations in the amorphous region between 5 and 15° 2 $\theta$ . Thus, this region was cut off from the diffractograms. At 600°C no sign of bulk crystallization was detected with the plates even after longer heat treatment times (6 hours). However, peaks indicating crystallization were identified on the top surface of the glass plates already after one hour of heat treatment. This indicates that only small crystals or a small fraction of crystals at levels below XRD's detection limits formed in the bulk glass. First distinct peaks from the analysis of the bulk sample were observed after one hour at 650°C.

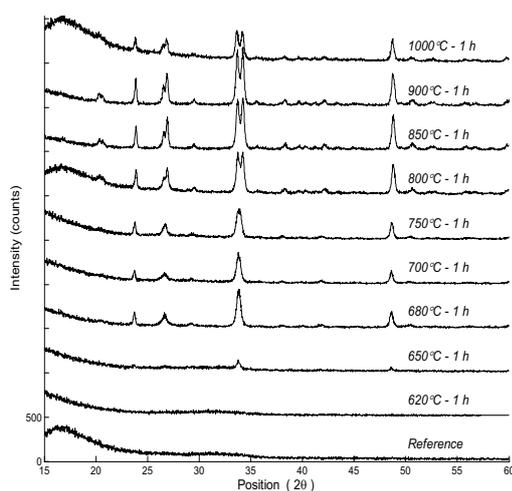


Fig. 4. Diffractograms of 45S5 heat treated for one hour at different temperatures (powdered plates).

The peak heights were found to increase linearly as a function of temperature up to 700°C. This suggests that the fraction and/or the size of the crystals increased linearly. In Fig. 5 the peak intensity evolution as a function of temperature is presented for three peaks at different angular locations. All the peaks follow the same trend. At 750°C an obvious decrease in the peak intensities was observed. Whether this is a real physical phenomenon or an experimental error was not properly verified, but a similar trend was measured for two parallel samples. Furthermore, at this temperature region a separation of the peak at the highest intensity (34° 2 $\theta$ ) started, indicating a change either in the crystal phase or lattice parameters. A similar peak separation was also reported by Lefebvre *et al.* [6]. At the same temperature also a separation of the smaller peak around 26° 2 $\theta$  was observed (Fig. 4).

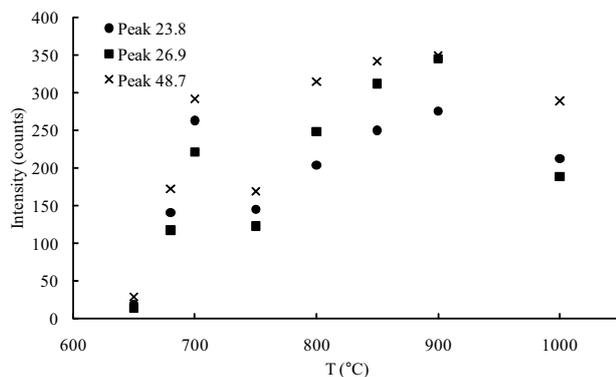


Fig. 5. Peak intensity (counts) evolution as a function of heat treatment temperature for three peaks at different angular locations.

Above 750°C the peak intensities increased again linearly until they started to decrease after one hour heat treatment at 1000°C. This implies that melting of the samples started. Partially crystallized 45S5 has been reported to start to melt within the temperature range around 1050-1200°C [6, 14]. When the full width at half maximum (FWHM) values of the different peaks were compared, no clear trends could be verified. Thus, no crystal size calculation was performed.

An unambiguous identification of the sodium calcium silicate crystal type was difficult, as expected also from the various data reported earlier. The overall best match was obtained with combeite Na<sub>2</sub>CaSi<sub>2</sub>O<sub>6</sub> (PDF 77-2189). The same pattern was suggested by Lefebvre *et al.*, Lin *et al.*, and Huang *et al.* [6, 9, 10]. A good fit was also gained with the Na<sub>2</sub>CaSiO<sub>4</sub> type of crystal pattern if considering the main intensity peak at 34° 2 $\theta$  to be a singlet. It is possible that a phase change caused the observed non-linearity in the peak intensity (Fig. 5).

The most often suggested so called 1N2C3S phase has a highly similar diffraction pattern to the combeite type, and was also found to fit well. The two crystal types may have interconnected structures making the identification difficult [10]. When the tape cast 45S5 glass was heat treated at temperatures between 800 and 1000°C, only 1N2C3S type was observed, and a densification of the structure was found to occur as a function of temperature [15]. Also for the tape cast 45S5 the main peak separated into a double peak.

