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MICROSTRUCTURE OF MICA GLASS-CERAMICS AND INTERFACE REACTIONS BETWEEN MICA GLASS-CERAMICS AND BONE

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Abstract

This review paper characterizes glass-ceramics containing mica as main crystal phase. The phase formation reactions in dependence of the chemical composition and the microstructure are shown. Microstructure of mica glass-ceramics has been studied by electron replica and scanning electron microscopic (SEM) techniques.

Mica glass-ceramics have previously been developed in SiO₂-B₂O₃-Al₂O₃-MgO-F⁻-base glasses. The material is machinable because of the precipitation of micas of fluorophlogopite-type. Also, a machinable glass-ceramic for dental applications was developed based on KMg_{2.5}(Si₄O₁₀)F₂-micas. We developed mica glass-ceramics in the SiO₂-Al₂O₃-MgO-Na₂O-K₂O-F glass system. Phase formation within these glasses was observed by SEM. A double controlled nucleation and crystallization of mica and apatite crystals was possible in glasses of the SiO₂-MgO-Na₂O-K₂O-F-CaO-P₂O₅-(Al₂O₃) system. The main crystal phases of phlogopite-type were characterized by SEM and energy dispersive x-ray spectroscopy (EDS) and apatite crystals Ca₅(PO₄)₃(OH,F) were analyzed by X-ray diffraction measurements. The glass-ceramics are useful biomaterials for bone substitution. EDS analysis shows the ion exchange between glass-ceramics and body fluids. The interface reaction is characterized by formation of a small phosphate layer, and particularly by alkali ion exchange.

Key Words: Glass-ceramics, mica, apatite, bone substitution, scanning electron microscopy, machinability, interface reactions, microstructure, phase formation, bioreactivity, ion diffusion.

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Introduction

The first machinable glass-ceramic, which contains mica as main crystal phase is MACOR[®] which was developed by Beall *et al.* (1971). The composition of the base glass is 47.2 SiO₂, 8.5 B₂O₃, 16.7 Al₂O₃, 14.5 MgO, 9.5 K₂ and 6.3 F.

A special method of controlled nucleation via phase separation and crystallization of silicate glasses has been used by Beall *et al.* (1971) to precipitate fluorophlogopite, namely KMg₃(AlSi₃O₁₀)F₂ as main crystal phase. The result was a glass ceramic which could be machined with standard metal working tools. Because of the combination of favorable properties, such as machinability and electrical isolation, very interesting technological applications can be considered. In order to ensure good machinability the precipitated mica crystals in the glass matrix need an optimal size and contact with each other. The material is machinable because of the preferred cleavage of the micas. Beall (1979) called the microstructure of the glass ceramic a "house of cards structure", which describes the orientation of the micas in the glassy phase.

Based on this development of Beall *et al.* (1971) further mica glass-ceramics (e.g., Beall, 1991) have been developed also for medical applications. The authors of the present paper review these developments (see chapters "glass-ceramic of DICOR[®]-type", "precipitation of micas rich in Ca²⁺-ions").

Further mica type glass-ceramics for technical purposes have been developed by Vogel *et al.* (1973) in the magnesium-aluminosilicate base glass system. Based on these investigations, the authors of this paper developed a phlogopite-type glass ceramic for medical application. This glass ceramic is biocompatible but not bioactive (see chapter "glass-ceramic of BIOVERIT[®] II-type").

The development of bioactive biomaterials has strongly been influenced by Hench *et al.* (1972) who developed the biomaterial BIOGLASS[®] from the SiO₂-Na₂O-CaO-P₂O₅-F system. The new biomaterials show bioactive properties and the materials are bonded to living bone. BIOGLASS[®] forms apatite on the surface

Figure 1. Microstructure of DICOR® glass ceramic observed during replica investigation of fracture surface in a transmission electron microscope (TEM). Specimen was etched for 5 seconds in 1 % HF.

Figure 2. SEM of cross-section through globular aggregates of curved phlogopite showing initial stage of crystallization. Polished sample and etched 2.5 seconds in 2 % HF.

Figure 3. Advanced stage of the precipitation of curved phlogopite crystals. SEM. Polished sample and etched 2.5 seconds in 2 % HF.

