EPR OF $LiNaGe_4O_9$:Mn CRYSTAL

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EPR spectra of manganese ions were studied in lithium-sodium tetragermanate $LiNaGe_4O_9$ crystal. The observed spectrum was typical for doping ions in tetravalent Mn^{4+}state ($3d^3$, S=3/2) and for main orientations of static magnetic field along the crystal axes (T=296 K) consisted of hyperfine sextuplet from electronic transition Ms= +1/2 ↔ – 1/2. Transitions Ms= ±3/2 ↔ ±1/2 were not detected owing to strong interaction of the spin system with crystal field as compared with electron Zeeman interaction in the X frequency range of EPR registration. The angular variations of the spectrum were measured for static field B rotated in three main crystal planes. Since only central transition (Ms= +1/2 ↔ – 1/2) was detected and the splitting of the fine structure remained unknown, the spectrum was described in the approximation of effective spin S_{eff}=1/2. The parameters of the spin Hamiltonian, including electron Zeeman and hyperfine interactions, were calculated. The magnetic multiplicity of the spectrum (k_m=2) evidenced that paramagnetic centers occupied the sites with monoclinic C_2 point symmetry. Taking into consideration the positional symmetry as well ionic charges and radii of the guest ion and the hosts, it was concluded that paramagnetic Mn^{4+}centers substituted for Ge^{4+} within oxygen octahedral complexes in the crystal lattice of $LiNaGe_4O_9$.

Keywords: lithium-sodium tetragermanate $LiNaGe_4O_9$ crystal, Mn doping ions, EPR.

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1. Introduction

Lithium-sodium tetragermanate $LiNaGe_4O_9$ crystal belongs to the family of germano-germanate complex oxides, which have framework-type structure formed by germanium-oxygen tetrahedral GeO_4 and octahedral GeO_6 complexes. Light alkali Li^+ and Na^+ ions occupy the special off-center positions within the structural channels formed by the Ge–O lattice skeleton [1,2]. At room temperature, the symmetry of the $LiNaGe_4O_9$ crystal structure corresponds to non-polar orthorhombic space group D_{2h}^8. On cooling below T_C≈113 K the crystal undergoes the transition to the ferroelectric phase (C_{2v}^7 space symmetry group) with spontaneous polarization oriented along [100] axis [2].

Study of $LiNaGe_4O_9$ electrical properties in [3] showed that on heating above 400 K conductivity σ became strongly anisotropic. Along [001] axis it was the highest and exceeded in two orders the σ values measured along [100] and [010] directions. In crystalline solutions $Li_{2-x}Na_xGe_4O_9$ conductivity was found to be dependent on the sodium concentration x [4]. Conductivity of $Li_{1.5}Na_{0.5}Ge_4O_9$ (x=0.5) had the comparable values along all three main crystal axes whereas in $Li_{1.8}Na_{0.2}Ge_4O_9$ (x=0.2) σ was maximal along [100] and [010] axes and in one order exceeded conductivity along [001] direction [5]. Thus, decrease of x from 1 to 0.5 and to 0.2 changed the anisotropy of σ for the opposite character. In total, the data published in [3,4] made it possible to suppose that charge transfer in $LiNaGe_4O_9$ crystal was contributed by lithium interstitials A_{Li} moved along the channels of the framework structure. Nevertheless, this supposition needs additional arguments for confidence.

Previously, using macroscopic and local experimental techniques, charge transfer was studied in detail in lithium heptagermanate $Li_2Ge_7O_{15}$ [5,6] which had the similar crystal structure. Among other things, it was shown that small amounts of aliovalent dopants strongly influenced conductivity of $Li_2Ge_7O_{15}$ [7,8]. Doping increased σ if charge compensation of impurity was provided by lithium ions interstitials A_{Li} and vice versa, suppressed conductivity in the case of appearance of charge compensating lithium vacancies V_{Li}. The doping effects unequivocally evidenced that charge transfer in $Li_2Ge_7O_{15}$ was determined by mobile interstitials A_{Li}. In the same way, analysis of doping effects on conductivity can help to elucidate the mechanism of charge transfer in $LiNaGe_4O_9$ crystal. Of course, interpretation of the experimental data needs the justified models of impurity centers in the lattice. The aim of this paper is to propose and substantiate the model of manganese impurity ions in $LiNaGe_4O_9$ crystal structure by studying EPR spectra.

