

## Oriented strontium fresnoite glass-ceramics prepared by electro-chemically induced nucleation

R. KEDING, C. RÜSSEL

*Otto-Schott-Institut, Jena University, Fraunhoferstraße 6, 07743 Jena, Germany*  
*E-mail: ccr@rz.uni-jena.de*

Fresnoites possess an acentric structure [1] and hence polar properties. They are non-ferroelectric, piezoelectric [2] as well as pyroelectric [3] and furthermore show non-linear optical effects [4], such as second harmonic generation. The crystal structure of fresnoites is fairly unusual with respect to the titanium coordination. Titanium is located inside square pyramids and hence possesses fivefold coordination. Due to their permanent polarity and high piezoelectric coefficients, fresnoites have a high potential for high stability and high temperature piezoelectric applications [2]. Usually, glass-ceramics as well as sintered ceramics contain randomly oriented crystals, thus in these materials, anisotropy as well as piezoelectricity is not observed. Nevertheless, if an orientation, also with respect to the polar axis can be achieved, piezoelectric properties are possible. In the literature, mainly two methods for the preparation of oriented glass-ceramics are described [6, 7]: plastic deformation of a partially crystalline melt and surface crystallization. To achieve orientation by plastic deformation, e.g. extruding anisometric crystals are required. Although, if it is possible to arrange needle-like polar crystals with their polar axis parallel to extrusion direction, this does not enable piezoelectricity because parallel and antiparallel orientation will occur in the same extent. By contrast, it is possible to prepare polar glass-ceramics by surface crystallization. Unfortunately, surface crystallization only enables the preparation of fairly thin (<500  $\mu\text{m}$ ) surface layers. Another method, developed in the past few years is the electrochemically induced nucleation [8, 10], which has already been applied to the preparation of mullit [8], richterite/diopsid [9],  $\text{Sr}(\text{PO}_3)_2$  and barium fresnoites glass ceramics [10].

This letter describes the formation of strontium fresnoites glass-ceramics from a melt with the composition  $2\text{SrO}\cdot\text{TiO}_2\cdot 2.75\text{SiO}_2$ . The glass was melted in a platinum crucible at  $1500^\circ\text{C}$ , homogenized by stirring 1 h and subsequently soaked for another 1 h. Then a platinum wire (diameter: 1 mm) was introduced into the melt which subsequently was cooled to  $1200^\circ\text{C}$ . Then a dc-potential of around 1.2 V was attached between the platinum crucible and the platinum wire, which led to a current flow of 30 mA. The platinum wire acted as cathode. After 2 min, the formation of crystals at the cathode was observed. The crystallization front proceeded from the cathode. After 30 min, the crystals grew around 2 cm. Then the wire with the adherent crystalline material was drawn out of the melt. Within 0.5 mm around

the platinum wire, a dark coloration was observed. The crystalline sample was cut, ground and polished. It was characterized by X-ray diffraction (Siemens D 5000), electron microscopy (Zeiss DSM 940A). Pole-figures were recorded using a Phillips x-pert diffractometer. The initially glassy sample was characterized by DTA (Netzsch STA 429).

During heating, the DTA-profile exhibited an exothermic peak at around  $947^\circ\text{C}$  and a subsequent endothermic peak at  $1233^\circ\text{C}$ . Endothermic effects were still visible until  $1290^\circ\text{C}$ . During subsequent cooling at  $1010^\circ\text{C}$  another exothermic peak is observed. As proved by tempering experiments at constant temperatures, the exothermic peak at  $947^\circ\text{C}$  is caused by the crystallization of the melt. Here  $\text{Sr}_2\text{TiSi}_2\text{O}_8$  (a phase with fresnoites structure, ICPDS: 35-212) is formed. At  $1233^\circ\text{C}$  the solidus and at  $1290^\circ\text{C}$ , the liquidus temperature is reached. During cooling, the melt crystallizes at  $947^\circ\text{C}$  (exothermic peak). Fig. 1 shows an SEM micrograph (back scattering electrons) of a sample cut perpendicular to the growth direction. The light phase seen is crystalline strontium fresnoite. A fairly regular structure is seen. The fresnoites crystals possess a size of around 2 to 10  $\mu\text{m}$ . In the higher magnification shown in Fig. 2, the structure between the crystals is seen. It is composed by two phases, a light phase, supposedly also strontium fresnoites and a dark phase in which the residual  $\text{SiO}_2$  is concentrated. In Fig. 3, a pole-figure of the 002-peak is presented. One main maximum located at a  $\Psi$ -angle of around  $4^\circ$  is seen. This proves a high degree of orientation: the crystallographic  $c$ -axis of the fresnoites is oriented perpendicular to the surface. Hence, the  $c$ -axis is oriented in the growth direction.

