IRSTI 29.19.11, 47.09.48 https://doi.org/10.26577/RCPh.2021.v76.i1.05

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STUDY OF MORPHOLOGICAL FEATURES OF LITHIUM-CONTAINING CERAMICS OBTAINED BY SOLID-PHASE SYNTHESIS

This work is devoted to the study of various morphological features of $Li_xTi_{1-x}O_3$ ceramics obtained by solid-phase synthesis and subsequent thermal annealing. Interest in these ceramics is due to the great potential for their use as materials for breeders or blankets for tritium reproduction. The choice of synthesis technology is due to the wide possibilities of changing morphological features and elemental composition, due to mixing of various components in different stoichiometric ratios. During the research, it was found that for lithium-containing ceramics, thermal annealing at a temperature of 800°C leads to the following changes: for ceramics with a lithium content of X=0.1-0.2, a change in shape is observed from rhomboid and cubic to diamond-like and hexahedral, with a sharp increase in grain sizes, which is associated with sintering processes. An increase in lithium concentration in the ceramic structure of X=0.3 leads to the formation of large grains, the size of which varies from 300 nm to 500 nm.

Key words: lithium-containing ceramics, solid-phase synthesis, titanium dioxide, agglomerates, thermal annealing.

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Қатты фазалық синтез арқылы алынған литий бар керамиканың морфологиялық ерекшеліктерін зерттеу

Бұл жұмыс қатты фазалық синтез және кейінгі термиялық күйдіру арқылы алынған $Li_xTi_{1-x}O_3$ керамикасының әртүрлі морфологиялық ерекшеліктерін зерттеуге арналған. Бұл керамикаға деген қызығушылық оларды бридерге арналған материалдар немесе тритийді көбейту үшін бланкеттер ретінде пайдаланудың үлкен әлеуетіне байланысты. Синтез технологиясын таңдау әртүрлі стехиометриялық қатынастардағы әртүрлі компоненттердің араласуына байланысты морфологиялық белгілер мен элементтер құрамының өзгеруінің кең мүмкіндіктеріне байланысты. Зерттеу барысында литий бар керамика үшін 800°C температурада термиялық күйдіру келесі өзгерістерге әкелетіні анықталды: литий X = 0.1 – 0.2 бар керамика үшін форманың кубтан гауһар тәрізді және алтыбұрышқа дейін өзгеруі байқалады, бұл түйірлердің мөлшерінің күрт артуымен байланысты. Сонымен қатар, барлық концентрациялар үшін форманың сфералық немесе дендрид тәріздіден ромбоид немесе кубқа өзгеруі байқалады. Пішіннің мұндай өзгеруі тордағы атомдардың жылу тербелістерінің өзгеруі нәтижесінде пайда болатын фазалық айналдыру процестерінің басталуымен, сондай-ақ нүктелік ақаулар мен қызуға байланысты. Керамикалық құрылымдағы литий концентрациясының жоғарылауы X = 0.3 үлкен дәндердің пайда болуына әкеледі, олардың мөлшері 300 нм-ден 500 нм-ге дейін.

Түйін сөздер: құрамында литий бар керамика, қатты фазалы синтез, титан диоксиді, агломераттар, термиялық күйдіру.

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Исследование морфологических особенностей литийсодержащих керамик, полученных методом твердофазного синтеза

Данная работа посвящена исследованию различных морфологических особенностей $Li_xTi_{1-x}O_3$ керамик, полученных методом твердофазного синтеза и последующего термического отжига. Интерес к данным керамикам обусловлен большим потенциалом их применения в качестве материалов для бридеров или бланкетов для размножения трития. Выбор технологии синтеза обусловлен широкими возможностями изменения морфологических особенностей и элементным составом, за счет смешивания различных компонент в разных стехиометрических соотношениях. В ходе проведенных исследований, было установлено, что для литийсодержащих керамик термический отжиг при температуре 800°С приводит к следующим изменениям: для керамик с содержанием лития X=0.1-0.2 наблюдается изменение формы с ромбовидной и кубической на алмазоподобную и шестигранную, с резким увеличением размеров зерен, которое связано с процессами спекания. При этом для всех концентраций наблюдается изменение формы от сферической или дендридоподобной до ромбовидной или кубической. Такое изменение формы связано с инициированием процессов фазовых превращений, происходящих в результате изменения тепловых колебаний атомов в решетке, а также с отжигом точечных дефектов и нагревом. Увеличение концентрации лития в структуре керамик выже X=0.3 приводит к образованию больших зерен, размеры которых варьируют в пределах от 300 нм до 500 нм.