2. Crystal growth and experimental technique

The single crystals of $LiNaGe_4O_9$, doped with Mn, were grown from the melts by Czochralski method. The dopant MnO (0.1 wt %) was added to the initial charge previously. The crystal growth technology was briefly described in [9]. Doping with Mn led to a slightly yellowish coloration of the crystal obtained. The samples for EPR spectra measurements were cut off as parallelepipeds with the edges oriented along the crystal axes. The EPR spectra were recorded by using the conventional radiospectrometer operating in *X* frequency band.

3. Experimental results

The EPR spectrum of $LiNaGe_4O_9$:Mn recorded for static field orientations along the crystal axes **B**||**a**, **b**, **c** (T=296 K) represents the sextuplet of nearly equidistant lines with near the same intensities. Such spectrum arises from hyperfine (HF) interaction of electron spin S with nuclear spin of isotope ^{55}Mn (I=5/2). The detected HF sextuplet is attributed to central electronic transition Ms= +1/2 ↔ – 1/2 of the spectrum of tetravalent Mn^{4+} ions ($3d^3$, S=3/2). Two outer sextuplets (Ms= ±3/2 ↔ ±1/2) are not observed because of high spin levels splitting in zero magnetic field. Strong interaction of the spin system with crystal field shifts slow-field HF sextuplet to the region of negative magnetic fields whereas high-field sextuplet appears in the experimentally unachievable region at B>0.7 T.

Complete description of the Mn^{4+}EPR spectrum requires including into the spin Hamiltonian (SH) the terms of electron Zeeman interaction, zero-field splitting due to interaction with crystal field and HF interaction of electron spin S=3/2 with nuclear one I=5/2. But in the experiment only central transition (Ms= +1/2 ↔ – 1/2) has been detected and there is no information about other spectral components. The lack of information about the splitting of the fine structure impairs the accuracy of determining the parameters of axial D and rhombic E crystal field. Since only the central fine transition is detected, the spectrum can be described phenomenologically by using effective electronic spin S_{eff}=1/2. In such case, the SH can be written as a sum of electron Zeeman and HF interaction energies

$$H = \beta \mathbf{S}_{\text{eff}} \boldsymbol{g}_{\text{eff}} \mathbf{B} + \mathbf{S}_{\text{eff}} A \mathbf{I}. \tag{1}$$

Here β is Bohr magneton, effective g-factor (g_{eff}) corresponds to S_{eff}=1/2 and does not coincide with true g-factor, A is HF interaction tensor.Fig.1 shows the angular variation of g_{eff} calculated from the central point of Ms= +1/2 ↔ – 1/2 fine transition for magnetic field **B** rotating in the main crystal planes. For the main orientations of the static field **B**||**a**, **b**, **c**,as in (**ac**) and (**cb**) planes, the single HP sextuplet is observed. If the field **B** rotates in (**ab**) plane, the sextuplet splits into two conjugated spectra from paramagnetic centers located in structurally equivalent sites. The calculated values of the SH (1) parameters, as well the set of magnetic axes **XYZ** with respect to the crystal axes **abc**, are presented in Table 1.

4. Discussion

The angular variation of the EPR spectrum (Fig.1) reflects the point symmetry of the site, occupied by Mn^{4+} centers. A doublet splitting of the HF sextuplet in (**ab**) plane demonstrates that the magnetic multiplicity of the spectrum is k_m=2 and testifies that Mn^{4+} centers occupy the structurally equivalent positions of d or e type with monoclinic symmetry C_2.

The studies of the crystal structure in [1,2] show that in the paraelectric phase of $LiNaGe_4O_9$ germanium ions occupy three structurally inequivalent sites. Ge1 (4(*d*) type position, C_2 point symmetry) and Ge3 (8(*f*) position, C_1 local symmetry) are coordinated byoxygen tetrahedra. Ge2 (4(*e*) position, C_2 point symmetry) are located within oxygen octahedra. Ions of alkali metals Li^+ (8(*f*), C_1 symmetry) and Na^+ (4(*e*), C_2 symmetry) occupy the sites within strongly distorted oxygen octahedra. Thus, the symmetry of Mn^{4+} EPR spectrum corresponds to the positions of Ge1, Ge2, and Na host ions. It should be noted that ionic charges and radii of the host germanium Ge^{4+} and foreign manganese Mn^{4+} ions coincide ($r = 0.53$ Å for coordination number IV; $r = 0.67$ Å for coordination number VI) [10]. Hence, the scheme $Mn^{4+}\rightarrow Ge^{4+}$represents the most probable substitution and both tetrahedrally (Ge1, Ge3) and octahedrally (Ge2) coordinated sites should be considered. For bothGe1 and Ge3 sites within tetrahedra the substitution can be expected as equiprobable. But the experimental spectrum corresponds to the single structurally equivalent position of the manganese centers. Thus, we can conclude that paramagnetic Mn^{4+} ions substitute for $(Ge2)^{4+}$ hosts within oxygen octahedra. This conclusion is consistent with the results of luminescence spectra analysis in$LiNaGe_4O_9$:Mn crystals performed in [11].

