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Pyroelectric composites based on $LaBSiO_5$ stillwellite

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Abstract

Synthesis of ferroelectric materials by glass crystallisation is attractive to produce both high-quality textures and composites. In the present work, composites based on ferroelectric stillwellite-like $LaBSiO_5$ and glasses having compositions near to compounds $Pb_5Ge_3O_{11}$, $PbLiPO_4$ and $PbBPO_5$ were synthesised and their dielectric and pyroelectric properties examined. A pyroelectric coefficient of about 0.5 nC/cm^2 K may be obtained by liquid-phase sintering of pellets. Preliminary data on crystallisation processes of the lead-containing glasses as well as on the chemical interactions between stillwellite-like $LaBSiO_5$ and glasses at the sintering temperature are reported.

Keywords: Composites; Ferroelectric properties; Glass ceramics; $PbBPO_5$; $Pb_5Ge_3O_{11}$; $PbLiPO_4$; Pyroelectric properties

1. Introduction

The $LaBGeO_5$ stillwellite-like crystal shows a favourable combination of physical properties such as a high pyroelectric coefficient, 8–10 nC/cm^2 K, low values of the dielectric constant ε, about 10, and of the dielectric losses tanδ, about 0.001, and high electric resistance up to 500°C. These data indicate the stillwellite family as promising pyroelectric materials.[1] However, the growth of large crystals is very difficult, especially for stillwellite-silicates and stillwellite-phosphates. Therefore information on the physical properties of stillwellite-like single crystals are very scarce, except for $LaBGeO_5$.

In this context, the preparation of stillwellite ceramics, composites, glass-ceramics and glass-ceramic textures to investigate their properties is well timed. Taking into account the data on the anisotropy of crystal growth forms[2] and the anisotropy of thermal expansion of $LaBGeO_5$[3] we can suppose that all the members of the stillwellite family have a high crystal anisotropy, which in combination with the high melting points of stillwellites (1350°C for $LaBSiO_5$; see Ref. 4) makes the sintering of stillwellite ceramics difficult.

We have obtained dense glass ceramic materials based on stillwellites using two ways. The first way is the synthesis of glass-ceramic textures as already carried out in the lanthanum borogermanate system.[2,5] Unfortunately, attempts to produce macroscopic textures by the crystallisation of lanthanum borosilicate glasses failed,[6] and there is no information about the obtaining of such textures in other stillwellite-forming systems. The second way is more general, being a conventional ceramic method. Dense ceramic composites, with negligible porosity, have been obtained by the addition of glasses to help the sintering process. The literature in the field of the synthesis of polar ceramics containing glassy components concerns mainly crystals in the perovskite family with pseudocubic symmetry;[7] information on polar ceramics and on composites with significantly anisotropic crystals is rare.

The present work is devoted to preparing composites based on $LaBSiO_5$ stillwellite and to studying their dielectric and pyroelectric properties. An advantage of $LaBSiO_5$

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crystals is the low temperature of the ferroelectric phase transition, $T_c = 130–140°C$,[4] when compared with other members of the stillwellite family; however, a pyroelectric response of $LaBSiO_5$ has not yet been measured.

Liquid-phase sintering may be promoted by adding a glass with low T_g value and from which it is possible to precipitate crystals with low melting points. Some glasses with compositions near the stoichiometry in the polar phases $Pb_5Ge_3O_{11}$, $PbLiPO_4$ and $PbBPO_5$, and hence containing large amounts of PbO, have the required characteristics. Moreover using these glasses for the liquid-phase sintering of the "$LaBSiO_5$/glass" composite, it should be possible to crystallise the glassy part to obtain a two-phase ferroelectric composite with very small amounts of residual glass.

