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Crystallization Behavior of Potassium Niobium Silicate Glasses

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Crystallization behavior of potassium niobium silicate (KNS) glasses having compositions expressed by the general formula $xK_2O{\cdot}xNb_2O_5{\cdot}(1-2x)SiO_2$, with $x = 0.167$, 0.182, 0.200, 0.220, and 0.250, has been studied by DTA, X-ray diffraction, second harmonic optical generation (SHG), and electron microscopy. Bulk crystallization of potassium niobates in glasses with compositions near $K_2O{\cdot}Nb_2O_5{\cdot}2SiO_2$, as well as surface crystallization of $KNbSi_2O_7$ phase, has been established. Transparent glass-ceramics, based on potassium niobates with remarkable SHG signal values, can be obtained from glasses with the lowest silica content, by heat treatment at temperatures just above T_g, while at higher temperatures from all of the glasses under investigation the main crystallizing phase is $KNbSi_2O_7$ ferroelectric. Applying a dc electric field, grain-oriented crystallization is produced in KNS glasses with development of significantly anisotropic arrangements of $KNbSi_2O_7$ crystallites.

I. Introduction

FERROELECTRIC glass-ceramics have been known for more than 30 years. Mainly precipitation of perovskite ferroelectrics from multicomponent silicate glasses have been studied.[1–5] Ferroelectric grain-oriented glass-ceramics with distinct pyroelectric properties have also been obtained in PbO–GeO_2[6,7] and La_2O_3–B_2O_3–GeO_2[8,9] systems based on $Pb_5Ge_3O_{11}$ and $LaBGeO_5$ ferroelectrics, respectively. For the system La_2O_3–B_2O_3–GeO_2 the range of stable glass formation is near the composition of the corresponding ferroelectric crystal. Most likely, lanthanum borogermanate stillwellite glass-ceramics[9] is the single example of a ferroelectric glass-ceramic synthesized from a glass having the same composition as the ferroelectric crystal. The closeness of the compositions of initial glass and ferroelectric phase allows minimization of the residual glass content. Moreover, texturing of glass-ceramics offers new perspectives on ferrolectric glass-ceramic technology. Therefore, the search for new glass-forming systems with ferroelectric phases is of great interest.

In the last few years new information on ferroelectric phases in glass-forming systems has been published and we think that special attention should be devoted to the ferroelectric $KNbSi_2O_7$ (potassium niobyl cyclotetrasilicate $K_2(NbO)_2Si_4O_{12}$).[10] Owing to difficulties in growing large $KNbSi_2O_7$ crystals, studies of glasses, glass-ceramics, and ceramics of similar compositions have become quite topical. Tetragonal polar $KNbSi_2O_7$ crystals (*P4bm*, $a = b = 8.741$, $c = 8.136$, $Z = 2$) are characterized by very high optical nonlinearity, with their second harmonic generation (SHG) signal approximately 500 times greater than the one for α-quartz. They remain in a ferroelectric state up to congruent melting at 1180°C[10] and show valuable ionic conductivity along the *c* axis above 300°C as well as its structural analogue $KTaSi_2O_7$.[11] The acentric character of the structure of $KNbSi_2O_7$ is mainly due to a sequence of short niobyl (0.176 nm) and long Nb–O (0.231 nm) bonds along the 4-fold axes. It is important to emphasize that the $KNbSi_2O_7$ composition lies in the glass-forming range of the ternary system K_2O–Nb_2O_5–SiO_2, and according to data from Ref. 12, potassium niobium silicate (KNS) glasses also contain strongly distorted Nb^{5+} polyhedra.

