Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of the European Ceramic Society 24 (2004) 1063–1067
www.elsevier.com/locate/jeurceramsoc

Surface and bulk stillwellite textures in glasses of the La_2O_3–B_2O_3–GeO_2 system

V.N. Sigaev[a], P.D. Sarkisov[a], P. Pernice[b,*], A. Aronne[b], A.M. Datsenko[a], S.Yu. Stefanovich[c], V.I. Fertikov[a], O.A. Pozhogin[a], D.A. Zakharkin[a]

[a]Mendeleev University of Chemical Technology of Russia, Miusskaya Square, 9, 125190 Moscow, Russia
[b]Department of Materials and Production Engineering, University of Naples Federico II, P. le Tecchio, 80125 Naples, Italy
[c]L. Ya. Karpov Institute of Physical Chemistry, Vorontzovo pole 10, Moscow 103064, Russia

Abstract

Both surface and bulk textures penetrating the whole volume of the glass may be formed in glasses of the La_2O_3–B_2O_3–GeO_2 system near the stoichiometry of $LaBGeO_5$ stillwellite. These textures cause non-linear optic, ferroelectric and pyroelectric properties of crystallized glasses. The present work represents SEM study of surface and bulk grain-oriented crystallization of stillwellite glasses for different conditions of synthesis of both planar surface (non-linear optic) and bulk (ferro/pyroelectric) textures based on oriented needle-shaped crystals of $LaBGeO_5$ stillwellite.

Keywords: Pyroelectricity; Stillewellite; Texture

1. Introduction

Many efforts are undertaken now to develop new non-linear optic media based on glasses. Plenty of work is devoted to electrical poling of glasses, leading to second harmonic generation (SHG) effect,[1,2] there are also attempts to create SHG-active nanostructured glasses.[3–6] Many investigations concern synthesis of thin transparent oriented layers of non-linear optic crystals on glassy surface.[7–9] Takahashi et al.[10–12] made an attempt to obtain firstly planar waveguide based on oriented ferroelectric crystals of $LaBGeO_5$ stillwellite. Earlier grain-oriented crystallization of lanthanum borogermanate (LBG) glasses was examined by authors[13,14] who synthesized glass ceramic textures of $LaBGeO_5$ stillwellite exhibiting promising pyroelectric properties.

Authors[10–12] offered original schedule of synthesis of surface transparent texture of $LaBGeO_5$ by preliminary heat treatment of initial polished glass plates at temperature near T_g to create nuclei of crystallization in the bulk of the glass and then by a final treatments at 725–750 °C forming textured surface layer. The conclusions of the paper[10–12] were done starting from DTA and XRD data without illustrations of textured layers by EM at appropriate magnifications. In particular, it is not clear what is the morphology of the stillwellite crystals of 25–30 μm in diameter found by Takahashi et al.[10] In our opinion, it is difficult to find a simple link of bulk nucleation process in glasses with their surface crystallization. Moreover, the authors[13–15] consider bulk nucleation as an antagonist of grain-oriented crystallization of glasses.

For the above reasons, we tried to explore by SEM the flow of surface crystallization of stillwellite glasses using different heat treatments including both conventional treatments in an electrical furnace and crystallization of glasses under temperature gradient fields for different temperature difference between "hot" and "cold" sides of glassy plates. The fine structure of well-textured samples is illustrated and discussed.

2. Experimental

The La_2O_3–B_2O_3–$2GeO_2$ glasses were melted in corundum crucibles placed in an electric furnace at 1300 °C for 30 min using reagents of La_2O_3, H_3BO_3 and GeO_2. The batch weights were from 30 to 100 g. The glassy

* Corresponding author. Tel.: +39-81-768-2411; fax: +39-768-2595.
E-mail address: pernice@unina.it (P. Pernice).

0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00424-2

melts were poured onto a steel plate and then pressed with another steel plate to a thickness of 0.8–1.5 mm.