Figure 4. Curved phlogopite crystals in glass ceramics (BIOVERIT® II-type) having high translucency. SEM. Polished sample and etched 2.5 seconds in 2 % HF.

in contact and reaction with the body fluid and the living bone. On the basis of the knowledge of this apatite formation in BIOGLASS®, further bioactive glass-ceramics, containing apatite crystals, have been developed (Blencke *et al.*, 1977; Strunz *et al.*, 1978).

Kokubo *et al.* (1982) showed a preferred bonding of bone and apatite-wollastonite glass ceramic, and an additional apatite formation in reaction with simulated body fluid could be shown on the surface of the biomaterial (Kokubo *et al.*, 1990).

The authors of this present paper developed a machinable bioactive glass-ceramic consisting of two crystal phases, namely mica and apatite, and a glassy phase. The microstructure and the properties, especially the interphase reactions between mica and bone are presented (see chapter "BIOVERIT® I-type glass-ceramics"). Other glass-ceramics containing micas and phosphates are reviewed (see "glass-ceramics containing micas and CaO-, P₂O₅-additives").

Glass-Ceramic of DICOR®-Type (Mica Glass-Ceramic)

Grossman (1972, 1983) crystallized glasses consisting essentially of 45-70 % SiO₂, 8-20 % MgO, 8-15 % MgF₂, 5-35 % R₂O and RO; where R₂O consists of K₂O, Rb₂O and Cs₂O and RO consists of SrO or BaO and other alkaline earth oxides. Additions, such as ZrO₂, Al₂O₃ and colourants were used. These investigations have been the basis for the development of a glass of the composition (in weight percent): 60.9 SiO₂, 0.6 Al₂O₃, 17.1 MgO, 13.8 K₂O, 4.9 F, 4.7 ZrO₂, 0.05 CeO₂ (Adair, 1984). CeO₂ can give the glass-ceramic fluorescence. This glass was heat treated and the microstructure was investigated by scanning electron microscopy (SEM) (Grossman, 1989; Adair, 1984).

Grossman (1989) showed that the base glass is phase separated and mica crystals of KMg_{2.5}Si₄O₁₀F₂-type grow during heat treating the glass from 625 to 1075 °C. A typical microstructure is shown in Figure 1 (the preparation technique is indicated in the caption of the Figure). The glass ceramic shows excellent properties, such as machinability, translucency and good bend-

ing strength. Hence, the material is used in dental medicine as crowns.

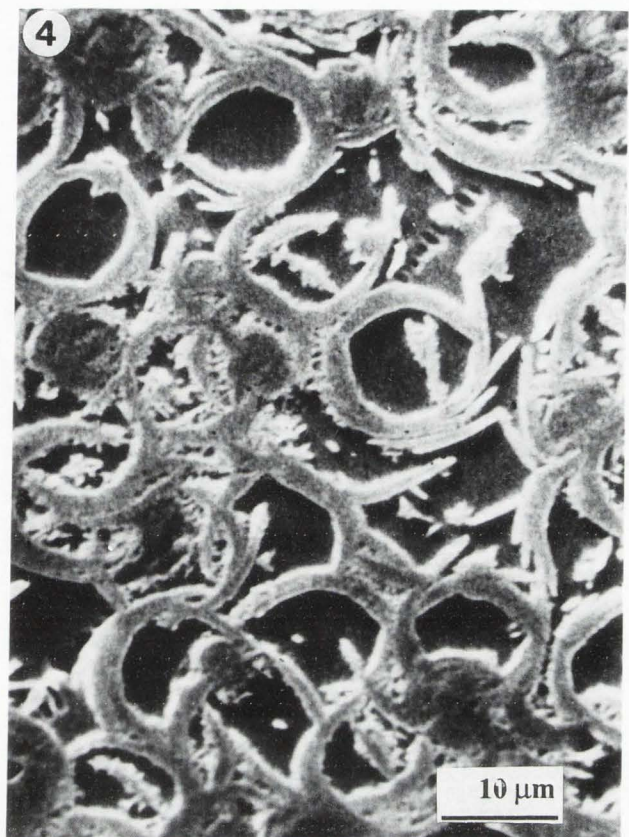
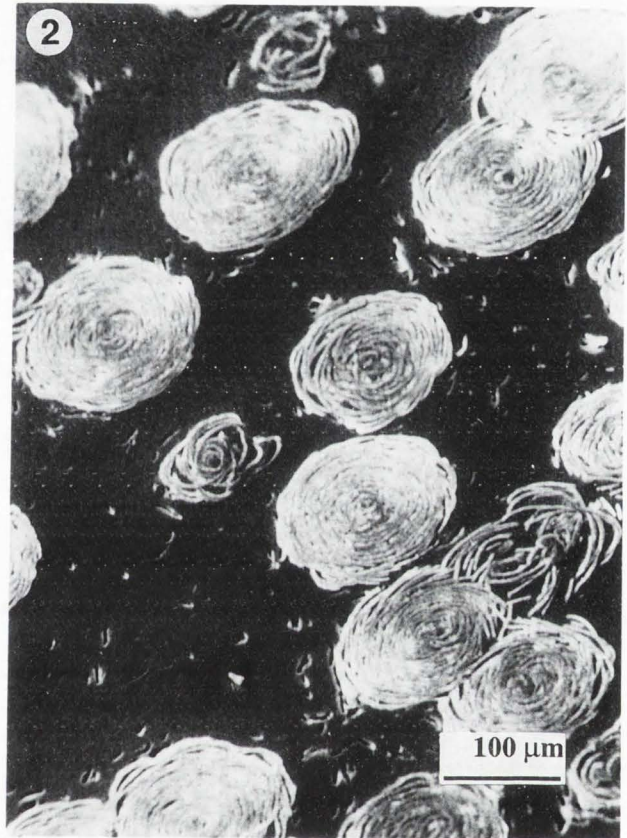
Glass-Ceramics of BIOVERIT® II-Type (Mica Glass-Ceramic)