The existence of the $KNbSi_2O_7$ phase makes the KNS system more profitable than the sodium niobium silicate one, in which transparent glass-ceramics, based only on $NaNbO_3$ perovskite-like phase, have been synthesized[3,13,14] In the KNS system it is possible that glass-ceramics based on both potassium niobates and $KNbSi_2O_7$ can be synthesized. Considering that the SHG signal of the $KNbO_3$ perovskite exceeds by about 700 times the one for the $NaNbO_3$ crystals,[15] transparent glass-ceramics could be prepared, in the KNS system, having higher optical nonlinearity than $NaNbO_3$ glass-ceramics, even if only a small amount of $KNbO_3$ nanometric crystallites precipitate from the glass matrix. This possibility is very important, taking into account also numerous attempts to produce SHG signals from electrically poled glasses.[16–18] In this connection, transparent glass-ceramics containing $KNbO_3$ crystals would look more advantageous than the usual glasses. Moreover, polar glass-ceramics based on $KNbSi_2O_7$ phase may be considered as prospective materials with ferroelectric, ion-conductive, or nonlinear optical properties. Therefore, taking into account the high quality of glass-ceramic textures obtained in PbO–GeO_2 and La_2O_3–B_2O_3–GeO_2 systems,[6–9] any attempt to obtain textures in the KNS system should be done.

The properties of KNS glasses have been recently studied in detail.[19] The same authors assert, by visual inspection of melted glasses, the existence of phase-separation phenomena in a wide compositional range near a K_2O/Nb_2O_5 ratio equal to 1.[19] Nevertheless, information on crystallization behavior of

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KNS glasses is poor,[20,21] contrary to Na_2O–Nb_2O_5–SiO_2[3,13,14,20] and K_2O–Nb_2O_5–TeO_2 glasses proposed as new types of nonlinear optical glass-ceramics.[22]

The aim of this work is to study the crystallization behavior of KNS glasses having compositions close to the stoichiometry of the $KNbSi_2O_7$ phase and in a wider compositional range where presumably phase separation occurs.[19] As a result, both transparent glass-ceramics with nonlinear optic properties and nontransparent ferroelectric glass-ceramic samples can be obtained. Their microstructure and nonlinear properties will also be examined by electron microscopy and SHG, respectively.

II. Experimental Procedure

Glasses, whose compositions are reported in Table I, were prepared from reagent-grade KNO_3 (or K_2CO_3), Nb_2O_5, and SiO_2. Well-mixed batches calculated to yield 300 g of glass were melted for 1.5 h at 1530–1560°C in Pt crucibles. The compositions of glasses 1 to 5 may also be expressed by the general formula $xK_2O{\cdot}xNb_2O_5{\cdot}(1-2x)SiO_2$, $x = 0.167$, 0.182, 0.200, 0.220, and 0.250.

The glasses were quenched by pouring out the melt into another crucible and then were annealed for 1 h at temperatures close to T_g as determined by DTA. From the glasses obtained small bulk samples were cut, having sizes suitable for the DTA sample holder. Part of the glasses were ground in an agate mortar and then used as powder samples. Flat bubble-free glass samples with sizes of about 10 mm × 10 mm and 1–4 mm thickness were polished and coated with Pt electrodes by sputtering technique. Crystallization of Pt-coated plates was carried out by placing them in a furnace at temperatures of about T_g and under dc electric fields of about 0.05–1 kV/cm, and treating them in an intermittent regime to preserve the samples from excessive heating due to ionic conductivity of the KNS glasses.

DTA curves were recorded for bulk or powdered (<45 μm) specimens of about 50 mg in air at a heating rate 10 $K{\cdot}min^{-1}$, using a Netzsch DSC 404 high-temperature thermoanalyzer with Al_2O_3 as a reference material. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and the sample holder. X-ray diffraction (XRD) data were obtained using a Philips PW1710 and a DRON-3M diffractometer (Cu$K\alpha$, Ni filter). Identification of the $KNbSi_2O_7$ phase was carried out by direct comparison of XRD patterns of tested glass-ceramics with that of powdered $KNbSi_2O_7$ pure crystal obtained by heating glass 1 for 5 h at 1050°C. The lattice distances (d) and intensities (I) of Bragg reflections measured for this sample are reported in Table II and agree well with those reported by Crosnier *et al.*[23] for $KNbSi_2O_7$ prepared by a solid-state reaction. Scanning electron microscopy (SEM) of crystallized glasses was carried out using a Tesla BS-301 electron microscope at magnifications from 100× to 10000×.[9]

