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Ferroelectric composites and ceramics based on stillwellite-like solid solutions

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Abstract

Stillwellite-like $LaBGeO_5$ exhibits promising pyroelectric properties that were observed for both single crystal and glass-ceramic textures. To increase pyroelectric coefficient in the room temperature range, it is worth trying to create stillwellite-like solid solutions diminishing ferroelectric phase transition point, T_c. However such an attempt has been carried out only for $LaBSiO_5$ stillwellite doped with $Pb(Ca)BPO_5$. Taking into account the higher pyroelectric activity of $LaBGeO_5$ as compared to $LaBSiO_5$, in the present work existence of solid solutions in the $LaBGeO_5$–$LaBSiO_5$ and $LaBGeO_5$–$Pb(Ca)BPO_5$ systems was explored and T_c composition dependency was determined. It can be supposed that compositions in the range $LaBGe_{0.2\text{-}0.4}Si_{0.8\text{-}0.6}O_5$ are good candidates to develop new high-effective pyroelectrics in form of ceramics, composites or textures.

Keywords: Ferroelectrics; Solid solution; Stillwellite

1. Introduction

Preparation of low-porosity ceramics based on stillwellite-like $LaBGeO_5$ is very problematic owing to the strong anisotropy of their physical properties, embarrassing the realization of its favourable pyroelectric properties on an industrial scale. Accordingly[1,2] $LaBGeO_5$ stillwellite is characterized by significant pyroelectric coefficient, 8–10 nC cm^{-2} K^{-1} and T_c value of 520–530 °C, it has very low dielectric constant (~11) and dielectric losses (~0.001) at room temperature, and conserve high electric resistance up to ~400 °C.

Nevertheless high quality glass-ceramic textures with remarkable pyroelectric efficiency were recently developed[3,4] as well as composites based on $La_{(1-x)}Pb_xSi_{(1-x)}P_xO_5$ solid solutions were synthesized.[5] Taking into account the above-mentioned pyroelectric and dielectric properties of $LaBGeO_5$, the synthesis of $La_{(1-x)}Pb_xBGe_{(1-x)}P_xO_5$ or $LaBGe_{(1-x)}Si_xO_5$ solid solutions looks very promising. In the present paper, we report data on solid-state synthesis of solid solutions in the borogermanate–borosilicate and borogermanate–borophosphate systems, testing the synthesis products by X-ray diffraction (XRD) and by their temperature dependencies of dielectric constant.

2. Experimental

Synthesis of one-phase stillwellite-like powders has been carried out by conventional solid-state chemical reactions. Lanthanum and lead oxides, silica, germanium dioxide, calcium carbonate, phosphoric and boric acids were used as reagents. In the case of the $LaBGeO_5$–$RBPO_5$ system, where R = Ca, Pb, $LaBGeO_5$ crystalline powders were mixed with appropriate amounts of additives either in the form of crystalline powders of $PbBPO_5$ ($CaBPO_5$) or batches corresponding to stoichiometry of these compounds, see Table 1. In the case of the $LaBGeO_5$–$LaBSiO_5$ system, powdered $LaBSiO_5$ was mixed with batches corresponding to appropriate amounts of $LaBGeO_5$. The $LaBGe_{0.2}Si_{0.8}O_5$ batch composition was prepared in two ways: as a mix of

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Table 1
Solid state synthesis of stillwellite-like solid solutions in the $CaBPO_5$–$LaBGeO_5$, $PbBPO_5$–$LaBGeO_5$, $LaBSiO_5$-$LaBGeO_5$

