Reactivity of T-Nb$_2$O$_5$ or H-Nb$_2$O$_5$ towards Li$_2$CO$_3$

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The literature survey has shown that Li$_2$O – Nb$_2$O$_5$ system has been the subject of many investigation. As a result of these works the phase diagram of the Li$_2$O – Nb$_2$O$_5$ system has been constructed [1]. Despite numerous works there are still controversies concerning the number, real compositions, conditions of synthesis, physical properties and thermal stability of described in literature phases. There are known nine polymorphic modifications of Nb$_2$O$_5$, but in the most of cases authors of works do not put attention to the type of polymorphic modification of Nb$_2$O$_5$ used for the synthesis. The results of our earlier investigations have revealed however, that type of used polymorphic modification of niobium(V) oxide can affect the type of intermediate and final products of the reaction [2]. LiNbO$_3$ is the most frequently investigated phase forming in the Li$_2$O – Nb$_2$O$_5$ system. Single crystals and thin films containing LiNbO$_3$ are materials of great importance because of their potential application as elements in optical waveguides, random access memories, and high dielectric constant capacitors. The complicating factor in application of LiNbO$_3$ is the non-stoichiometry of obtained samples, which influence highly their physical properties [3]. The excess or deficiency of Li$_2$O is compensated by formation of Li$_2$NbO$_4$ and LiNb$_3$O$_8$ phases, whereas in the case of optical applications, stoichiometric LiNbO$_3$ single crystals and thin films are preferred. The aim of this work is to conduct comparative studies concerning synthesis of LiNbO$_3$, Li$_2$NbO$_4$ and LiNb$_3$O$_8$ phases in the solid state using two niobium(V) oxide modifications: T-Nb$_2$O$_5$ and H-Nb$_2$O$_5$.

The reactants used for the synthesis of the phases were Li$_2$CO$_3$ a.p. (POCH, Gliwice, Poland), H-Nb$_2$O$_5$ high purity, (CBMM, Brazil), T-Nb$_2$O$_5$ 99.9% (Aldrich, Germany) and mixture of M and H-Nb$_2$O$_5$ obtained from T-Nb$_2$O$_5$ 99.9% (Aldrich, Germany) by heating at 1000°C for 10 minutes. The reactants weighed in appropriate proportions were ground in an agate mortar and next calcined at 600, 650, 700, 750 and 800°C for 24 hours in the atmosphere of air. Before calcination prepared mixtures of reactants were subjected to investigation with the aid of DTA-TGA methods. After each calcination cycle the contents of the preparations were determined by XRD method. Mixtures of starting components and final products were additionally investigated with the help of IR and UV-Vis-NIR measuring techniques.

To estimate the conditions of synthesis of the phases, mixtures of reactants before first calcination stage were subjected to investigations with the help of DTA-TGA methods. Analysis of the shape of TGA curves have revealed, that considerable mass loss of samples, which can be connected with the run of the reaction between reactants, starts at 600°C in the case of mixtures containing T-Nb$_2$O$_5$. This temperature is much lower than the melting temperature of Li$_2$CO$_3$, equal to 723°C. On the other hand, the process connected with mass loss commences at higher temperatures for mixtures prepared using H-Nb$_2$O$_5$. It is worth to note, that the onset temperatures of effects recorded in DTA curves are considerable lower for mixtures prepared using the T-Nb$_2$O$_5$. Moreover the shape of DTA curves is much more complex in this case. The results of XRD phase analysis have revealed that regardless of composition of sample and type of used modification of Nb$_2$O$_5$, the synthesis process starts at 600°C. The pure phases LiNb$_2$O$_6$, LiNbO$_3$ and Li$_3$NbO$_4$ were obtained after heating stage at 650°C when the reactant was T-Nb$_2$O$_5$, but at 700, 750 and 750°C respectively, by using H-Nb$_2$O$_5$. The IR and UV-Vis-NIR spectra of selected samples were recorded. The analysis of UV-Vis-NIR spectra has revealed the shift of absorption bands towards shorter waves with increase of lithium content in obtained phases. On the other hand, the IR spectra are very useful in detection of small amounts of carbonates in obtained samples.