LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES 2012, N 6 (I)

DOI: 10.2478/v10047-012-0034-0

EPR SPECTRUM ANGULAR DEPENDENCES IN LiYF4 CRYSTAL

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Electron paramagnetic resonance (EPR) measurements have been made for two perpendicular planes in a LiYF₄ crystal before and after x-ray irradiation at room temperature. Analysis of the EPR spectrum angular dependence shows the presence of two defects – an impurity ion, which was embedded during the crystal growth process, and an x-ray induced defect with the g-factor of approx. 2.0. Spectral parameters and possible defect models are discussed.

Key words: *EPR spectrum, LiYF*₄ *crystal.*

1. INTRODUCTION

Due to its optical properties, lithium yttrium fluoride (LiYF₄) can be used in solid-state lasers and scintillation detectors; therefore, studying its structure defects is important. So far, the main area of interest has been LiYF_4 crystals doped with trivalent rare-earth elements, since they replace Y^{3+} ions and do not require additional charge compensation [1].

To be suitable in optical devices, $LiYF_4$ should not have too many impurities such as oxygen which easily incorporates into the crystal during its growth. Recently, possible locations of the oxygen impurity have been studied (see *eg* [2]).

Studies of radiation-induced defects have shown that it is possible to generate the intrinsic defects such as F- and V_{K} -centres in LiYF₄; however, they are unstable at room temperature (RT) [3]. In our recent research, a radiation defect which is stable at RT was observed, and a qualitative analysis has been made; however, due to complexity of the hyperfine structure of EPR spectrum a defect model has not been created [4].

In the present work, the EPR spectrum angular dependences of RT stable radiation defect are simulated, and a defect model is proposed based on the spectrum parameters.

2. METHODS

The LiYF₄ crystal has a tetragonal structure belonging to the I4₁/a space group with C_{4h}^{6} symmetry. Each Li⁺ ion is surrounded by four equidistant F⁻ ions. The Y³⁺ ion (with local S₄ point symmetry) is at the centre of a dodecahedron of 8 F⁻ ions [5].

A nominally undoped LiYF₄ sample was grown at the Institute of Solid State Physics by Czochralski's technique. The c-axis of the sample was determined using an optical microscope; the sample was irradiated with *x*-rays (50 kV, 10 mA, 30 min) at RT [4].

The EPR spectra and their angular dependences were obtained at the liquid nitrogen temperature (77 K) using an RE 13-06 spectrometer by rotating the crystal around either of two perpendicular axes, both oriented perpendicularly to the applied magnetic field. The rotation axes were selected in the following ways: 1) parallel to the crystal c-axis; 2) around an arbitrary direction perpendicular to the *c*-axis. In a coordinate system fixed to the crystal axes this resulted in rotation of the magnetic field in two perpendicular planes (referred to below as "A" and "B", respectively). The microwave frequency was 9.080 GHz.

For analysis of the LiYF₄ geometric structure, VESTA (a 3D visualization program) was used, in which a model of LiYF_4 was created from the coordinates of atom positions found in literature [6]. The inter-atomic distances and the relevant angles formed with the crystal c-axis were determined with the software.

The spectrum modelling was done with EasySpin [7] program, which uses the Matlab environment for calculations. For convenient parameter input a graphical user interface was created. The spin-Hamiltonian used for the calculations was:

$$\hat{H} = \mu_B \vec{B} \tilde{g} \hat{S} + \sum_i \hat{S} \tilde{A}_i \hat{I}_i$$

where

the first term is responsible for the electron Zeeman interaction,

 μ_B – Bohr magneton;

 \vec{B} – magnetic induction;

 \tilde{g} – g-tensor;

 \hat{S} – electron spin operator,

and

the second - for the electron hyperfine interactions with surrounding nuclei,

 \tilde{A} – hyperfine coupling tensor;

 \hat{I} – nuclear *spin* operator.

3. RESULTS

The EPR spectrum angular dependences of two different defects were observed – the first before x-ray irradiation (Fig. 1 and Table 1), and the second defect appeared after the irradiation (Fig. 2 and Table 2).

Figure 1 shows the EPR spectrum angular dependences of the LiYF₄ sample before irradiation. The isotropic spectra observed in plane A are simulated in a paramagnetic centre model, which has its g-tensor z-axis oriented along the crystal c-axis of crystal. The anisotropy observed in plane B arises from the differences in g-tensor components g_{\perp} and g_{\parallel} . To simulate the hyperfine structure of a spectrum when the LiYF₄ c-axis orientation is 90° in respect to the external magnetic field, two anisotropic interactions with fluorine nuclei are necessary.



Fig. 1. EPR spectrum angular dependences of the non-irradiated LiYF₄ sample.

Table 1

Modelling parameters for Fig. 1

g⊥=1.890		$g_{\parallel}\!=1.979$			
Euler angles of g-tensor z-axis			Hyperfine interactions with fluorine nuclei		
α, °	β, °	γ, °	Quantity	A⊥, MHz	A_{\parallel}, MHz
0	0	0	2	15	8



Fig. 2. EPR spectrum angular dependences of the irradiated LiYF₄ sample.

