ISSN 2616-8685. JOURNAL OF PHYSICS AND ELECTRONICS Vol. 29(1), 2021. DOI 10.15421/332110

OPTICAL ABSORPTION OF $LiNaGe_4O_9$:Mn CRYSTAL

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The paper reports the results of optical absorption spectra studying in $LiNaGe_4O_9$ crystal doped with Mn. It is shown that Mn impurity causes the appearance of the additional absorption bands. The intensities of these bands change in different ways in the range of the ferroelectric phase transition. Semi-empirical version of the crystal field theory is used to discuss localization and charge state of Mn impurity ions in the $LiNaGe_4O_9$ structure.

Keywords: lithium-sodium tetragermanate LiNaGe4O9 crystal, doping with Mn, optical absorption, local symmetry.

Received 05.06.2021; Received in revised form 12.07.2021; Accepted 15.08.2021

1. Introduction

Design and study of new materials with functional characteristics make a basis for development of modern information technologies. Ferroelectrics attract special attention since in the range of structural phase transitions their properties become extremely sensitive to external fields. Currently, the ferroelectric crystals of lithium tetragermanate $Li_2Ge_4O_9$ (LG4) and lithium sodium tetragermanate $LiNaGe_4O_9$ (LNG) are being the subjects of intensive investigations. The attention is devoted to the crystal structure [1] and dielectric properties [2-4]. Nevertheless, up to now optical properties of LG4 and LNG have been studied very poorly. One can expect that doping with transition ions should significantly modify the properties of LG4 and LNG crystals. For example, recently it was shown that doping $Li_{2-x}Na_xGe_4O_9$ crystals ($x = 0.28$) with Cr ions shifted the temperature T_C of the ferroelectric phase transition from 257 to 267 K, while doping with Mn ions practically did not change T_C [5]. The authors of [6] studied optical and EPR spectra and concluded that chromium ions in trivalent charge state Cr^{3+} substituted for Ge^{4+} host ions in the LNG crystal lattice. However, the data available do not allow to find out the reasons for the different effects of Cr and Mn ions doping on the temperature T_C of the ferroelectric phase transition.

This paper is devoted to an experimental study of optical absorption in the temperature ranges of para- and ferroelectric phases of LNG crystals doped with manganese (LNG:Mn). The obtained results give information on the charge state and localization of Mn impurity ions in the LNG crystal structure.

2. The experimental technique

The studied LNG:Mn single crystals were grown by Czochralskii method [4]. An impurity of MnO was added to the charge in an amount of 0.1 wt %. In the experiments we used the samples prepared as the plates cut off parallel to the crystallographic plane (100). The main planes of the samples were polished and had the dimensions 10×8 mm^2, the samples thickness d was 0.15 and 2 mm. The optical transmission spectra $t(\nu)$ were registered using the spectrophotometer Specord M40 in the range of wave numbers $\nu = 45000 \div 11000$ cm^{-1} where $\nu = 1/\lambda$, λ is the wavelength. The temperature of the samples was stabilized in the intervals of paraelectric ($T_1 = 300$ K) and ferroelectric ($T_2 = 88$ K) phases of LNG crystal. The optical absorption spectra were calculated by using the formulae $\alpha(\nu) = \frac{1}{d} Ln \frac{1}{t(\nu)}$.

3. The experimental results and discussion

The obtained results show that LNG:Mn crystals are optically transparent in the whole investigated spectral interval. The fundamental optical absorption edge is in the range $\nu = 45600 \div 40600$ cm^{-1}. One can see that the transition from the paraelectric phase

(T_1= 300 K) to the ferroelectric one (T_2 = 88 K) is accompanied by a significant shift of the absorption edge. This shift is shown in Fig. 1, where absorption α is presented as a function of energy $h\nu$ of light quanta. For α = 600 cm^{-1}, the isoabsorption band gap is equal to ΔE_{g1} = 5.43 and ΔE_{g2} = 5.64 eV at the temperatures T_1 and T_2, correspondingly. In addition, the absorption band with $h\nu_{max}$ = 5.59 eV (ν_{max} = 45112 cm^{-1}) is registered on the low-temperature α($h\nu$) dependence. In the range ν = 44000 – 11000 cm^{-1}, the α(ν) spectra are represented by broad and structured absorption bands (Fig. 2).

