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TEXTURE FORMATION IN A GLASS CERAMIC OF $Li_2O \cdot 2\ SiO_2$ COMPOSITION

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Glass ceramics of the composition $Li_2O \cdot 2\ SiO_2$ were prepared with an oriented microstructure. The oriented crystalline phase is orthorhombic lithium disilicate. This orientation was achieved by crystallization of glass fibers and bulk glasses in a temperature gradient and under isothermal conditions. Both bulk and surface crystallization were achieved. Further, oriented crystalline films were prepared on glassy and crystalline substrates by a sol-gel method. Scanning electron microscopy and atomic force microscopy were used to characterize the microstructure. The degree of orientation was investigated by X-ray pole figure measurements from which orientation distribution functions and inverse pole figures were calculated. The (002) plane of the surface crystallized material shows a strong fiber texture parallel to the surface of the sample.

KEY WORDS: Glass ceramic, lithium disilicate, oriented microstructure

1. INTRODUCTION

Glass ceramics are polycrystalline materials containing a residual glassy phase. They are obtained by controlled crystallization of glasses (McMillan, 1979). Crystallization is accomplished by subjecting a suitable base glass to a controlled heat treatment which results in nucleation and growth of crystallites within the glass. The properties of the resulting glass ceramic depend on the crystalline phase and on the microstructure. Through a proper choice of composition and thermal treatment, it is possible to obtain materials with a desired microstructure and with widely ranging properties.

Normal glass ceramics are aggregates of crystallites of random orientation and are therefore materials with isotropic properties. However, it is possible to produce glass ceramics with an oriented microstructure which are expected to exhibit a marked anisotropy.

Glass ceramics with oriented crystals have been formed by extruding glass at a temperature near the crystallization temperature with compositions in the fluoramphibole, fluor-mica or lithium disilicate systems (Ashbee, 1974; Atkinson and McMillan, 1977) and near the nucleation temperature (Durschang *et al.*; 1994). However, the products showed partial crystal alignment only. Booth and Rindone (1964) and Rindone (1962) have reported on oriented surface crystallization of lithium disilicate glass. But no attempt was made to put the determination of the texture on a quantitative level.

Another way to produce an oriented microstructure involves the sol-gel method. The preparation of sol-gel films is possible for a broad spectrum of glass and ceramic systems and their application has the potential of yielding high performance glass and ceramic materials (Klein, 1991). Sol-gel procedures have potential interest in microelectronics, which generally require the deposition of materials at low temperatures. The sol-gel

route to glass formation and subsequent crystallization is based on the possibility of forming a glass network by polymerization of suitable compounds in the solution state. The formation of the glass film takes place below the transformation temperature without melting of the glass.

It is the aim of this work to produce glass ceramics with a highly oriented microstructure by different preparation conditions (surface crystallization and bulk crystallization in a temperature gradient, crystallization of glass fibers and of sol-gel produced coatings) and to determine the degree of orientation from orientation distribution functions (ODF) and inverse pole figures, which are calculated from pole figure measurements. The techniques used to grow oriented glass ceramics and the resulting microstructure are briefly discussed.

2. TEXTURE MEASUREMENTS OF GLASS CERAMIC MATERIALS

Quantitative texture measurements of glass ceramics are not well established yet. In general, the crystalline phases in glass ceramics have a low crystallographic symmetry and the materials consist often of various crystalline phases. The peaks of the X-ray diffraction pattern overlap, they are weak and it is difficult to separate these different peaks. Thus texture analysis in glass ceramics is more difficult than in the case of metallic materials.

For pole figure measurements it is necessary to have the exact knowledge of the lattice parameters. However the lattice parameters of the crystalline phases in a glass ceramic and thus the peak positions in the diffraction pattern vary with preparation conditions and with the composition of the base glass (Benedetti *et al.*, 1983; West and Glasser, 1981).

Glass of the composition of $Li_2O \cdot 2SiO_2$ was selected for a number of reasons. The only crystalline phase in the resulting glass ceramic is lithium disilicate with an orthorhombic crystallographic symmetry. The rate of crystal growth is sufficiently high and observations of preferred surface crystallization have been reported in the literature.

