

Reactivity of T-Nb₂O₅ or H-Nb₂O₅ towards Li₂CO₃

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The literature survey has shown that Li₂O – Nb₂O₅ system has been the subject of many investigation. As a result of these works the phase diagram of the Li₂O – Nb₂O₅ 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 Nb₂O₅, but in the most of cases authors of works do not put attention to the type of polymorphic modification of Nb₂O₅ 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]. LiNbO₃ is the most frequently investigated phase forming in the Li₂O – Nb₂O₅ system. Single crystals and thin films containing LiNbO₃ 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 LiNbO₃ is the non-stoichiometry of obtained samples, which influence highly their physical properties [3]. The excess or deficiency of Li₂O is compensated by formation of Li₃NbO₄ and LiNb₃O₈ phases, whereas in the case of optical applications, stoichiometric LiNbO₃ single crystals and thin films are preferred. The aim of this work is to conduct comparative studies concerning synthesis of LiNbO₃, Li₃NbO₄ and LiNb₃O₈ phases in the solid state using two niobium(V) oxide modifications: T-Nb₂O₅ and H-Nb₂O₅.

The reactants used for the synthesis of the phases were Li₂CO₃ a.p. (POCH, Gliwice, Poland), H-Nb₂O₅ high purity, (CBMM, Brazil), T-Nb₂O₅ 99,9% (Aldrich, Germany) and mixture of M and H-Nb₂O₅ obtained from T-Nb₂O₅ 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-Nb₂O₅. This temperature is much lower than the melting temperature of Li₂CO₃, equal to 723°C. On the other hand, the process connected with mass loss commences at higher temperatures for mixtures prepared using H-Nb₂O₅. It is worth to note, that the onset temperatures of effects recorded in DTA curves are considerable lower for mixtures prepared using the T-Nb₂O₅. 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 Nb₂O₅, the synthesis process starts at 600°C. The pure phases LiNb₃O₈, LiNbO₃ and Li₃NbO₄ were obtained after heating stage at 650°C when the reactant was T-Nb₂O₅, but at 700, 750 and 750°C respectively, by using H-Nb₂O₅. 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.

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[2] P. Tabero, E. Filipek, M. Piz, *Cent. Eur. J. Chem.* **7** (2009) 222-7.

[3] A. Bartaszyte *et al.*, *J. Phys. Condens. Matter* **25** (2013) 205901-9.