Effect of Cr and Mn doping on ferroelectric and dielectric properties of Li$_{1.72}$Na$_{0.28}$Ge$_4$O$_9$ single crystals

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**Effect of Cr and Mn doping on ferroelectric and dielectric properties of Li$_{1.72}$Na$_{0.28}$Ge$_4$O$_9$ single crystals**

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Li$_{1.72}$Na$_{0.28}$Ge$_4$O$_9$ single crystals pure and slightly doped with chromium and manganese, obtained by Czochralski growth, were investigated for their ferroelectric and dielectric properties. The change in stoichiometry of Li$_{2-x}$Na$_x$Ge$_4$O$_9$ ($x = 0.28$) crystals doped with Cr and Mn (0.1 mol.%) had an influence on the value of ferroelectric-to-paraelectric phase transition temperature, $T_c$. The applied doping affects the $T_c$ value by no more than 10 K. Moreover, we observed strong anisotropy of physical properties of lithium tetragermanate crystals. It has been found that Li$_{1.72}$Na$_{0.28}$Ge$_4$O$_9$ crystal doped with transition metal ions reveals ferroelectric activity in the $b$-crystallographic direction, (010 in $Pcma_2_1$ space group), below $T_c = 260$ K. This activity, measured by the value of electrical permittivity, is much less for doped crystals than pure ones. Dielectric permittivity $\varepsilon'$, conductivity and loss tangent of the crystals, all as the function of temperature in the range of 113–433 K, at frequency between 1 Hz to 1 MHz were measured. The values of conductivity activation energies, $E_a$, were estimated. Hysteresis loops as well as coercive field and spontaneous polarization were measured and calculated. Switching current transients were analyzed.

**Keywords:** ferroelectric properties; dielectric properties; tetragermanate single crystals; doping

1. Introduction

Li$_{2-x}$Na$_x$Ge$_4$O$_9$ ($0 < x < 1$) single crystals pure and doped reveal ferroelectric properties. The LiNaGa$_3$O$_9$ ($x = 1$), has been studied in most detail [1–4] ($T_c = 110$ K). In this compound critical slowing down of the polarization relaxation process at frequencies below 1 kHz and a Debye frequency dispersion has been observed in the megahertz range near the phase transition [2]. The spontaneous polarization of LiNaGa$_3$O$_9$ crystal can be considered as the order parameter [5]. Due to the small values of dielectric permittivity, spontaneous polarization and Curie–Weiss temperature the Li$_{2-x}$Na$_x$Ge$_4$O$_9$ can be classified as pseudoproper [6] or weak [7] ferroelectric. Pure single crystals with $x = 0.23$ composition were analyzed previously by Kudzin et al. [8]. Below, $x = 0.2$ single crystals of

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the above stoichiometry show multiphase structure and could not be obtained as single crystals. Up to now mainly pure crystals were investigated for its dielectric properties. The phase temperature transition, $T_c$, in the crystals very strongly depends on a composition and slightly on a kind of doping. For $\text{Li}_2\text{Ge}_4\text{O}_9$ ($x=0$) it is $\sim180$ K while for $\text{Li}_{1.8}\text{Na}_{0.2}\text{Ge}_4\text{O}_9$ ($x=0.2$) it is about $320$ K [5,8].

Previously reported results confirmed a second-order type of the phase transition in the $\text{Li}_2\text{Ge}_4\text{O}_9$ ($x=0$) and $\text{LiNaGe}_4\text{O}_9$ ($x=1$) single crystals but the small value of the transition entropy implied that the mechanism of the phase transition is not typical of an order-disorder one, so it not only involves ordering of constant dipole moments [5]. Simultaneous presence of order-disorder and displacement types of ferroelectric transitions was reported for $\text{Li}_2\text{Ge}_7\text{O}_{15}$ single crystal [1,3,9,10]. All the crystals seem to be similar in structure. At room temperature, the unit cell of the $\text{LiNaGe}_4\text{O}_9$ crystal is orthorhombic with a space group $D_{2h}^8$-$Pcca$ [2]. The crystal structure consists of [GeO$_3$]$_n$-chains of tetrahedrally coordinated Ge-atoms that are connected by [GeO$_6$] octahedral into a three dimensional network. Alkali metal atoms (Li and Na) are disordered between two equivalent positions (8f, 4c) inside the channels formed by GeO polyhedral [11,12]. We believe that the same mixed type of phase transition may take place for $\text{LiNaGe}_4\text{O}_9$ and the secondary crystals. One of the methods allowing to clearly distinguish the two mechanisms of the phase transition is doping of the crystal with ions enhancing one of the two types of the above mechanisms. Mn$^{2+}$ ions substitute for Li$^+$ ions and are sensitive to structure changes having ordering character. Cr$^{3+}$ ions substitute for germanium ions forming sublattice sensitive to displacement type structural distortions in the crystal. Analysis of the dominating type of phase transition may be done by EPR analysis of the EPR line widths below $T_c$. It was confirmed partially by Trubitsyn et al. in [9]. We decided to obtain and investigate the crystals pure and doped with Cr, Mn and doubly doped with Cr and Mn to analyze the influence of the kind of doping onto their dielectric properties. The goal of co-doping with Cr and Mn was enhancing the optical activity of chromium ions, what was confirmed by us using photoluminescence measurements. Taking into account the multiphase limitation we have grown $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$ single crystals with $x=0.28$ [11].