Lattice parameters of lithium disilicate were determined by powder diffractometry and using the Rietveld structure analysis in the Institut für Mineralogie und Mineralische Rohstoffe, TU Clausthal. The values obtained are a = 0.5813 nm; b = 1.4635 nm; c = 0.4783 nm and are in fair agreement with those obtained by Liebau (1961) and with those reported by Rindone (1962).

Qualitative texture estimations were performed by Ashbee (1974) and Atkinson and McMillan (1977). They estimated the crystallographic orientation of the lithium disilicate crystals in extruded specimens. The intensities of the (hkl) reflections of X-ray diffraction patterns were measured and compared relative to those from the (111) plane of the lithium disilicate phase in different samples.

3. EXPERIMENTS

3.1 Materials and heat treatment

Batch mixtures of 100 g were prepared from reagent grade chemicals of SiO_2 (Strem) and Li_2CO_3 (Merck). The chemicals were mixed, melted in a Pt5%Au crucible for 5 h at 1450°C in an electric furnace and poured into steel molds. The molds were

rectangular with dimensions 20 mm × 30 mm for the surface crystallization samples, and they were cylindrical with a diameter of 8 mm and height of 30 mm for the temperature gradient samples. The samples were annealed at 400°C for 1 h before further treatment. No nucleating agent or nucleation step was used to suppress the growth of spherulites in the bulk of the samples. For surface crystallization, the samples were heat treated at 650°C for 1 h.

Transparent glass fibers were drawn by hand from a glass melt. The diameters of the glass fibers were in the range of 100 to 500 μm. The fibers were crystallized by heat treatment at 650°C for 1 h.

Glass rods were crystallized in a temperature gradient furnace. The temperature at the bottom of the glass rod was in the range of the crystallization temperatures (650 to 750°C). The temperature gradient in the axial direction was about 400 K/cm. The glass rods were moved in the furnace with a constant velocity of 13 μm/s which is approximately the crystal growth rate.

3.2 Crystallization of sol-gel films

Gel layers were deposited on glass slides, on platinum and silicon substrates by the dip coating process from suitable solutions described by Helsch (1993). Proper thermal treatment at 500°C was necessary to convert the gel into glass and subsequently into the crystalline films.

3.3 Characterization techniques

Crystalline phases were studied using X-ray diffraction techniques (XRD with Bragg-Brentano geometry, Seifert). The microstructure was investigated by scanning electron microscopy (SEM; JSM-U3, Jeol) and with atomic force microscopy (AFM; Nanoscope II, Digital Instruments). The pole figures were measured with an ATEMA-C apparatus (Institut für Metallkunde und Metallphysik, TU Clausthal).

4. RESULTS AND DISCUSSION

4.1 Surface and bulk crystallization

SEM investigations show that needlelike crystals form the surface layer of the sample (Figure 1). In the bulk of the material the crystals were randomly oriented. The thickness of the surface layer with oriented crystals was in a range of 100 μm to 1 mm. This thickness depended on the preparation conditions, the surface roughness and the thermal treatment. Because of the marked texture observed with SEM of the surface layer, it was selected for the first pole figure measurements and texture calculations. The diffraction spectra using CuKα radiation are shown in Figure 2. Figure 2a displays the diffraction spectrum taken in the regular sample position of the bulk material. The crystalline fraction possesses well-developed peaks of lithium disilicate with the (hkl) indexing specified in the diffraction spectrum. Figure 2b shows the diffraction spectra taken for various representative sample tilt angles of the sample with surface crystallization. Already the qualitative inspection of the diffraction spectra displays a sharp texture of this surface crystallized material.

