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X-RAY ANALYSIS OF $Li_{2-x}Na_xGe_4O_9$ CRYSTALS

X-ray phase analysis is carried out for $Li_{2-x}Na_xGe_4O_9$ crystals with different values of *x*. X-ray diffraction is studied in monochromatic Cu K*α* radiation. Unit cell parameters are calculated by the main interference maxima of $LiNaGe_4O_9$ system. It is found that for large *x* values the lattice parameters vary slightly. Starting with *x* = 0.4, a marked decrease of the parameters is observed. The minimal values of the lattice parameters are determined for compound with *x* = 0.21, for which intensity of the reflexes corresponding to $LiNaGe_4O_9$ decreases, and the peaks characteristic for $Li_2Ge_7O_{15}$ compound appear. Two-phase composition does not enable to grow single crystals with *x* < 0.2. Anomalies of the concentration dependence of the lattice parameters for x values in the range 0.4 - 0.2 correlate with the data of studying dielectric properties of $Li_{2-x}Na_xGe_4O_9$ crystals. The results are discussed on the basis of structural features. Reduction in the number of sodium ions with *x* decreasing in $Li_{2-x}Na_xGe_4O_9$ leads to the experimentally observed changes of the lattice parameters.

Keywords: germanogermanates, $Li_{2-x}Na_xGe_4O_9$ crystals, X-ray phase analysis.

Проведено рентгенофазовий аналіз кристалів системи $Li_{2-x}Na_xGe_4O_9$ для різних значень *x*. Дифрактометричні досліди проводились у монохроматичному випромінюванні Cu K*α*. Параметри елементарної ґратки розраховувались за основними інтерференційними максимумами системи $LiNaGe_4O_9$. Виявлено, що в області великих значень *x* параметри ґратки змінюються не значно. Помітне зменшення параметрів спостерігалось, починаючи з *x* = 0.4. Мінімальне значення параметрів ґратки відзначалось для складу з *x* = 0.21, для якого зменшується інтенсивність максимумів, що відповідають складу $LiNaGe_4O_9$, і з'являються піки, які характерні для складу $Li_2Ge_7O_{15}$. Двофазність складу не дозволяє отримати монокристали з величинами *x* < 0.2. Аномалії концентраційної залежності параметрів ґратки для значень *x* в області 0.4 - 0.2 корелюють із даними вивчення діелектричних властивостей кристалів $Li_{2-x}Na_xGe_4O_9$. Отримані результати обговорюються з урахуванням особливостей структури досліджуваних кристалів. Зниження вмісту іонів натрію при зменшенні *x* у складах $Li_{2-x}Na_xGe_4O_9$ призводить до змін параметрів ґратки, які спостерігаються експериментально.

Ключові слова: германогерманати, кристали $Li_{2-x}Na_xGe_4O_9$, рентгенофазовий аналіз.

Проведен рентгенофазовый анализ кристаллов системы $Li_{2-x}Na_xGe_4O_9$ для различных значений *x*. Дифрактометрические исследования осуществлялись в монохроматическом излучении Cu K*α*. Параметры элементарной ячейки рассчитывались по основным интерференционным максимумам системы $LiNaGe_4O_9$. Обнаружено, что в области больших значений *x* параметры решетки изменяются незначительно. Заметное уменьшение параметров наблюдалось, начиная с *x* = 0.4. Минимальные значения параметров решетки отмечаются для состава с *x* = 0.21, для которого уменьшается интенсивность максимумов, соответствующих составу $LiNaGe_4O_9$, и появляются пики, которые характерны для состава $Li_2Ge_7O_{15}$. Двухфазность состава не позволяет получить монокристаллы с величинами *x* < 0.2. Аномалии концентрационной зависимости параметров решетки для значений *x* в области 0.4 - 0.2 коррелируют с данными изучения диэлектрических свойств кристаллов $Li_{2-x}Na_xGe_4O_9$. Полученные результаты обсуждаются с учетом особенностей структуры исследуемых кристаллов. Снижение содержания ионов натрия при уменьшении *x* в составах $Li_{2-x}Na_xGe_4O_9$ приводит к наблюдаемым экспериментально изменениям параметров решетки.

Ключевые слова: германогерманаты, кристаллы $Li_{2-x}Na_xGe_4O_9$, рентгенофазовый анализ.