The SHG experiments were carried out using a LTI-PCh-7 solid-state pulsed laser operating in the Q-switching mode at a frequency of 12.5 Hz at room temperature. The thin polished plates cut out from the sythesized glasses and powder samples both in the initial state and at different stages of crystallization were studied using transmission and reflection schemes, respectively. The reported SHG signal, $I_{2\omega}$, indicates the ratio between the intensity of the second harmonic radiation from a test sample and that from a reference α-quartz powder with a dispersion of approximately 3 μm. The SHG technique applied to glasses was the same as described in a previous work.[24]

Table I. Glass Compositions and T_g Values of the Studied Glasses, $xK_2O{\cdot}xNb_2O_5{\cdot}(1-2x)SiO_2$

Sample	x	Composition (mol%) K_2O	Nb_2O_5	SiO_2	T_{g1} (°C)	T_{g2} (°C)
1	0.166	16.7	16.7	66.6	733	
2	0.182	18.2	18.2	63.6	724	
3	0.200	20.0	20.0	60.0	721	1022
4	0.220	22.2	22.2	55.6	705	†
5	0.250	25.0	25.0	50.0	688	†
6		16.7	19.6	63.8	768	1063

†Glass transition not detected.

Table II. *d* Spacing and Relative Intensity

d (Å)†	Intensity†	d (Å)‡	Intensity‡
—	—	8.12	2
—	—	6.19	67
4.52	46	4.38	74
4.02	76	4.08	93
3.91	20	3.92	100
—	—	3.86	9.0
3.57	38	3.53	63
—	—	3.40	36
3.01	86	3.09	40
2.99	69	2.98	59
2.96	100	2.82	55
2.80	48	2.77	96
2.60	11	2.46	6
2.39	16	2.32	3
2.26	11	2.29	8
2.17	5	2.19	4
2.10	8	2.12	15
—	—	2.05	3
2.01	35	2.04	26
1.96	16	1.96	90
1.91	6	1.93	14

†Glass sample $x = 0.25$ heated, at 10°C/min, up to 1050°C and then quenched.
‡Glass sample $x = 0.25$ heated at 1050°C and held 5 h.

III. Results and Discussion

(1) Glass Transition and Devitrification Behavior

Clear glasses were obtained in all of the compositional range under investigation. The present data for 300 g batches for which both KNO_3 and K_2CO_3 were used as potassium reagents confirm the extensive glass-forming region found by Vernacotola and Shelby[19] in the K_2O–Nb_2O_5–SiO_2 system for 15 g batches. The same authors found phase separation in glasses with SiO_2 ranging from approximately 40 mol% to more than 70 mol%. When we used K_2CO_3 reagent, some parts in the obtained glass were nontransparent or crystallized while the glasses prepared using KNO_3 were transparent. Therefore, in order to avoid any doubt, the results reported in this paper refer exclusively to glasses melted with KNO_3 as starting material.

The DTA curves of the bulk glasses are shown in Fig. 1. All curves exhibit a change in slope that may be attributed to the glass transition. In this work, the inflection point at the slope change in the DTA curves (see the arrows in Fig. 1) was taken as the glass transition temperature, T_g. The reproducibility of the T_g values was 2 K. The DTA curves of bulk samples of glasses 1 ($x = 0.167$) and 2 ($x = 0.182$) show one change in slope due to glass transition, which is typical of a homogeneous glass, while the DTA curves of the bulk samples of glasses 3 ($x = 0.200$) and 6 (Fig. 2) show clearly two glass transitions, T_{g1} and T_{g2}, indicating that these glasses are or become phase separated during the DTA run. The second, high-temperature, glass transition for samples 4 ($x = 0.220$) and 5 ($x = 0.250$), if it exists, is covered by a strong endothermic peak (see Fig. 1). The glass transition temperature values are reported in Table I and agree well with the data from Ref. 19.

The DTA curves of bulk samples of the high-silica glasses (1, 2, and 3, Fig. 1) do not exhibit any exothermic peak. This indicates that these glasses do not crystallize during DTA. Two exothermic peaks appear in the DTA curves of bulk samples of low-silica glasses 4 and 5 ($x = 0.220$ and 0.250), indicating that they crystallize during the DTA run. This is confirmed by XRD analysis (Fig. 3) of glass samples heated, at 10°C/min in the DTA furnace, up to the temperature of the first and second