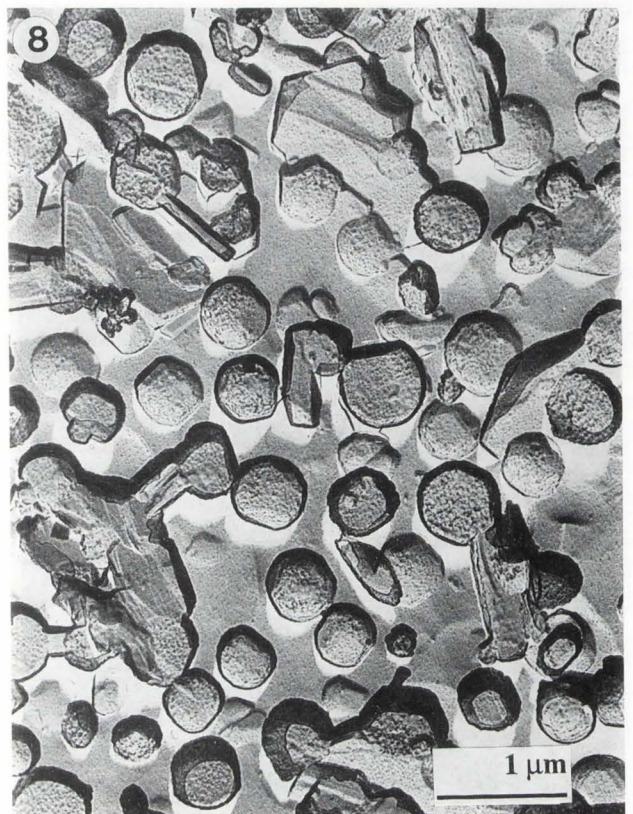
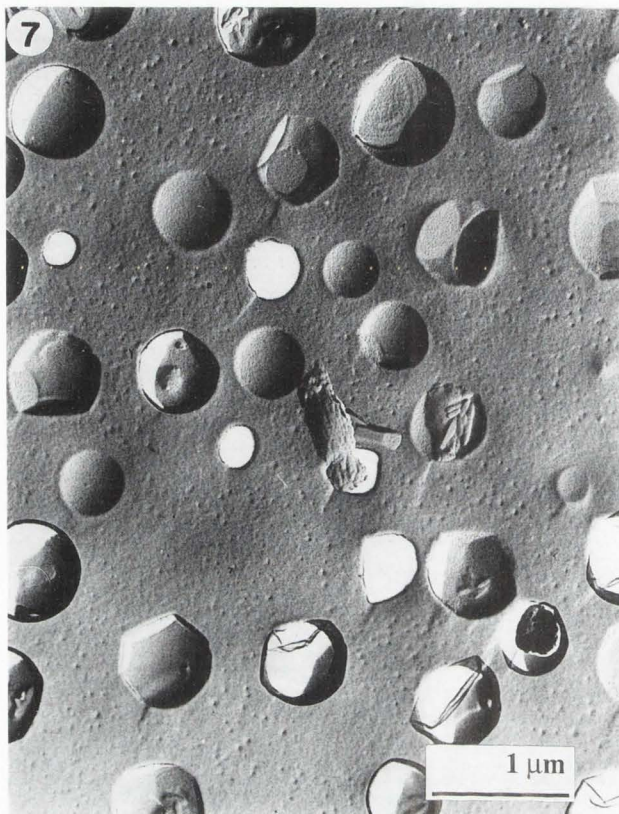
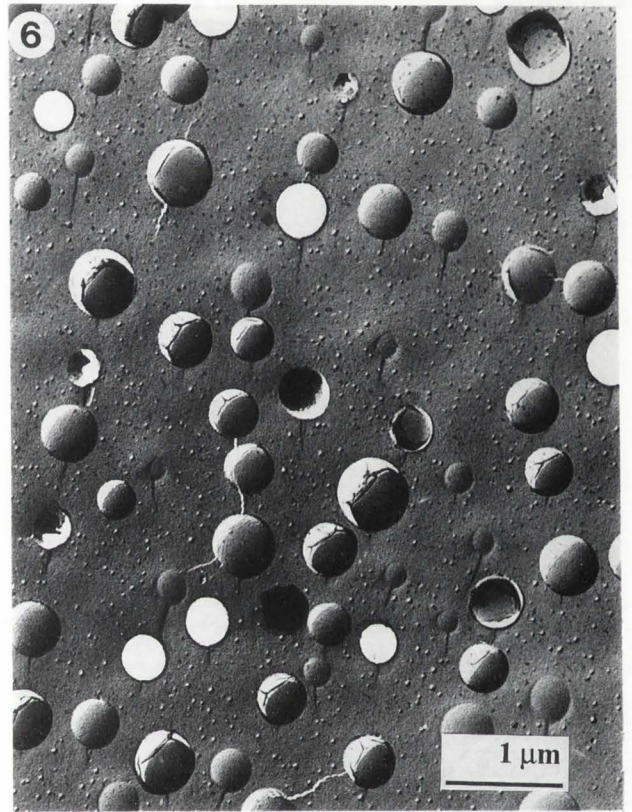
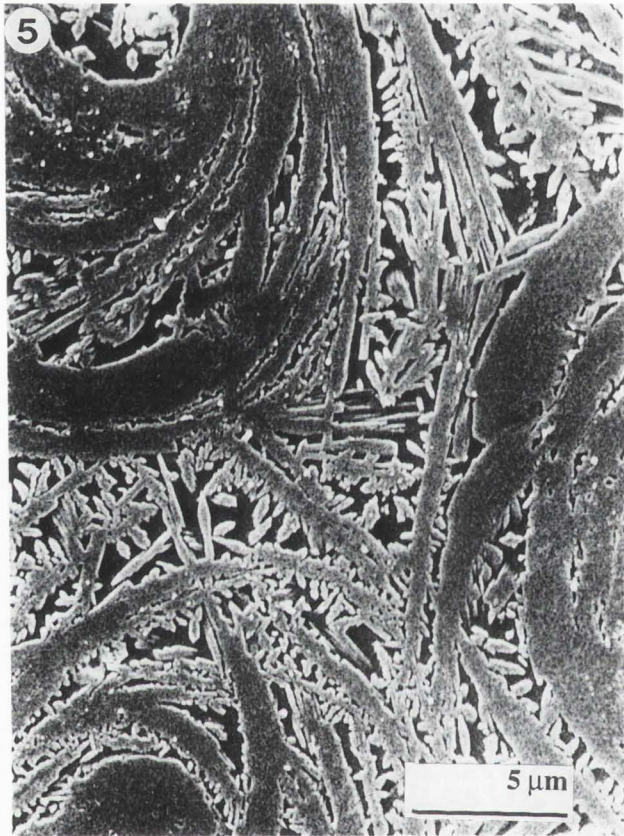
The crystallization behavior of magnesium-alumino-silicate base glasses was investigated by Vogel *et al.* (1973). Na₂O, K₂O and F were added to SiO₂-Al₂O₃-MgO-glasses and the mica precipitation has been studied. Based on these results, Höland *et al.* (1981) analyzed the phase formation processes in glasses of the composition: 43-50 SiO₂, 26-30 Al₂O₃, 11-15 MgO, 7-10 R₂O, 3.3-4.8 F, 0.01-0.6 Cl, 0.1-3 CaO, 0.1-5 P₂O₅, wherein R₂O is the sum of 3-5.5 wt. % Na₂O and 4-6 wt. % K₂O. A new type of phlogopite in a curved shape was precipitated in a glass ceramic. The formation of this new phlogopite was investigated in a glass with the chemical composition (wt. %): 44.5 SiO₂, 29.9 Al₂O₃, 11.8 MgO, 4.2 F, 4.4 Na₂, 4.9 K₂O, 0.1 CaO, 0.1 P₂O₅, 0.1 Cl by TEM and SEM (Höland *et al.*, 1991a). The chemical composition of this new curved mica, (Na_{0.18}K_{0.82})(Mg_{2.24}Al_{0.61})(Si_{2.78}Al_{1.22})O_{10.10}F_{1.90} could be analyzed by energy dispersive spectroscopy (EDS) (Höland *et al.*, 1991a).

