EPR and dielectric spectroscopy of reorienting Cr\(^{3+}\)– Li\(^{+}\) pair centres in Li\(_2\)Ge\(_7\)O\(_{15}\) crystal

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Earlier it has been shown that in the lithium heptagermanate Li\(_2\)Ge\(_7\)O\(_{15}\) structure the chromium doping ions substitute the germanium hosts and create Cr\(^{3+}\)– Li\(^{+}\) pair centres. In the paper EPR and dielectric spectra of Li\(_2\)Ge\(_7\)O\(_{15}\):Cr\(^{3+}\) crystal are studied in the temperature range 300 ÷ 500 K. The thermally activated reorientation of Cr\(^{3+}\)– Li\(^{+}\) pairs has been detected through EPR line width broadening and dielectric relaxation.

Key words: impurity ions, electron paramagnetic resonance, dielectric loss and relaxation

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1. Introduction

It is known that Cr\(^{3+}\) doping ions in the structure of Li\(_2\)Ge\(_7\)O\(_{15}\) (LGO) crystal substitute the Ge\(^{4+}\) host ions within oxygen octahedral complexes [1]. Incorporation of chromium ions into oxygen octahedra changes the local symmetry of the lattice site from monoclinic \(C_2\) group to triclinic \(C_1\) group. The local symmetry lowering is attributed to the effect of the additional defect compensating the charge misfit of Cr\(^{3+}\) ion at the Ge\(^{4+}\) site. Taking into account a weak coupling of lithium ions with the germanium–oxygen lattice framework [2], the interstitial Li\(^{+}\) is considered to be the most probable charge compensating defect, located within the structural cavity near the octahedral CrO\(_6\) complex. Subsequent measurements of optical spectra have confirmed the model of Cr\(^{3+}\)– Li\(^{+}\) pair centres in the LGO crystal structure [3,4].

The available data make it possible to assume that electric dipole moments of Cr\(^{3+}\)– Li\(^{+}\) pairs are directed along the crystal axis \(a\). Interstitial Li\(^{+}\) ions locally break the symmetry axis \(C_2\|b\) of the sites within the oxygen octahedral complexes [2]. As a result, there are two equivalent configurations of the pair centres which are conjugated by broken \(C_2\) axis and have dipole moments with opposite orientations. It may be assumed that pair centres can reorient due to thermal activation. Reorientation of the pair centres should be accompanied by: i) shortening of the configuration lifetime and ii) switching of defect dipole moments.

The paper is devoted to the detection of thermally activated Cr\(^{3+}\)– Li\(^{+}\) reorientation in LGO:Cr\(^{3+}\) crystal through measurements of EPR spectra and dielectric permittivity.

2. EPR lines width broadening

Angular variations of LGO:Cr\(^{3+}\) EPR spectra [1,5] have shown that for arbitrary orientations of static magnetic field \(B\) with respect to the crystal axes there are four \((k_m = 4)\) conjugated spectra of triclinic symmetry \(C_1\). For magnetic field \(B\) rotating in the main crystal planes two structurally equivalent Cr\(^{3+}\) spectra are registered. If Cr\(^{3+}\) centres kept the monoclinic local symmetry \(C_2\) of the perfect lattice sites, then the magnetic multiplicity of the spectrum would be \(k_m = 2\) with unique direction along axis \(b\) [6]. In this case, for a magnetic field rotating in \((ab)\) and \((bc)\) planes one spectrum would be observed, whereas in \((ac)\) plane two conjugated spectra would be detected. Therefore, doubling of the spectra in \((ab)\) and \((bc)\) planes results from lowering of the positional
symmetry $C_2 \rightarrow C_1$ due to the formation of $\text{Cr}^{3+}-\text{Li}^+$ pair centres. Assuming that at high temperatures the probability of reorientation between equivalent states should increase, it may be supposed that in $(ab)$ and $(bc)$ planes EPR spectra should broaden on heating [7]. It may be expected that a fast enough reorientation between equivalent configurations should average the local distortions produced by pair centres, and effectively restore point symmetry $C_2$ of the perfect lattice site.