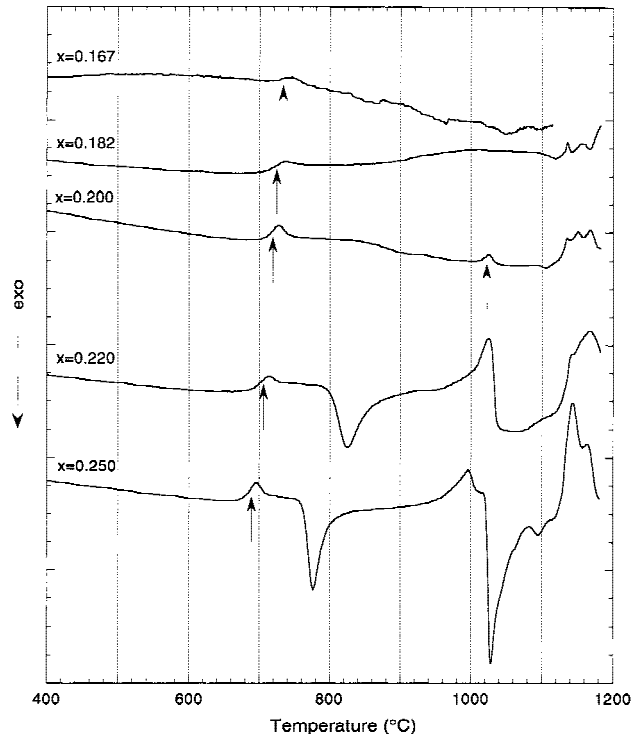

Fig. 1. DTA curves of bulk samples of the studied glasses.

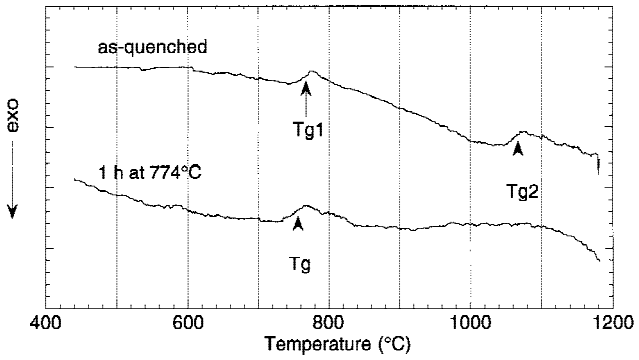

Fig. 2. DTA curves of bulk samples of glass 6.

exothermic peaks. The XRD pattern of the sample heated to the temperature of the first exothermic peak shows only a few broad and low-intensity peaks, indicating the growth of very small and not well-shaped crystals, as often observed for glass samples crystallized during a DTA run. Therefore, to identify the crystalline phases formed in this stage is difficult, because under these conditions from a multicomponent glass system more than one crystalline phase may grow. Nevertheless in this XRD pattern some peaks may be assigned to potassium niobate; the others are due to unidentified phases. At temperatures above T_{g2} (about 1000°C) a second exothermic peak leads to the crystallization of phases different from those formed at the first DTA peak since in the XRD pattern of a glass sample heated in the DTA furnace up to the temperature of the second exothermic peak (Fig. 3) the Bragg reflections of the phases previously formed completely disappear. Even in this case no crystalline phase between those known in the system under investigation may be identified for certain. Moreover, it is important to note that often during the nonisothermal crystallization of a glass, especially when crystallization starts from surface nuclei, grain-oriented crystallization occurs and that as a consequence in the XRD pattern some peaks may be more intense than they should be while some others may be completely absent.[25,26] Nevertheless, comparing the lattice distance relative to the XRD pattern in Fig. 3 (II exo) with those of a well-crystallized $KNbSi_2O_7$ glass sample (Table II), we may suppose that an unknown slightly different form or a preform of $KNbSi_2O_7$ crystallizes at this stage. This hypothesis seems to be well confirmed as the crystalls, formed during the DTA run, change in $KNbSi_2O_7$ by prolonged heating. The DTA curves of glasses 4 and 5 ($x = 0.220$ and 0.250) also show two

