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EPR HYPERFINE STRUCTURE OF RADIATION DEFECT IN OXYFLUORIDE GLASS CERAMICS

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We have investigated the samples of thermally treated oxyfluoride glass ceramics $50SiO_2–25LiO_2–20YF_3–3ErF_3–2YbF_2$ by means of electron paramagnetic resonance (EPR) techniques. After irradiation of the samples with X-rays, in the EPR spectra a hyperfine structure characteristic of F-centres could be observed in different fluoride crystals. The structure of F-centre in the oxyfluoride glass ceramics containing $LiYF_4$ crystallites is discussed.

Key words: *electron paramagnetic resonance, defects, glass ceramics*.

1. INTRODUCTION

Ceramic materials based on fluoride components are perspective materials for various optical applications, like materials for solid laser and scintillator technology, especially when doped with rare-earth ions [1]. Properties of these materials depend on the impurity defects and the defects created by irradiation. Oxyluoride glass ceramics consists of a glass matrix and fluoride crystalline parts which are created by thermal treatment [2].

In this work, we used the electron paramagnetic resonance (EPR) as a structure-sensitive method to investigate the nearest coordination of irradiation defects in oxyfluoride glass ceramics.

Recently, F-centre as a radiation defect in fluorine crystals has been studied in detail in [3] for $LiBaF_3$ crystals and in [4] for $LiYF_3$ crystals. At the same time, no reports could be found on the resolved hyperfine (HF) structure of the EPR spectra of F-centres in the disordered structures like oxyfluoride glass and oxyfluoride glass ceramics.

In this work, the EPR spectra of investigated oxyfluoride glass ceramics samples after thermal treatment and irradiation with X-rays have shown hyperfine interactions, which we describe below as belonging to a radiation defect (F-centre) in $LiYF_4$ crystals.

2. EXPERIMENTAL

Oxyfluoride glass and glass ceramics of the following composition were obtained at the Institute of Solid State Physics (in mol%):

$$50SiO_2–25LiO_2–20YF_3–3ErF_3–2YbF_2$$

These components were mixed together in a corundum melting crucible and heated in air or in another atmosphere up to 1450 ^{o}C. After the heat treatment, in order to avoid crystallization of the samples, they were quickly cooled down between two iron plates to increase the temperature drop. The produced glass samples were thermally treated at 550 ^{o}C for 20 min to reach a crystallization of the fluorine-rich parts. All EPR measurements were performed at liquid nitrogen temperature (77 K) using a standard X-band EPR spectrometer with the microwave frequency of ~9.1 GHz. The measurements were made several times, and the experimental data were averaged to achieve a better signal-to-noise ratio. After the thermal treatment, the samples were X-ray irradiated (50 kV, 10 mA) for 1 h at room temperature (RT). The EPR spectra were recorded for the samples before the thermal treatment, after the thermal treatment, and after the irradiation.

3. RESULTS AND DISCUSSION

The EPR spectra of investigated oxyfluoride glass and glass ceramics samples are shown in Fig. 1, where (*a*) is the oxyfluoride glass EPR spectrum, and (*b*) is the EPR spectrum of oxyfluoride glass ceramics obtained by the heat treatment of glass. The creation of a crystalline phase was confirmed by X-ray diffraction (XRD) measurements.

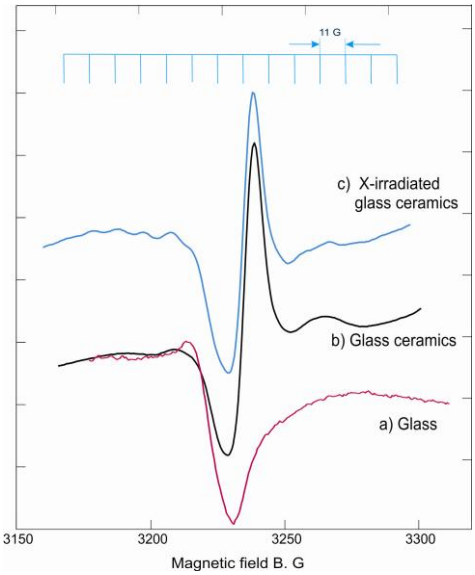

Fig.1. EPR spectra of: *a*) as-prepared oxyfluoride glass; *b*) oxyfluoride glass ceramics obtained by 20 min heating at 555 ^{o}C; *c*) X-ray irradiated oxyfluoride glass ceramics.