In this connection, high lead glasses of compositions $5PbO{\cdot}3GeO_2$, $2PbO{\cdot}Li_2O{\cdot}2P_2O_5$ and $2PbO{\cdot}B_2O_3{\cdot}P_2O_5$ have been chosen as sintering agents. The first composition corresponds to well-known ferroelectrics.[8] The second is located near to the $PbLiPO_4$ ferroelectrics,[9] the composition of which is located far from the glass-forming region.[10] Here we have used the $2PbO{\cdot}Li_2O{\cdot}2P_2O_5$ glass but enriched in P_2O_5. The third composition corresponds to the stillwellite-phosphate $PbBPO_5$ which, as established recently, is piezoelectric[11] but it is not ferroelectric. However, as shown in previous work,[12] solid solutions may be synthesised in the system $LaBSiO_5$–$PbBPO_5$, with T_c values close to the range of room temperature.

In this first paper on the synthesis of ferroelectric composites, our main goals are to study the crystallisation behaviour of the glasses and to verify the existence of ferroelectric and pyroelectric properties of $LaBSiO_5$ composites obtained by sintering in the presence of high lead glasses. The subsequent crystallisation of glasses is expected to lead to the formation of either a second polar phase or to a stillwellite-like solid solution.

The high reactivity of the Pb containing melts poses the necessity to study the chemical interactions between crystalline and liquid phases during the sintering process. Therefore following this investigation of the synthesis of the composites and their pyroelectric activity, results from differential thermal analysis (DTA) and X-ray diffraction (XRD) of the initial powders and mixtures as well as of the sintered pellets will be published in a following paper.

2. Experimental

Solid state synthesis of $LaBSiO_5$ was carried out[4] in an electric furnace using stoichiometric mixtures of reagents grade SiO_2, $La_2O_3{\cdot}3H_2O$ and H_3BO_3 placed into a corundum crucible. 5 h heat treatments at temperatures from 900 to 1300°C with 50°C steps and grinding of the products at each step make it possible to obtain one-phase powders with stillwellite-like structure (trigonal cell, $a_{hex} = 6.81$, $c_{hex} = 6.74$ Å). The grinding after each step accelerates the chemical reaction while the low temperature steps permit to minimize the boron loss by volatility. The synthesised phase was identified by XRD using a diffractometer DRON-3.0 (Cu K_α, with a Ni filter).

The $5PbO{\cdot}3GeO_2$, $2PbO{\cdot}Li_2O{\cdot}2P_2O_5$ and $2PbO{\cdot}B_2O_3{\cdot}P_2O_5$ glasses were melted in corundum crucibles at 1000°C for 30 min and then quenched between two steel plates. The crystallisation behaviour of the glass powders was examined[5] by DTA and XRD. From the DTA curves, the glass transition temperature (inflection point), T_g, and the temperatures of exothermic crystallisation peaks, T_{cr} were determined as well as melting points of the crystallising phases.

Both crystalline $LaBSiO_5$ and the synthesised glasses were ground up to a dispersivity of less than 20 μm in an agate mortar or in a ball mill. After mixing of the crystal and glass powders in the ratio of 9:1, pellets 10 mm in diameter and 2 mm thick were prepared by dry pressing. Sintering of the pellets was carried out at 1000–1100°C for approximately 20 min, to avoid the growth of the $LaBSiO_5$ grains.

Pellets with uniform microstructure were selected, following visual and optical microscopy inspection, for the preparation of plane-parallel plates 0.5–1 mm thick. These plates were coated with electrodes by applying a silver paste and heating at 400°C. The dielectric permittivity ε was measured in the frequencies range from 1 kHz to 1 MHz and over a 200°C interval around the T_c values, using a P5083 bridge (30 Hz–100 kHz) and a E7-12 bridge (1 MHz).

Some samples displaying a distinct maximum at the T_c temperature on the $\varepsilon(T)$ curves were poled by a d.c. field perpendicular to the surface of the samples in the temperature range from T_c to room temperature. The pyroelectric measurements of the poled samples were carried out by the quasistatic method with a V7-30 microvoltmeter, during a uniform temperature increase at the rate of 10 K/min.