The mechanism of the electrochemical nucleation and the formation of the oriented strontium fresnoites structure can be explained as follows: at  $1200^\circ\text{C}$ , the melt is around 90 K below the liquidus temperature, however, as seen from the DTA-profile, homogeneous nucleation does not yet occur. After attaching a dc-current, nuclei are formed. This is due to the reduction of the melt at the cathode. Here,  $\text{Ti}^{4+}$  incorporated as network former is reduced to  $\text{Ti}^{3+}$  which predominantly acts as network modifier (see also dark color around the cathode; see also [10]). At the anode, the glass network is reduced to gaseous oxygen. This leads to a smaller rigidity of the network and to a drop in viscosity. According to the classical nucleation theory, the latter causes an increase in the nucleation rate. The orientation of the sample should not be caused by epitaxial

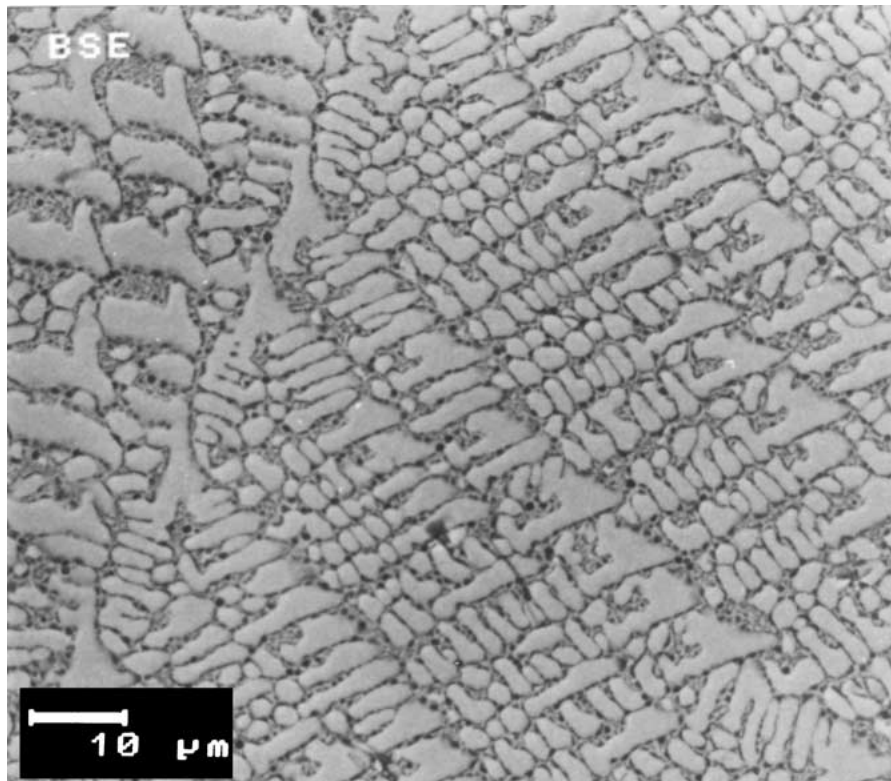


Figure 1 SEM micrograph of a strontium fresnoite glass-ceramics cut perpendicular to the growth direction (low magnification).