Sample	Composition, mole%				Heat treatment
	$LaBGeO_5$		Additives		
	Crystalline powder	Batch	Crystal	Batch	
1	97		3 $PbBPO_5$		850 °C—10 h +950 °C—14 h + 1050 °C— 60 h
2	90		10 $PbBPO_5$		850 °C—10 h +950 °C— 14 h + 1050 °C— 60 h
3	97			3 $PbBPO_5$	1000 °C—7 h + 1050 °C—14 h
4	90			10 $PbBPO_5$	1000 °C—7 h + 1050 °C—14 h
5	97		3 $CaBPO_5$		850 °C—7 h +950 °C— 184 h + 1000 °C—17 h + 1050 °C—60 h
6		10	90 $LaBSiO_5$		1000 °C—7 h + 1150 °C—14 h
7		20	80 $LaBSiO_5$		1000 °C—7 h + 1150 °C—14 h
8		20		80 $LaBSiO_5$	1000 °C—7 h + 1150 °C—14 h
9		50	50 $LaBSiO_5$		1000°—7 h + 1150°—14 h
10		80	20 $LaBSiO_5$		1000 °C—7 h + 1150 °C—14 h

crystalline $LaBSiO_5$ and $LaBGeO_5$ batch and as a mix of both batch components.

Pellets acceptable for dielectric measurements were pressed and then heat-treated according to data reported in Table 1. Pellets were reground after each 4 or 5 h of heat treatment and then new pellets were pressed.

3. Results and discussion

Temperature dependences of dielectric constants were obtained at frequencies from 1 kHz to 1 MHz. As it appears clear from Fig. 1, the position of dielectric anomaly maximum does not change with frequency, pointing out the ferroelectric nature of the phase transition, T_c, at 520–530 °C by analogy with the single

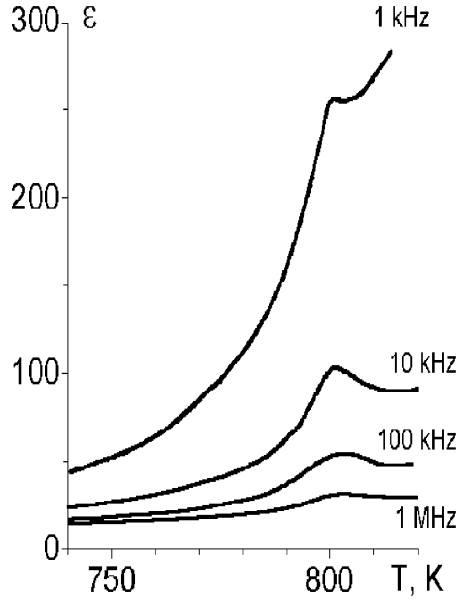

Fig. 1. Typical temperature dependence of dielectric constant, ϵ, of stillwellite-like composites at different frequencies.

crystal $LaBGeO_5$ data.[1,2] Fig. 2 shows $\epsilon(T)$ curves of the samples reported in the Table 1. The absence of a distinct shift of T_c on x allows us to conclude that the formation of $La_{(1-x)}Ca_xBGe_{(1-x)}P_xO_5$ and $La_{(1-x)}Pb_xBGe_{(1-x)}P_xO_5$ solid solutions is strongly embarrassed as compared to the $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$ system, for which solid solutions were synthesized at x values up to 0.1.[5] Most likely heterovalence substitutions of La by Ca(Pb) and of Ge by P are hindered due to too a large difference in dimensions of tetrahedra of PO_4 and GeO_4. Because for the samples 1 and 3, and 2 and 4 (see the Table 1) similar $\epsilon(T)$ curves were attained for shorter treatments of batched samples, (Fig. 2), probably more prolonged treatments of batched pellets would allow us to obtain solid phospho-germanate stillwellite-like solid solutions for $x \sim 0.1$. However it does not look promising since diminishing of T_c of $LaBGeO_5$ from 520–530 °C is expected to be very moderate, while T_c of $LaBSiO_5$ is 130–140 °C and $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$ solutions have a T_c about 100 °C.

An opposite situation is observed in the $LaBGe_{(1-x)}Si_xO_5$ system for which solid solutions may be formed at all x values from 0 to 1 because $\epsilon(T)$ curves show maxima in a wide temperature range depending on the x value (Fig. 2). It should be underlined that $\epsilon(T)$ curves of samples 7 and 8 of the $LaBGe_{0.2}Si_{0.8}O_5$ composition are similar. It means that both mixes based on crystalline $LaBSiO_5$ and $LaBGeO_5$ or on both batch components permit us to achieve a solid solution state in the same time.

