The synthesis of Li$_2$ZnTi$_3$O$_8$ and Li$_2$Zn$_3$Ti$_4$O$_{12}$ powders for Low Temperature Cofired Ceramic (LTCC) production

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Abstract. The powders of different phase compositions in the Li$_2$O-ZnO-TiO$_2$ system were prepared. These powders can be used as major components in microelectronic devices production using Low Temperature Cofired Ceramic (LTCC) technology. The influence of factors such as the synthesis temperature and holding time on phase transformations processes and composition of synthesized powders were studied. It was determined that the synthesis of Li$_2$ZnTi$_3$O$_8$ and Li$_2$Zn$_3$Ti$_4$O$_{12}$ compounds can be carried out at 850-900 °C. At the same time, the synthesized phases are extremely sensitive to the ratio of the initial components.

1. Introduction

A rapid progress of ceramic technology with low dielectric loss became a reason of development of the field of high-frequency communication because of possibility of the miniaturization and the price decrease of electronic devices [1]. Thereby, titanium dioxide is widely considered by science community as a major component of electronic materials due to its dielectric properties: its relative dielectric permittivity $\varepsilon_r$ is in the range of 20-50, and $tg \delta$ is lower than $1 \cdot 10^{-3}$. Moreover, these materials can be produced using LTCC technology because of the low sintering temperature. In this technology such materials as silver and gold are used as metallic conductors and they can be introduced into the material during the sintering stage [2]. Such systems as Li$_2$O-MgO-TiO$_2$, Li$_2$O-ZnO-TiO$_2$, ZnO-Nb$_2$O$_5$ and so on can be considered as the most promising materials for microwave devices production [1, 2]. At the same time, thermally stabilized forms and conditions of synthesis of said compounds are not properly studied. Therefore, the information about conditions of synthesis of those systems varies in different sources.

In this research, in order to determine conditions of synthesis of compounds with required phase composition, the powders of one of the most promising system Li$_2$O-ZnO-TiO$_2$ were synthesized and studied. There are 8 individual compounds in this system with Li$_2$TiO$_3$, Li$_2$ZnTi$_3$O$_8$ and Li$_2$Zn$_3$Ti$_4$O$_{12}$ being considered as the ones that possess the best dielectric properties (oxides ratio are 1:0:1, 1:1:3 and 1:3:4, respectively) [3]. The synthesis temperature of these compounds varies in the range 700-900 °C [4-7]. The Li$_2$ZnTi$_3$O$_8$ and Li$_2$Zn$_3$Ti$_4$O$_{12}$ are solid solutions that are not studied completely, which makes their identification more complicated. Thus, in the research phase transformations of three-phase compounds were studied.

2. Experimental procedure

High-purity Li$_2$CO$_3$, ZnO and TiO$_2$ powders were used as the starting materials for the three-phase compounds synthesis. Stoichiometric amounts of the powders were mixed together and ball milled in
acetone medium for 24 h. The resultant slurry was dried at 75 °C and disaggregated. Prepared powders were investigated using differential thermal analysis (DTA). At the end, powders were synthesized in air under following conditions:
1) Li$_2$ZnTi$_3$O$_8$ at 700 °C/ 4 h, 850 °C/4 h and 900 °C/4 h;
2) Li$_2$Zn$_3$Ti$_4$O$_{12}$ at 900 °C/4 h and 900 °C/8 h.
Phase compositions of powders were analyzed using X-ray diffractometry (XRD) and petrographic analysis.

3. Results discussion
Figure 1 shows the DTA results of powders that were used for Li$_2$ZnTi$_3$O$_8$ synthesis. Heating rate is 25 °C/min. The initial deviation of curve from zero in the range 50-400 °C can be explained by the difference between thermal conductivity of sample and reference. The endothermic peak registered at 496 °C highlights a mass loss of 8.5%. This can be explained by a lithium carbonate decomposition. There are two exothermic reactions that start at 676 °C. The first reaction is the Li$_2$TiO$_4$ formation that starts at 676 °C and supposedly ends at 774 °C. The second exothermic effect hits its peak at 813 °C and is considered to be a Li$_2$ZnTi$_3$O$_8$ formation.

A complex of instrumental methods must be used for study of phase transformations of this system since diffraction peaks register at almost identical 2θ values in XRD method.
XRD results of powders obtained from Li$_2$ZnTi$_3$O$_8$ synthesis are shown in Fig. 2. At the synthesis temperature of 700 °C (Fig. 2, a) the phase Li$_2$O-TiO$_2$ and oxides Li$_2$O, ZnO, TiO$_2$ are observed. At 850 °C (Fig. 2, b) the phase Li$_2$O-TiO$_2$, along with TiO$_2$, can be observed. Additionally, petrographic analysis confirms a presence of little amounts of Li$_2$O and ZnO.
At the synthesis temperature of 900 °C (Fig. 2, c) the formation of required compound Li$_2$ZnTi$_3$O$_8$ is observed. Also, a small amount of anatase TiO$_2$ (~3 wt. %) was registered. A presence of said phases was confirmed using petrographic analysis.

Figure 1. DTA results of the powder for Li$_2$ZnTi$_3$O$_8$ synthesis.
Figure 2. XRD results of the powders obtained from \( \text{Li}_2\text{ZnTi}_3\text{O}_8 \) synthesis:
   - a) 700 °C, b) 850 °C, c) 900 °C.

Thus, the synthesis of a required compound starts at the temperature of 850 °C, and at 900 °C the maximum amount of this compound was obtained. A small amount of anatase TiO\(_2\) (3 wt. %) in its composition can be a reason of an incomplete synthesis process. Nevertheless, because of the high value of \( \varepsilon_r \) that TiO\(_2\) possesses, it is possible that its extra amount can positively affect dielectric properties of a produced material.