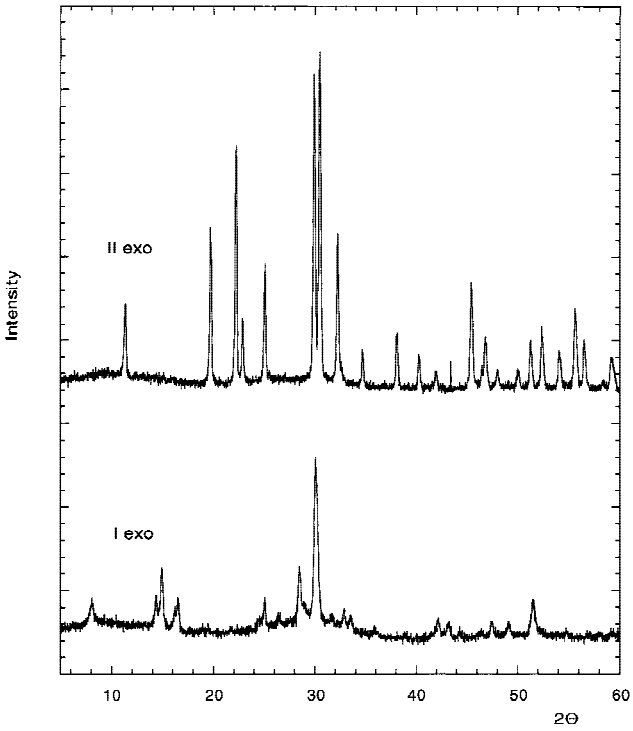

Fig. 3. XRD patterns of glass sample 5 heated in DTA furnace up to the temperatures of the first and second exothermic peak.

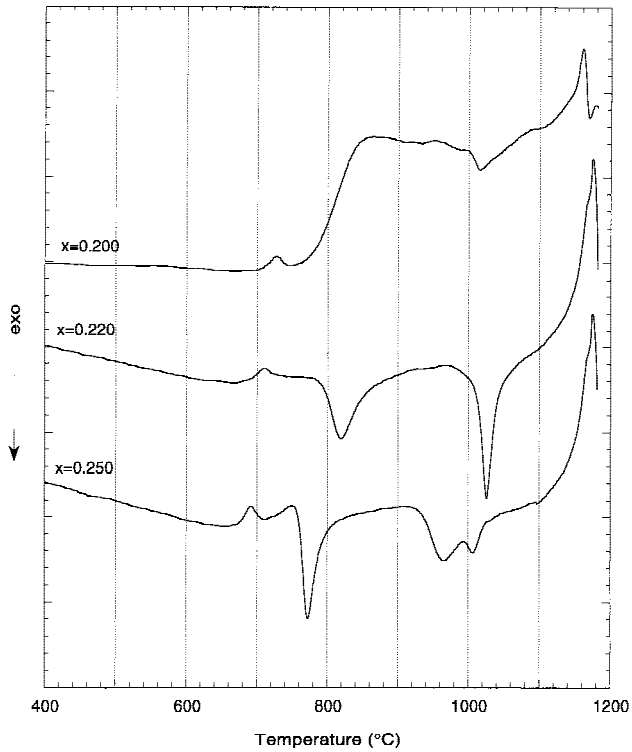

Fig. 4. DTA curves of powdered samples.

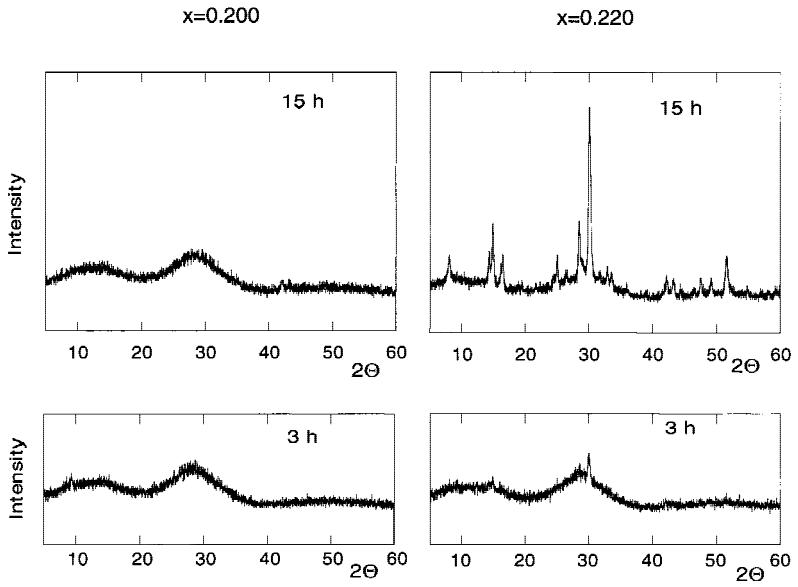

Fig. 5. XRD patterns of glass samples 3 and 4 heat-treated at 730°C.