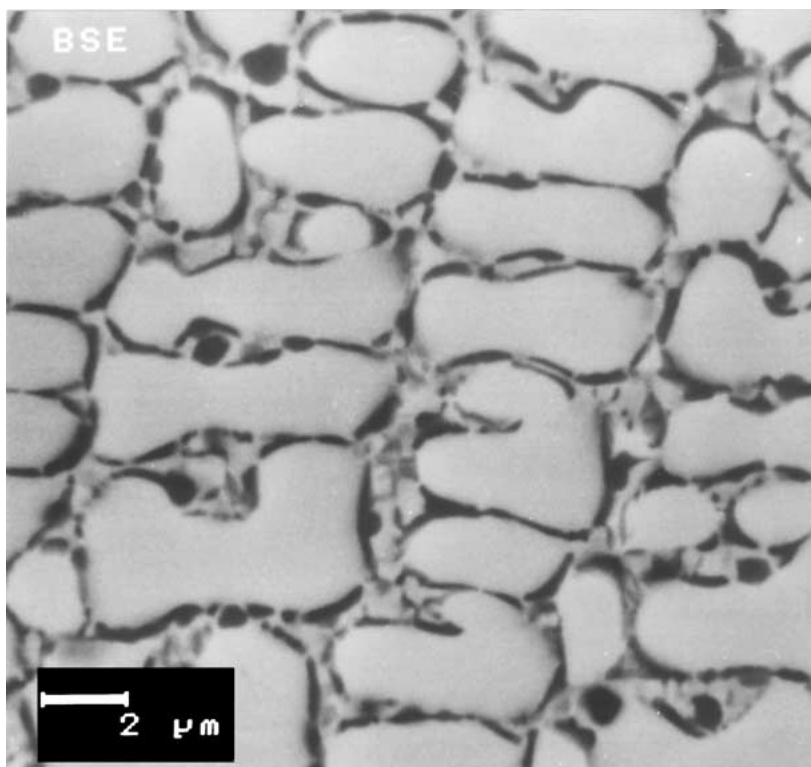


Figure 2 SEM micrograph of a strontium fresnoite glass-ceramics cut perpendicular to the growth direction (high magnification).

growth on the surface of the cathode, since it consists of polycrystalline platinum. However, the growth rates seem to be very different in different crystallographic directions. By analogy to surface nucleation, an initially random orientation may also result in oriented materials [7, 10]. Those crystals which are not oriented perpendicular to the surface with their fast growing crystallo-

graphic direction will hinder each other during crystal growth. Hence, only those crystals with the right orientation will continuously grow. This leads to the high degree of orientation. In the system studied, the crystal growth velocity is  $11 \mu\text{m}\cdot\text{s}^{-1}$ . Hence, the temperature of  $1200^\circ\text{C}$  is attributed to a negligible nucleation rate, however, to a large crystal growth velocity. It should

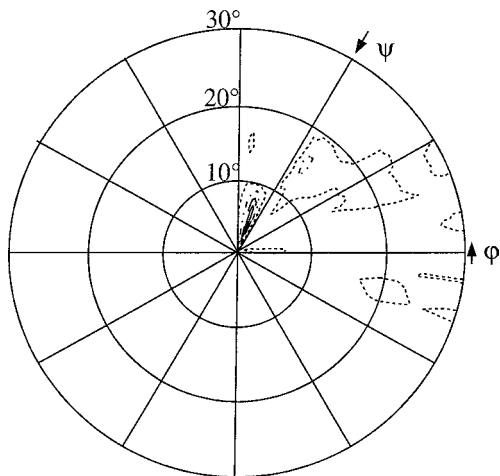


Figure 3 Pole-figure of a sample cut perpendicular to the growth direction (002-peak) relative intensities: ···: 176, ---: 340, —: 505, - - - : 669 and —·—: 834.

be assumed that at 1200 °C, only the large crystals as shown in Fig. 2 are formed, however, the crystalline structures between the fresnoites crystals are formed during subsequent cooling.

Stoichiometric strontium fresnoites melt incongruently [11] and hence, by contrast to barium fresnoites, the growth of single crystals from a melt is difficult. However, for some optical applications, such as second harmonic generation, barium fresnoite is not suitable,

due to poor phase matching. Due to its high degree of orientation, near to that of a single crystal, the as prepared strontium fresnoite glass-ceramics might be an interesting alternative for single crystalline materials. In further studies, the non-linear optical properties will be studied.

## References

1. P. B. MOORE and J. LOUISNATHAN, *Z. Kristallog.* **130** (1969) 438.
2. A. HALLIYAL, A. S. BHALLA and R. E. NEWNHAM, *Ferroelectrics* **62** (1985) 27.
3. H. SCHMIDT, P. GENEQUAND, H. TIPPMANN, G. POUILLY and H. GUEDU, *J. Mater. Sci.* **13** (1978) 2257.
4. Y. TAKAHASHI, Y. BENINO, T. FUJIWARE and T. KOMATSU, *Appl. Phys. Lett.* **81** (2002) 223.
5. A. HALLIYAL, A. SAFARI, B. S. BHALLA, R. E. NEWNHAM and L. E. CROSS, *J. Amer. Ceram. Soc.* **67** (1984) 331.
6. Y. DING, Y. MIARA and A. OSAKA, *ibid.* **77** (1994) 2905.
7. C. RÜSSEL, *J. Non-Cryst. Solids* **219** (1997) 212.
8. G. VON DER GÖNNA, R. KEDING and C. RÜSSEL, *ibid.* **243** (1998) 109.
9. R. KEDING, D. STACHEL and C. RÜSSEL, *ibid.* **283** (2001) 137.
10. R. KEDING and C. RÜSSEL, *ibid.* **219** (1997) 137.
11. T. HÖCHE, W. NEUMANN, S. ESMAEILZADEH, R. UECKER, M. LEUTRON and C. RÜSSEL, *ibid.* **166** (2002) 15.

Received 16 June

and accepted 16 September 2003