

Electric conductivity of $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ crystals

O.A. Bibikova, M.D. Volnianskii, M.P. Trubitsyn

*Oles' Gonchar Dnipropetrovsk National University,
prosp. Gagarina 72, 49010, Dnipropetrovsk, Ukraine*

Crystals of $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{GeO}_2$ system belong to the germane-germanates family, in which charge transfer is determined by lithium ionic conduction. Conductivity σ of $\text{LiNaGe}_4\text{O}_9$ crystals doped with Cu ions is studied in the paper. Measurements were performed in AC field ($f=1$ kHz) in the temperature interval 300 – 800 K. It is shown that in contrast to the nominally pure crystals, anisotropy of σ in $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ is practically absent and conductivity has near the same values along three main directions. Activation energy of conductivity in $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ crystals are higher, approximately, one and a half times in comparison with nominally pure samples. Influence of Cu doping on temperature behavior $\sigma(T)$ is discussed with the help of EPR spectroscopy data. According to the results of EPR studying, in $\text{LiNaGe}_4\text{O}_9$ lattice lithium ions are substituted for bivalent copper centers $\text{Cu}^{2+} \rightarrow \text{Li}^+$. Lithium or sodium vacancies can compensate excess charge introduced by impurity. It is assumed that doping with Cu ions changes mechanism of charge transfer from interstitial to vacancy.

Keywords: lithium-sodium germane-germanates crystals, impurity ions, ionic conduction.

Кристаллы системы $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{GeO}_2$ принадлежат семейству германо-германатов, перенос заряда в которых определяется ионной проводимостью по литию. В работе исследуется электропроводность σ кристаллов $\text{LiNaGe}_4\text{O}_9$, легированных Cu. Измерения проведены в переменном поле ($f=1$ kHz) в интервале температур 300 – 800 K. Показано, что в отличие от номинально чистых кристаллов, для $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ анизотропия σ практически отсутствует, и электропроводность имеет близкие значения вдоль трех главных направлений. Энергия активации электропроводности в кристаллах $\text{LiNaGe}_4\text{O}_9:\text{Cu}$, примерно, в полтора раза выше по сравнению с номинально чистыми образцами. Влияние примеси Cu на температурное поведение $\sigma(T)$ обсуждается на основе данных ЭПР спектроскопии. Согласно результатам изучения ЭПР, в решетке $\text{LiNaGe}_4\text{O}_9$ двухвалентные центры меди гетеровалентно замещают ионы лития $\text{Cu}^{2+} \rightarrow \text{Li}^+$. В качестве компенсаторов заряда могут выступать вакансии лития либо натрия. Предполагается, что введение примесных ионов Cu приводит к изменению механизма переноса заряда от междоузельного к вакансионному.

Ключевые слова: кристаллы литиево-натриевых германо-германатов, примесные ионы, ионная проводимость.

Кристали системи $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{GeO}_2$ належать до сімейства германо-германатів, перенос заряду в яких визначається іонною провідністю по літію. У роботі досліджується електропровідність σ кристалів $\text{LiNaGe}_4\text{O}_9$, легованих Cu. Виміри проведені в змінному полі ($f=1$ kHz) в інтервалі температур 300 – 800 K. Показано, що на відміну від номінально чистих кристалів, для $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ анизотропія σ практично відсутня, та електропровідність має близькі значення вздовж трьох головних напрямків. Енергія активації електропровідності у кристалах $\text{LiNaGe}_4\text{O}_9:\text{Cu}$, приблизно, у півтора рази вища порівняно з номінально чистими зразками. Вплив домішки Cu на температурну поведінку $\sigma(T)$ обговорюється на основі даних ЕПР спектроскопії. Згідно результатам вивчення ЕПР, у ґратці $\text{LiNaGe}_4\text{O}_9$ двоцвалентні центри міді гетеровалентно заміщують іони літія $\text{Cu}^{2+} \rightarrow \text{Li}^+$. В якості компенсаторів заряду можуть виступати вакансії літія або натрія. Припускається, що введення домішкових іонів Cu призводить до зміни механізму переносу заряду від міжвузольного до вакансійного.

Ключові слова: кристали літєво-натрієвих германо-германатів, домішкові іони, іонна провідність.