endothermic peaks at 1142° and 1164°C. They may be attributed to melting of crystalline phases, as the melting point of pure $KNbSi_2O_7$ is 1180°C and the melting points of the different potassium niobate phases lie in the range 1000–1050°C. Moreover, the endothermic peak at about 1000°C lies in the range of the second glass transition and covers it.

Even though a detailed study of the nucleation and crystallization mechanisms will be performed and reported in a following paper, to get preliminary information DTA runs were carried out on powdered samples of glasses 3, 4, and 5 ($x = 0.200$, 0.220, and 0.250) and the resulting curves are reported in Fig. 4. As is known,[27,28] the nonisothermal method allows easy evaluation of the influence of the specific surface area of the sample on the nucleation mechanism. For a given heating rate, the higher the total number of nuclei N (bulk and/or surface), the lower the temperature of the maximum of the DTA exothermic peak, T_p, according to the following equation: $\ln N = a(1/T_p) + b$, where a and b are constants.[28] For glasses 4 and 5 ($x = 0.220$ and 0.250) the temperature of the first exothermic peak is the same as that of the corresponding bulk sample. This indicates that potassium niobates grow mainly from bulk nuclei. The higher-temperature exothermic peak, due to the crystallization of $KNbSi_2O_7$, shifts toward lower temperature with respect to the bulk sample peaks, indicating that for this phase surface nucleation is dominant. On the other hand, the DTA curves for the powdered glass sample 3 ($x = 0.200$) do not show any peak at low temperature, confirming that postassium niobates do not nucleate from surfaces. The large change of baseline is due only to the softening of the glass powder. On the other hand, a small exothermic peak appears just above 1000°C. This demonstrates that some crystallization occurs in the temperature range of $KNbSi_2O_7$ growth, confirming that this crystalline phase grows from surface nuclei. The DTA curves in Fig. 4 show also the endothermic peak due to the melting of $KNbSi_2O_7$ phase while the melting peak of potassium niobates is completely masked by the crystallization of $KNbSi_2O_7$.

To investigate the initial stage of the crystallization process we have performed isothermal heat treatment at 730°C, for 3 and 15 h, on samples of glasses 3 ($x = 0.200$) and 4 ($x = 0.220$). The chosen temperature is just above the T_{g1} value of glass 3 and lies in the range where the anionic network reaches the mobility required for structural rearrangements as nucleation and/or phase separation. The sample of glass 3, which during the DTA run does not crystallize, after 3 h heat treatment becomes opalescent, while the sample of glass 4, which