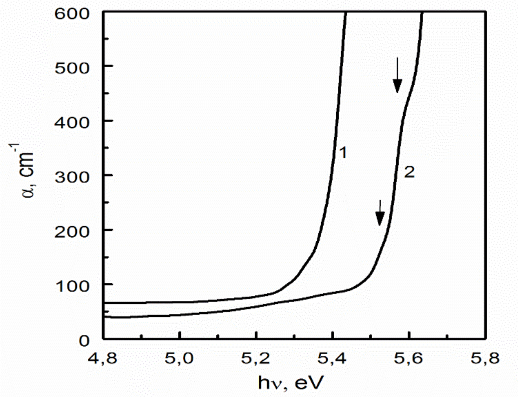

Fig. 1. The optical absorption spectra α(*h*ν) of LNG:Mn crystal in the region of the fundamental absorption edge, measured at 300 (1) and 88 K (2); *d* = 0.15 mm.

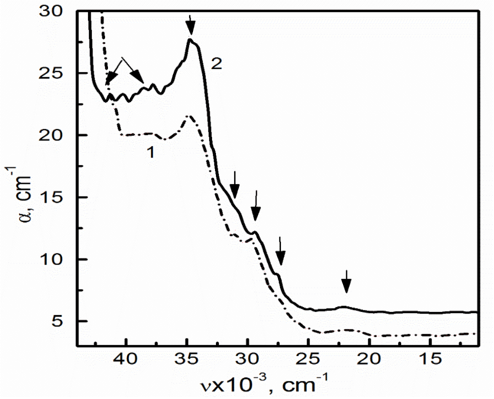

Fig. 2. The optical absorption spectra *α(ν)* of LNG:Mn crystals in ultraviolet and visible region of the edge, measured at 300 (1) and 88 K (2), *d* = 2 mm.

To interpret these results, it is necessary to take into consideration the structure of LNG crystal and its changes at the ferroelectric phase transition (PT).

In the paraelectric phase (T_1= 300 K) LNG crystal lattice belongs to an orthorhombic space symmetry group $D_{2h}{}^8$ and has four formula units per unit cell. The cell contains six of [GeO$_4$] tetrahedra, which form a three-dimensional framework through the links with [GeO$_6$] octahedra. Ge^{4+} ions are distributed within the oxygen coordination polyhedra of two types. One Ge from the formulae unit is located within an oxygen octahedron, the other three Ge are within oxygen tetrahedra of different sizes. Average (Ge-O) distance in octahedra is 1.87 Å; the (Ge-O) distances in tetrahedra change from 1.72 to 1.79 Å. Na$^+$ ion is located within distorted oxygen octahedron: the (Na-O) distances change in the interval 2.27 ÷ 3.09 Å. Li$^+$ ion is also surrounded by six neighboring oxygens: four ligands at distances in the range 1.83÷2.05 Å and two at 2.29 and 3.01 Å, correspondingly [1]. In the ferroelectric phase, the symmetry of LNG crystal structure reduces to orthorhombic space group $C_{2h}{}^5$ [1]. The ferroelectric phase transition in LNG crystal, as in LG4, is somewhat unusual and combines the features peculiar for both order-disorder and displacive mechanisms of structural changes [3].

Thus, the determination of the charge state and localization of Mn ions is complicated due to the presence of nonequivalent cationic positions in the LNG crystal lattice, as well as by impurity polyvalence (from Mn^{2+} (3d^5) to Mn^{5+} (3d^2) in the various studied crystals). It is known that in weakly distorted oxygen polyhedra Mn^{3+} (3d^4) state is unstable and usually either oxidizes to the Mn^{4+} (3d^3) state, which can be stabilized by the crystal field, or reduces to Mn^{2+} state with the most stable 3d^5 electronic configuration. The unstable 3d^4 configuration is still possible in distorted oxygen octahedra for Mn^{3+} ions with a degenerate ground *E*-state [7].