T_c values smoothly grow from 130–140 ($LaBSiO_5$) to 520–530 °C ($LaBGeO_5$) supposing the range of change of first-order phase transition (LaBSiO5) to second-order phase transition ($LaBGeO_5$) at $x \sim 0.1$ (Fig. 3). This figure summarises also all published data on stillwellite-like solid solutions. Low-temperature phase transitions are observed only for silicate systems, $La_{(1-x)}Sm_xBSiO_5$, $Pr_{(1-x)}Sm_xBSiO_5$ (Fig. 3a)[6] and

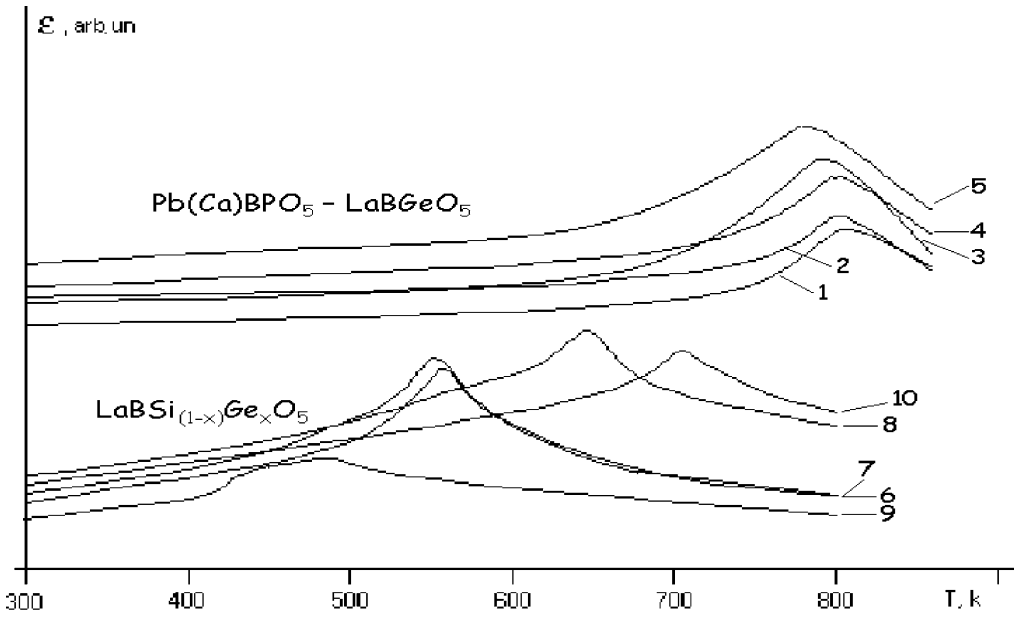

Fig. 2. Temperature dependence of dielectric constant, ϵ, at 1 MHz.