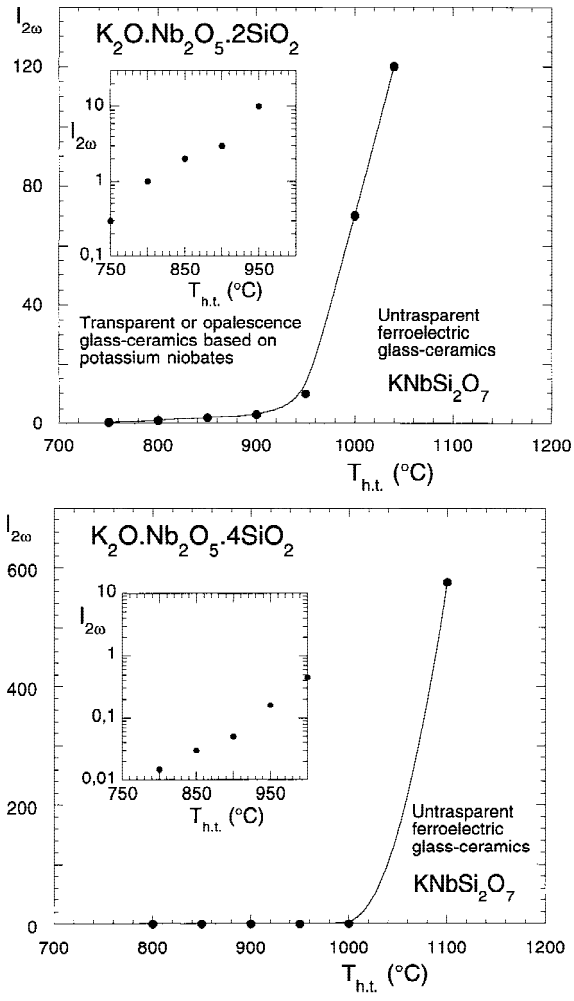

Fig. 6. SHG signals of glasses 1 and 5 heat-treated 4 h at different temperatures.

during the DTA run crystallizes, becomes nontransparent. After 15 h heat treatment the sample of glass 3 is still opalescent but the sample of glass 4 appears completely crystallized. The XRD patterns of the heat-treated samples (Fig. 5) show that

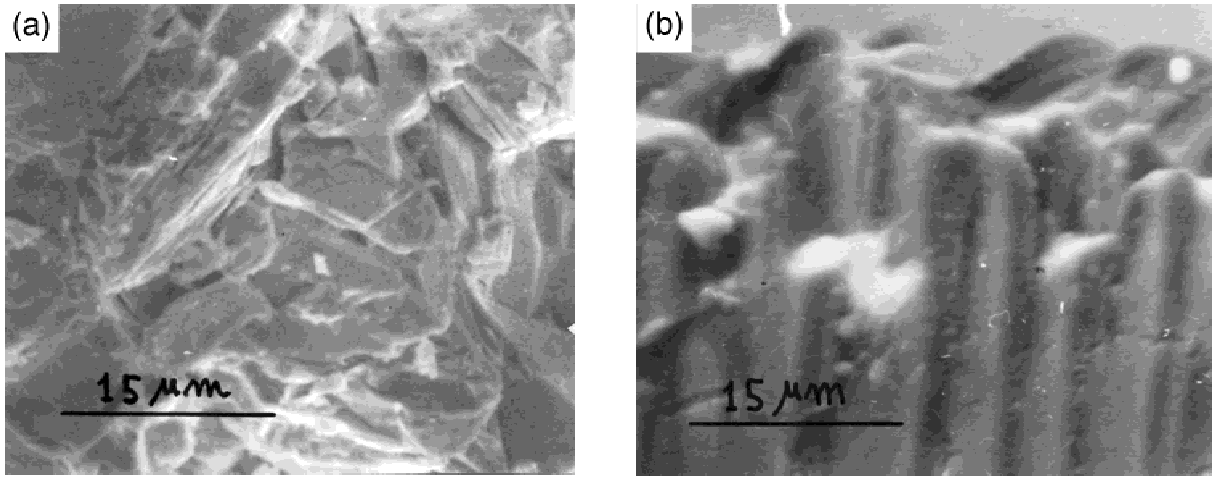

Fig. 7. SEM micrographs of untextured (a) and textured (b) ferroelectric glass-ceramics based on $KNbSi_2O_7$ phase.

glass 3 remains amorphous after 3 and 15 h heat treatment at 730°C, so its opalescence is due to the enhancement of phase separation. Glass 4 begins to crystallize after 3 h treatment and is well crystallized in 15 h. Moreover, we have prepared a glass (6) in the composition range where Vernacotola and Shelby[19], found evident phase separation. This composition may be considered to be derived from glass 1, replacing SiO_2 by Nb_2O_5. The DTA curve of this glass shows two glass transitions as it is phase separated (Fig. 2), but in the DTA curve of a glass sample previously heated for 1 h at 774°C, the second glass transition T_{g2} disappears. This clearly shows that it becomes homogeneous during the heat treatment and that its composition is close to the metastable immiscibility cupola, a boundary of which lies between 730 and 774°C.

