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Nanostructuring in potassium titanium phosphate glasses containing SiO_2

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Abstract

Glasses from which the ferroelectrics phase $KTiOPO_4$ can crystallise have been prepared and studied. Namely, two glasses having the $92(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}8SiO_2$ (KTP-8Si) and the $88(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}12SiO_2$ (KTP-12Si) molar compositions have been synthesised by the melt quenching technique. They were examined by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The KTP-8Si glass devitrifies in a single step forming $KTiOPO_4$ phase, whereas the KTP-12Si glass firstly crystallises in an unknown phase and then, at higher temperatures, $KTiOPO_4$ crystallites grow. Proper heat treatments performed on the KTP-8Si glass at temperatures just below the glass transition range produce transparent samples the glassy matrix of which contains crystalline nanostructure of the KTP phase.

Keywords: Crystallisation; $KTiOPO_4$; Nanostructured glasses

1. Introduction

Glassy materials have been usually considered as a typical structural material. Recently, many attempts are been done to make functional glassy materials. Particularly, as concerned the second-order non-linear optical properties, this objective was realised by means of two main methods. In the first, named as ''poling'', the functionality was achieved by exposing the glass to an appropriate external excitation field. In the second nano- or micro-crystallites of ferroelectric or other highly polarizable phases were grown in the glassy matrix by thermal treatment. In this way, recently, nanostructured glasses (NG), i.e. transparent or slightly opalescent crystal-glass nano- or micro- composites, have been obtained based on phases as β-BaB_2O_4,[1,2] $LaBGeO_5$,[3] $LiNbO_3$,[4] $KNbO_3$ and $KNbSi_2O_7$[5,6] which were distributed either in the bulk of glasses or in the form of surface texture. The preparation of NG containing ferroelectric nanocrystals of potassium titanil phosphate ($KTiOPO_4$ or KTP) looks promising, since these crystals have very high nonlinear optical coefficients, high optical damage threshold, wide acceptance angles and thermally stable phase-matching properties.[7] The lack of literature data regarding crystallisation of KTP from bulk glasses prepared by conventional melt quenching techniques is related to difficulties to obtain glasses having compositions close to the KTP stoichiometry. Indeed such glasses show high devitrification tendency owing to a relatively low content of the glass forming oxide. This problem was firstly overcome by Li et al.[8] using the sol-gel technique. They synthesized glassy KTP/SiO_2 composites with crystallites sizes less than 100 nm.[8] Sigaev et al.[9] have obtained transparent glasses by the traditional melt-quenching technique adding glass-forming oxides SiO_2 or P_2O_5 to the KTP composition.[9] Particularly, for the glass having the molar composition 90KTP-10SiO_2 (KTP-10Si), transparent samples exhibiting second-order non-linear optical properties were obtained by proper isothermal heat treatments at temperature not far from the glass transition one.[9]

In the present paper, that is a part of more general study concerning the synthesis, the structural characterization and the crystallisation behaviour of glasses with composition close to the KTP stoichiometry, glass

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forming from the melt of new compositions in the KTP-SiO_2 system has been explored and preliminary data on the crystallisation behaviour have been obtained. We have searched for more suitable glass compositions and heat treatments for obtaining single-phase KTP-based NGs.

2. Experimental

Two glasses having the $92(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}8SiO_2$ (KTP-8Si) and the $88(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}12SiO_2$ (KTP-12Si) molar compositions were prepared from reagent grade K_2CO_3, TiO_2, $(NH_4)_2HPO_4$ and SiO_2. Well mixed batches calculated to yield 30 g of glass were melted in a corundum crucibles for 1 h at 1480 °C. The glasses were quenched by pouring out the melt on a massive metal form and then pressed by another metal plate up to about 1 mm thickness. From the glasses obtained small bulk samples appropriated to DTA sample holders were selected.

The non-isothermal crystallisation of the glasses was studied by differential thermal analysis (DTA). DTA curves of bulk specimens of about 50 mg were recorded in air at heating rate 10 K min^{-1}, using a high temperature DTA unit with Al_2O_3 powder as reference material. Powdered Al_2O_3 was also added into holders to improve heat transfer between bulk samples and the sample holder. Characteristic temperatures detected by DTA curves were reproducible within ±1 K.

To investigate the amorphous nature of the as-quenched glass and to identify the crystalline phases grown during the DTA runs, the thermally processed samples were finely ground and analysed in a computer-assisted X-ray (CuK_α) powder diffractometer. X-ray diffraction (XRD) patterns were matched to JCPDS (Joint Committee on Powder Diffraction Standards) data and corresponding phases were identified.

To test the microstructure of the studied glasses a scanning electron microscope was used. Freshly fractured glass surfaces were etched in 2% HF for approximately 60 s. The etched samples were coated with a thin Au film.