Ключевые слова: литийсодержащие керамики, твердофазный синтез, диоксид титана, агломераты, термический отжиг.

Introduction

The use of new types of materials for thermonuclear reactors requires special attention to assess their applicability, temperature drop resistance, high-dose radiation load, mechanical strength and resistance to degradation [1-5]. In case of thermonuclear reactors, one of the key points affecting the operability of the reactor is the accumulation and generation of tritium in the reactor system, as well as control over its transportation and retention [6-10]. At the same time, one of the most effective methods of controlling the rate of tritium accumulation is the use of lithium-containing ceramics, the use of which allows to significantly increase the efficiency of tritium generation, as well as significantly reduce the probability of emergency situations to a minimum and significantly increase the safety of thermonuclear reactors [11-13].

The use of lithium-containing ceramics as a basis for thermonuclear blankets (breeders) is the most promising material for these purposes, interest in them is due to such characteristics as a high release coefficient of tritium, good indicators of thermophysical and thermomechanical properties, the ability to withstand prolonged exposure to radiation, in particular neutron radiation, as well as high temperatures, with different temperature gradients [13-15]. At the same time, high thermal stability and chemical stability to external influences makes lithium-containing ceramics, such as Li_2O, $LiAlO_3$, Li_2TiO_3, Li_2ZrO_3, Li_4SiO_4, the best candidates for materials for fusion reactors in terms of durability and radiation safety [16-20].

Based on the above, the aim of this work is to comprehensively study the effect of stoichiometry and sintering temperature on the geometry and shape of particles based on $Li_xTi_{1-x}O_3$ ceramics obtained by solid-phase synthesis.

Experimental part

Solid-phase synthesis was chosen as a method for preparing lithium-containing ceramics with various variations of lithium and titanium. This method is the most effective method for producing ceramics with uniform size distribution and phase composition. The method is based on grinding the initial salts in specified stoichiometric ratios in a planetary mill or agate mortar to obtain a powder that is uniform in consistency. At the same time, the use of planetary mills, in contrast to agate mortars, makes it possible to carry out phase transformations and obtain solid substitution solutions, as well as to grind powders to nanoscale.

For the synthesis of lithium-containing ceramics $Li_xTi_{1-x}O_3$, TiO_2 and $LiClO_4\cdot 3H_2O$ (99.99 % Sigma Aldrich) were used as initial salts in specified stoichiometric ratios. The content of component x varied from 0.1 to 0.5. After weighing, the initial mixture was mixed in an agate mortar, and after a planetary mill at a speed of 400 rpm for an hour. The choice of the grinding time and the number of revolutions is due to the prevention of thermal heating and sintering of the samples during grinding.

After mixing and grinding, the obtained samples were subjected to thermal annealing in an oxygen-containing atmosphere in the temperature range from 400 to 1000°C for 5 hours. The samples were cooled down together with a muffle furnace until reaching room temperature. The choice of isochronous annealing in such a wide temperature range is due to the possibility of initiation of phase transformation processes, as well as the formation of stable Li_2TiO_3 phases in various structural modifications.

The analysis of morphological features and the size and shape of particles was carried out using the method of scanning electron microscopy (JEOL JEM – 1400 Plus, JEOL, Japan).

Results and discussion

Figure 1 shows SEM images of the studied lithium-containing ceramics after grinding in a planetary mill with different lithium concentrations.

As can be seen from the presented data, an increase in the lithium content in the structure results into an increase in the grain size and their coarsening. For samples with X=0.1, the average grain size varies from 20 to 50 nm, and the formation of dendrite-like agglomerates of irregular shape is observed. An increase in the concentration of lithium X=0.2-0.3 leads to an enlargement of the size up to 70-100 nm, and a rise in the number of dendritic structures. For samples with a concentration of X=0.4-0.5, the formation of diamond-shaped and spherical particles is observed, the size of which varies from 50 to 120 nm. At the same time, for these grains, the formation of small growths in the form of spherical particles, the size of which does not exceed 10-15 nm, is observed.