Figure 3a presents two representative pole figures, (002) and (111), of the surface crystallized material and Figure 3b the pole figures, (170) of the surface and the bulk

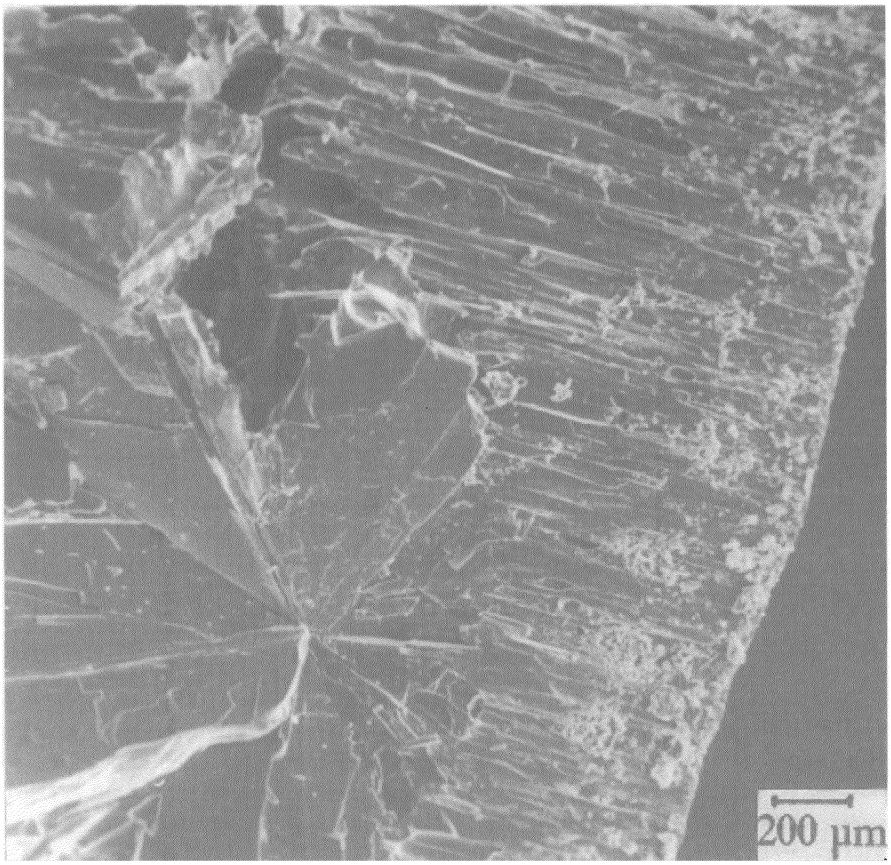


Figure 1 SEM micrograph of a fracture surface of a lithium disilicate glass ceramic.

material respectively. The contour levels of the pole figures are the measured intensities. Texture calculation with ODF results in an axially symmetric texture of the surface - crystallized material. Because of the axial symmetry the presentation in inverse pole figures is more appropriate than in orientation distribution functions. The inverse pole figures give the distribution of a particular sample direction in the coordinate system of the crystal. For the surface crystallization, the inverse pole figure in the normal direction is the most important (see Figure 4a, b and Table 1).

These results show a strong fiber texture of crystals. The strongest fiber of the (002) plane is to be seen in the pole figure (Figure 3a) and the inverse pole figure (Figure 4a). The crystals grow with their (002) planes parallel to the surface. These results correlate with qualitative investigations of the oriented surface layer described in literature (Rindone 1962). Rindone found the lithium disilicate crystals to be oriented with the (002) plane parallel to the surface of the glass ceramic by comparing the intensities of the (111) and (002) planes of the X-ray diffraction peaks.

Figure 5 shows the reasonable agreement between the measured and the calculated pole figures of (170).