3. Results and discussion

In a previous work[9] some glass compositions in the KTP-SiO_2 system have been studied. The results have shown that as-quenched glasses with more than SiO_2 20 mol% are phase separated. Interesting results were obtained for a glass composition with SiO_2 10 mol% for which transparent or opalescent amorphous samples exhibiting optical non-linear activity were obtained by heat treatment for 2 h at 640 °C.[9] It was seen that further investigations around this composition are necessary. Actually, it is important to explore the glass-forming toward the KTP stoichiometry in order to obtain single-phase KTP-based NGs. On the other hand, it is also important to synthesize a stable and homogeneous glass in order to control easily the nanostructuring by proper heat treatments. Therefore, two KTP-glasses with the SiO_2 amount equal to 8 and 12 mol% were synthesized. Transparent and slightly yellow coloured glasses, without any inclusion, were obtained for both compositions. The presence of small amount of Ti^{+3}, formed during the melting, was supposed to cause the glass coloration. Moreover it cannot be ruled out that during the melting a certain amount of aluminium oxide dissolves in the glass.

The DTA curves of the as-quenched bulk glasses are shown in Fig. 1, where, for comparison, the DTA curves of the KTP-10Si and KTP-20Si glasses[9] are also reported. All curves exhibit a slope change that may be attributed to the glass transition. This transformation of the glassy matrix occurs in a temperature range but it is usually indicated as single value, T_g. The slope change appears clear-cut only into the DTA curve of the KTP-20Si glass while, for the other glasses, it is not well distinct as a drift of the base line in a large temperature range is observed in their DTA curves (Fig. 1). This makes difficult an accurate determination of the glass transition temperature as the inflection point at the slope change. Therefore, in order to obtain the more reproducible values (within ±5 K) the extrapolated onset at the slope change on the DTA curve is taken as

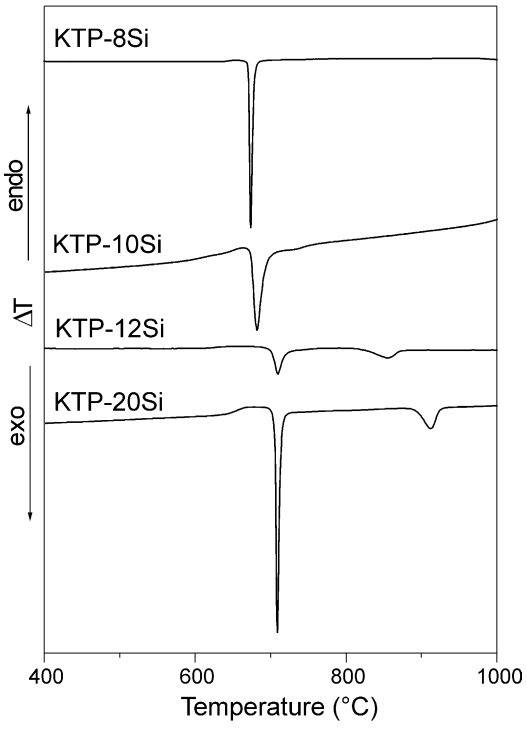

Fig. 1. DTA curves recorded in air at 10 K/min of the as-quenched bulk glasses.

T_g. In this limit of uncertain it was found that the four glasses, in spite of their different nominal composition, exhibit the same T_g value (634 °C). This behaviour could suggest that the as-quenched glasses are phase separated. However, SEM microphotographs have shown that all the glasses are homogeneous except than KTP-20Si. Nevertheless these results do not rule out the possibility that the amorphous matrix of these glasses are inhomogenous on the nanometric scale.

The DTA curve of the KTP-8Si glass exhibits a single sharp exothermic peak just above T_g at 674 °C that is related to the precipitation in the amorphous matrix of KTP microcrystals (JCPDS card No. 350802) as shown by XRD pattern. On the contrary, the DTA curve of the KTP-12Si glass shows two exothermic peaks, the first of which occurs at the same temperature (710 °C) of the corresponding peak of the KTP-20Si glass. At this stage, for both glasses, the crystallisation of the same unknown phase occurs.[9] The growth of KTP phase takes place only at 856 °C for the KTP-12Si and 912 °C for the KTP-20Si glass.

Taking into account DTA/XRD data and the goal to obtain NG containing KTP crystals, isothermal heat treatments at the temperatures in the glass transition range or just below have been performed on the KTP-8Si glass for 2 h. Each heat treated sample was examined by XRD and the corresponding DTA curves, shown in Fig. 2, were also recorded. The heat treatments were firstly performed at 632 °C that is close to the T_g value.

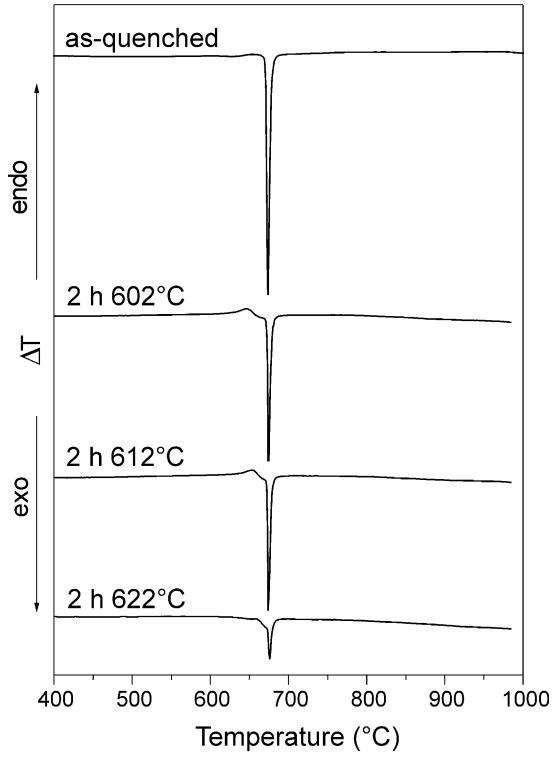

Fig. 2. DTA curves recorded in air at 10 K/min of the KTP-8Si glass.