According to DTA, XRD, and petrographic analysis results, it is shown that formation of a required phase begins at the temperature of 676 °C, at which \( \text{Li}_2\text{CO}_3 \) decomposes with the \( \text{Li}_2\text{O} \) formation. The \( \text{Li}_2\text{O} \)-TiO\(_2\) phase formation was shown to begin at 676 °C, and at 813 °C the \( \text{Li}_2\text{ZnTi}_3\text{O}_8 \) formation is observed. A slight difference between the synthesis temperatures of phases registered by DTA and XRD analyses can be explained by different quantities of powders that were used in both methods.

Fig. 3 shows DTA results of the powder for \( \text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12} \) synthesis. Heating rate is 25 °C/min.
Figure 3. DTA results of the powder for Li$_2$Zn$_3$Ti$_4$O$_{12}$ synthesis.

The endothermic peak shows a mass loss to 92.4 % and highlights a lithium carbonate decomposition. A phase formation starts at the temperature higher than 700 °C and hits it peak at 753 °C. The observed exothermic peak highlights an additional phase formation. At the temperature of 840 °C both phases supposedly form completely and further fall of DTA curve is explained by the difference between thermal conductivity of sample and reference. However, the presence of a plateau at the temperatures of 947 °C and 984 °C cannot be fully explained.

XRD results of the powders obtained from Li$_2$Zn$_3$Ti$_4$O$_{12}$ synthesis are shown in Fig. 4.

Figure 4. XRD results of powders obtained from Li$_2$Zn$_3$Ti$_4$O$_{12}$ synthesis: a) 900 °C/4 h b) 900 °C/8 h

Both synthesis were carried out at 900 °C. At 900 °C/4 h (fig. 4, a) Li$_2$Zn$_3$Ti$_4$O$_{12}$ (60 wt. %) and Zn$_2$TiO$_4$ (40 wt. %) are observed. Oxides of the initial components are not present at this temperature. At 900 °C/8 h (fig. 4, b) the differences in quantity composition of phases are not observed. It is possible that due to lack of Li$_2$O, the process of formation of Li$_2$Zn$_3$Ti$_4$O$_{12}$ happens as long as Li$_2$O is present in the system, and then the additional Zn$_2$TiO$_4$ phase begins to form from the remained ZnO and TiO$_2$ oxides. Nevertheless, the synthesis temperature of 900 °C is enough for the phase formation as evidenced by the Li$_2$Zn$_3$Ti$_4$O$_{12}$ phase presence. Change of diffraction peak intensity caused by the holding time increase can be explained by the improvement of crystal lattice of both phases.
4. Results discussion
According to DTA, XRD, and petrographic analysis results, the synthesis process of Li$_2$ZnTi$_3$O$_8$ ends completely at 900 °C/4 h. At the lower temperatures of synthesis, the remains of initial oxides are present. Thus, 850 °C is the most optimal temperature for synthesis in case of increased holding time. At the synthesis temperature of 850 °C it is possible to maintain a small particle size of powders as well as high amount of defects, and avoid crystal growth.

In the process of Li$_2$Zn$_3$Ti$_4$O$_{12}$ synthesis, the presence of Li$_2$Zn$_3$Ti$_4$O$_{12}$ and Zn$_2$TiO$_4$ phases is observed. The presence of Zn$_2$TiO$_4$ phase is explained by the lack of Li$_2$CO$_3$ in the system. The right stoichiometric amounts of initial components must help to avoid the additional phase formation. Nevertheless, it was established that 900 °C/4 h is the most optimal temperature for the synthesis. The holding time more than 4 hours will only lead to the improvement of crystal lattice which is a negative outcome as it decreases the powder activity to the sintering process.

Acknowledgments
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References
[1] Sebastian M.T., Ubic R., Jantunen H. Low-loss dielectric ceramic materials and their properties // International Materials Reviews. 2015. Iss. 60, № 7. P. 392-412.
[2] Sayyadi-Shahraki A. et al. A new temperature stable microwave dielectric ceramic with low-sintering temperature in Li$_3$TiO$_3$–Li$_2$Zn$_3$Ti$_4$O$_{12}$ system // Journal of alloys and compounds. 2014. Iss. 597. P. 161-166.
[3] Zhang Y.D., Zhou D. Pseudo phase diagram and microwave dielectric properties of Li$_2$O–MgO–TiO$_2$ ternary system // Journal of the American Ceramic Society. 2016. Iss. 99. № 11. P. 3645-3650.
[4] Liu C.Y. et al. Influence of B$_2$O$_3$ additive on microwave dielectric properties of Li$_2$ZnTi$_3$O$_8$ ceramics for LTCC applications // International Journal of Applied Ceramic Technology. 2013. Iss. 10. P. E49-E56.
[5] Zitani M.K. et al. Microstructural and microwave dielectric properties of LZT (Li$_2$ZnTi$_3$O$_8$) ceramics sintered in presence of bismuth borate glass for LTCC applications // Ceramics International. 2018. Iss. 44. №. 4. P. 4016-4026.
[6] Hou M., Chen G., Bao Y., Yang Y., Yuan C. Low-temperature firing and microwave dielectric properties of LBS glass-added Li$_2$ZnTi$_3$O$_8$ ceramics with TiO$_2$ // Journal of Materials Science: Materials in Electronics. 2012. № 23. P. 1722-1727.
[7] Sayyadi-Shahraki A., Taheri-Nassaj E. Low temperature cofirable Li$_2$Zn$_3$Ti$_4$O$_{12}$ microwave dielectric ceramic with Li$_2$O-ZnO-B$_2$O$_3$ glass additive. Journal of Materials Science: Materials in Electronics. 2014. № 25. P. 355-360.