Both sides of glassy plates were polished and undergone different heat treatments. A series of samples was treated at 740, 750 and 760 °C for 5 h (one step heat treatment). Another part of plates was preliminary treated at temperatures from 650 to 680 °C with step 5° for 1.5 h covering interval of maximum nucleation rate reported in the paper,[10–12] and then these samples were kept at 750 °C (two steps heat treatment). A third series of samples was treated in a temperature gradient furnace for different temperatures and different values of temperature gap ΔT between "hot" and "cold" sides of the glassy plate. For all the three series, both sides of plates were examined by SEM because down side surface had contact with fine powder of corundum while upper surface was in air.

SEM micrographs were obtained on electron microscope BS-340, Tesla, using fresh fractured pieces of samples that were coated with Cu.

XRD patterns were recorded using powder diffractometer DRON-3M (CuK_α radiation).

3. Results and discussion

First of all it should be noted that all the three types of heat treatments produce oriented crystalline layer on the both sides of glassy surfaces (Figs. 1 and 2). In all cases we observed needle-shaped crystals of $LaBGeO_5$ well oriented along *c* axis and with typical value of diameter of 1–2 μm. Lattice parameters of trigonal $LaBGeO_5$ crystallized on the surface layer of the glass almost exactly corresponded to those of single crystal ($a = 6.99$; $c = 6.86$ Å) for all the heat treatments performed. Because values of refractive indexes of $LaBGeO_5$ crystals and LBG glass were the same in all textured samples, transparency of the surface layers of different samples was similar.

Typical micrograph of glasses after one-step heat treatment is shown on Fig. 1a. Dense layer of $LaBGeO_5$ penetrated in the bulk of the glass on a depth of about 20 μm for a treatment at 740 °C for 6 h. An increase of temperature leads to progressive increasing of crystalline layer thickness.

The two steps heat treatment (650–680 °C, steps through 5° for 1.5 h and 750 °C, 5 h) is somewhat like that reported in the paper[10–12] (initial glass samples kept at the maximum of nucleation rate 670 °C for 10 h and 750 °C, 5 h). The glass samples treated in two steps show a microstructure of very long needle-shaped crystals of some μm in diameter (Fig. 1b) with a depth of crystallized layer 60 μm corresponding well to the data in Ref. 10.

Glassy plates treated in a temperature gradient furnace exhibit the same crystallization behavior. Fig. 1c shows a well-formed texture as a result of the heat treatment at 770 °C ("hot" side) and $\Delta T \sim 50$ °C for 5 h. When ΔT was increased to ~ 150 °C quality of texture was worsened (Fig. 1d) probably due to a too fast growth of needle-shaped crystals. Raising the temperature to 850 °C, it was possible to achieve full crystallization of the glassy plate in agreement with Ref. 13 Fig. 1e reproduces textured structure of LBG glass penetrated whole volume of the sample. Such textures cause distinct pyroelectric effect that was discovered in Refs. 13 and 14. Existence of high pyroelectric coefficient of LBG textures firmly testifies that indeed texture occupies most part of the volume of the glass and that needle-shaped crystals link opposite sides of the sample. SEM micrographs of well-crystallized textured samples obtained for higher magnifications permit to observe individual $LaBGeO_5$ crystals (Fig. 2). One can conclude that typical morphology of $LaBGeO_5$ crystals in LBG textures is needle (fiber) of the stillwellite-like $LaBGeO_5$ of 1–2 μm in diameter propagating on hundreds μm inside the glass (Fig. 2a). Later stages of crystallization is connected with growth of "oriented spherulites" when new stillwellite crystals begin to grow as "ellipsoidal flowers" from some ranges of needles (Fig. 2b and c) conserving predominantly orientation of new crystals almost in parallel to needles formed earlier.

The scenario of crystallization of LBG glasses described by SEM micrographs of Figs. 1 and 2 may be classified as significantly surface grain-oriented crystallization starting from the glass surface and occupying the whole volume of the glass under appropriate regimes of heat treatments.