The most probable is isovalent substitution of Ge^{4+} host ions in oxygen octahedral with Mn^{4+} impurity ions. In addition, substitutions such as "Mn^{2+}→Li$^+$" and/or "Mn^{2+}→Na$^+$" are also possible. Despite the heterovalent nature, such substitutions can be consistent with the concepts of isomorphism. For example, the substitution of “$Mn^{2+} \rightarrow 2Li^{+}$” type was found in lithium heptagermanate $Li_2Ge_7O_{15}$ crystal [8], which are structurally similar to LNG. The broad absorption bands indicate a complex formation of the α(ν) and α(*h*ν) spectra. In the para- and ferroelectric phase, the following groups of Gaussian components can be distinguished: at $\nu_1 \approx 20500 \div 22000$, $\nu_2 = 27300 \div 32000$, $\nu_3 = 34390 \div 35200$ cm^{-1} (Fig. 2). A narrow band appears in the ferroelectric phase in the interval $\nu_4 = 44800 \div 45000$ cm^{-1} (Fig. 1). In the α(ν) spectra, the components at ν_1, ν_2, and ν_4 correspond to the spectral position of the known electronic *d-d* transitions in Mn^{4+} ($3d^3$) ions: $^4A_2 \rightarrow {}^4T_{2g}$ (*U*-band), $^4A_2 \rightarrow {}^4T_1$ (*Y*-band), $^4A_2 \rightarrow {}^4T_1$ (*V*-band). These components are compared also with the theoretically calculated electronic transitions in Mn^{4+} ($3d^3$) ions in octahedral crystal fields by using Tanabe-Sugano diagrams (Fig. 3). The diagrams are plotted in the scale E/B vs Δ/B, where E is the energy of the electronic transition, B and Δ are the parameters of the crystal field theory [7]. The best agreement has been obtained for the Racah parameter $B = 690$ cm^{-1} and the crystal field strength $\Delta = 2140$ cm^{-1} (Fig. 3, a, b). A small value of B indicates a significant degree of covalence of the $Mn^{4+} – O^{2-}$ bonds. *V*-band (transition $^4A_2 \rightarrow {}^4T_1$) falls into the ultraviolet region of the spectrum (Fig. 1). Narrow bands near ν_3 can be attributed to intercombinative transitions from the $^4A_2$ ground state to the excited ones.

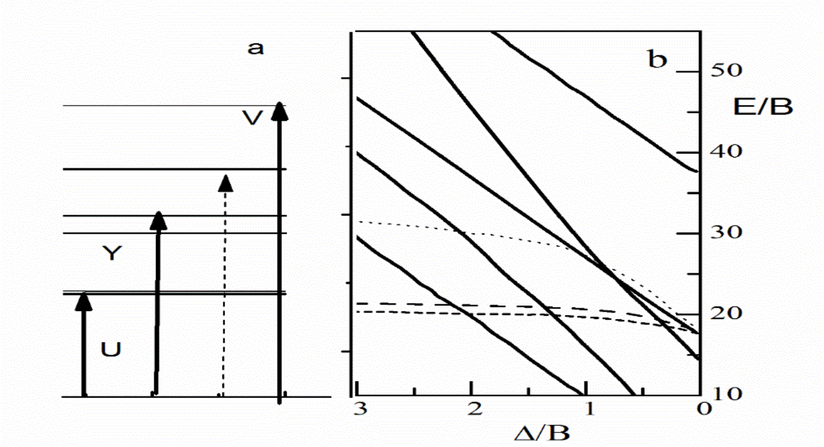

Fig. 3. Comparison of the scheme of electronic transitions in Mn^{4+} ions, obtained from the analysis of the α(ν) spectra in LNG:Mn crystal (a), with the theoretical Tanabe-Sugano diagram for the $3d^3$ electronic configuration in an octahedral crystal field (b).

A characteristic feature of the α(ν) spectra is a set of narrow bands in the near ultraviolet region with $\nu_5 = 37000 \div 45000$ cm^{-1} (Fig. 2). The similar bands were observed for Cr^{3+} ions, which have the isoelectronic to Mn^{4+} ions $3d^3$ configuration.

It should be accounted that the structure of the α(ν) and α(*h*ν) spectra can be also contributed by electronic transitions in Mn^{3+} ($3d^4$) and in Mn^{2+} ($3d^5$). Thus, in the intervals ν_1, ν_2 and ν_3 the transition from the paraelectric phase to the ferroelectric one is accompanied by the appearance and/or an increase in the intensity of absorption bands, which cannot be attributed to the transitions in Mn^{4+} ($3d^3$) ions. These are the components with $\nu_{max} \approx 20500$, 24400 cm^{-1} and the narrow bands with $\nu_{max} \approx 25000 \div 26000$ cm^{-1} (Fig. 2), which were observed in many crystals and can be attributed to transitions in Mn^{3+} ($3d^4$) and Mn^{2+} ($3d^5$) ions in distorted octahedra [7]. However, more experiments are needed to clear up the origin of these bands.

