EPR of radiation defects in lithium-oxyfluoride glass ceramics

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Abstract. We studied oxyfluoride composites based on lithium silicate glasses with yttrium fluorides and rare-earth dopants. The electron paramagnetic resonance (EPR) has been used to obtain information about radiation induced defects in these materials. Spectra have been measured before and after X-ray irradiation at room temperature and at liquid nitrogen temperature. Fluoride crystallites within samples were created by means of thermal treatment at specific temperatures. EPR spectra of radiation induced defects in oxyfluoride glass ceramics, in which crystallites have not been yet created, show no explicit hfs interaction of fluorine nuclei. However, in glass ceramics, which already contains fluoride crystallites, the hfs characteristic to fluorine nuclei appears in the EPR spectra. EPR hyperfine structure could be explained within a model of an F-type centre in YF$_3$ crystalline phase.

1. Introduction
Composite materials, consisting of a glass matrix with introduced micro/nano-crystallites (called also glass-ceramics), can possess properties either of the glass matrix or the crystallites, as well as new properties, that extend the scope of their applications. Fluoride nano-crystals have been obtained recently in fluorozirconate glasses, a novel application of fluorozirconate glass-ceramic has been proposed as an x-ray storage phosphor [1]. Less investigated are fluoride crystallites in oxyfluorides, new interesting properties of the so-called up-conversion have been reported in [2,3]. Most of the studies concern the up-conversion process in oxyfluoride glass-ceramics doped with rare earth element activators. After a specific treatment, rare earth ions incorporate into the fluoride crystallites. The intensity level of the luminescence is higher than in the glass material. However, electron paramagnetic resonance studies are rare in this field.

2. Experimental
In the present work, we studied oxyfluoride composites based on lithium silicate glasses with fluorides, obtained at the Institute of Solid State Physics of University of Latvia. Oxyfluoride glass has been prepared from the following ingredients mixture containing 50 mol% SiO$_2$, 25 mol% Li$_2$CO$_3$, 20 mol% YF$_3$, 3 mol% ErF$_3$ and 2 mol% YbF$_3$. Fluoride crystallites within samples have been created by means of thermal treatment at approximately 555°C temperature for 20 minutes. To obtain information about radiation induced defects in these materials we used a standard X-band electron paramagnetic resonance (EPR) spectrometer. Spectra were measured before and after X-ray irradiation at room temperature (RT) and at liquid nitrogen temperature (LNT).
3. Results

EPR spectra of radiation induced defects were obtained in both glass and glass-ceramics materials. No EPR signal could be detected prior to irradiation. After the irradiation various absorption lines appeared in the EPR spectra (see figure 1). Comparing EPR spectra of the glass and the glass-ceramics, considerable qualitative additional features could be observed in the glass-ceramics: 1) intense line at 1500 Gs, could probably be attributed to a Fe$^{3+}$ impurity in oxide glasses, 2) two broad bands between 1500 Gs and 3000 Gs 3) two broad lines at 3250 Gs, one with a g-factor $g = 1.975$ obscuring partially resolved hyperfine structure (hfs) of the spectrum (see details in figure 2). A sharp line at 3200 Gs is common in both material states and is attributed to some typical irradiation defect in silicate glasses. Radiation induced defects in oxyfluoride glass ceramics, in which crystallites have not been yet created, show no explicit hfs interaction of fluorine nuclei. Hypefine lines could be resolved only at 77 K and after warming to RT the hfs spectrum disappears.

4. Discussion

Our analysis of the obtained EPR spectra is based on our previous knowledge about radiation induced defects in fluoride single crystals. EPR spectra of such defects often showed well-pronounced hyperfine structure (hfs) caused by interaction with neighboring flourine nuclei (LiF [4], LiBaF$_3$ [5] and others).