Figure 1. Fragment of LGO:Cr$^{3+}$ EPR spectrum: four conjugated lines corresponding to electronic transition $|M_S| = 1/2 \rightleftharpoons 3/2$.

Figure 2. Temperature dependencies of the line width of the spectral components depicted in the figure 1: a) the total peak-to-peak line width; b) the line width, contributed by $\text{Cr}^{3+}-\text{Li}^+$ centres reorientation.

At low enough temperatures the so-called slow reorientation limit is valid [7]. The spectra from equivalent configurations are observed separately. EPR lines broaden on heating and the line width is inversely proportional to the life time $\tau'$ of the equivalent configurations

$$\delta B = \delta B_0 + \frac{h}{g\beta} \frac{1}{2\sqrt{3}\pi} \left(\tau'\right)^{-1},$$

where $\delta B_0$ is the background line width contributed by all other mechanisms except for the pair centres reorientation, $h$ is Planck constant, $g$ is the spectroscopic factor, $\beta$ is Bohr magneton, the life time $\tau'$ and relaxation rate $(\tau')^{-1}$ exponentially depend on the inverse temperature $(\tau'/2) = \tau = \tau_0 \exp(U/kT)$, $(\tau_0)^{-1}$ is frequency of oscillations near potential minima, $U$ is activation energy, $k$ is Boltzmann constant.

EPR spectra of LGO:Cr$^{3+}$ were measured using a conventional X-band spectrometer. The temperature of the samples was regulated by a standard gas flow cryostat. To detect the assumed local kinetics, the magnetic field $B$ was rotated from $c$ axis to $b$ axis by 26$^\circ$ and then tilted from $(bc)$ plane by $\approx 0.8^\circ$. For such an orientation, all four conjugated spectra are distinctly resolved. The group of conjugated EPR lines corresponding to the electronic transition $|M_S| = 1/2 \rightleftharpoons 3/2$ (figure 1) was measured in the temperature interval 290 ÷ 500 K. The line shape was described by a Lorentzian, the temperature dependencies of the line width are depicted in figure 2a. For all components the studied linewidths demonstrate non-monotonous temperature dependencies $\delta B(T)$. The decrease of $\delta B$ on heating in the interval 290 ÷ 380 K is obviously connected with ferroelectric phase transition ($T_C = 283.4$ K) which is accompanied by an EPR line width anomaly [5]. The anomalous line width broadening has been described by the Curie-Weiss law, and for the background line width in (1) the following expression was used

$$\delta B_0 = \delta B_0^0 + \frac{C_{\text{CW}}}{T-T_C}.$$  

The temperature dependence $\delta B_0$ in (2) being taken into account enables us to derive the line width contributed by the pair centres reorientation. The temperature dependencies of the line width originated from the pair centres dynamics are presented in figure 2b.

The oscillation frequency $(\tau_0)^{-1}$ was estimated from the Debye temperature which has a typical value of $\theta_D \approx 200$ K for the crystals of germanate family [8]. The activation energy is estimated
as \( U = 0.55 \pm 0.05 \text{ eV} \) from the line width of the four components registered. Evidently, in the temperature interval studied the line width broadening is too small (\( \sim 7\% \) from the background line width) and the activation energy is determined with low accuracy. Nevertheless, one can estimate in what temperature and frequency range the permittivity anomalies from \( \text{Cr}^{3+} - \text{Li}^+ \) reorientation can be detected.