The same conclusion may be drawn considering the crystallization behavior of lower and upper surfaces of LBG plates that are characterized by significant difference of texturing (Fig. 3). XRD patterns of upper surface of the glass, in contact only with air confirm data[10] about random distribution of crystals on the glass surface (Fig. 3a). On the contrary, surface of lower side of the plate, in contact with fine powder of corundum, appears to be distinctly textured as clearly indicated by the strong decreasing of (110) reflex and dominating of (200) one (Fig. 3b). Thus, the XRD data of Fig. 3 as well as SEM micrographs of LBG glasses undergone to different heat treatments supports the hypothesis that surface grain-oriented crystallization strongly depends on surface conditions and that bulk nucleation does not promote texture formation.

It is worth emphasizing that the quality of the glasses strongly influences on quality of textures. The working of glasses by pressing cannot provide high quality of glassy plates. The most perfect LBG textures, exhibiting excellent pyroelectric properties, were obtained[13] by gradient crystallization of polished glassy plates cut from massive block of optical quality without bubbles,

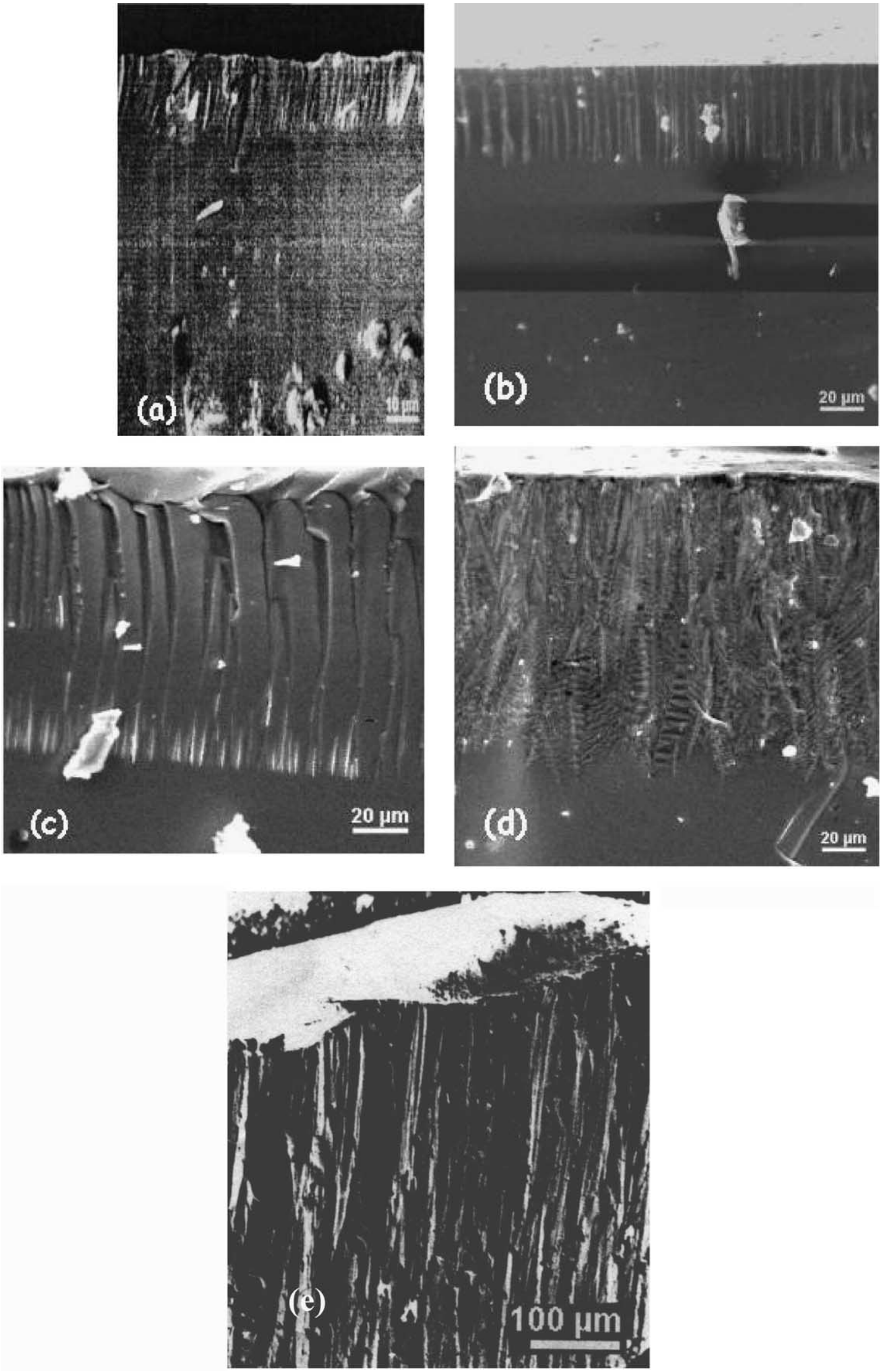

Fig. 1. SEM microphotographs of LBG glass-ceramics surface layer, fractured samples: (a) one step at 740 °C; (b) two steps; (c) temperature gradient 5 h at 770 °C, $\Delta T \sim 50$ °C; (d) temperature gradient 5 h at 800 °C, $\Delta T \sim 150$ °C; (e) temperature gradient 12 h at 870 °C, $\Delta T \sim 50$ °C.