To separate EPR spectra of the glass and the glass-ceramics spectra the glass spectrum was subtracted from the spectra of the glass ceramics (see figure 1c) so distinction between both is seen in more details.
There are several possibilities for creation of crystalline phases. Most probable phases are as following: oxides – LiYSiO$_4$, Y$_2$SiO$_5$, Li$_2$SiO$_3$ and fluorides – YF$_3$, LiF and LiYF$_4$. It is well known that hfs interaction with fluorine nuclei often leads to a well-pronounced hfs structure in the EPR spectra. EPR of intrinsic defects induced with irradiation in fluoride single crystals are well studied [4,5,6]. g-factor <2 indicates that our discussed defect is rather an electron centre. In our case, an F-type centre as a most probable model could be considered. Similar centres have been reported in LiF and LiBaF$_3$ [4,5].

Spin Hamiltonians (1) and (2) could describe the interaction of a paramagnetic electron with its nearest surrounding ions with nonzero nuclear spins in the case of interaction with fluorine and lithium ions:

\[
\hat{H} = \mu \hat{g} \mathbf{B} + \sum_{i=1}^{N_F} SA^F_i I^F_i + \sum_{j=1}^{N_Y} SA^{Y_j} I^{Y_j} \tag{1}
\]

\[
\hat{H} = \mu \hat{g} \mathbf{B} + \sum_{i=1}^{N_F} SA^F_i I^F_i + \sum_{j=1}^{N_Li} SA^{Li_j} I^{Li} \tag{2}
\]

Nuclear spins of possible fluoride crystalline components are $I^F_y=1/2$, $I^F_x=1/2$, $I^{Li}=3/2$ (only Li$^7$ isotope is taken into account). A number of specific nuclei is denoted accordingly with $N_F$, $N_Y$ and $N_{Li}$. For evaluation of a proper number of nearest neighbors a crystalline structure of possible crystalline phases should be considered. Hyperfine structure in this case should be caused by a certain number of equidistant fluorine nuclei $N_F$, equidistant yttrium nuclei $N_Y$ and/or equidistant lithium nuclei $N_{Li}$. Since the hfs of the spectrum is partially obscured by the two broad EPR lines, we cannot precisely resolve the number of lines. Thus we base our simulated spectra on a qualitative coincidence with the common width of the spectrum and relative intensities of the hfs lines. The most probable model of the crystalline phase would be that of YF$_3$. It allows us to consider a hfs interaction of the electron with $N_F=10$ and $N_Y=4$ nuclei. Resulting simulated spectrum shows a rather good coincidence with the experimental spectrum (see figure 3). Other possibilities, which included an hfs interaction with Li nuclei, do not seem so reasonable. In any case, by adding of two lithium nuclei to the model, the number of fluorine nuclei should be decreased by at least three nuclei, which is not reasonable in any considerable model of the crystalline phase.

Figure 2. Part of the experimental EPR spectra of radiation defects in oxyfluoride glass (G) and glass-ceramics, whereby only the crystalline part (C) is shown.
The hfs of the F-centre in LiF includes hf interaction with six Li\textsuperscript{7} and two F\textsuperscript{19} nuclei [4], but F-type center in LiBaF\textsubscript{3} possess hf interaction with two Li\textsuperscript{7} and eight F\textsuperscript{19} nuclei [5]. Thus the Li hf interaction has been excluded from our present analysis. The XRD data on our samples confirm possibility of both YF\textsubscript{3} and LiYF\textsubscript{4} phases in the material. However, it is still not clear, which crystallographic structure obtained crystallites could possess.

![Experimental EPR spectra of radiation defect in oxyfluoride glass and glass-ceramics compared with a simulated EPR spectrum taking into account hfs with 10 fluorine and 4 yttrium nuclei.](image)

**Figure 3.** Experimental EPR spectra of radiation defect in oxyfluoride glass and glass-ceramics compared with a simulated EPR spectrum taking into account hfs with 10 fluorine and 4 yttrium nuclei.

5. Conclusions
Radiation defects have been studied in X-irradiated glass-ceramics crystalline phases, where clearly distinguishable hfs interaction in the EPR spectrum could be observed. Hyperfine structure of the spectrum could be explained within a model of an intrinsic radiation defect - F-type centre in the YF\textsubscript{3} crystalline phase. Following isotropic parameters have been estimated: $g = 1.975$, $A_F = 56$ MHz, $A_Y = 23$ MHz.

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