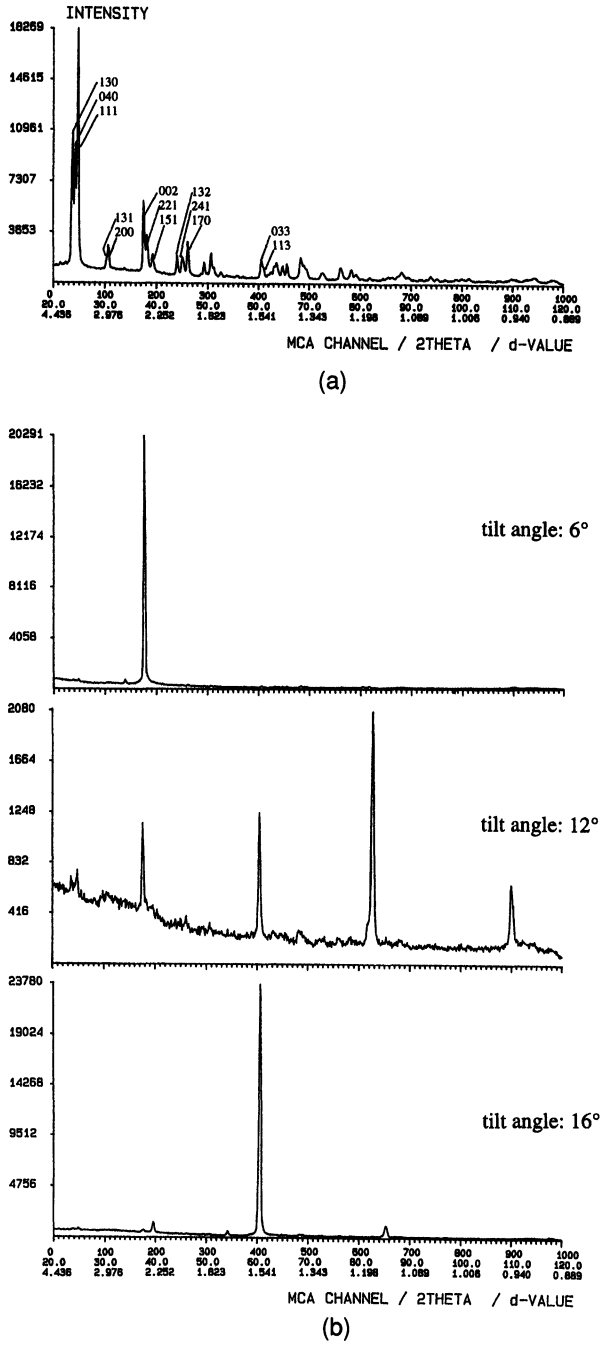


Figure 2 Diffraction spectra of lithium disilicate glass ceramics. a) Sample from the bulk material after removal of the surface layer (nearly random). b) Highly oriented surface layer at different tilt angles.

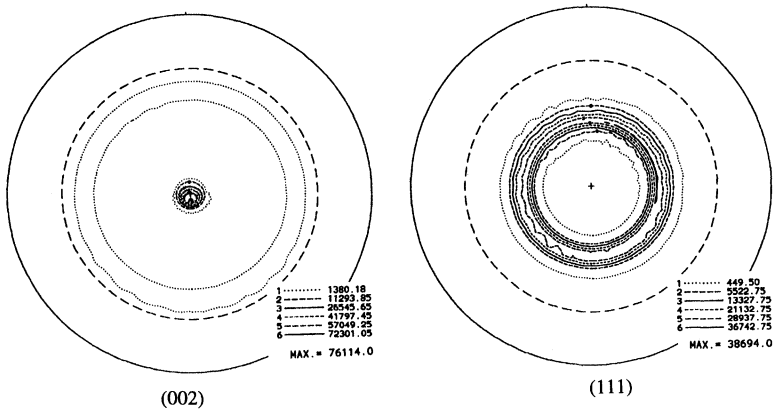


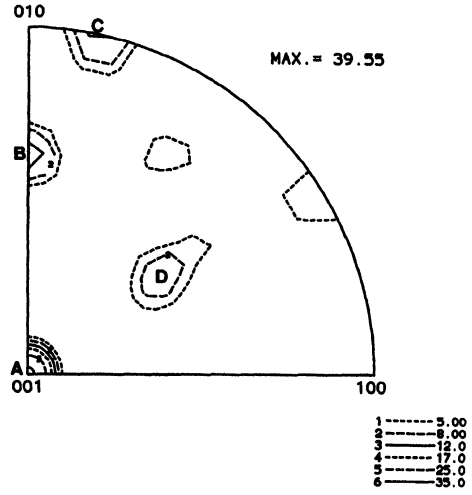
Figure 3 Representative pole figures. a) Surface crystallization. b) (170) surface crystallization and (170) bulk crystallization.