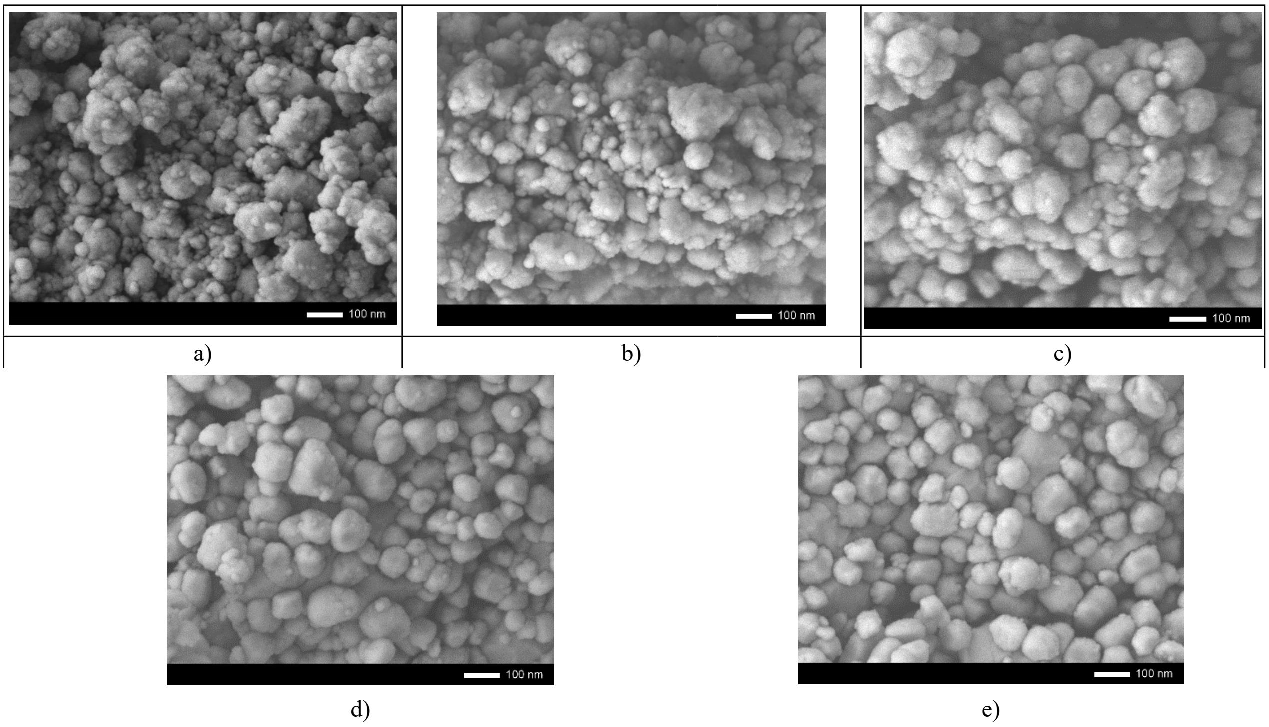


Figure 1 – SEM images of lithium-containing ceramics with different lithium content in the structure: a) X=0.1; b) X=0.2; c) X=0.3; d) X=0.4; e) X=0.5

Thus, it has been established that an increase in the concentration of lithium in ceramics upon grinding under specified conditions leads to structural transformations and a change in the morphology of ceramics grains, which, in turn, can be associated with phase transformations and changes in the structural parameters, as well as the density of ceramics.

Figure 2 shows the results of changes in the morphology of ceramics during thermal annealing at a temperature of 400°C for 5 hours.

According to the data presented in Figure 2, the grain morphology at an annealing temperature of 400°C does not undergo changes, which indicates the absence of sintering processes at this temperature. Figure 3 shows SEM images of lithium-containing ceramics after annealing at 600°C.