Introduction

In recent years an interest to the crystals of germane-germanates family is growing due to the need for new dielectrics with high ionic conductivity. In particular, among the superionics there is a large group of solid solutions based on lithium orthogermanate Li_4GeO_4 . The best known compound of this group is lison $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$ ($x=0.75$), electrical conductivity of which is about $\sigma \sim 0.13 \text{ Ohm}^{-1}\text{cm}^{-1}$ at $T=573 \text{ K}$ [1]. Among the family representatives, the crystals of lithium-sodium germane-germanates $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$, undergoing ferroelectric phase

transition, are actively investigated [2]. Electrical properties of nominally pure $\text{LiNaGe}_4\text{O}_9$ crystals were studied earlier in AC field [3]. Significant anisotropy of σ was observed for $T>500 \text{ K}$. It was shown, that highest conductivity σ was detected for measuring field directed parallel to [001] axis, along which there were structural channels containing Li ions [4]. Conductivity of $\text{LiNaGe}_4\text{O}_9$ crystals doped with Mn and Cr was studied in [5]. It was shown that doping with Mn didn't practically change typical values and character of σ anisotropy. On the contrary, doping with Cr increased σ approximately in one order, anisotropy of σ

remained as in undoped crystals and highest conductivity was detected along [001] direction. Available data showed that in $\text{LiNaGe}_4\text{O}_9$ structure Ge^{4+} host ions located within oxygen octahedra were substituted for Mn^{4+} and Cr^{3+} doping ions [6, 7]. These data allow to suppose that conductivity of $\text{LiNaGe}_4\text{O}_9$ crystals is determined by motion of interstitial lithium ions (A_{Li}).

Conductivity of $\text{LiNaGe}_4\text{O}_9$ crystals doped with Cu is studied in the paper. The data obtained are discussed on the basis of the first results of EPR spectra measuring in $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ crystals.

Experimental results

$\text{LiNaGe}_4\text{O}_9$ single crystals, doped with Cu ions (0.07 wt.%), were grown from the melt by Czochralski method. Conductivity σ was measured in AC field ($f=1\text{kHz}$) by bridge method along main crystallographic directions in the temperature intervals 300–800 K. Samples for σ measuring were prepared as the plates with dimensions $5 \times 5 \times 1 \text{ mm}^3$ and main faces parallel to (100), (010) and (001). Silver electrodes were deposited by vacuum evaporation method. EPR spectra were recorded in X-range frequency by using the serial radiospectrometer.

It is well known, that thermally activated growth of electric conductivity can be described by exponential function

$$\sigma(T) = \frac{A}{T} \cdot \exp\left(-\frac{W}{kT}\right), \quad (1)$$

where proportionality coefficient A depends on carrier's charge, concentration and jump length, W – activation energy of charge transport, k – Boltzmann constant, T – absolute temperature [8]. According to (1), temperature dependences of conductivity in $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ crystals are plotted in fig.1 in Arrhenius scale for measuring

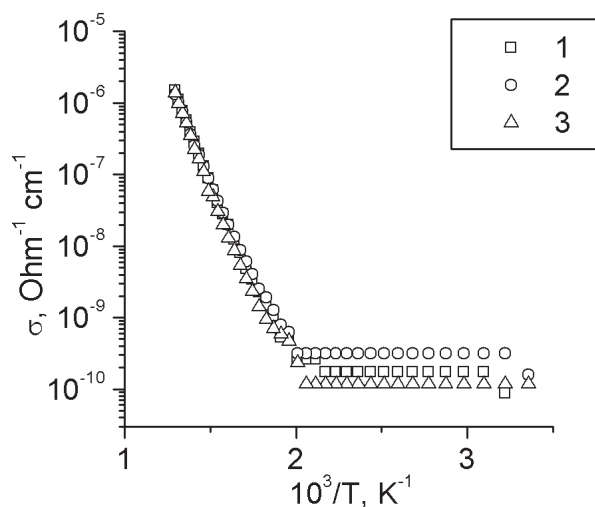


Fig. 1. Dependences $\sigma(1/T)$ for $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ crystals, measured in AC field ($f=1 \text{ kHz}$) along axes: 1 – [100]; 2 – [010]; 3 – [001].

field directed along [100], [010] and [001]. One can see that along main crystallographic directions σ has similar temperature behavior and values. Activation energy of conductivity is about 1.2–1.3 eV at $T > 500 \text{ K}$.