3. Dielectric relaxation of \( \text{Cr}^{3+} - \text{Li}^+ \) pair centres

The permittivity of pure and \( \text{Cr}^{3+} \) doped (0.1 wt.) LGO crystals was measured using a bridge method in the temperature interval \( 300 \div 500 \text{ K} \) and frequency range \( 0.5 \div 10 \text{ kHz} \). Dependencies of real \( \varepsilon' \) and imaginary \( \varepsilon'' \) parts of LGO:Cr\(^{3+}\) permittivity measured along \( a \) axis are plotted in figures 3a, b. There is a distinct \( \varepsilon'(T) \) step-like anomaly and \( \varepsilon''(T) \) maximum which shift to high temperature side with the increasing of measuring field frequency \( f \). Along \( b \) and \( c \) axes the quantities \( \varepsilon' \) and \( \varepsilon'' \) of LGO:Cr\(^{3+}\) do not demonstrate any anomalies and slightly depend on temperature. For nominally pure LGO crystal, the real and imaginary parts of permittivity monotonously depend on temperature and do not show any anomalous features.

The anomalies of the LGO:Cr\(^{3+}\) permittivity are typical of a thermal polarization process [9]. The experimental data show that \( \varepsilon', \varepsilon'' \) anomalies are contributed by chromium dipole moments directed mainly along \( a \) axis. To determine the parameters of pairs centres reorientation, the real and imaginary parts of complex permittivity \( \varepsilon^*(T) \) (figure 3) are described by means of the Debye model

\[
\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + i\omega\tau},
\]

where \( \varepsilon_0 - \varepsilon_{\infty} = C/T, C \) is Curie constant, \( \omega \) is angular frequency of measuring field and \( \tau = \tau_0 \exp(U/kT) \) is relaxation time.

Fitting of (3) to the experimental data was carried out for the imaginary part of permittivity, since processing of \( \varepsilon''(T) \) maxima enables us to determine the parameters in (3) to a higher accuracy in comparison with less pronounced step-like \( \varepsilon'(T) \) anomalies. At high temperatures the background component of \( \varepsilon''(T) \) sufficiently increases as it may be described by the expression \( \varepsilon''_{\text{bg}} = \varepsilon''_{\text{bg}}^0 + A \exp(-W/kT) \), where \( \varepsilon''_{\text{bg}}^0 \) is the temperature independent part and \( W = 0.85 \text{ eV} \) is the activation energy for the exponential growth of the background component. The dependencies calculated by using (3) are shown in figure 3 by solid lines, the parameters used are

\[
\begin{align*}
\varepsilon_{\infty} &= 7.59 \pm 0.017, \\
\tau_0 &= (4.5 \pm 2) \cdot 10^{-13} \text{ s},
\end{align*}
\]

\[
\begin{align*}
C &= 907 \pm 14 \text{ K}, \\
U &= 0.66 \pm 0.02 \text{ eV}.
\end{align*}
\]

The comparison of the measured data and the calculated dependencies reveals that the Debye model makes it possible to describe the experimental results. The temperature dependence of...
the relaxation rate $\tau^{-1}$, obtained from $\varepsilon''(T)$, may be described by the Arrhenius law with good accuracy (figure 4).

It may be noted that the activation energy $U$ determined from the dielectric measurements (4) is close enough to the value (0.55 ± 0.05 eV), estimated from the EPR spectra. The frequency $(\tau_0)^{-1}$ (4) agrees well with independent measurements of the Debye temperature $\theta_D \approx 200$ K [8].

4. Conclusions

Investigations of EPR and permittivity spectra have made it possible to detect the thermally activated reorientation of $\mathrm{Cr}^{3+}$-- Li$^+$ pair centres in LGO crystal. The reorientation of $\mathrm{Cr}^{4+}$-- Li$^+$ pairs leads to a temperature EPR line width broadening and results in relaxation anomalies of the dielectric permittivity.

The reorientation of the pair centres is apparently realized by the hopping of interstitial Li$^+$ ions through the channels of LGO structure. It is obvious that the spatial location of $\mathrm{Cr}^{3+}$ ions is fixed within the oxygen octahedral complexes.

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