Modelling	parameters	for	Fig.	2
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g⊥=2.007	'		$g_{\parallel}\!=2.028$			
Euler angles of g-tensor z axis			Hyperfine interactions with fluorine nuclei			
α, °	β,	0	γ, °	Quantity	A⊥, MHz	A_{\parallel}, MHz
0	12	27	0	1	28	28
270	12	27	0	4	9	9
241	1	5	0			
150	16	55	0			
14	6	7	0			
195	6	7	0			

Figure 2 shows the EPR spectrum angular dependences of the irradiated LiYF_4 sample. The best fit of a simulated spectrum with the experimental one was obtained taking the sum of the spectra generated by six paramagnetic centre orientations with a spin s = 1/2 located in a fluorine position with axial g-tensors in the directions to the six closest fluorine nuclei. The width and shape of spectral lines was simulated by five hyperfine interactions where one was significantly stronger than the other four.

4. DISCUSSION

4.1. Impurity centre

The spectrum (Fig. 1) of non-irradiated sample can be best described with a g-tensor that has its z-axis oriented along the LiYF_4 crystal c-axis. There are different ion pairs in this crystal that have such orientation, the closest of them being Li-Y ion pairs (5.37 Å). As the defect was observable before irradiation, it is reasonable to suggest that it is an impurity which is incorporated into the crystal during its growth process; however, further investigation is needed to determine the structural model of this defect.

4.2. Radiation defect

The structure of radiation defect EPR spectra shown in Fig. 2 is more complex: anisotropy is seen in both planes. For simulation of the spectrum parameters different defect geometries were considered; however, with most of them it was not possible to achieve a good fit of the simulated spectra with the experimental angular dependence "frames" in both rotation planes simultaneously. The best fit was achieved in a model where the defect is located in a fluorine position and its g-tensor's z-axis is oriented in the directions to neighbouring fluorine ions. The hyperfine interaction tensors show that an oriented orbital of the unpaired electron should be used for interpretation of the spectrum parameters, because one of the hyperfine interactions is considerably stronger than others. This excludes the possibility of applying the F- or V_{K} -centre models.

The oxygen impurity O⁻- and O²⁻-centres have been observed in different materials with similar g-tensor values [8]. Oxygen is known as a common impurity in fluoride crystals. It usually forms composite defects with a fluorine vacancy nearby for charge compensation. In a LiYF₄ crystal, oxygen (its O²⁻ form) could take a fluorine position, and initially charge compensation would be necessary by a

fluorine vacancy located in one of the nearest six fluorine positions. After x-ray irradiation the charge of oxygen impurity would change to O^- ; thus, the centre becomes "EPR active". The oxygen O^- with $1s^22s^22p^5$ electron configuration has the outer orbital with a p-type wave function; therefore, one of the neighbouring fluorines could be located closer to the p-orbital density maximum and is to interact with the paramagnetic centre stronger than the other four nuclei. The above described model of the oxygen-vacancy defect in LiYF₄ is shown in Fig. 3.



Fig. 3. O⁻-centre as a model for the radiation defect in irradiated $LiYF_4$ crystal:

- Li lithium ion;
- Y yttrium ion;
- O^- oxygen impurity;
- V_F fluorine vacancy shown in one of the six possible fluorine sites;
- F nearby fluorine ions.

5. CONCLUSIONS

Two defects have been observed in the EPR spectrum of $LiYF_4$ crystal: one is an impurity centre created during the crystal growth process, the other one – a radiation induced defect.

The angular dependences of the impurity centre EPR spectrum can be simulated in a model of the paramagnetic centre oriented along the $LiYF_4$ c-axis and having two anisotropic interactions with fluorine nuclei. The first choice for such a direction in the crystal should be that towards the Li–Y site; however, a definite model has not been created yet.

The EPR spectrum angular dependences of the second (radiation) defect can be satisfactorily simulated with a sum of six paramagnetic centre orientations which correspond to a defect in the fluorine position with the axial g-tensor, its principal axis directed to one of the neighbouring fluorine ions. A proposed defect model is an O⁻-centre with a fluorine vacancy nearby for charge compensation and the other five fluorine nuclei creating the hyperfine structure of the spectrum.

ACKNOWLEDGMENTS

The authors thank the Latvian Council of Science, grant project No 09.1126, for financial support.

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EPR SPEKTRU LEŅĶISKĀS ATKARĪBAS LiYF4 KRISTĀLĀ

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Kopsavilkums

Darbā veikti elektronu paramagnētiskās rezonanses (EPR) un tās leņķisko atkarību mērījumi LiYF₄ kristālā, rotējot magnētisko lauku divās perpendikulārās plaknēs, pirms un pēc apstarošanas ar rentgenstariem istabas temperatūrā. EPR spektru leņķiskās atkarības liecina par divu defektu klātbūtni – piejaukuma jona, kas radies kristāla audzēšanas laikā, un radiācijas defekta ar aptuvenu g faktora vērtību 2,0. Darbā apspriesti spektru parametri un iespējamie defekta modeļi.

29.08.2012.