According to [4], Cr^{3+} ions with the $3d^3$ configuration (which is isoelectronic to Mn^{4+}) in $Li_{2-x}Na_xGe_4O_9$ crystals ($x = 0.28$) also substitute for Ge^{4+} ions within oxygen octahedra; however, such substitution $Cr^{3+} \rightarrow Ge^{4+}$ is aliovalent and requires charge compensation. The authors of [9] (see also the references therein) considered the substitution $Cr^{3+} \to Ge^{4+}$ in lithium heptagermanate $Li_2Ge_7O_{15}$ crystal and proposed Li^+ ions interstitials (A_{Li}) as the local charge compensators. Afterwards this model as well as the formation of $Cr^{3+}–A_{Li}$ paired dipolar centers was experimentally confirmed in [10]. For $Mn^{4+} \to Ge^{4+}$ substitution charge compensation is not required. Moreover, Mn^{4+} and Ge^{4+} ions for a coordination number CN = VI have the same ionic radii r = 0.67 Å. Hence, charge perturbation and structural deformations accompanying $Mn^{4+} \to Ge^{4+}$ substitution can be assumed as unessential. Just the absence of charge and mechanical disturbances explains the zero doping effect on the PT temperature in LNG:Mn crystal [5]. In contrast, strong influence of doping on the PT point in LNG:Cr crystal can be associated with significant local disturbance of the structure induced by $Cr^{3+}–A_{Li}$ pair dipolar centers which were discussed earlier in [9 – 10].

4. Conclusions

1. The band gap width in the para- and ferroelectric phases of LNG:Mn crystal has been determined as $\Delta E_{g1} = 5.43$ and $\Delta E_{g2} = 5.64$ eV, respectively.
2. It is shown that the main features of the absorption spectra of LNG:Mn crystal are due to electronic transitions in Mn^{4+} ions, which substitute for Ge^{4+} host ions within oxygen octahedra. The crystal field strength $\Delta = 2140$ cm^{-1} and the Racah parameter $B = 690$ cm^{-1} were calculated from the absorption spectra.

References

1. **Iwata, Y.A.** Neutron diffraction study on the phase transition in ferroelectric $LiNaGe_4O_9$/ Y. Iwata, N. Koyano, M. Machida, M. Wada, A. Sawada // J. Korean Phys. Soc. – 1998. – Vol. 32. – P. S195–S198.
2. **Wada, M.** Ferroelectric phase transition in $Li_{2-x}Na_xGe_4O_9$ (x=0,5) /M. Wada, Y. Yamashita, A. Sawada, Y. Ishibashi // J. Phys. Soc. Jpn. – 1993 – Vol. 62. – P.14–17.
3. **Cach, R**. Dielectric studies of ferroelectric phase transition in LNG crystal/ R. Cach, I. Cebula, M.D. Volnyanskii //Mater. Sci. Eng. –2002. – Vol. B90. – P.72–78.
4. **Kudzin, A.Yu.** Dielectric nonlinearity of crystals $Li_{2-x}Na_xGe_4O_9$(x ≈ 0,23)/ A.Yu. Kudzin, D.M. Volnyanskii // Phys. Solid State. –1999. – Vol.41 (6). – P.1070–1072.
5. **Jasik, A**. Effect of Cr and Mn doping on ferroelectric and dielectric properties of $Li_{1.72}Na_{0.28}Ge_4O_9$ single crystals / A. Jasik, S.M. Kaczmarek, K. Matyjasek, J. Barczynski, M. Berkowski// Phase Transition. – 2013. – Vol. 86. – P. 230–237.
6. **Jasik, A.** Grown, Optical and EPR properties of $Li_{1.72}Na_{0.28}Ge_4O_9$ single crystals. Pure and slightly doped with Cr/ A. Jasik, M. Berkowski, S.M. Kaczmarek, A. Suchocki, A. Kaminska, G. Leniec, P. Nowakowski, V. Domukhovski // Cent. Eur. J. Phys. – 2012. – Vol. 10(2). – P.506–513.
7. **Sviridov D. T.** Optical spectra of transition ions metals in crystals/ D. T. Sviridov, R. K. Sviridova, Yu. F. Smirnov // Nedra, M. – 1976. – 263 p.
8. **Trubitsyn M. P.** EPR of Mn^{2+} ions in lithium heptagermanate crystals/ M.P. Trubitsyn M.D. Volnianskii, A.Yu. Kudzin // Crystallography. – 1991.– Vol. 36. – P.1472–1476.
9. **Kaplyanski, A.A.** Ferroelectric Transition Induced Dipole Moments in Probe Ions in $Li_2Ge_7O_{15}$ Crystals Doped with Mn^{4+} and Cr^{3+} /A. A. Kaplyanski, S. A. Basun, S. P. Feofilov // Ferroelectrics. – 1995. – Vol. 169. – P.245–248.
10. **Volnianskii, M.D.** EPR and dielectric spectroscopy of reorienting $Cr^{3+}–Li^+$ pair centres in $Li_2Ge_7O_{15}$ crystal/ M. D. Volnianskii, M. P. Trubitsyn, Yahia A. H. Obaidat // Condensed Matter Physics. – 2007. – Vol.10. – P.75–78.