It is clear that the pyroelectric coefficient must depend on the electric poling conditions, sample thickness, and porosity of samples. At this stage, we have not investigated these factors in detail. Samples with rough and porous microstructure were for the most part destroyed during poling so that only samples with acceptable microstructure were conserved for pyroelectric measurements.

Because only well-sintered pellets show the remarkable dielectric anomaly on the $\varepsilon(T)$ curves and a distinct pyroelectric response, the dielectric measurements, the poling process and the pyroelectric measurements can be considered as a measure of the quality of sintered pellets.

3. Results and discussion

3.1. Thermal analysis

DTA curves for the powder glasses synthesised are presented in Fig. 1. All three glasses are characterised by low values of T_g, by intense exothermic peaks at temperatures T_{cr} from 420 to 543°C and by the low temperatures of the endothermic peaks connected with the melting of crystalline phases. The values of T_g, T_{cr} and $T_{m.p.}$ are reported in Table 1. The XRD patterns of glass powders heat-treated at temperatures just above the respective T_{cr} value show that the main crystallising phase, from each glass, is $Pb5Ge_3O_{11}$, $PbLiPO_4$ and $PbBPO_5$ respectively. The $T_{m.p.}$ values (Table 1), agree well with the literature data[8–11] for each crystalline phase, supporting the XRD data of heat treated samples.

There are literature DTA data for the $5PbO.3GeO_2$ glass.[13,14] The crystallisation temperatures, T_{cr}, reported in these papers (380 and 395°C) are lower than the value (420°C) shown in Fig. 1. This indicates that the crystallisation behaviour of this glass is affected by its thermal history. A lower crystallisation peak temperature indicates a higher number of nuclei in the glass. Moreover the α–β transformation of $Pb_5Ge_3O_{11}$ reported[13,14] as an exothermic peak at around 500°C, is seen in Fig. 1 as a low intensity peak. Information on the crystallisation behaviour of these glasses will be investigated afterwards. However from the data reported in Fig. 1 and Table 1, we infer that liquid-phase sintering of $LaBSiO_5$ composites should be possible at temperatures higher than 900°C for the above three glasses, while crystallisation of the liquid phase could occur only during the cooling of the sintered pellets depending on the cooling rate.

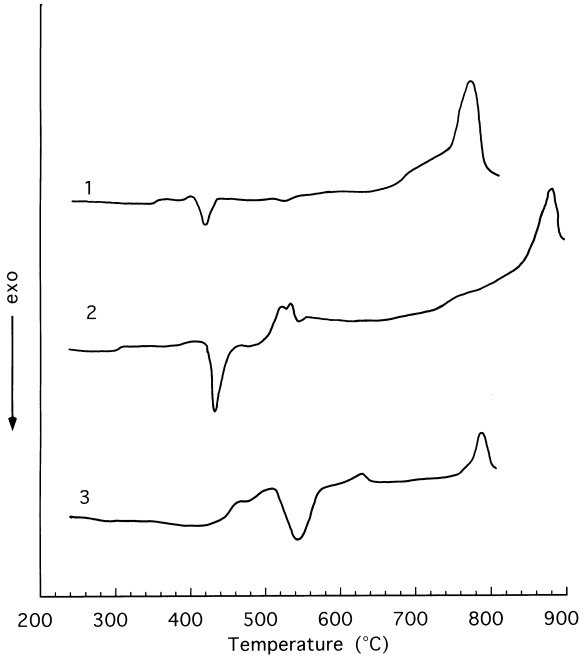

Fig. 1. DTA curves, 10°C/min, of powder glasses having composition: $5PbO.3GeO_2$ (1), $2PbO.Li_2O.2P_2O_5$ (2) and $2PbO.B_2O_3.P_2O_5$ (3).