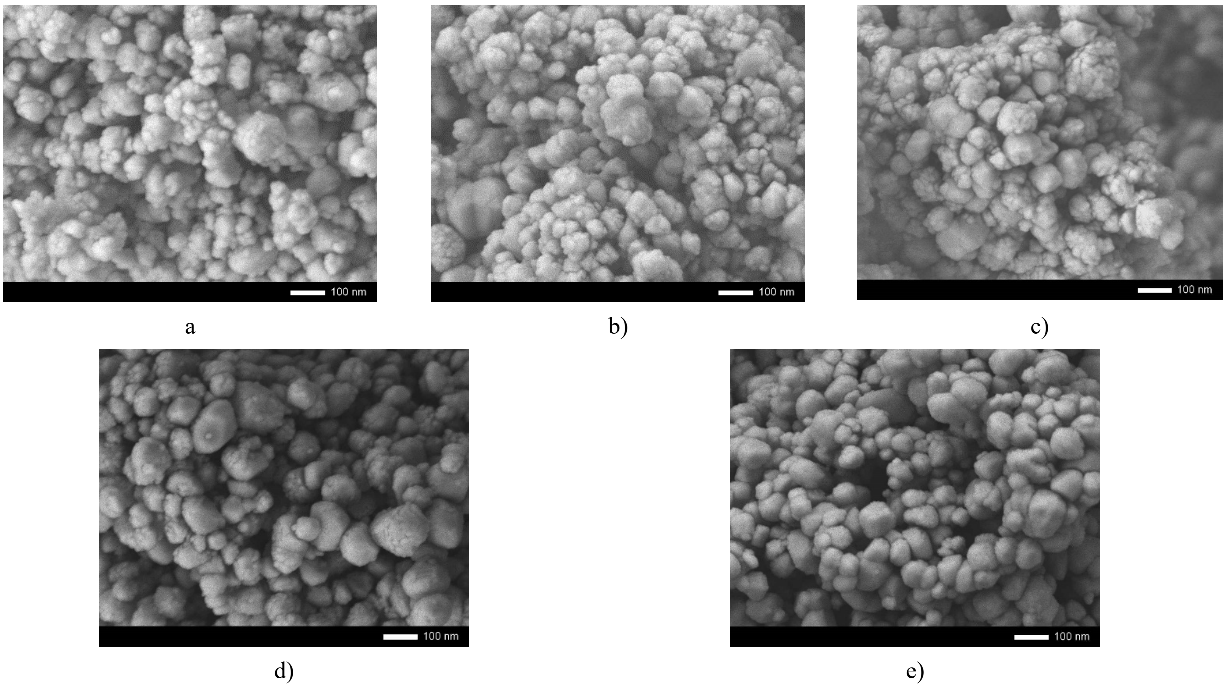


Figure 2 – SEM images of lithium-containing ceramics with different lithium content in the structure after annealing at 400°C: a) X=0.1; b) X=0.2; c) X=0.3; d) X=0.4; e) X=0.5

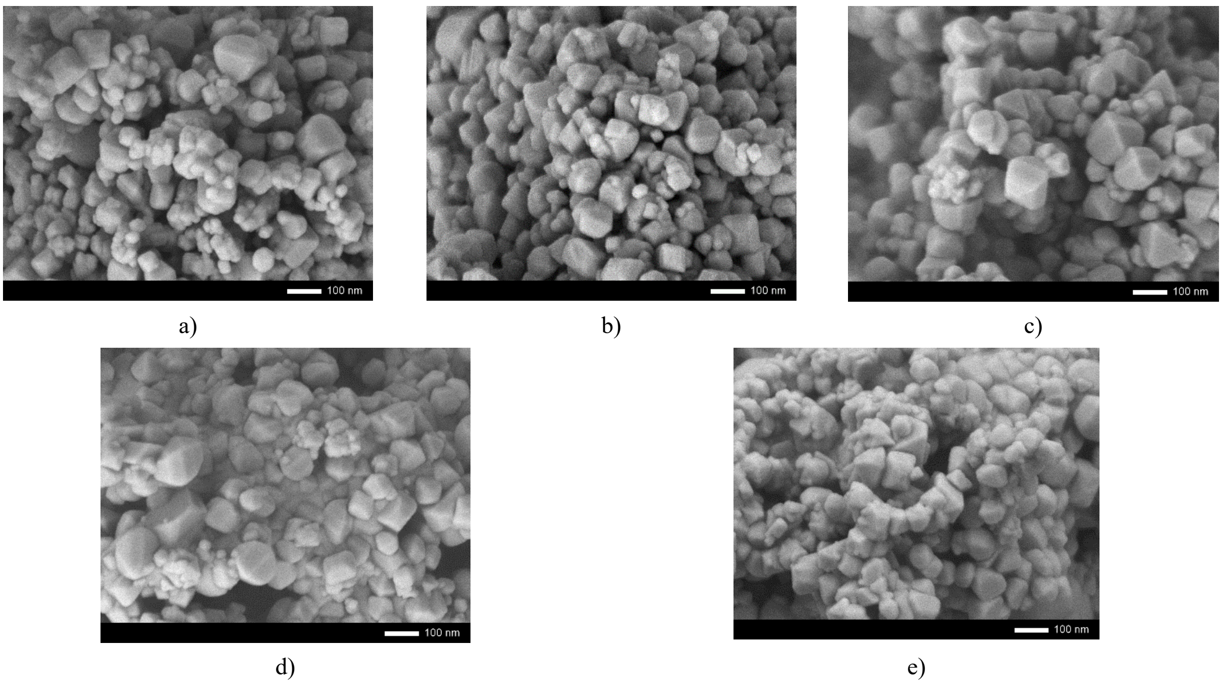


Figure 3 – SEM images of lithium-containing ceramics with different lithium content in the structure after annealing at 600°C: a) X=0.1; b) X=0.2; c) X=0.3; d) X=0.4; e) X=0.5