Discussion

It should be noted that for $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ crystals anisotropy of σ is practically absent in contrast to strong anisotropy observed in undoped crystals [3]. Besides the data in fig.1 show that activation energy of conductivity for Cu doped crystals (1.2–1.3 eV) is higher one and a half times, than for nominally pure crystals (0.8–0.9 eV) [3].

Dependencies $\sigma(1/T)$ for nominally pure and Cu doped $\text{LiNaGe}_4\text{O}_9$ crystals are compared in fig.2 ($E_{\parallel[001]}$). It can be seen that in the studied temperature interval for $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ crystals σ is noticeably lower than for undoped crystals. Moreover, greater slope of $\sigma(1/T)$ dependence indicates that comparing with pure crystals, in Cu doped samples charge carriers should overcome higher potential barriers moving between quasi equilibrium positions. Obviously, that small concentration of Cu dopant (0.07 wt.%) cannot change so strongly the potential relief of the structure. One can assume that Cu doping is accompanied by appearance of additional charged defects and causes changing type of the major charge carriers.

The data on Cu ions state and localization in the structure could clarify the mechanism of copper impurity influence on conductivity in $\text{LiNaGe}_4\text{O}_9$ crystals. Such information can be obtained by EPR spectroscopy. EPR spectra, shown in fig.3, evidence that in $\text{LiNaGe}_4\text{O}_9$ lattice copper ions are in bivalent state Cu^{2+} . Accounting the ratio between radiuses and charges of the impurity and host cations in $\text{LiNaGe}_4\text{O}_9$ formula unit ($r_{\text{Cu}^{2+}}=0.72 \text{ \AA}$, $r_{\text{Li}^+}=0.68 \text{ \AA}$, $r_{\text{Na}^+}=0.97 \text{ \AA}$, $r_{\text{Ge}^{4+}}=0.53 \text{ \AA}$), one can assume substitution

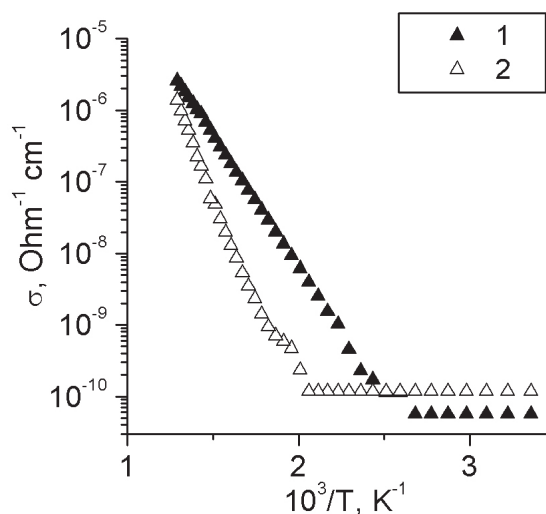


Fig. 2. Dependences $\sigma(1/T)$ for $\text{LiNaGe}_4\text{O}_9$ (1) and $\text{LiNaGe}_4\text{O}_9\text{:Cu}$ (2) crystals, measured along [001] axis.

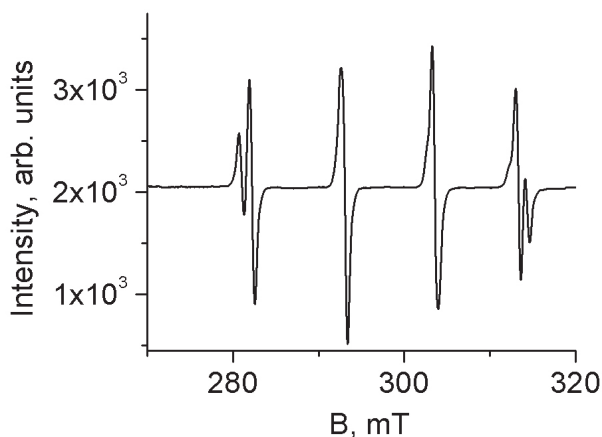


Fig. 3. EPR spectrum of $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ crystals, $B_{\parallel}[001]$, $T=300\text{K}$.