2. Experimental

Single crystals of $\text{Li}_{2-x}\text{Na}_x\text{Ge}_4\text{O}_9$ with starting composition $x=0.28$ (LNG), pure and doped with Cr (0.02 mol.%), Mn (0.1 mol.%) and Cr together with Mn (0.1 mol., 0.1 mol.%) were grown by the Czochralski method in an inductively heated platinum crucible under ambient pressure in the air. The mixture of $\text{Li}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3$, $\text{Ge}_2\text{O}_5$ and $\text{Cr}_2\text{O}_3$ or $\text{MnO}$ powders of 99.99% purity were used as starting materials. They were heated at 300°C for 4 hours before weighing, mixing in stoichiometric ratios and melting. Crystal growth process of the crystals doped with TM ions was described in detail elsewhere [11]. Samples of 1 mm in thickness and 1 cm$^2$ in area were cut, both sides polished and coated with silver electrodes.

Dielectric permittivity dependence on temperature and frequency was measured by HP 4284A LCR meter with an accuracy of 0.2 K. We registered values of $\varepsilon'$, $\varepsilon''$, $\tan\delta$ in heating and cooling mode. The electrical measurements were carried out with air-drying silver paste as electrodes. Hysteresis loops (D-E dependence) were recorded using a modified Sawyer–Tower circuit by using an ac field of 50 Hz and digital oscilloscope. The switching currents were measured by applying square-wave electric pulses (two positive pulses
followed by two negative ones) amplified with a Kepco bipolar amplifier. The voltage across the 50 Ω resistor, connected in series with the crystal sample, was measured using a digital oscilloscope. A real switching transient, which is almost independent of the circuit conditions, was then obtained by subtracting the nonswitching current from the full current pulse. The electrical measurements were carried with air-drying silver paste as electrodes. Electrical treatment can be seen as a standard technique allowing a fast characterization of the ferroelectric crystal. The switching current data were integrated in order to obtain the temporal dependence of the switched polarization $P(t)$.

3. Results and discussion

3.1. Dielectric properties

LNG single crystals crystallize in the $Pcca$ space group with lattice constants: $a = 9.3191\AA$, $b = 15.8410\AA$, $c = 4.6486\AA$, $V = 686.25\AA^3$, $Z = 4$ [11]. We have first measured the dielectric permittivity in the (001) crystallographic direction, because the orientation of our samples was performed taking into account the Pca2$_1$ space group. We found that at the point characteristic for second order ferroelectric-to-paraelectric phase transition the dielectric permittivity, $\varepsilon'$, is very low. As one can see from Figure 1(a), for a frequency as high as 10 kHz, a value of $\varepsilon'$ is very small, lower than 20. $T_c$ of pure LNG crystal was found to be about 267 K while that of LNG:Cr, Mn was about 260 K. Doping always shifts the position of $T_c$ towards higher temperatures, from 256.7 K for pure crystal up to 267 K for chromium doped one. Manganese doping moderates changes in $T_c$.

Dielectric permittivity for all other crystallographic directions was measured mainly for LNG:Cr, Mn single crystals. As one can see from Figure 1(b), the value of $\varepsilon'$ in (100) direction is at least six times larger than registered for the (001) direction. Curie–Weiss temperature depends, moreover, on the temperature mode (heating or cooling). The difference between the values measured in heating and cooling modes is as high as 4 K.

Changes of dielectric permittivity and loss tangent with frequency for the (100) LNG:Cr, Mn crystal orientation are typical as can be seen from Figure 2. In Figure 3 we presented the ac conductivity dependences versus temperature for LNG:Cr, Mn plates oriented along the (100) direction. We derived the conductivity activation energies and found that there are very small. They change from 0.032 ± 0.004 eV for 10 kHz to 0.044 ± 0.005 eV for 1 Hz. For other two directions (010) and (001) they are slightly higher. However, the values are not accurate, because the linear character of $\ln(s)$ versus $1/T$ dependence is limited to a part only of experimental points, at high temperatures.