After irradiation of the sample with X-rays, the EPR measurements show additional absorption lines of radiation defects (Fig. 1*c*). The radiation defects created by X-irradiation are decaying within approx. one hour at the liquid nitrogen temperature and within few minutes at RT.

In order to evaluate the changes in the EPR spectra after X-irradiation in the most precise way, average of up to 40 spectra was obtained – both before and after the irradiation, and then the difference was calculated. Figure 2*b* shows the changes in the EPR spectra due to irradiation; approx. 12 to 14 equidistant EPR HF lines

could be observed. A similar hyperfine structure with a large number of hyperfine lines was observed earlier for the F-centres in LiF [3] and $LiBaF_3$ [4] crystals, leading us to the conclusion that in glass-ceramics we also observe the EPR of F-centres.

The $LiYF_4$ crystalline phase is the most pronounced one in the XRD spectrum. However, some smaller XRD lines could be associated with other crystalline phases.

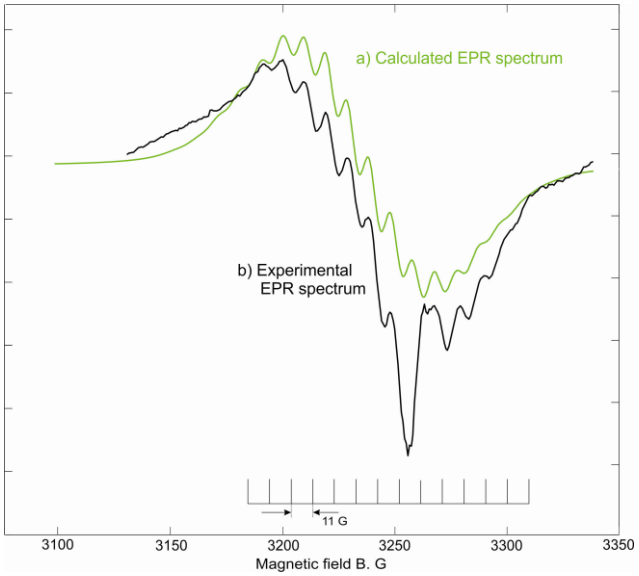

Fig. 2. a) Calculated EPR spectrum of the F-centre in the oxyfluoride glass ceramics containing $LiYF_4$ crystallites; *b*) experimental EPR spectrum taken as a difference between the spectra after and before X-irradiation.

The observed hyperfine structure of EPR spectrum could be satisfactorily calculated within the F-centre model with the following spin-Hamiltonian:

$$\hat{H} = \mu S\, g\, B + \sum_{i=1}^{N_F} SA_i^F I_i^F + \sum_{j=1}^{N_Y} SA_j^Y I_j^Y + SA^{Li} I^{Li},$$

where μ is the Bohr magneton,
A_i^F, A_j^Y, A^{Li} are hyperfine interaction constants for fluorine, yttrium and lithium nuclei,
I_i^F, I_j^Y, I^{Li} denote corresponding nuclear spins,
N_F and N_Y are the numbers of neighbouring fluorine and yttrium nuclei, respectively.

Six fluorine neighbours are the closest to the fluorine vacancy, (the distances are from 2.67 Å to 2.80 Å, with differences less than 5%); other fluorine atoms are more distant and cannot contribute to the HF structure to the same extent. To calculate the HF interaction in an F centre model the following parameters were taken: electron (S =1/2, g~2.00) – interacts isotropically with six fluorine nuclei (A^F = 53.8 MHz, N_F = 6); two yttrium nuclei (A^Y = 26.9 MHz, N_Y = 2); and one lithium nucleus (A^{Li} = 26.9 MHz). The microwave frequency was ν = 9.1 GHz and

the line width was 11 G. We included the interaction with only one nearest Li neighbour (fluorine vacancy – lithium distance 1.71 Å), because the next nearest Li neighbour is already at a much larger distance (2.91 Å).

For the simulations of EPR spectra we used the Easyspin Matlab package [5]. The calculated EPR spectrum is shown in Fig. 2*a*.

Calculations have also been performed on other models, including different HF interactions and numbers of neighbouring Li, Y and F nuclei. However, only the F-centre model in $LiYF_4$ demonstrates a good coincidence with the hyperfine structure of the experimental data.