of lithium or sodium for copper ions as the most probable. This assumption was verified by studying the angular dependences of EPR spectra. It was shown that four conjugated Cu^{2+} spectra from structurally equivalent centers were registered for the arbitrary orientations of magnetic field B with respect to the crystal axes. According to [9], magnetic multiplicity $k_m=4$ indicates that paramagnetic centers occupy positions of triclinic point symmetry group C_1 in $\text{LiNaGe}_4\text{O}_9$ lattice (space symmetry group D_{2h}^8). As shown in [4], in $\text{LiNaGe}_4\text{O}_9$ unit cell Li^+ ions are located in the sites with point symmetry C_1 , whereas sodium ions occupy positions of monoclinic symmetry C_2 . Comparing the positional symmetry of the impurity and the host ions, one can suppose substitution of lithium ion for copper one $\text{Cu}^{2+} \rightarrow \text{Li}^+$. In that case, an excess charge introduced by impurity can be compensated by remote vacancies of lithium V_{Li} or sodium V_{Na} .

Thus, heterovalent substitution $\text{Cu}^{2+} \rightarrow \text{Li}^+$ increases concentration of vacancies V_{Li} or V_{Na} . The last ones can act as the traps for interstitials A_{Li} , mobility of which determines conductivity in undoped $\text{LiNaGe}_4\text{O}_9$ crystals [5]. Obviously, concentration of copper dopant significantly exceeds equilibrium content of A_{Li} for studied temperature interval. Therefore in $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ crystals lithium interstitials are captured effectively and concentration of A_{Li} significantly decreases. Oppositely, content of vacancies V_{Li} or V_{Na} is significantly higher than equilibrium one, it is determined by dopant concentration and weakly depends on temperature. It seems obvious, that V_{Li} hopping from the regular position to the neighboring free site should overcome more high potential barriers in comparison with motion of A_{Li} through quasi-equilibrium interstitial sites. Considering noticeable difference in activation energies (fig.2) and all mentioned above, one can assume that charge transfer in doped $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ crystals is determined by mobile vacancies V_{Li} or/and V_{Na} in contrast with A_{Li} interstitials conduction regime in undoped crystals.

Conclusions

The results obtained show that Cu doping significantly affects conductivity of $\text{LiNaGe}_4\text{O}_9$ crystals. Unlike nominally pure crystals, conductivity of $\text{LiNaGe}_4\text{O}_9:\text{Cu}$ is almost independent of the measuring field direction. Activation energy of conductivity in the doped crystals is higher one and a half times than in the undoped samples.

Study of EPR spectra allow to suppose that in $\text{LiNaGe}_4\text{O}_9$ lattice lithium host ions are substituted for bivalent copper Cu^{2+} ones. The excess charge introduced by heterovalent substitution $\text{Cu}^{2+} \rightarrow \text{Li}^+$ can be compensated by vacancies V_{Li} or/and V_{Na} which are surplus with respect to equilibrium vacancy content. Based on the EPR data it is supposed that doping $\text{LiNaGe}_4\text{O}_9$ crystals with copper changes charge transfer mechanism from the interstitial to the vacancy.

1. Yu.Ya. Gurervich, Yu. I. Kharkatz. *Superionnye provodniki*, Nauka, M. (1992), 288 p.
2. M.D. Volnianskii, A.Yu. Kudzin, V.F. Katkov. *FTT*, 34, 1, 309 (1992).
3. M.D. Volnianskii, M.P. Trubitsyn, O.A. Bibikova. *Ferroelectrics*, 443, 16 (2013).
4. H. Völlenkle, A. Wittmann, H. Nowotny. *Monatshefte für Chemie*, 100, 79 (1969).
5. M.D. Volnianskii, O.A. Bibikova, M.P. Trubitsyn, *Vestnik KhNU*, 1076, 13 (2013).
6. K.S. Omelchenko, O.V. Khmelenko, T.V. Panchenko, M.D. Volnianskii. *Physics of the Solid State*, 56, 4, 751 (2014).
7. A. Jasik, M. Berkowski, S. M. Kaczmarek, A. Suchocki, A. Kaminska, G. Leniec, P. Nowakowski, V. Domukhovski. *Cent. Eur. J. Phys.*, 10(2), 506 (2012).
8. Yu.M. Poplavko. *Fizika dielektrikov. Vyscha shkola*, K. (1980), 400 p.
9. M.L. Meilman, M.I. Samoilovich. *Vvedenie v spektroskopiyu EPR aktivirovannyh monokristallov*. Atomizdat, M. (1977), 272 p.