4.2 Glass ceramic fibers

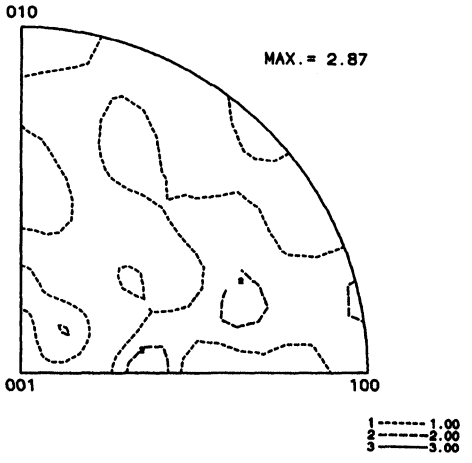
The SEM shows needlelike crystals growing from the surface into the core of the fiber (see Figure 6). The texture investigations show the crystallites have grown radially with the c axis directed from the surface towards the core of the fiber.

4.3 Crystallization in a temperature gradient

Another goal was to produce an oriented microstructure in the bulk of the glass ceramic material by starting nucleation at the surface of the glass and allowing the crystallites to grow into the bulk of the sample and, at the same time, carefully avoiding the growth of spherulites.



(a)



(b)

Figure 4 Inverse pole figures. a) Surface crystallization. b) Bulk crystallization.

Table 1 Axis directions and intensities of the points A-D marked in the inverse pole figures

component	axis direction	intensity
A	normal to (0 0 1)	39.55
B	normal to (0 10 2)	15.11
C	normal to (1 13 0)	12.57
D	normal to (1 2 1)	11.05

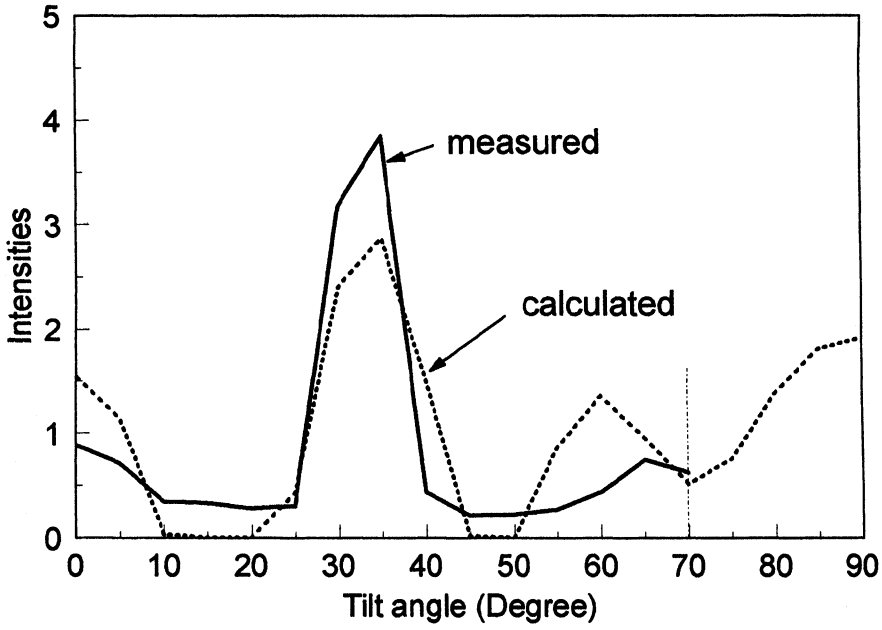


Figure 5 Measured and calculated lineplot of the (170) pole figure.