In contrast to the samples annealed at a temperature of 400°C, for which no change in grain morphology was observed, for the samples annealed at a temperature of 600°C, changes are observed associated with both a change in shape and size. For all concentrations, a change in shape from spherical or dendrid-like to rhomboid or cubic is observed. This change in shape is associated with the initiation of phase transformation processes that occur as a result of changes in thermal vibrations of atoms in the lattice, as well as the annealing of point defects and heating. Also, a change in shape leads to crushing of the grains and a decrease in their size.

Figure 4 shows the data on changes in the grain morphology of lithium-containing ceramics as a result of thermal annealing at a temperature of 800°C.

As can be seen from the presented data, for lithium-containing ceramics, thermal annealing at a temperature of 800°C leads to the following changes: for ceramics with a lithium content X=0.1-0.2, a change in shape is observed from rhomboid and cubic to diamond-like and hexagonal, with a sharp increase in grain size, which associated with sintering processes. An increase in the concentration of lithium in the structure of ceramics higher than X=0.3 leads to the formation of large grains, the size of which varies from 300 nm to 500 nm. In this case, grains are sintered into large dendrid-like structures.

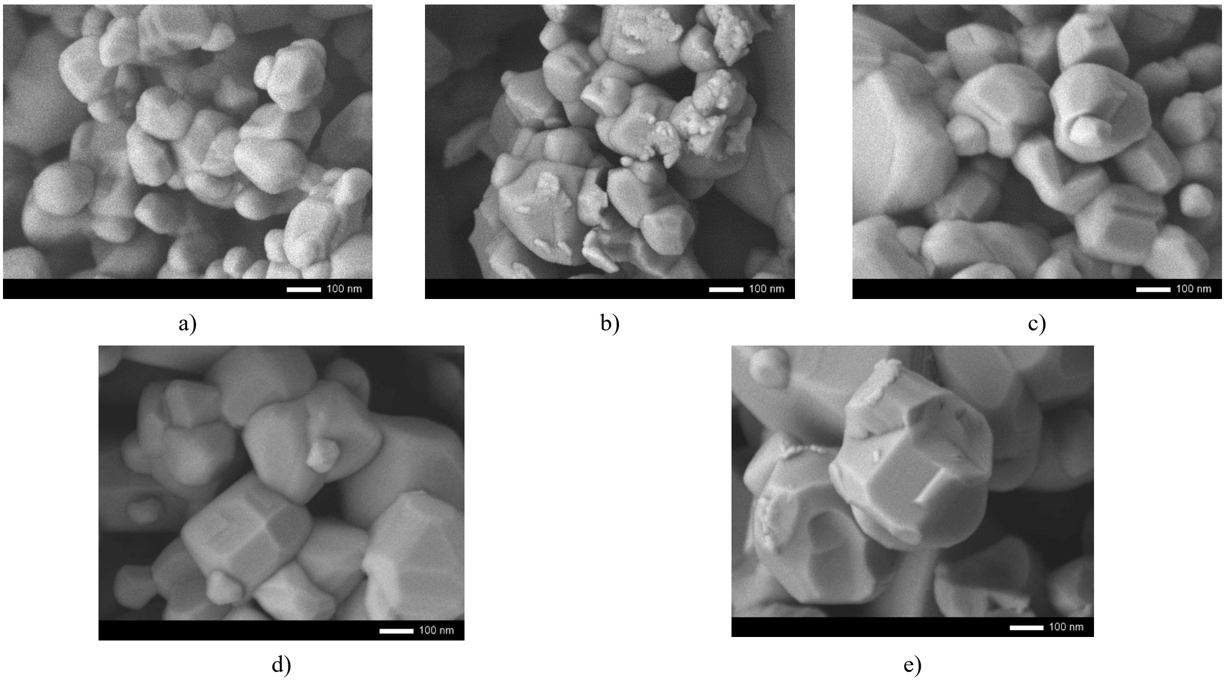


Figure 4 – SEM images of lithium-containing ceramics with different lithium content in the structure after annealing at 800°C: a) X=0.1; b) X=0.2; c) X=0.3; d) X=0.4; e) X=0.5