3.2. Hysteresis loop measurements

Figure 4(a) presents the shape of hysteresis loops (H-L) obtained at various amplitudes of the ac-field at frequency 50 Hz. At low electric field H-L has a near flat shape relative to P-E axis. At higher E, the H-L becomes more slanted. Figure 4(b) illustrates the H-Ls taking at various temperatures, measured close to $T_c$ temperature. The temperature dependence of the hysteresis loop exhibits a behavior typical of crystals with second-order phase transitions. Only LNG crystals with $T_c > 300$ K are characterized by a double hysteresis loops [13]. Typical ferroelectric H-Ls are observed up to 259 K when electric fields up to 3 kVcm$^{-1}$ were applied. At 260 K and higher, typical linear dielectric responses are observed, suggesting that the investigated LNG:Cr, Mn crystal becomes paraelectric at macroscopic scale. In Figure 5 spontaneous polarization versus temperature, calculated
based on the results presented in Figure 4 is shown. As one can see, $P_s$ decreases with temperature. It vanishes when temperature reaches $T_c$ value, at 260.2 K. In the same figure temperature dependence of dielectric permittivity is also shown. Its maximum is at least four times lower than the one registered for pure LNG single crystals with $x=0.3$ [14]. It may be due to the doping of LNG crystals.

3.3. Switching current measurements

More comprehensive information about the fast switching process can be obtained from switching current curves, representing the reverse polarization as a function of the pulse duration for a constant electric field. Figure 6(a) show switching currents for several amplitudes of the electric field, while Figure 6(b) presents the time dependence of the switched polarization obtained after integration of the switching curves for several amplitudes of the electric field for LNG:Cr, Mn single crystal. For normal ferroelectrics,
Figure 2. Dielectric permittivity as a function of a frequency for LNG : Cr, Mn single crystal of (100) orientation (a), Loss tangent dependence as a function of frequency in the same case (b).

Figure 3. Conductivity vs. temperature for LNG : Cr, Mn sample of (100) orientation at different frequencies.
Figure 4. Hysteresis loops for several amplitudes of electric field (a) and at various temperatures (b) for (100) orientation of LN:Cr, Mn.

Figure 5. Dependence of spontaneous polarization on temperature on the background of electric permittivity for (100) orientation of LN:Cr, Mn.
as the electric field increases, the switching curves shift to shorter times and the domain switching time is known to be of the order of microseconds, when external electric field approaches $E_c$.

The switching kinetics in homogeneous ferroelectrics crystals can be well described by the Kolmogorov–Avrami–Ishibashi (KAI) model, which is based on the classical statistical theory of nucleation and unrestricted domain growth [15]. In the KAI model, the time dependence of the switched polarization is expressed by formula, called as Avrami function $P(t) = P_0[1 - \exp(-t/\tau)^n]$, where $P_0$ is the switchable polarization, $\tau$ characteristic switching time and $n$ is effective dimensionality of the domain growth. The parameter $n$ depends on the rate of nucleation and the shape of the reversed domains being between 1 and 3. The experimental data are well fitted (dashed lines) with the Avrami function, however the resulting growth exponents attain values $n < 1$ (Figure 6) and thus differs from that predicted by the KAI model. This is probably brought about by a spatially nonuniform distribution of domain nuclei and restricted domain growth in the examined single crystal. The KAI model is formulated to ideal infinite media, assuming that a great number of nuclei are randomly distributed over the volume of the crystal.

Figure 6. Switching currents (a) and switched polarization (b) vs. time; dashed lines mark fitting using Avrami function.
4. Conclusion

Dielectric permittivity measured for LNG:Cr, Mn single crystal is about four times lower than that measured for pure LNG crystals [13,14]. Doping always shifts the position of Curie temperature, $T_c$, towards higher temperatures, from 256.6 K for pure crystal up to 267 K for chromium doped one. Manganese doping or co-doping moderates changes in $T_c$ position. The difference between the value measured in heating and cooling modes is as high as 4 K. The experimental data for switched polarization are well fitted with the Avrami function [15], however the resulting growth exponents attain values $n < 1$, and thus differ from that predicted by the KAI model. This is probably brought about by a spatially nonuniform distribution of domain nuclei and restricted domain growth in the examined single crystal.

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