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ELECTRON SPIN RESONANCE STUDY OF THERMAL DEFECTS IN SrLaAlO₄ AND SrLaGaO₄ High-T_c SUBSTRATES

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The effect of annealing SrLaAlO₄ (SLA) and SrLaGaO₄ (SLG) crystals in oxidizing and reducing atmospheres in the temperature range of 950°C-1300°C was investigated. Three kinds of anisotropic defects D_1 , D_2 , and E at the temperature range of 4-300 K were found. By diagonalization of orthorhombic spin-Hamiltonian parameters: $|D| = 0.0541(10) \text{ cm}^{-1}$, $|E| = 0.0108(10) \text{ cm}^{-1}$, $g_{\parallel} = 0.883(5)$, and $g_{\perp} = 1.922(5)$ for D_1 defects for SLG and SLA were calculated and they had the same values within the margin of error.

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1. Introduction

Single crystals of SrLaAlO₄ (SLA) and SrLaGaO₄ (SLG) are considered as the promising substrates for HTSC films. Both, SLA and SLG, compounds crystallize in a tetragonal structure similar to that of K_2NiF_4 . This structure has I4/mmm space group symmetry [1]. There is little information in literature about thermal defects detected by electron spin resonance spectroscopy (ESR). It was reported [2] that as SLA crystals change colour from green-yellow to colourless the intensity of ESR signal is lowered, respectively. It was also reported [3] that crystals of SLG grow with different colours, green amber and yellow. Thermal defects denoted D and E were shown in Ref. [4]. These investigations are continued in this work.

2. Experiment

Single crystals of SLA and SLG were grown by the Czochralski technique with the use of iridium crucible. Both types of crystals contained iron impurity lower than 10^{-3} at.%. The samples typically $3.5 \times 3.5 \times 2$ mm³ were measured in a BRUKER ESP-300 ESR spectrometer (X-band). The spectrometer was equipped with a helium flow cryostat type ESR- 900 Oxford Instruments. The ESR lines were observed in the temperature range from 4 K to 300 K.

3. Results and discussion

The angular dependence of ESR spectrum at 20 K is depicted in Fig. 1. The variation of ESR spectrum from $H \parallel c$ to $H \perp c$ in (110) plane are shown in Fig. 2. Figure 2a depicts the spectrum obtained from the as-grown SLG sample and Fig. 2b shows a series of spectra of samples annealed in a dynamic vacuum of 10^{-5} torr at 1300°C for 1 h. The intensity of D_1 and D_2 spectra decreases and new "E" spectra appears (see Fig. 2b). In both figures we see two lines of D_1 and one line D_2 that have a large line width for $H \parallel c$ ($\Delta H = 100 \text{ mT}$) and for $H \perp c$ lines of D_1 and D_2 are placed in the lowest magnetic field and have a minimal line width ($\Delta H = 20 \text{ mT}$). In all spectra on the left we see the typical ESR spectra of iron doped samples. In the investigated crystals iron existed only as a residual impurity. After heat treatment in the dynamic vacuum the sample was annealed at 1200°C for 6 h under a pressure of 10 kbar in 20% O₂ and 80% Ar atmosphere. The disappearance of "E" spectra and an increase in D_1 , D_2 spectra were observed. The as-grown SLA sample was treated under the same conditions and changes of ESR spectra were not observed.



Fig. 1. Angular dependence of X-band spectra. Open squares are related to D_1 -spectrum, the solid lines are calculated from spin-Hamiltonian with the effective spin S = 1, solid circles and open triangles are related to D_2 and E defect, respectively. Fig. 2. The variation of D_1 , D_2 , and E shape lines for SLG crystal obtained for X-band at T = 20 K. The series of spectra are shown from $H \parallel c \ (0^\circ)$ to $H \parallel c \ (90^\circ)$ in (110) plane, (a) as-grown sample, (b) annealed in a dynamic vacuum of 10^{-5} torr at 1300°C for 1 h.

The spin Hamiltonian

$$\mathcal{H} = g\beta \boldsymbol{H} \cdot \boldsymbol{S} + D\left[\boldsymbol{S}_{z}^{2} - \frac{1}{3}\boldsymbol{S}(\boldsymbol{S}+1)\right] + E(\boldsymbol{S}_{x}^{2} - \boldsymbol{S}_{y}^{2})$$

with S = 1 was used to fit the experimental data with the theoretical calculations. The best fitting was obtained with the following parameters: $g_{\parallel} = 0.883(5)$, and $g_{\perp} = 1.922(5)$, $|D| = 0.0541(10) \text{ cm}^{-1}$, $|E| = 0.0108(10) \text{ cm}^{-1}$ for D_1 defects for SLG and SLA and they had the same values within the margin of error.

4. Conclusions

Considering the crystal structure of both compounds it can be concluded that the position of oxygen in the lattice, O1 laying on the *ab* plane, is more stable than the oxygen O2 laying along the axis *c*. The results of ESR investigation have been interpreted as related to defects in which the oxygen O2 is missing (the spectrum marked D_1 , D_2). The intensity of these lines depends on the colour of the crystals. The change of colour from colourless through yellow, green to dark-green correlates with the increasing of the number of defects represented in the ESR spectrum by lines D_1 , D_2 (see Fig. 3). The observed splitting of the ESR line (see Fig. 4) can be interpreted in the case of better crystallographic perfection of the crystal and in consequence a lower width of the lines. In such case the ESR lines related to the particular defects D_1 , D_2 can be separated from each other.



Fig. 3. ESR intensity signals for variously coloured crystals related to the intensity of D_1 line shown in the spectrum of the inset. Spectra are given at X-band, T = 20 K, and P = 2 mW.

Fig. 4. The line shape of the ESR spectrum for different concentrations of defects.

References

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