In comparison to glasses which form flat mica crystals, the control of the reduced phase separation process allowed the formation of the new curved mica crystals (Höland *et al.*, 1981). Because of a low concentration of nucleating centers, curved micas and cordierite crystals (as secondary crystal phase) grow in the range 700-1050 °C. The phase formation and the structure of curved mica crystals, that are typical for glass-ceramics of BIOVERIT® II-type, have been studied in comparison to flat crystals (Vogel and Höland, 1982; Höland *et al.*, 1983b; Elsen *et al.* 1989). Crystal structure investigation by X-ray diffractometry of phlogopite micas showed that the curved mica has a still higher content of aluminum ions in the octahedral coordination.

Small glassy phase separated droplets are the nucleating centers of the curved phlogopite. Curved phlogopites grow as isolated ball shaped aggregates (Figure 2). The crystallization up to 980 °C can be controlled so that the curved crystals come into contact with each

Mica glass-ceramics, structure and reactions





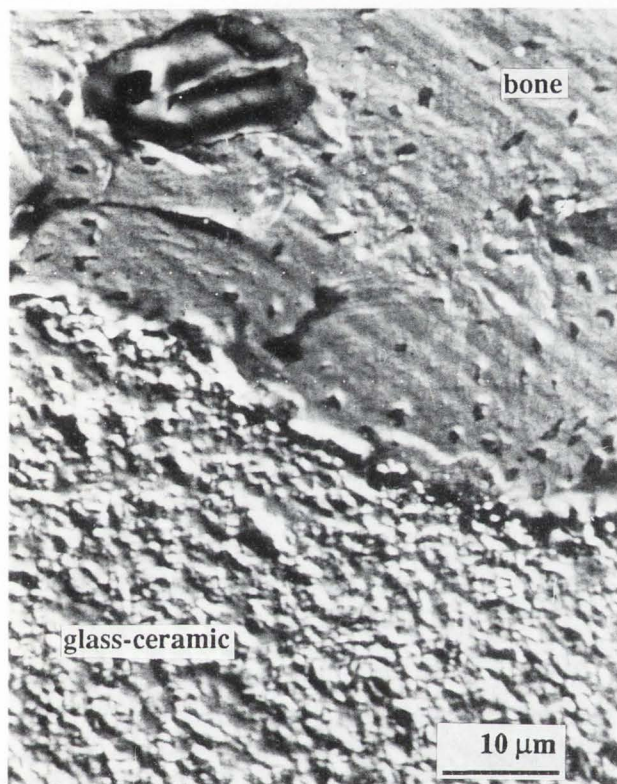


Figure 9. Interface between bone (guinea pig) and mica-apatite glass ceramic (BIOVERIT® I) one year after implantation.