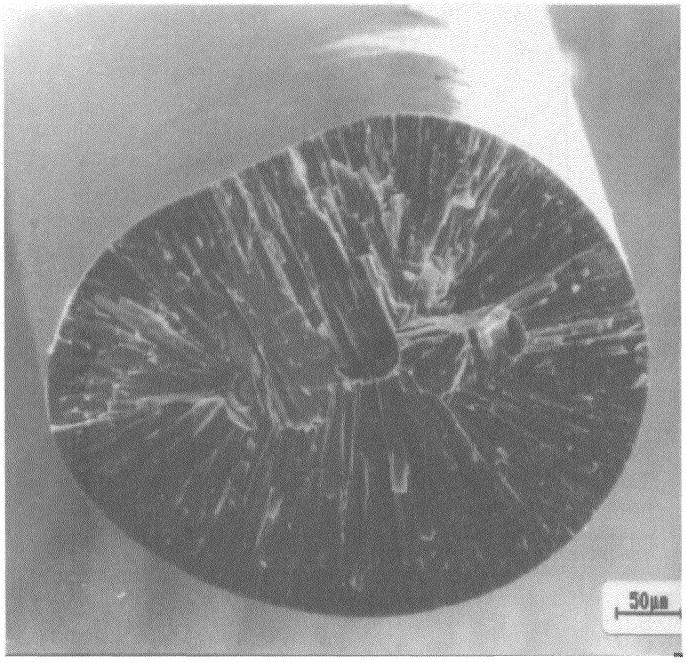


Figure 6 SEM micrograph of a fracture surface of a lithium disilicate glass ceramic fiber.

Crystallization starts at the bottom surface of the rod into the bulk. Figure 7 shows the oriented crystallites of a fracture surface. The oriented region from the bottom into the bulk of the sample was about 6 mm.

Texture interpretation with pole figure measurement and ODF show the same behaviour as the surface crystallization.

4.4 Crystallized sol-gel films

The crystal phase of the crystallized sol-gel film was identified by X-ray diffraction as lithium disilicate. A film thickness of 5 μm was obtained by multiple coating. This high thickness is necessary to obtain sufficient intensity for the X-ray diffraction patterns and for the measurements of the pole figures (Helsch, 1993).

Texture interpretation of sol-gel films is more difficult than for conventionally produced glass ceramics. The X-ray intensities of the sol-gel films are weak and less peaks are observed. Further, it is not possible to determine the exact dimensions of the lattice parameters of the sol-gel obtained crystalline films. But some of the measured pole figures can be compared with those of the conventionally produced glass ceramics. Figure 8 shows the pole figures of a crystallized sol-gel film. The intensities of the sol-gel film are weaker but show similar characteristics as the surface crystallization of a conventionally crystallized glass ceramic (see Figure 3a)

Investigations with SEM and AFM support the texture investigations of the sol-gel crystallized films. Figure 9 shows the surface of a crystalline sol-gel film deposited on a platinum substrate. The AFM shows the orientation of the crystallites.

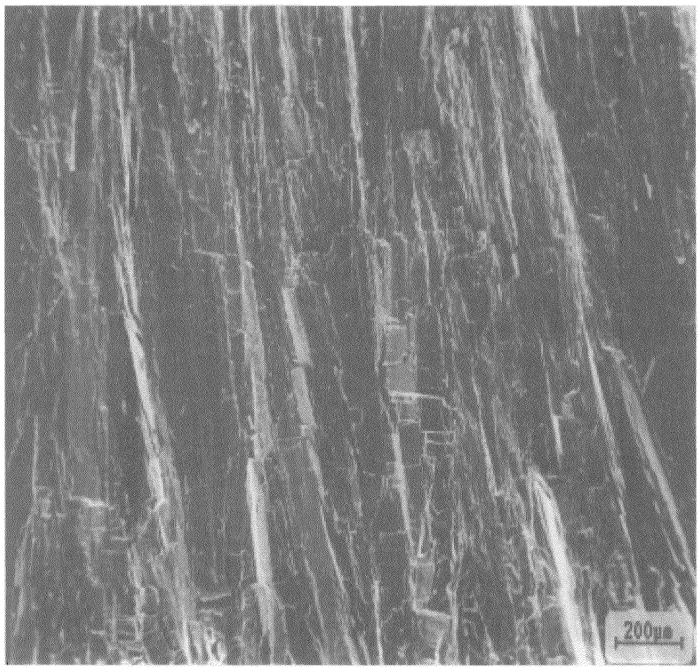


Figure 7 SEM micrograph of a glass ceramic fracture surface prepared in a temperature gradient furnace. The surface of the sample is perpendicular to the needlelike crystals.