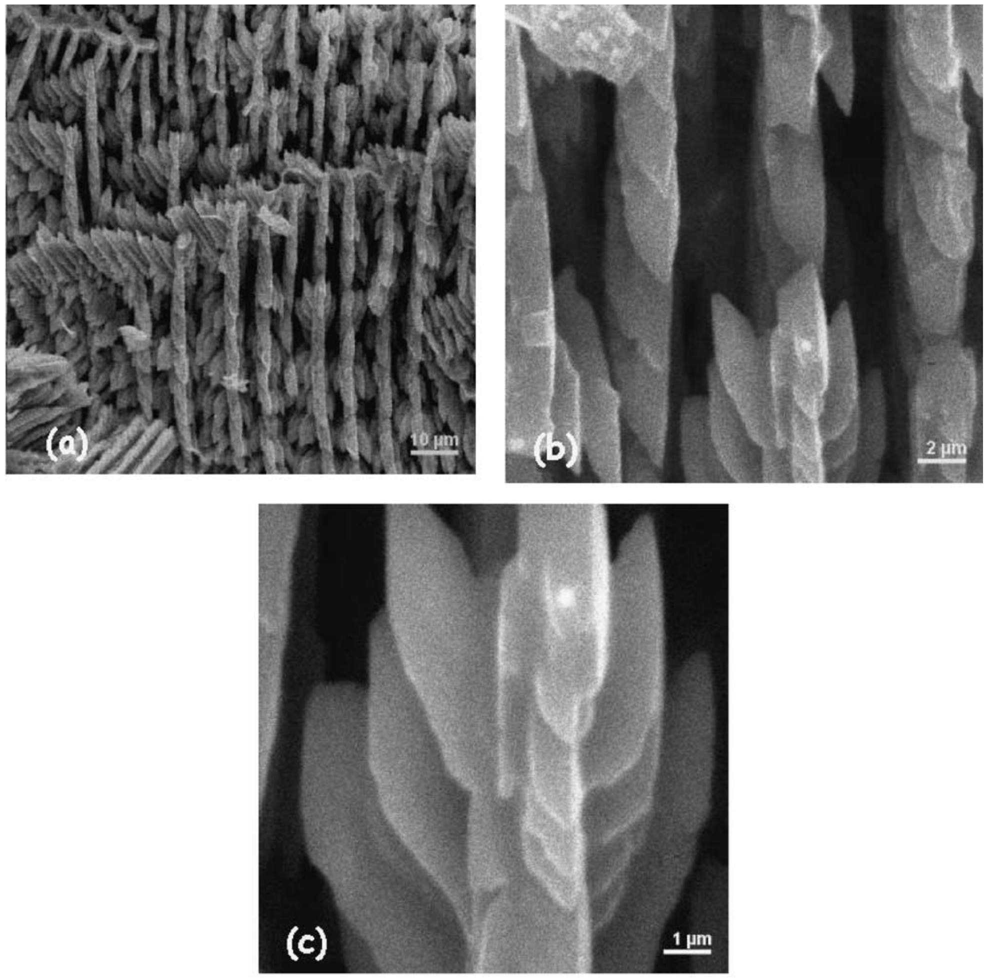

Fig. 2. SEM microphotographs at different magnifications of LBG glass-ceramics texture.

cords and any crystallization nuclei. Moreover, in spite of similarity of volume thermal expansion coefficients of LBG glasses and $LaBGeO_5$ stillwellite crystal, the great structural anisotropy of $LaBGeO_5$, leading to great differences in linear thermal expansion coefficients along axis *c* ($+20\times10^{-6}$ K^{-1}) and *a* (-2×10^{-6} K^{-1}),[16] may produce stresses and defects, especially during cooling of textured samples. Probably small diameter (about 1–2 μm) of needle-shaped crystals of stillwellite growing from glass surface diminishes the risks of cracks near the boundary between glass and front of propagation of texture.

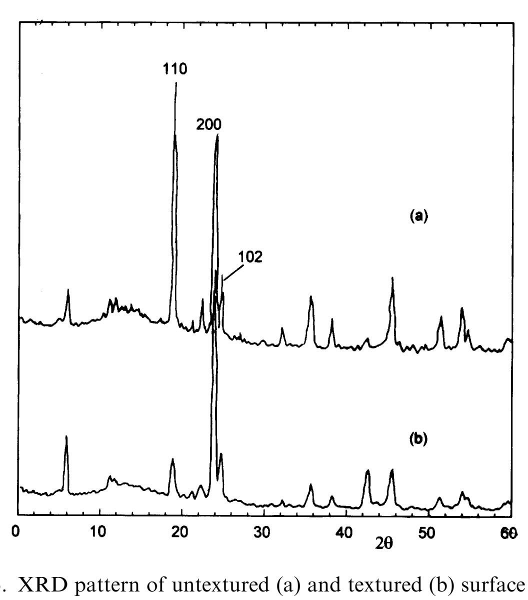

Fig. 3. XRD pattern of untextured (a) and textured (b) surface layer.

4. Conclusion

Crystallization of the La_2O_3–B_2O_3–$2GeO_2$ glass is characterized by formation of surface textured layer consisting of needle-shaped stillwellite-like $LaBGeO_5$ crystals. During following stages of crystallization, under appropriate conditions, texture penetrates the whole volume of the glass. The SEM micrographs of LBG glasses, which undergone different types of heat treatments support the hypothesis that surface grain-oriented crystallization strongly depends on surface conditions and that bulk nucleation does not, promoted texture formation.

Acknowledgements

This work was financially supported by the NATO Science for Peace Program (grant no. SfP-977980), Italian Ministry of Foreign Affaires and Landau Network-Centro Volta, Ministry of Atomic Industry and Ministry of Education of Russia (grant no. 2.08-23) and Russian Foundation for basic Research (grant no. 02-03-32105).