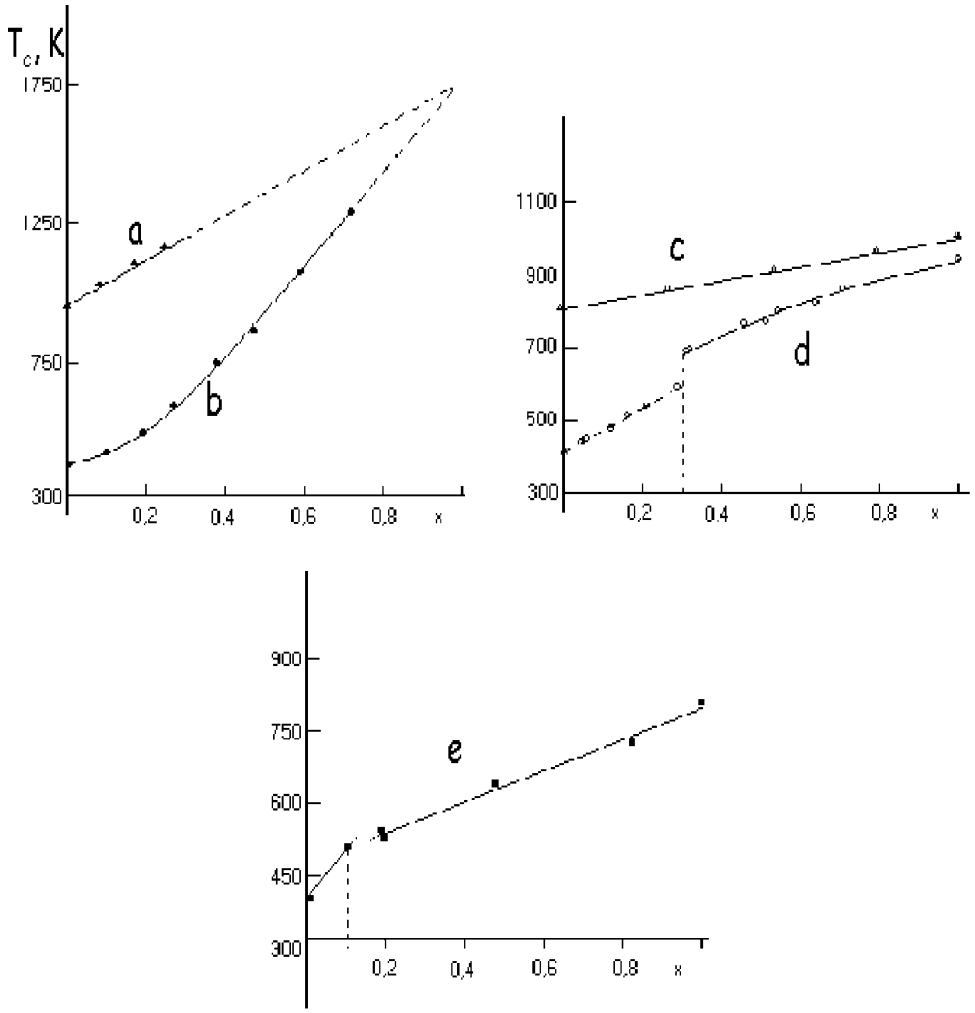

Fig. 3. Ferroelectric phase transition points, T_c, of stillwellite-like solid solutions: (a) $Pr_{(1-x)}$ Sm_xBSiO_5 (b) $La_{(1-x)}$ Sm_xBSiO_5, (c) $La_{(1-x)}$ Pr_xBGeO_5, (d) $La_{(1-x)}$ Pr_xBSiO_5, (e) $LaBGe_{(1-x)}$ Si_xO_5.

$La_{(1-x)}Pr_xBSiO_5$ (Fig. 3b),[7,8] which is not characterized by high pyroelectric activity. Among germanate stillwellite-like solid solutions the $LaBGe_{(1-x)}Si_xO_5$ system looks the most promising, especially that in the compositional range of $x = 0.2$–0.4, for which T_c values lie at 250–350 °C as well as excellent properties of $LaBGeO_5$ stillwellite are expected to be reproduced at lower temperatures.

4. Conclusions

Stillwellite-like solid solutions $LaBGe_{1-x}Si_xO_5$ have been synthesized and their ferroelectric phase transition points determined. The compositions in the range $LaBGe_{0.2-0.4}Si_{0.8-0.6}O_5$ are a good candidate to develop new high-effective pyroelectrics in the form of ceramics, composites or textures. Formation of $La_{(1-x)}Ca_xGe_{(1-x)}P_xO_5$ and $La_{(1-x)}Pb_xBGe_{(1-x)}P_xO_5$ stillwellite-like solid solutions is strongly embarrassed as compared to $La_{(1-x)}Pb_xBSi_{(1-x)}P_xO_5$.

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