Table 1
Glass transition temperature, T_g, and crystallisation temperature, T_{cr}, of investigated glasses, and melting temperature, $T_{m.p.}$, of the crystallising phases by DTA data

Glass compositions	Main crystalline phase	T_g (°C)	T_{cr} (°C)	$T_{m.p.}$ (°C)
$5PbO.3GeO_2$	$Pb_5Ge_3O_{11}$	351	420	742
$2PbO.Li_2O.2P_2O_5$	$PbLiPO_4$	297	430	850
$2PbO.B_2O_3P_2O_5$	$PbBPO_5$	452	543	770

3.2. Sintering

In the present work, the sintering of "$LaBSiO_5$–glass" composites was carried out at 1000–1100°C for 10–20 min. More prolonged sintering leads to unwanted growth of the $LaBSiO_5$ grains. The XRD analysis of the sintered pellets indicates that only the stillwellite-like phase is present in the $LaBSiO_5$–$PbBPO_5$ composites. In the cases of the $Pb_5Ge_3O_{11}$ and $PbLiPO_4$ glasses, the XRD patterns of the sintered pellets are more complex.

In order to check whether chemical interaction between the $LaBSiO_5$ grains and the liquid Pb-containing glasses occurs at the sintering temperatures, the XRD patterns of mixtures of the initial powders and powders obtained by the grinding of sintered pellets has been collected. The similarity of XRD patterns in the case of the "$LaBSiO_5$–$PbBPO_5$ glass" composite indicates the absence of any pronounced interaction in this system.

3.3. Dielectric behaviour

Typical temperature dependencies of the ε values of the synthesised pellets are displayed in Fig. 2. There are three different types of curve. In the first, the imperfections of the microstructure, such as excessive porosity, cause the absence of the distinct maximum on the $\varepsilon(T)$ curve, expected from the ferroelectric nature of the crystalline phase. The poling causes the destruction of such samples already at 0.2–0.5 kV/mm confirming their deficient microstructure. This type of curve is characteristic of the composites sintered at less than 900°C. Secondly, high quality pellets, able to bear a poling of up to 5 kV/mm strength, may be synthesised at temperatures of about 1000–1100°C. They are characterised by an $\varepsilon(T)$ curve with sharp a maximum at 125–135°C corresponding almost exactly to the ferroelectric phase transition point, T_c of $LaBSiO_5$ stillwellite-like crystals. Thirdly, when a composite "$LaBSiO_5$–$PbBPO_5$" is preliminarily heat treated at 1000°C for a long time, up to 100 h, the maximum on the $\varepsilon(T)$ curve shifts to about

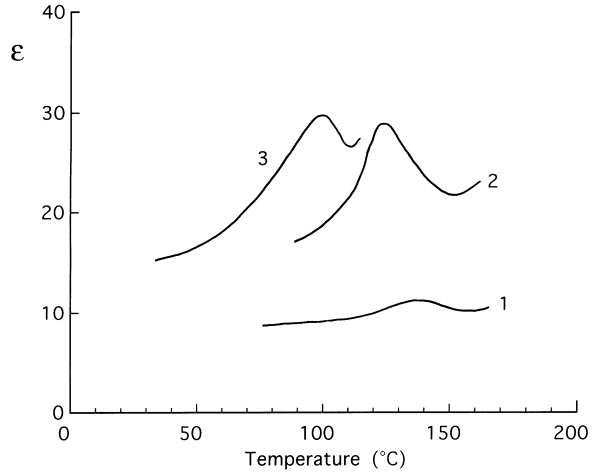

Fig. 2. Temperature dependencies of dielectric permittivity ε at 1 MHz frequency. Ill-sintered (1) and well-sintered (2) pellets of composites based on $LaBSiO_5$ and well-sintered pellet of the composite based on $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$ solid solutions (3).