When comparing the diffractograms of the plate samples (Fig. 4) with the heat treated 25-45  $\mu$ m powder samples (Fig. 6), no big differences can be observed. However, the crystallization is clearly noticed after one hour at 600°C for the glass powder. Again, the separation of the main intensity peak occurred in the same temperature region.

The separation of the main intensity peak (34° 2 $\theta$ ) as a function of the heat treatment temperature followed a linear dependence (Fig. 7). Highly similar values were obtained for both the heat treated plates and the 25-45  $\mu$ m powder samples. A similar trend of the peak separation has been reported also for a fine powder

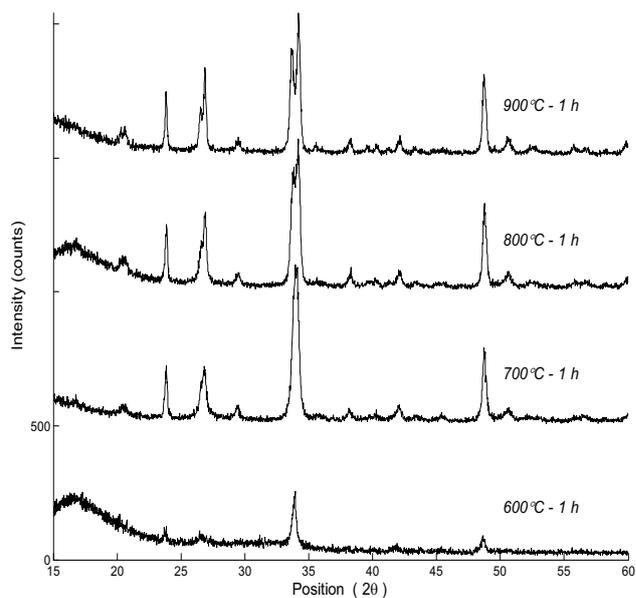


Fig. 6. Diffractograms of 45S5 (25-45 $\mu$ m powder) heat treated for one hour at different temperatures.

(1  $\mu\text{m}$ ) of 45S5 heat treated at different temperatures for 5 min [6]. The separation was assumed to be due to the lattice parameter change rather than to a phase change.

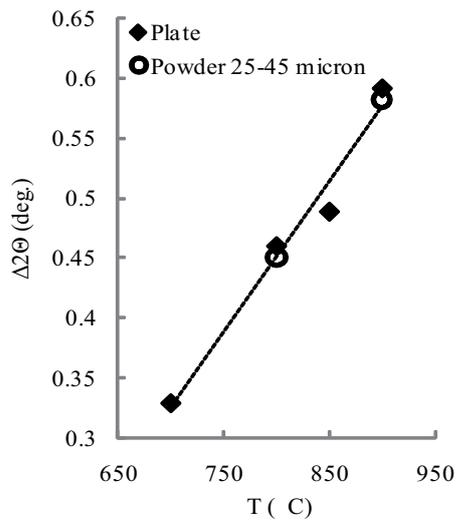


Fig. 7. Separation of the two peaks around  $34^\circ$  as a function of heat treatment temperature for crystallized plates and 25-45  $\mu\text{m}$  powder samples of 45S5.

The phosphate rich crystalline phase suggested by the SEM-EDX analysis could not be identified with certainty neither in the heat treated plates nor powder samples with XRD. A beginning of a new peak formation was observed near the main intensity peak in same temperature range as reported for the silicorheanite ( $\text{Na}_2\text{Ca}_4(\text{PO}_4)_2\text{SiO}_4$ ) [6].

The silicorheanite pattern (PDF 32-1053) suggested by Lefebvre *et al.* [6] was fitted to diffractograms of the powdered plates, and a relatively good match was obtained. The diffractogram of the top surface of after four hours at  $900^\circ\text{C}$  (cf. Fig. 3) shows a clear new peak around  $32^\circ 2\theta$  (Fig. 8). In this figure the fitting of PDF 77-2189 (light) and PDF 32-1053 (black) is shown.