Figure 5. Mica-cordierite glass-ceramic (BIOVERIT® II-type). The precipitation of cordierite takes place between the curved mica plates. SEM. Polished sample and etched 2.5 seconds in 2 % HF.

Figure 6. Base glass of mica-apatite glass-ceramic. The glass consists of three glassy phases. TEM/replica. Fractured surface etched 5 seconds in HCl.

Figure 7. Precipitation of $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$ apatite within the $\text{CaO-P}_2\text{O}_5\text{-F}$ rich droplet phase. TEM/replica. Fractured surface etched 5 seconds in HCl.

Figure 8. Mica apatite glass-ceramic after one week in Ringer's solution. TEM/replica.

other (Figure 3). The content of crystals within the glass-ceramic can be varied, e.g., lowered in comparison to Figure 3 and the translucency becomes higher (Figure 4).

Varying the chemical composition, to add more MgO and Al_2O_3 to the melt, it is possible to increase the content of the second crystal phase, cordierite (Figure 5). Therefore, the properties of the glass-ceramic, such as translucency, mechanical properties and thermal expansion coefficient can be controlled depending on the particular application in medicine (Höland *et al.*, 1991a).

The experiences of the surgeon (Beleites *et al.*, 1988) showed that middle ear implants have to have a very good machinability, that means a high content of curved micas (Beleites *et al.*, 1988) and dental products should show a special translucency.

Precipitation of Micas Rich in Ca^{2+} -Ions

Silicate glasses rich in CaO were developed by Ehrt and Heidenreich (1978), and Kasuga and Kasuga (1991). A characteristic composition which has been investigated by Ehrt and Heidenreich was 50 % SiO_2 , 18 % Al_2O_3 , 7 % MgO, 10 % CaO, 3.5 % Na_2O , 4.5 % K_2O , 7 Ma. % F. Kasuga and Kasuga (1991) could get glass-ceramics of the composition 43.5 SiO_2 , 12.7 Al_2O_3 , 25.5 MgO, 6.5 CaO, 1.7 K_2O and 10.1 F. The main crystal phase is a mica rich in Ca^{2+} -ions and secondary phases, such as diopside, anorthite, richterite and others were precipitated in the glass-ceramic (Kasuga and Kasuga, 1991).

Developments of Ehrt and Heidenreich (1978) and Kasuga and Kasuga (1991) to increase the CaO-content in mica type glass-ceramics had given the possibility to develop machinable glass ceramics with high mechanical strength (bending strength 210-300 MPa). The microstructure of the glass ceramic formed by Kasuga and Kasuga contains mica and diopside crystals and a glass matrix phase. An application for dental crowns was proposed by Kasuga and Kasuga (1991).

BIOVERIT® I-Type Glass-Ceramics (Mica-Apatite Glass-Ceramics)

A combination of different properties within a glass ceramic material, especially the combination of machinability and bioactivity was possible in multi-component glasses of the $\text{SiO}_2\text{-(Al}_2\text{O}_3\text{)-MgO-Na}_2\text{O-K}_2\text{O-F-CaO-P}_2\text{O}_5$ system. Typical compositions are 35.9 SiO_2 , 18.1 Al_2O_3 , 6.5 MgO, 5.1 Na_2O , 4.0 K_2O , 16.7 CaO, 11.2 P_2O_5 and 2.5 wt. % F₋ or 38.7 SiO_2 , 1.4 Al_2O_3 , 27.7 MgO, 6.8 K_2O , 10.4 CaO, 8.2 P_2O_5 and 1.9 wt. % TiO_2 (Höland *et al.*, 1983a, Höland *et al.*, 1991a).