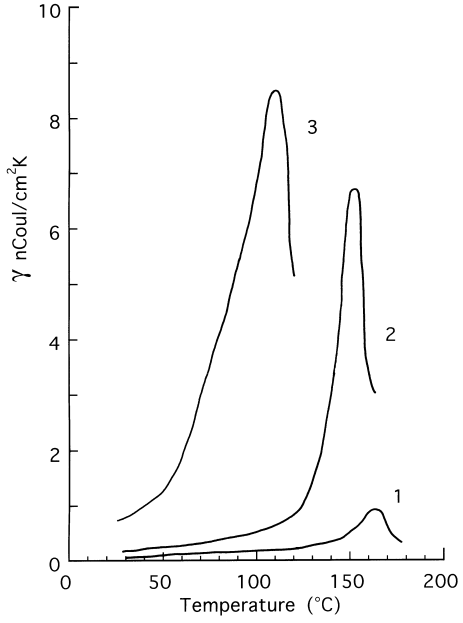

Fig. 3. Temperature dependencies of coefficient of pyroelectricity γ. Ill-sintered (1) and well-sintered (2) pellets of composites based on $LaBSiO_5$ and well sintered pellet of the composite based on $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$ solid solutions (3).

100°C indicating the formation of a solid solution with the heterovalent substitutions $La^{(III)}$ by $Pb^{(II)}$ and $Si^{(IV)}$ by $P^{(V)}$.[12] The maximum on the $\varepsilon(T)$ curve certainly has a distinct ferroelectric nature because its position does not depend on the frequency of the applied field.

3.4. Pyroelectric behaviour

The temperature dependency of the pyroelectric current flowing through a composite plate was typical for pyroelectrics; as changing from heating to cooling, the direction of the current flow is suddenly reversed. This behaviour confirms the pyroelectric nature of the measured current. An additional confirmation of the pyroelectric origin of the current is the change of the EMF sign when the sample is reversed in the holder.

Temperature dependencies of the coefficient of pyroelectricity $\gamma(T)$ (Fig. 3), are similar to those of the $\varepsilon(T)$ curves. Curve 1 of Fig. 3 reflects the pyroelectric properties of a knowingly ill-sintered composite "0.9 crystalline $LaBSiO_5$–0.1 glassy $LaBSiO_5$" owing to the impossibility of achieving liquid-phase sintering. All the pellets containing PbO but sintered at low temperatures, less than 900°C, show the same behaviour analogous to the $\varepsilon(T)$ curves of Fig. 2. On increasing the temperature, the sintering is accomplished to the dense state so that a strong pyroelectric effect is observed with maximum near the T_c value of $LaBSiO_5$. The T_c of the composites decreases owing to the formation of the solid solution $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$,[12] so the maximum of the pyroelectric effect shifts towards room temperature and the γ values, at 20–50°C, rise to 0.3–0.8 nC/cm^2 K. The latter values are comparable with those obtained for glass-ceramic non-ferroelectric textures.[15] The asymmetric shape of the curve 3 in Fig. 3 as well as that of curve 3 in Fig. 2 may be attributed to the coexistence in the composite of a wide continuous series of solid solutions with T_c values approximately between 70 and 110°C. The value of spontaneous polarisation P_s at room temperature for $LaBSiO_5$ composites was evaluated as 0.3–0.4 μC/cm^2 by integrating the $\gamma(T)$ curves over temperature.

The existence of ferroelectric composites with clear pyroelectric properties in the "$LaBSiO_5$–glass" systems suggests the synthesis of similar composites based on $LaBGeO_5$ and $LiTaO_3$ for which fovourable pyroelectric properties may be expected.

4. Conclusions

It is easy to obtain glass–ceramic ferroelectric composites containing high lead glasses. The T_c of such composites based on $LaBSiO_5$ decreases owing to the formation of solid the solution $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$; the maximum of pyroelectric response correspondingly shifts towards room temperature, with a rise of the γ values at 20–50°C to 0.3–0.8 nC/cm^2 K.

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