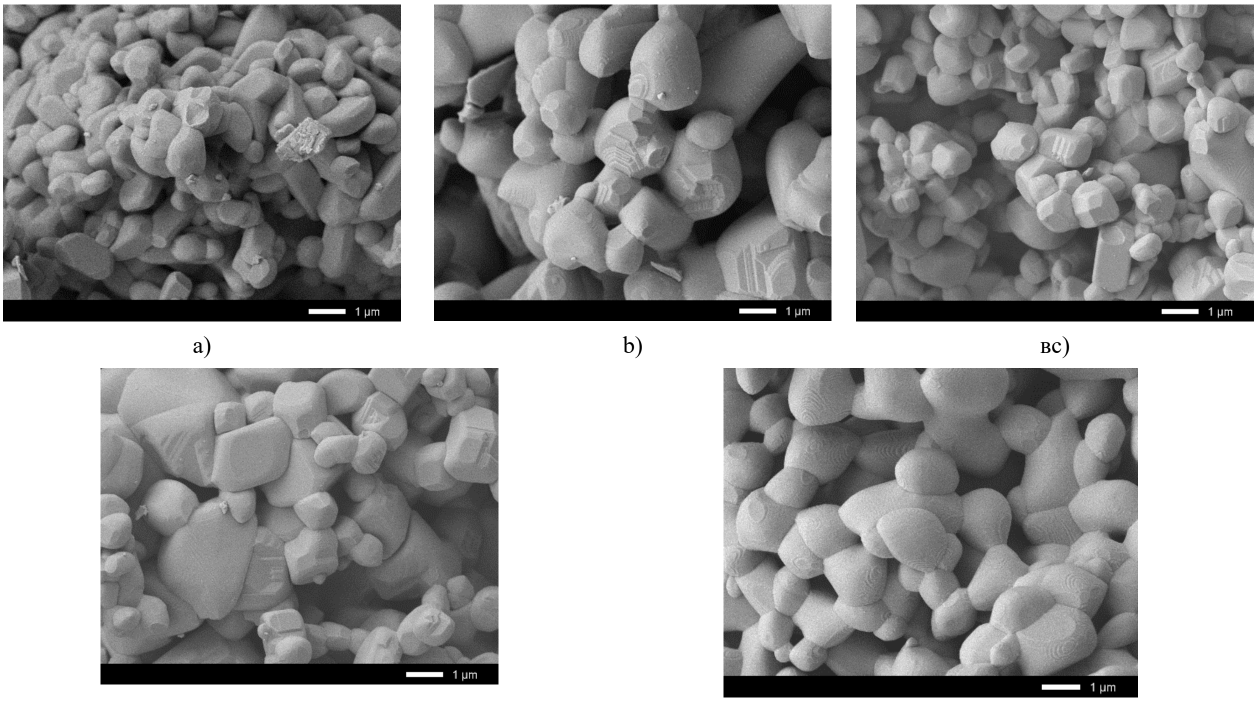
Figure 5 shows SEM images of lithium-containing ceramics annealed at 1000°C.

A further increase in the annealing temperature to 1000°C leads to sintering of ceramics into large agglomerates and enlargement of grain sizes, which reach up to 1-5 μm in transverse size.

Conclusion

Thus, during the experiments on synthesis, the effect of both the annealing temperature and the concentration of lithium in the structure of ceramics on the grain size and shape was established. Thermal annealing was carried out in an oxygen-containing atmosphere in the temperature range from 400 to 1000°C for 5 hours.

It was found that for all lithium concentrations at a temperature of 600°C, a change in shape from spherical or dendrid-like to diamond-shaped or cubic is observed. This change in shape is associated with the initiation of phase transformation processes that occur as a result of changes in thermal vibrations of atoms in the lattice, as well as the annealing of point defects and heating.



a) b) вс)

d) e)

Figure 5 – SEM images of lithium-containing ceramics with different lithium content in the structure after annealing at 1000°C: a) X=0.1; b) X=0.2; c) X=0.3; d) X=0.4; e) X=0.5

It was found that for lithium-containing ceramics, thermal annealing at a temperature of 800°C leads to the following changes: for ceramics with a lithium content X=0.1-0.2, a change in shape is observed from rhomboid and cubic to diamond-like and hexagonal, with a sharp increase in the grain size, which is associated with the processes sintering. An increase in the concentration of lithium in the structure of ceramics higher than X=0.3 leads to the formation of large grains, the size of which varies from 300 nm to 500 nm.

Funding

This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (No. AP08855734).

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