(2) SHG Measurements and Textured Glass-Ceramics

Glasses 1 and 5 have been chosen to be heat-treated and studied by electron microscopy and SHG methods. These two glasses are representative of different crystallization behavior. Glass 1 ($K_2O{\cdot}Nb_2O_5{\cdot}4SiO_2$), corresponding to the stoichiometry of $KNbSi_2O_7$, crystallizes predominantly from the surface with precipitation of $KNbSi_2O_7$ ferroelectrics, whereas low-silica glass 5 ($K_2O{\cdot}Nb_2O_5{\cdot}2SiO_2$) is characterized by bulk nucleation of potassium niobates at temperatures near T_g.

Glass samples 1 and 5 were heat-treated at temperatures ranging from 700° to 1100°C for 0.5–4 h and their SHG signals measured (Fig. 6). Two temperature regions are clearly seen in the curves of Fig. 6. At temperatures up to about 950–1000°C slow growth of SHG signals with the increase of heat treatment temperature is connected predominantly with bulk precipitation of potassium niobates (glass 5) or with the beginning stage of surface crystallization of $KNbSi_2O_7$ (glass 1). It is important to emphasize that for glass 5 the range of $I_{2\omega}$ values from 0 to about 1–3 units of α-quartz (Fig. 6) corresponds to transparent or slightly opalescent glass-ceramics based on potassium niobates. $I_{2\omega}$ values become higher than ≈5 when in glasses of both compositions intensive crystallization of the $KNbSi_2O_7$ phase occurs, leading to nontransparent ferroelectric glass-ceramics. Therefore, transparent poreless glass-ceramics with intrinsic SHG activity about some units of α-quartz may be obtained in the KNS system. At the same time, well-crystallized ferroelectric glass-ceramics based on $KNbSi_2O_7$ phase with high SHG signals, about 500 units of α-quartz, may be synthesized in a wide range of compositions from glasses 1 to 5 (Fig. 6). In contrast with dense, nonporous and transparent glass-ceramics having the composition of glass 5, the microstructure of well-crystallized samples of $KNbSi_2O_7$ composition is coarse and porous (Fig. 7(a)).

To control the surface crystallization and to obtain ferroelectric $KNbSi_2O_7$ glass-ceramics with acceptable microstructure, conventional powder technology with the use of high-pressure techniques (hot pressing, hydrostatic pressing, etc.) may be used. But a completely reorganized microstructure of $KNbSi_2O_7$ glass-ceramics can be alternatively obtained, orienting the crystalline grains by means of different external anisotropic actions. In the case of polar crystals such as $KNbSi_2O_7$, it is supposed that the grain-oriented crystallization of mother glasses can be obtained by high temperature gradient, hot extrusion, dc fields, etc.[6–9,29–35] The results of oriented crystallization of $KNbSi_2O_7$ by hot extrusion and heat treatment of glasses in a high temperature gradient will be published in a following work. Here we report only preliminary data on crystallization of KNS glass plates coated with Pt electrodes under a dc field. Using a dc field of about 0.05–0.1 kV/cm in an intermittent regime and at temperatures between T_{g1} and T_{cr2}, $KNbSi_2O_7$ crystallites grow along the dc field direction yielding a high-quality anisotropic microstructure (Fig. 7(b)). The depth of propagation of textured regions into glass may reach about 0.5 mm from the surface. At the present time the main goal is to obtain large dense uniform samples suitable for measurements of the anisotropy of properties like the temperature dependence of dielectric parameters, electrical conductivity, SHG, etc., similar to the measurements carried out in Ref. 9. The properties of the obtained textures and the characterization of their structure will be published later.

IV. Conclusion

The crystallization behavior of K_2O–Nb_2O_5–SiO_2 glasses with K_2O/Nb_2O_5 equal to 1 and silica contents from 50 to 66.6 mol% were studied. In low-silica glasses at first bulk crystallization of potassium niobates occurred. At higher temperature intensive growth of ferroelectric crystals ($KNbSi_2O_7$) took place from surface nuclei, while in high-silica glasses only $KNbSi_2O_7$ crystallization was observed.

Transparent glass-ceramics based on nanometric crystallites of potassium niobates with nonlinear optical properties were synthesized, and their SHG was estimated to be some units of α-quartz as a reference.

It was established that well-textured ferroelectric glass-ceramics based on $KNbSi_2O_7$ phase can be obtained by crystallization of starting glass in a dc field.

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