The effect of the heat treatment time on the XRD diffractograms is shown in Figs. 9 and 10. The heat treatment time did not have a great influence on the crystallization at  $700^\circ\text{C}$ . The results indicate that the main intensity peak separation does not depend on the kinetics, but on the thermodynamics

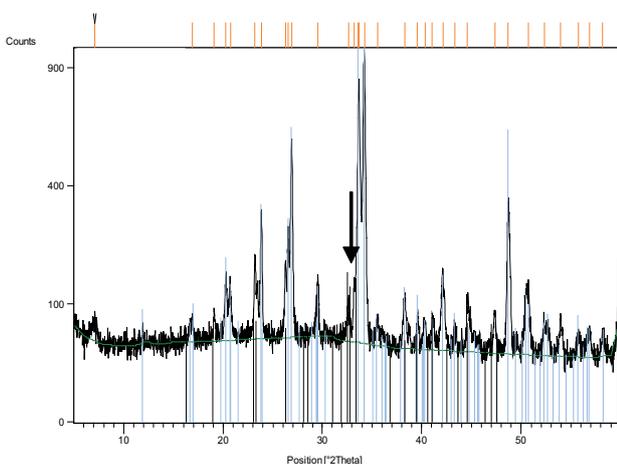


Fig. 8. Diffractogram of the top surface of a after 4 h at  $900^\circ\text{C}$  (PDF 77-2189 as light and PDF 32-1053 as black).

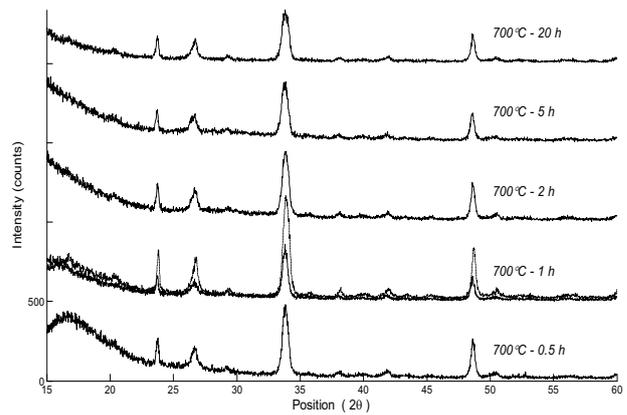


Fig. 9. Diffractograms of 45S5 (plates) heat treated for different times at  $700^\circ\text{C}$ .

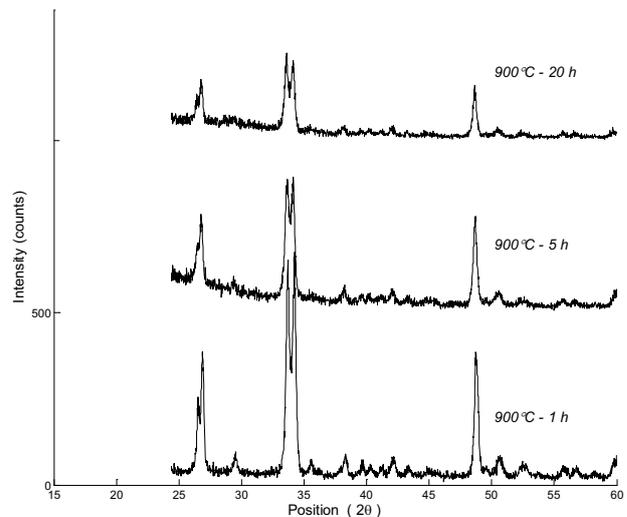


Fig. 10. Diffractograms of 45S5 (plates) heat treated at  $900^\circ\text{C}$  for different times.

because even after 20 h no big changes in the structure occurred. Thus, a certain activation energy barrier needs to be exceeded in order to initiate a lattice parameter or a phase change causing the peak splitting.

At  $900^\circ\text{C}$  the intensity of the peaks was again observed to decrease, but the peak width increased after a 20 h heat treatment (Fig. 10). No secondary phases were identified for the sample heat treated for 20 h.

## 4. Conclusions

Crystallization of plates of 45S5 at isothermal treatments for up to six hours at ten different temperatures ( $600$ - $1000^\circ\text{C}$ ) was studied by using XRD, SEM, and optical microscope. Also some powdered samples were heat treated.

A phase separation was observed to start around  $600^\circ\text{C}$ . The first signs of crystallization of the powdered samples were observed at this temperature while for the plates the first peaks indicating crystallization were noticed at  $650^\circ\text{C}$ .

Crystal aggregates found in the bulk showed a truncated cube-like morphology. In this study only sodium calcium silicate crystals were identified with certainty. However, the exact empirical formula is still unclear. Nevertheless, the formation of phosphorus -rich secondary crystals at higher

temperatures (800°C) was considered to be highly probable. The sodium calcium silicate peaks were assumed to mask at least partially the phosphorus containing crystals signals.

An evident broadening of the main peak (at  $2\theta \approx 34^\circ$ ) leading to separation into two peaks was observed around 700°C; the separation of the peaks increased linearly as a function of temperature. The separation was considered to be a thermodynamically rather than kinetically limited process because even after prolonged heat treatments at 700°C no clear changes were observed for the main peak.

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