1 Introduction

The structural framework of single crystals of the family of germanogermanates is formed by germanium tetrahedral and octahedral complexes. The monovalent cations Li^+ and Na^+ are located in the cavities of Ge-O structural skeleton. The single crystals of $LiNaGe_4O_9$ - $Li_2Ge_4O_9$ ($Li_{2-x}Na_xGe_4O_9$, $0 \le x \le 1$) series undergo the ferroelectric phase transition (PT), and therefore are studied in more details. By now there are papers devoted to study of dielectric [1-3], thermal [4] and structural [5, 6] properties of $LiNaGe_4O_9$ (LNG) crystal.

At room temperature, LNG has an orthorhombic structure with a space symmetry group D_{2h}^{8} [5]. The unit cell contains four formula units and has the following parameters: a = 9.31, b = 4.68 and c = 15.88 Å. The ferroelectric PT in LNG was studied by neutron diffraction [7]. It was shown that the low-temperature structure belongs to the orthorhombic space group C_{2v}^{5} with Z = 4. The PT is accompanied by ordering of Li and Na atoms in one of two equiprobable above T_C positions, while the ordering mechanisms for Li and Na are different [7]. In addition, in the ferroelectric phase there is a slight translation of germanate groups perpendicular to the direction of spontaneous polarization P_S [7].

Further studies were devoted to influence of Li–Na non-stoichiometry on the properties of $LiNaGe_4O_9$ - $Li_2Ge_4O_9$ crystals. It was found anomalously high, non-monotonic shift of the PT temperature T_C with a change of x in $Li_{2-x}Na_xGe_4O_9$ system [8]. On x decreasing from 1 to 0.3, T_C increases linearly with a factor 2 K /%, where x = 1 corresponds to 100%. In a concentration range $0.2 \le x \le 0.3$, T_C shifts with concentration x more considerably – with a factor 4.5 K /%. Within the latter x range unusual nonlinear dielectric and polarization properties of $Li_{2-x}Na_xGe_4O_9$ crystals were detected [9-11]. As it was noted in [5], smooth changes of the lattice parameters make it possible to believe that there is a series of solid solutions in $LiNaGe_4O_9$ - $Li_2Ge_4O_9$ series. However, all attempts to grow $Li_{2-x}Na_xGe_4O_9$ single crystals in a range $0 < x < 0.2$ were unsuccessful [8].

The aim of this work is to study X-ray diffraction of $Li_{2-x}Na_xGe_4O_9$ single crystals in a wide range of concentration x.

2 Results and discussion

Single crystals of $Li_{2-x}Na_xGe_4O_9$ series were grown from a melt by Czochralski method. Stoichiometric mixtures of lithium, sodium and germanium oxides, corresponding to certain x value, were used as starting reagents. Obtained single crystals are up to 30 mm length. The crystals grown have good optical quality for x range from 1 to 0.21. Crystal boules are visually identical, clear, and colorless and have no colored inclusions. As it was mentioned above, growing of single crystals with sufficient quality for concentrations $x \le 0.15$ failed. For this x range boules consist of non-transparent milk-white color blocks. Some of these blocks have a pinkish color and pronounced facets. For $x \le 0.15$ differential thermal analysis shows presence of two different phases. The phase composition of $Li_{2-x}Na_xGe_4O_9$ crystals ($x \le 0.15$) was studied by X- ray diffraction by using of DRON 2.0 diffractometer operating with monochromatic Cu - Kα radiation. Fine powders, prepared from $Li_{2-x}Na_xGe_4O_9$ single crystals (x = 1, 0.02, 0.15, 0.21, 0.3, 0.4, 0.6, 0.8), were used as the samples.

Figures 1 and 2 show the diffraction patterns measured. Basic reflexes are identified with using ASTMPDF2 files.