In Fig. 2*a* it is seen that the calculated spectrum has a good agreement with the experimental data; the observed hyperfine structure could be explained as arising from the F-centre in $LiYF_4$ crystallites, where the electron with spin $S = 1/2$ interacts with 6 fluoride + 2 yttrium +1 lithium neighbor nuclear spins, as shown in Fig. 3.

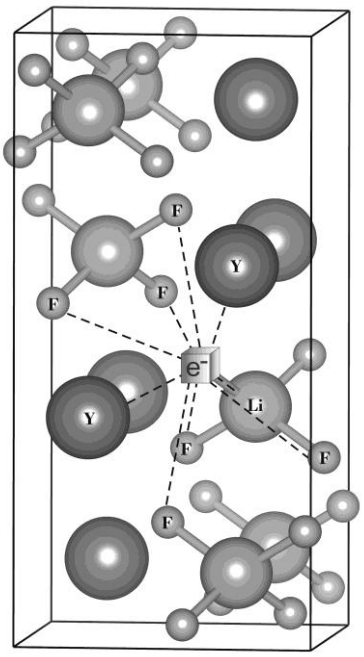

Fig. 3. Structure of the $LiYF_4$ crystal showing F-centre model and nearest Li, Y and F neighbours.

Six nearest fluorine nuclei are approximately at equal distance to the fluorine vacancy and seem to have nearly the same hyperfine interaction parameter A^F. The intensity distribution in the hyperfine structure of the spectrum is far from a binomial distribution. However, inclusion of additional hyperfine interactions with the Y and Li nuclei allows reproducing the hyperfine structure of the observed EPR spectrum (Fig. 2*b*). The relative amplitude of a couple of central EPR lines of the experimental spectrum could not be determined precisely enough due to the initial overlap with the intense and broad lines of other defects seen in the spectra of Fig. 1.

4. CONCLUSIONS

After X-irradiation of the oxyfluoride glass ceramics of $50SiO_2–25LiO_2–20YF_3–3ErF_3–2YbF_2$ composites, the EPR spectrum of a radiation defect with a pronounced hyperfine structure has been observed.

The defect is thermally unstable at room temperature.

The observed hyperfine structure could be explained as arising from the F-centre in $LiYF_4$ crystallites, where the electron with a spin $S = 1/2$ interacts with 6 fluorine + 2 yttrium +1 lithium neighbour nuclear spins.

ACKNOWLEDGEMENTS

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REFERENCES

1. Chen, D., Wang, Y., E. Ma, Y. Yu, Bao, F., Hu, Z., & Cheng, Y. (2006). Influences of Er^{3+} content on structure and upconversion emission of oxyfluoride glass ceramics containing CaF_2 nanocrystals. *Materials Chem. and Phys., 95*, 264.
2. Dejneka, M.J. (1998). Transparent oxyfluoride glass ceramics, *MRS Bulletin, 23*, 57.
3. Kaplan, R., & Bray, P.J. (1963). Electron-spin paramagnetic resonance studies of neutron-irradiated LiF. *Phys. Rev. B, 129*, 1919.
4. Fedotovs, A., Elsts, E., Rogulis, U., Gulans, A., Tale, I., Nikl, M., Ichinose N., & Shimamura, K. (2007). EPR Hyperfine Structure of F-type Centres in Pure $LiBaF_3$ .Crystal. *Phys. stat. sol., (c), 4* (3), 1284.
5. Stoll, S. & Schweiger, A. (2006). EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Res*., 178, 42.

RADIĀCIJAS DEFEKTA EPR HIPERSĪKSTRUKTŪRA OKSIFLUORĪDU STIKLA KERAMIKĀ

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K o p s a v i l k u m s

Oksifluorīdu stiklu keramikas $50SiO_2–25LiO_2–20YF_3–3ErF_3–2YbF_2$ radiācijas defektu īpašības pētītas, izmantojot elektronu paramagnētiskās rezonanses (EPR) metodi. Pēc paraugu apstarošanas ar rentgen stariem, EPR spektros tika novērota vairāku fluorīdu kristālu F-centriem raksturīga hipersīkstruktūra. Šajā darbā apskatīta F-centra struktūra oksifluorīdu stiklu keramikā, kura satur $LiYF_4$ kristalītus.

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