Mica-apatite glass-ceramics show a characteristic microstructure and phase formation reactions (Vogel and Höland, 1987). The base glass shows three glassy phases, a SiO_2 -rich glass matrix, a $\text{CaO-P}_2\text{O}_5\text{-F}$ -rich big droplet phase, and a $\text{Na}_2\text{O-K}_2\text{O-Al}_2\text{O}_3\text{-MgO-F}$ -rich big droplet phase (Figure 6). Heat treating the glass at temperatures between 610 and 1050 °C allowed a double controlled *in situ* crystallization of mica and apatite. Apatite grows inside the $\text{CaO-P}_2\text{O}_5\text{-F}$ -rich big droplet phase (Figure 7) and phlogopite formation is a result of a solid state reaction of the glass matrix phase and the small droplet phase (Figure 8). The apatite crystals of

$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$ -type could be determined by X-ray diffraction measurements and the flat phlogopite crystals, $(\text{Na}_{0.21}\text{K}_{0.81})(\text{Mg}_{0.52}\text{Al}_{0.44})(\text{Si}_{2.80}\text{Al}_{1.20})\text{O}_{10.18}\text{F}_{1.82}$ could be analyzed by EDS (Höland *et al.*, 1983 a, 1985).

The authors of the present paper assume that similar reactions take place in glasses containing low concentrations of Al_2O_3 (or Al_2O_3 -free glasses). The difference between the phase formation in glasses shown in Figures 6-8 is that the phases formed are very small and the mica consists of $\text{KMg}_{2.5}(\text{Si}_4\text{O}_{10})\text{F}_2$ -type.

Electron microprobe investigations carried out by Höland *et al.* (1991b) show a very good contact of mica-apatite glass-ceramic and bone. One year after operation, the reaction interface between bone (tibia of guinea pig) and mica-apatite glass-ceramic is less than $15\ \mu\text{m}$ (Figures 9 and 10). Apatite is present within the biomaterial but an additional small calcium phosphate layer will be formed on the surface of the glass-ceramic. Secondary ion mass spectroscopy (SIMS) investigations show the tendency that phosphate groups become enriched at the surface of BIOVERIT® I glass-ceramics under simulated conditions (Höland *et al.*, 1991b). Figure 11 shows that the peak positions 31, 47 and 63 are responsible for the enrichment of phosphate groups. Additionally an NaCl-rich layer from the simulated body fluid seems to be deposited onto the sample (position 35, 37).

The process of bioactivity seems to be of a complex nature. It includes solid state reactions (apatite-apatite reaction), ion diffusion processes (e.g. Na^{+-} , Ca^{2+-} diffusion), Ca-phosphate formation and a possible positive influence of silicates (Hench, 1991) on the bone regeneration reaction. This corresponds with results of bioactive behavior of glasses and glass-ceramics reported by Hench (1991), Kokubo *et al.* (1990), and Wilson (1991).

Glass-Ceramics Containing Micras and CaO , P_2O_5 -Additives

Shibuya *et al.* (1990) also formed glasses by adding CaO and P_2O_5 to SiO_2 - (Al_2O_3) - MgO - K_2O - F^- glasses, e.g.: 57.1 SiO_2 , 11.7 MgO , 13 K_2O , 5.9 F , 4.8 ZrO_2 , 3.1 CaO , 2.6 P_2O_5 and 1.84 CeO_2 . The formation of different crystal phases was investigated by X-ray diffraction measurements (Shibuya *et al.*, 1990).

Shibuya *et al.* (1990) developed a $\text{KMg}_{2.5}(\text{Si}_4\text{O}_{10})\text{F}_2$ -mica glass-ceramic containing also calcium phosphate groups. Apatite crystals have been analyzed by X-ray diffraction measurement after heat treating the glass up to 1050-1075 °C. Shibuya *et al.* (1990) reported also, that they have carried out scanning electron microscopic measurements which show that the crystals are in close contact with each other, they are cross-linked.

Conclusions

The results of the authors of papers cited in the bibliography and the authors of this paper showed that mica glass-ceramics are biocompatible materials which can be used for bone substitution in medicine.

DICOR®-type glass ceramic is used for dental restoration. Mica glass-ceramics of BIOVERIT® II-type and mica-apatite glass ceramics of BIOVERIT® I-type have been successfully applied in head and neck surgery and orthopaedic surgery in more than 600 patients (Schubert *et al.*, 1988; Höland *et al.*, 1990).

