THE PHASE TRANSITION OF SOL-GEL PREPARED LABSIO$_5$ STILLWELLITE

T.E. Konstantinova, G.K. Volkova, I.A. Danilenko, A.A. Saprikin, V.M. Pogibko, L.G. Gusakova
A.A. Galkin Donetsk Institute for Physics and Engineering
72 R.Luxemburg Str., Donetsk 83114, Ukraine

The stillwellites $LaBXO_5$ (X=Si, Ge) and stillwellite-based solid solutions of the type $La_{1-x}Pr_xBXO_5$ combine ferroelectricity with (i) low values of the dielectric permeability ε and dielectric losses tgδ out of the range of ferroelectrical phase transitions; (ii) high resistivity ρ_v at comparatively high temperatures; (iii) noticeable coefficient of pyroelectricity. The temperature of ferroelectrical phase transition can be varied in a wide range of values (from 130 to 750^{o}C) by directed change of the chemical composition of these materials (1,2).

The above mentioned combination of properties allows us to consider stillwellites to be perspective pyroelectrics. The investigations of the opportunity of obtaining of ferroelectric materials in a glass-crystal state are stimulated by the fact that the majority of compositions of stillwellites is located near areas of glass formation (3).

Pyroelectric materials can be used for tympanic thermometers, laser power meters and beam profiles, fire detection, pollution monitoring/gas analysis. The use of pyroelectric detectors for energy plants (e.g. SOFC) is also of great importance.

The obtaining of homogeneous small-grain state from hardened glass is known to be a complex problem because crystal nucleation in hardened glasses occurs mostly on the surface and is followed by the penetration into the bulk. Besides, the area of glass formation is restricted in a number of silicate and boron systems. Being melted, these compounds are separated in some range of concentration values to two liquids of different compositions. In this case, the process of phase separation does not include nucleation, i.e. it is a spinodal process. The metastable stratification is followed by the precipitation of extremely dispersed phases and the structure of the glass becomes laminar. That is why the study of another way of obtaining of a small-grain ceramics with stillwellite structure is of valuable interest. Sol-gel method is one of such ways. The obtained amorphous gel is similar to a glass which is transformed into a high-dispersed powder mass after heating. It is very important to know what transformations occur in the system and if the process of phase separation takes place. So the main aim of the present work was the study of the processes of phase transformation in La-B-Si-O system when sol-gel method of powder obtaining is used.

Boron acid is dissolved in the 100^{o}C heated gel of H_2SiO_3 at intermixing, the gel is poured into $La_2O_3{\cdot}3H_2O$ suspension and then the physically bound water is eliminated from the obtained mass in MW field (4).

We have taken into account that the character of the crystallization of La-B-Si materials differs sharply even at small deviations of the composition. Thus, we prepared by the above mentioned gel method three groups of powder materials with the metal concentration close to the stohiometry of stillwellite. The ratio of the components (i.e. La_2O_3:B_2O_3:SiO_2) was 33,3:33,3:33,3; 18:32:50; 20:30:50 mol % , in the first, second and third group correspondingly. SiO_2 was an amorphous substance in all the groups of samples.

The DTA of the sample of the first group has shown that the release of physically bound water occurs even after exposure at 105^{o}C till 120^{o}C. Three endopeacks at 320, 555 and 570^{o}C are observed on the curve of the mass loss rate and the rate of the change of thermal effects. Besides, a wide minimum is present on the DTA curve at 765^{o}C which is not followed by the mass loss. More explicit image of phase transitions in the studied system is given by X-ray analysis.

The process of synthesis can be divided into three stages. The first stage corresponds to low temperatures (<300^{o}C) and is characterized by crystal-amorphous mixture of the source components where three-hydrous lantan oxyde is the crystal phase. The second stage is the region from 300 to 700^{o}C characterized by the formation of intermediate phases. $La_2Si_2O_7$ and high-temperature $LaBO_3$ are formed first (at 300^{o}C). The last compound is transformed into the low-temperature modification at 500^{o}C. This transformation is fully completed at 700^{o}C. Besides, the amount of $LaBO_3$ increases as the temperature raises. Only this phase is left at 800^{o}C in the samples of all three groups. It should be mentioned that the $LaBO_3$ lattice parameter after anneal at 800^{o}C is larger than the table value.

The third stage (from 800 to 1175^{o}C is characterized by the formation of stillwellite $LaBSiO_5$. Its quantity is about 6% at 850^{o}C. The stillwellite co-exists with the low-temperature phase $LaBO_3$. The $LaBO_3$ percentage raises as the temperature of the synthesis increases.

The change of the composition of the source mixture does not affect the general character of the observed transformations but it changes essentially the ratio of the formed phases. The amount of low-temperature $LaBO_3$ falls from 95% to 57% as the contentment of lantan oxyde decreases from 33 to 22 mol.% and the contentment of SiO_2 rises from 33 to 50%. The influence of the initial composition of the mixture appears to be the most essential at the maximum (1175^{o}C) temperature of annealing. 100% part of stillwellite-like phase of $LaBSiO_5$ is formed only in the samples of the second group when the ratio of the components (i.e. La_2O_3:B_2O_3:SiO_2) is 17.6:31.8:50.6% and the minimum 49% amount was observed in the first group with the ratio of 33.3:33.3:33.3.

The results have confirmed the possible use of the sol-gel method for obtaining highly-dispersed crystal powders for pyroelectric materials on the base of $LaBSiO_5$ crystallite. It is estimated that the same phases appear both during the synthesis and during the crystallization of glasses of the same composition. But the formation of $LaBSiO_5$ starts 100^o C below the temperatures when this phase is formed from a glass. The source phase of stillwellite formation ($LaBO_3$) probably is a solid solution containing Si that is evidenced by the increase of the lattice parameter.

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