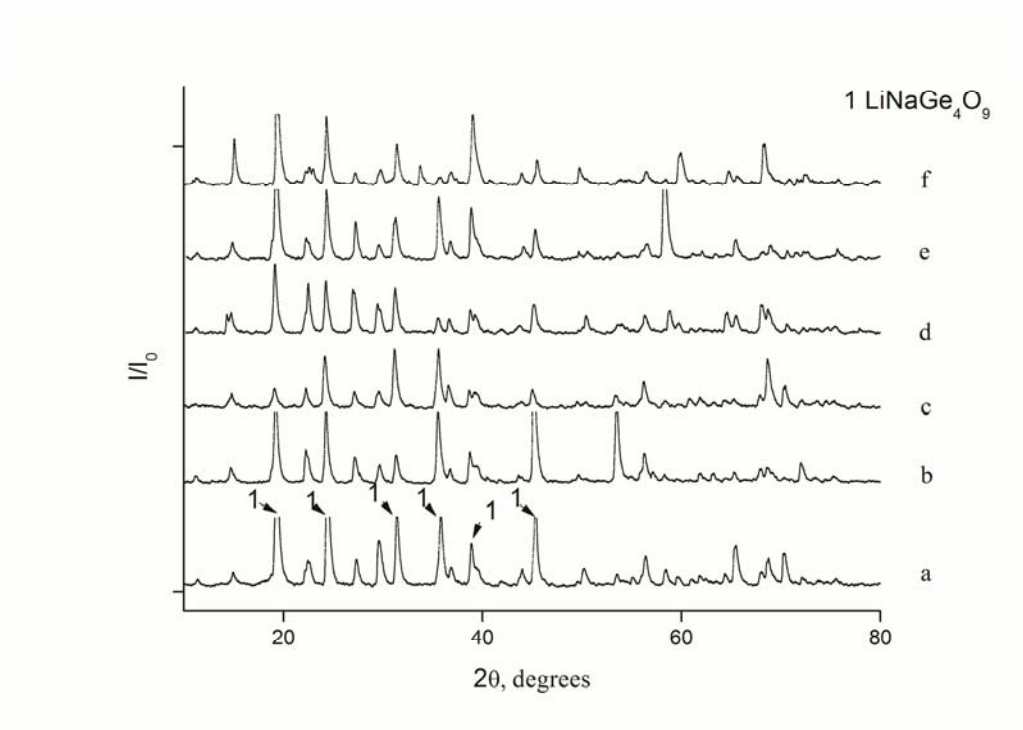

Fig.1 Diffraction patterns of $Li_{2-x}Na_xGe_4O_9$ with x = 1 (a) 0.8 (b) 0.6 (c) 0.4 (d), 0.3 (e), 0.21 (f), the main reflexes of $LiNaGe_4O_9$ structure are indicated.

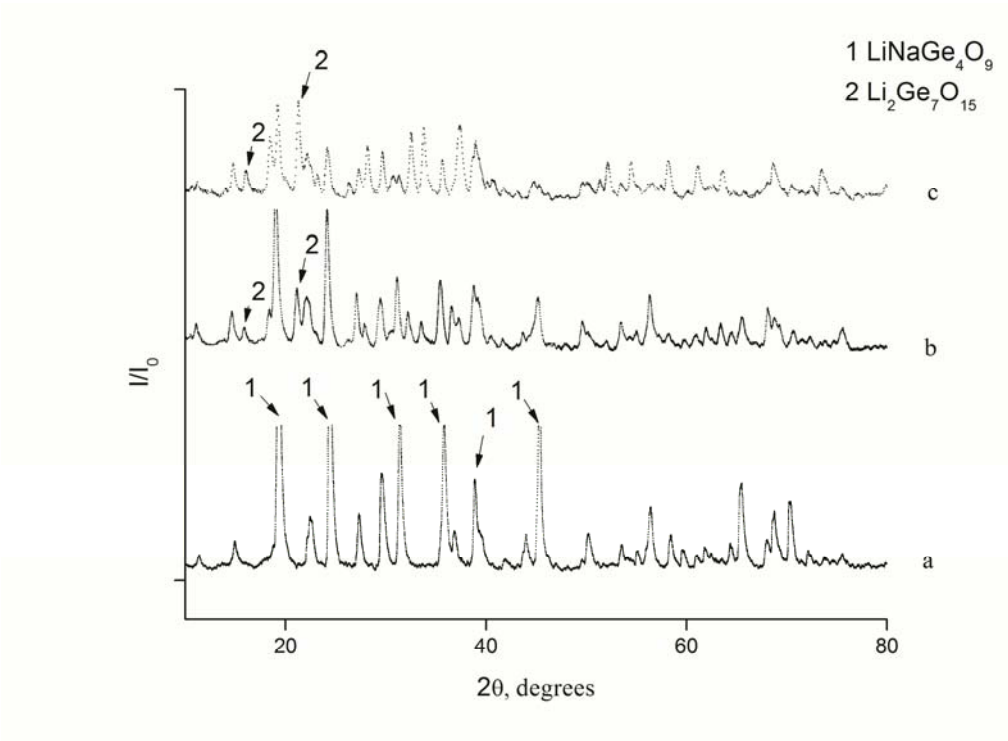

Fig.2 Diffraction patterns of $Li_{2-x}Na_xGe_4O_9$ with x = 1 (a), 0.15 (b), 0.02 (c). The main reflexes from $LiNaGe_4O_9$ and $Li_2Ge_7O_{15}$ structures are indicated.