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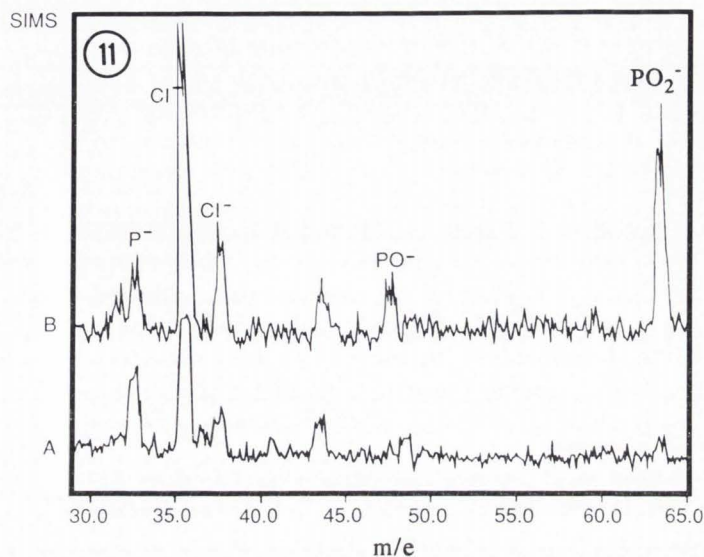
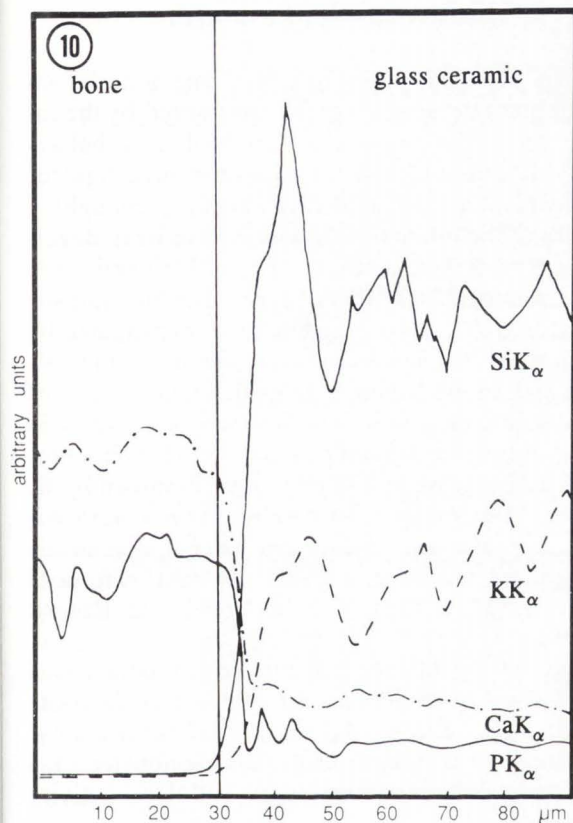


Figure 11 (above). Negative secondary ion mass spectra (SIMS) of BIOVERIT® I glass-ceramic before (A) and after soaking (B) in simulated body fluid (SBF) at 95 °C for 64 hours.

Figure 10 (at left). Electron microprobe investigation of the interface between mica-apatite glass ceramic and bone (16 weeks after implantation).

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Discussion with Reviewers

Reviewer III: The paper reviews some material aspects of glass-ceramics that are considered by the inventors to be biocompatible. The biological behavior of this type of material is neither investigated, nor documented, nor published carefully enough!

Authors: The biomaterials which have been developed at Otto-Schott-Institute of Jena University are glass-ceramic of BIOVERIT® type. The biocompatibility of BIOVERIT® I-type has been investigated by J. Gummel, T. Schubert, K.J. Schulze and W. Purath and are documented in qualification thesis of orthopaedic clinic, Dresden, Germany and partly in the text reference Schubert *et al.*, 1988. The biocompatibility of BIOVERIT® II-type is shown by E. Beleites, University Jena, clinic for otorhinolaryngology and the results are documented in his qualification theses and partly in text reference Beleites *et al.* (1988), and in Vogel and Höland (1987).

The well established cell culture test method was utilized for the determination of toxicity for both ceramic types. Neither the "bioactive" ceramics nor the "bioinert" reference materials demonstrated a significant influence on the cellular activity (proliferation).

Additional testing protocols are documented in the references listed previously. We have also performed further biocompatibility studies with laboratory animals: Sixteen weeks after subcutaneous implantation of Bioverit I, with its higher solubility, a stabilization of the cellular reaction was observed. The investigators concluded that this result can be interpreted as a sign of controlled surface solubility factors and excellent biocompatibility.