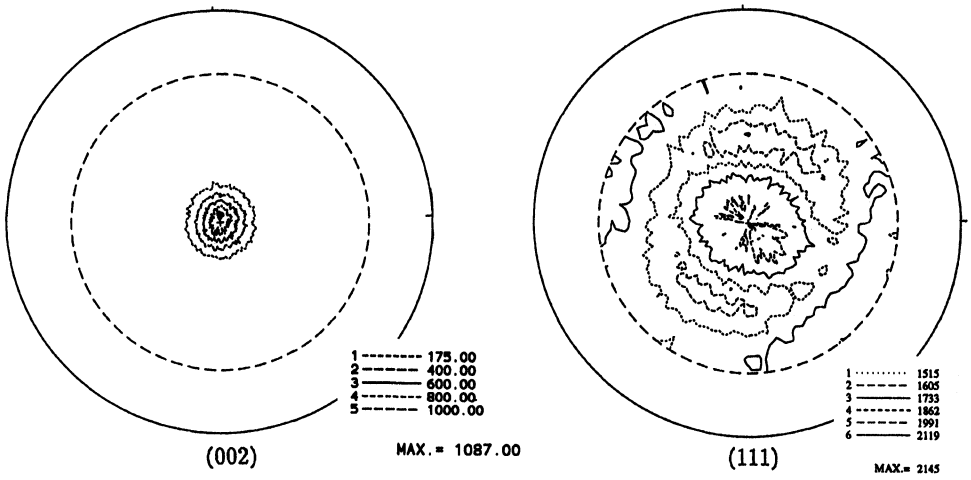


Figure 8 Pole figure of the (002) and the (111) plane of a sol-gel obtained film.

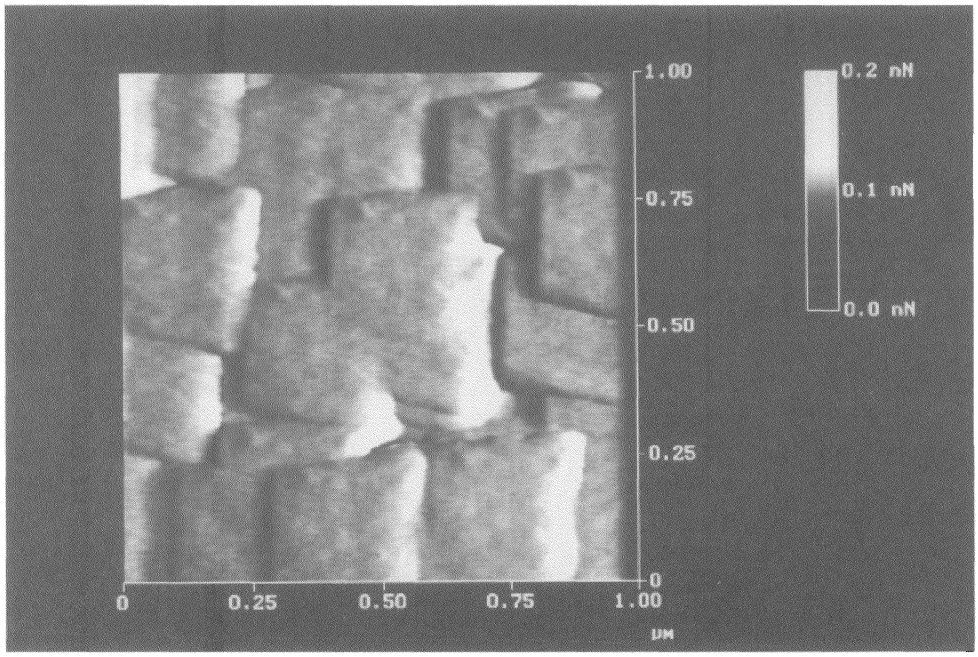


Figure 9 AFM micrograph of a lithium disilicate film on a platinum substrate.

5. CONCLUSIONS

Anisotropic glass ceramics were prepared and quantitative texture analysis was used to demonstrate the degree of orientation. The orientation distribution function and the inverse pole figures were calculated for the crystallization of glass ceramic surfaces, of fibers and of bulk material obtained under isothermal conditions and in a temperature gradient. The (002) plane shows a strong fiber texture parallel to the surface of the samples.

Atomic force microscopy and pole figure measurements of crystalline sol-gel films show a preferred orientation of the crystals.

6. *Acknowledgments*

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