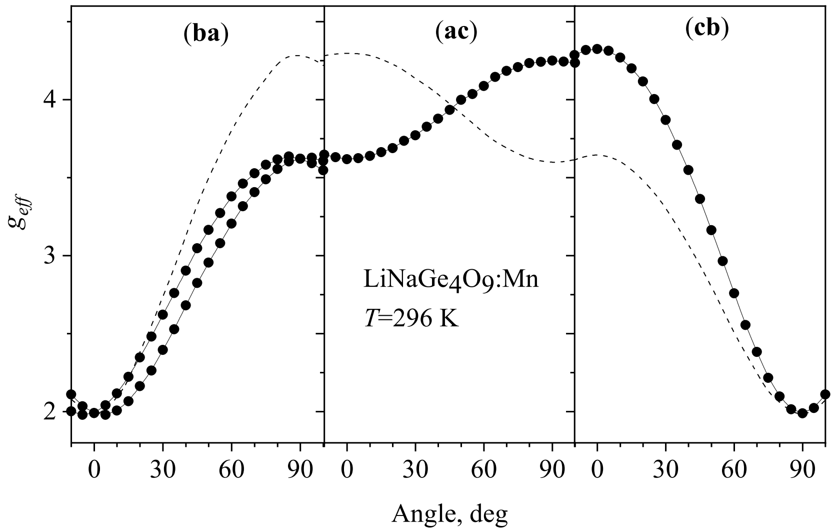

Fig. 2. Angular variations of g_{eff} for main crystal planes. The circles represent the positions of the intensive sextuplet (Ms= +1/2 ↔ – 1/2) of $LiNaGe_4O_9$:Mn EPR spectrum. The dashed line corresponds to the additional low intensive sextuplet (see the text).

Table 1

The parameters of spin-Hamiltonian (1) calculated for Mn^{4+} spectra (T=296 K)

Active center	Magnetic axes set	Components of g_{eff}	Components of HF tensor A, $10^{-4}cm^{-1}$
Mn^{4+}	∠**X**,**a**=4.4^0; **Y**‖**c**‖C_2; ∠**Z**,**b**=184.4^0	$(g_{eff})_x$= 3.625(4) $(g_{eff})_y$= 4.285(4) $(g_{eff})_z$=1.974(3)	A_x=72.0(5) A_y=71.0(5) A_z=75.5(5)

One should note that the additional low intensity HP sextuplet from Mn^{4+}ions could be distinguished in the spectrum. The amplitude of this spectrum is lower approximately in five times as compared with the main HP sextuplet. The angular variation of the additional HP sextuplet position is plotted in Fig.1 by the dashed line. One can see that at **B**||**b** the positions of the main and additional sextuplets practically coincide whereas the maximal splitting between them is observed at **B**||**a**,**c**. It is remarkable that the angular dependences of the low intensity sextuplet positions can be described by the same SH (1) with the parameters given

(Table 1) for the main spectrum but with the changing the magnetic axes **X** ↔ **Y**. Presumably the low-intensity Mn^{4+} spectrum appears due to twinning the crystal under study.

5. Conclusions

The EPR spectrum of Mn impurity was studied in lithium-sodium tetragermanate $LiNaGe_4O_9$ crystal at room temperature. The single hyperfine sextuplet detected at main orientations of magnetic field **B**||**a**, **b**, **c** was attributed to electronic transition $M_s = +1/2 \leftrightarrow -1/2$ of the spectrum of tetravalent Mn^{4+}ions ($3d^3$, S=3/2). Analysis of the angular change in the spectrum evidenced that paramagnetic ions occupied monoclinic positions with C_2 point symmetry and substituted for germanium host ions (Ge2) within oxygen octahedra. The proposed model of Mn centers can be useful for interpretation of the doping effects on ionic conductivity and anomalies of physical properties in the range of ferroelectric phase transition in $LiNaGe_4O_9$ crystal.

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