References

1. Nasu, J., Matsuoka, X. and Kamiya, K., Second- and third order optical non-linearity of homogeneous glasses. *J. Non- Cryst. Solids*, 1994, **178**, 23.
2. Fargin, E., Berthereau, A. and Cardinal, T., Optical non-linearity in oxide glasses. *J. Non- Cryst. Solids*, 1996, **203**, 96.
3. Kao, Y. H., Zheng, H., Makenzie, J. D., Perry, K., Bouhill, G. and Perry, G. W., Second harmonic generation in transparent barium borate glass ceramics. *J. Non- Cryst. Solids*, 1994, **167**, 247.
4. Shioya, K., Komatsu, T., Kim, H. G., Sato, R. and Matusita, K., Second harmonic generation from an electrically poled K_2O–Nb_2O_5–TeO_2– glasses. *J. Non- Cryst. Solids*, 1995, **189**, 16.
5. Sigaev, V. N., Stefanovich, S.Yu., Champagnon, B., Gregora, I., Pernice, P., Aronne, A., LePark, R., Sarkisov, P. D. and Dewhurst, C., Amorphous nanostructuring in potassium niobium silicate glasses by SANS and SHG: a new mechanism for second-order optical non-linearity of glasses. *J. Non-Cryst. Solids*, 2002, **306**, 238–248.
6. Sigaev, V. N., Pernice, P., Aronne, A., Akimova, O. V., Stefanovich, S.Yu. and Scaglione, A., $KTiOPO_4$ bulk precipitation from potassium titatium phosphate glasses, producing second harmonic generation. *J. Non-Cryst. Solids*, 2001, **292**, 59–69.
7. Ding, Y., Osaka, A. and Miura, Y., Enhaced surface crystallization of β-barium borate on glass due to ultrasonic treatment. *J. Am. Ceram. Soc.*, 1994, **77**, 749–752.
8. Ding, Y., Masuda, N., Miura, Y. and Osaka, A., Preparation of polar oriented $Sr_2TiSi_2O_8$ films by surface crystallization of glass and second harmonic generation. *J. Non-Cryst. Solids*, 1996, **203**, 88–95.
9. Ding, Y., Miura, Y. and Yamaji, H., Oriented surface crystallisation of lithium disilicate on glass and the effect of ultrasonic surface treatment. *Phys. Chem. Glasses*, 1998, **39**, 338–343.
10. Takahashi, Y., Benino, Y., Dimitrov, V. and Komatsu, T., Transparent surface crystallized glasses with optical non-linear $LaBGeO_5$ crystals. *J. Non- Cryst. Solids*, 1999, **260**, 155–159.
11. Takahashi, Y., Benino, Y., Dimitrov, V. and Komatsu, T., Transparent optical nonlinear crystallised glasses with ferroelectric $LaBGeO_5$. *Phys. Chem. Glasses*, 2000, **41**(5), 225–228.
12. Takahashi, Y., Benino, Y., Fujiwara, T. and Komatsu, T., Second harmonic generation in transparent surface crystallized glasses with stillwellite-type $LaBGeO_5$. *J. Appl. Phys.*, 2001, **89**(10), 5282–5287.
13. Sigaev, V. N., Lopatina, E. V., Sarkisov, P. D., Stefanovich, S.Yu. and Molev, V. I., Grain-oriented surface crystallisation of lanthanum borosilicate and lanthanum borogermanate glasses. *Mater. Sci. Eng. B*, 1997, **B48**, 254–260.
14. Sigaev, V. N., Sarkisov, P. D., Stefanovich, S.Yu., Pernice, P. and Aronne, A., Glass ceramic textures based on new ferroelectric complex oxides. *Ferroelectrics*, 1999, **233**, 165–185.
15. Halliyal, A. G., Bhalla, A. S., Newnham, R. E. and Cross, L. E. In *Glass and Glass-ceramics*, ed. M. H. Lewis. Chapman and Hall, London, 1989, p. 272.
16. Belokoneva, E. L., David, W. I. F., Forsyth, J. B. and Knight, K. S., Structural aspects of the 530 °C phase transition in $LaBGeO_5$. *J. Phys.: Condens. Matter*, 1997, **9**, 3503–3508.