The main reflexes in the diffraction patterns of the investigated samples practically do not shift or smear on x decreasing. Slight decrease of the main signals intensities is observed only for high angles 2θ (Fig. 1). For small x values the character of the diffraction pattern becomes somewhat different. As it can be seen from Figure 2, intensity of $LiNaGe_4O_9$ main peaks decreases. At the same time additional peaks from $Li_2Ge_7O_{15}$ structure arise. Increase of the peaks intensities shows that part of the new phase grows on x decreasing. However, even for x = 0.02 diffraction maxima from $LiNaGe_4O_9$, are observed, though their intensities decrease considerably.

Diffraction patterns are identified in orthorhombic crystal system. The dependences of the unit cell parameters on x are shown in Fig.1 for all samples studied. Calculations were performed by using of positions of the main peaks of $LiNaGe_4O_9$ structure. It can be seen, that at high x the unit cell parameters vary slightly. But in the x range from 0.4 to 0.2 unit cell parameters decrease with x more sufficiently. The minimal parameters values are observed for x = 0.21.

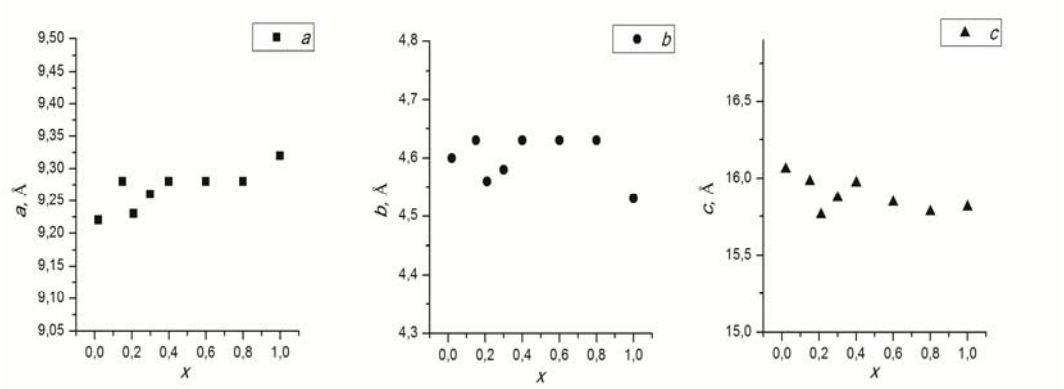

Fig. 3 The dependences of $Li_{2-x}Na_xGe_4O_9$ unit cell parameters *a, b, c* on concentration *x*.

Some specific features of $Li_{2-x}Na_xGe_4O_9$ crystals characteristics were pointed out in previous paper [8]. In particular, for compound with x = 0.2, temperature dependence of dielectric constant changes its character, whereas ε_{max} value decreases in about 3 times. Furthermore, in the range x = 0.3 - 0.2 the trend of PT temperature growing with x decreasing is changed. X-ray diffraction study shows that just in the same range of concentrations unit cell parameters demonstrate anomalous behavior and two phases $LiNaGe_4O_9$ and $Li_2Ge_7O_{15}$ coexist. Earlier it was noted, that germanates tend to form loose structural frameworks, which contain more positions for cations, than it is required for stoichiometric compositions [5]. Therefore, in the $Li_2Ge_4O_9$ - $LiNaGe_4O_9$ system Li ions can occupy not only the position of substituted sodium ions, but some new own positions. It is probable, that decreasing of sodium ions content in $Li_{2-x}Na_xGe_4O_9$ on x decreasing leads to release of these positions and, consequently, to decrease of the unit cell parameters.

3 Conclusions

Direct study of $Li_{2-x}Na_xGe_4O_9$ crystal structure by X-ray diffraction methods confirms that for compounds with x < 0.2 a new $Li_2Ge_7O_{15}$ phase arises and two phase system is formed. Changes of the lattice parameters, as well as reported previously anomalous behavior of other physical properties, indicate that $Li_2Ge_7O_{15}$ phase nucleation occurs in the $Li_2Ge_4O_9$ - $LiNaGe_4O_9$ system. For x < 0.2 fraction of additional phase is so significant that does not allow obtaining single crystals.

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