A sample heated at this temperature appears opaque and fully crystallized as confirmed by its XRD pattern as well as by the lack of the crystallisation peak on its DTA curve. Therefore the subsequent heat treatments were performed at lower temperatures. A sample heated at 622 °C appears opalescent suggesting that is partially crystallised as attested by the intensity of the DTA crystallisation peak lower than that of the as-quenched glass and by its XRD pattern showing few low intensity peaks on the amorphous background. Samples heated at lower temperature, 602 and 612 °C, appear transparent and fully uncoloured. The main difference between their DTA curves and the one of the as-quenched glass concerns the glass transition range. Actually, in these heat treated samples a clear-cut slope change is observed contrary to what occurs for the as-quenched glass. This result suggests that the low temperature heat treatments originate mainly structural modifications into the glassy matrix of the KTP-8Si glass. The SEM microphotograph of the transparent sample heat treated at 612 °C for 2 h is shown in Fig. 3. The microstructure of this sample looks as a typical phase separated glass containing inhomogeneities on nanometric scale. The comparison between the XRD patterns of the as-quenched and the heat treated (2 h at 612 °C) samples, Fig. 4, shows that negligible changing take place with the heat treatment. Nevertheless these changing correspond to the strongest Bragg peak of KTP phase, hence heat treatment in this range can originate a KTP crystalline nanostructure into the glassy matrix. Therefore, the obtained data indicate that for the KTP-8Si glass it is possible to control the nanostructuring of its glassy matrix by proper heat treatment and to produce transparent nanocrystallized samples. The same behaviour was already observed for the KTP-10Si glass[9] while for the KTP-12Si glass the different crystallisation behaviour excludes the possibility to produce precipitation of KTP nanocrystals in the glass matrix.

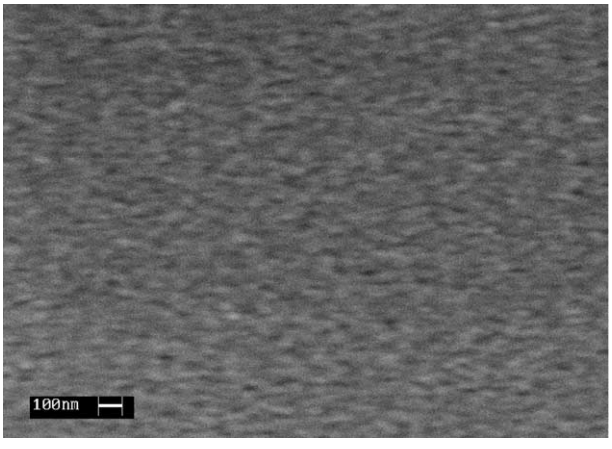

Fig. 3. SEM microphotograph of the KTP-8Si sample heat treated for 2 h at 612 °C.

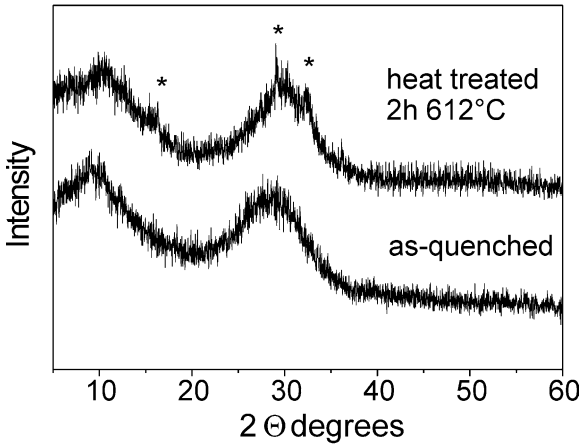

Fig. 4. XRD pattern of the of the KTP-8Si glass. Asterisks denote the higher intensity peaks of $KTiOPO_4$ phase (JCPDS card no. 35-802).

4. Conclusions

Transparent KTP glasses having the $92(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}8SiO_2$ and the $88(K_2O{\cdot}2TiO_2{\cdot}P_2O_5){\cdot}12SiO_2$ molar compositions were obtained by melt quenching technique. These glasses exhibit a different crystallisation behaviour: the KTP-8Si devitrifies in a single step forming the only $KTiOPO_4$ phase whereas the KTP-12Si crystallises in two steps producing at first a non-identified phase and then, at higher temperatures, $KTiOPO_4$ crystallites.

It has been established that heat treatments performed on the KTP-8Si glass at temperatures just below the glass transition range produce transparent samples the glassy matrix of which contains KTP based crystalline nanostructure.

Acknowledgements

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