

Optical Detection of Paramagnetic Centres in Activated Oxyfluoride Glass-Ceramics

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Electron paramagnetic resonance (EPR), magnetic circular dichroism (MCD) and EPR detected via MCD (MCD-EPR) investigations have been performed on rare-earth activated oxyfluoride glasses and glass-ceramics. Er³⁺, Gd³⁺, and Mn²⁺ activators in oxyfluoride glass-ceramics show paramagnetic MCD behaviour and the MCD-EPR has been detected. The results of the MCD-EPR measurements for the Er-doped oxyfluoride glass-ceramics showed that Er³⁺ ions in the CaF₂ crystallites in these ceramics embed only in the cubic symmetry environment, similarly to the previous observations of cubic Gd³⁺ centres in the glass-ceramics containing CaF₂. Finally, the correlation of optics and paramagnetic centres is discussed for Mn-doped YAlO₃ ceramics.

DOI: [10.12693/APhysPolA.133.785](https://doi.org/10.12693/APhysPolA.133.785)

PACS/topics: 76.70.Hb, 76.30.-v

1. Introduction

Oxyfluoride glass-ceramics are transparent composite materials consisting of the oxide glass matrix and fluoride micro- and nanocrystals obtained by a thermal annealing of the initial oxyfluoride glass [1]. Activated oxyfluoride glass ceramics have found an application as infrared converters [2], and are considered for applications as scintillators [3] and phosphors for white LED's [4].

Activator centres as well as colour centres are often paramagnetic (PM) and may affect the properties of the glass-ceramics significantly. Investigations of the paramagnetic centres by the conventional EPR techniques usually do not allow to directly attribute these centres to particular optical bands of the given sample. For this purpose the most convenient is the EPR optically detected via the magnetic circular dichroism (MCD and MCD-EPR) [5–7]. Usually the correlation between the optical and paramagnetic properties of point defects has been studied in crystalline materials, where the angular dependences of the magnetic resonances are well pronounced [5]. Nevertheless, the correlation of optical and paramagnetic properties of activator centres is an actual task also in glass-ceramics and ceramic samples [7].

In this work, we present the results of the MCD and the MCD-detected EPR measurements of the Er³⁺, Gd³⁺ [8], and Mn²⁺ doped oxyfluoride glass-ceramics. Through the MCD-EPR, the direct correlation between the optical absorption and the local structure of the activator centres in these glass-ceramics has been established. More complicated task is the attribution of the optical

spectra and paramagnetic centres for the ceramics, e.g. Mn-doped YAP ceramics [9]. EPR measurements on the Mn-doped YAlO₃ (YAP) ceramics show a presence of only Mn²⁺ centres, however, the luminescence measurements contain both Mn²⁺ and Mn⁴⁺ centres. The MCD is not available due to the opacity of the ceramics. In this case the only possibility is to establish the correlation by the MCD-EPR first in the half-transparent crystalline analogues and then to verify it for the corresponding ceramics.

2. Experimental

Aluminosilicate oxyfluoride glasses and glass-ceramics have been prepared at the Institute of Solid State Physics, University of Latvia. Glass-ceramics have been obtained by annealing of glasses at temperatures in the range from 600 °C to 700 °C. The composition of the melt (in mol.%) for the Er-doped samples was 46SiO₂–20.5Al₂O₃–8CaCO₃–25.5CaF₂–0.1Er₂O₃. For the Gd-doped samples the composition was 46SiO₂–20Al₂O₃–8CaCO₃–26CaF₂–0.1Gd₂O₃. The size of the crystallites in the Er- and Gd-doped glass-ceramic samples was estimated from the XRD data to be few tens of nm.

The composition for the Mn-doped samples was 55SiO₂–10Al₂O₃–15Na₂CO₃–10ZnO–10SrF₂–0.5MnF₂. Glass ceramics samples were at least partially transparent, which allows investigate them with the MCD.

The Mn-doped YAP ceramics sample IK6 was the same as the #6 in Ref. [9]: Y_{1.01}Al_{0.99}O₃–0.01Mn–0.1Hf. The YAP ceramics sample was not transparent.

MCD and MCD-EPR measurements have been performed with the custom-built spectrometer based on the Oxford Instruments magneto-optical cryostat, operating at magnetic fields up to 3 T, down to temperatures of 4.2 or 1.5 K, in the microwave range from 36 to 62 GHz. For

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the optical detection of the paramagnetic centres in the investigated aluminosilicate oxyfluoride glass-ceramics, we used the magnetic circular dichroism and MCD-EPR techniques similar as described in [5].

EPR measurements have been performed at 9.14 GHz microwave frequency at temperature 77 K.

3. Results and discussion

MCD-EPR could be observed in the MCD bands which have paramagnetic behaviour [5]. The intensity of the MCD spectra of the Er^{3+} -doped oxyfluoride glass-ceramics sample is nearly proportional to the reciprocal temperatures as it is characteristic for the paramagnetic MCD (see Fig. 1). We observed the paramagnetic MCD for the oxyfluorides activated by Mn^{2+} , Eu^{2+} , Gd^{3+} , Ho^{3+} , Sm^{3+} and Er^{3+} . Oxyfluorides activated by Tb^{3+} and Dy^{3+} showed no paramagnetic components in the MCD signal.

Nearly the same MCD has been observed in glasses and in the glass-ceramics. The MCD measurements alone do not allow to say if some of Er^{3+} ions could embed in the CaF_2 crystallites.

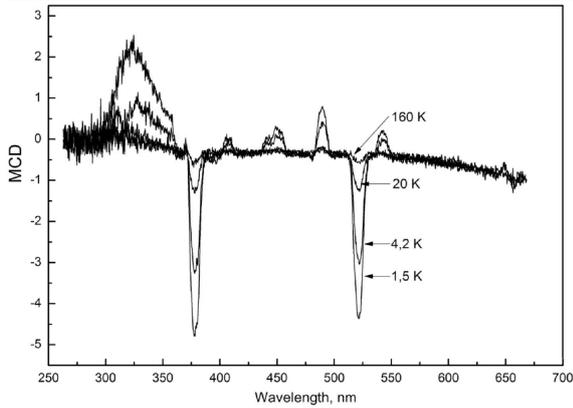


Fig. 1. Temperature dependence of the MCD spectrum of the Er-doped glass-ceramics sample measured at $B = 1$ T. So-called paramagnetic behaviour for all the MCD bands has been observed.

In the initial Er-doped glass, no MCD-EPR signal could be observed. For the glass-ceramics sample, the MCD-EPR signal has been observed only at the magnetic field of about 655 mT (see Fig. 2), which corresponds to the Er^{3+} ions in the CaF_2 in the cubic environment [10].

The resonances of the Er^{3+} ions in tetragonal and trigonal [10] environment in the CaF_2 have not been observed in the MCD-EPR. Therefore, Er^{3+} ions in the CaF_2 crystallites in these ceramics embed only in the cubic symmetry environment. Similar MCD-EPR results have been observed in the Gd^{3+} -doped oxyfluoride glass-ceramics (for details, see [8]).

Figure 3 shows the MCD-EPR and the corresponding MCD spectrum (inset) of the Gd-doped glass ceramics. Again, only the MCD measurements do not allow draw conclusions about the embedding of the Gd^{3+}

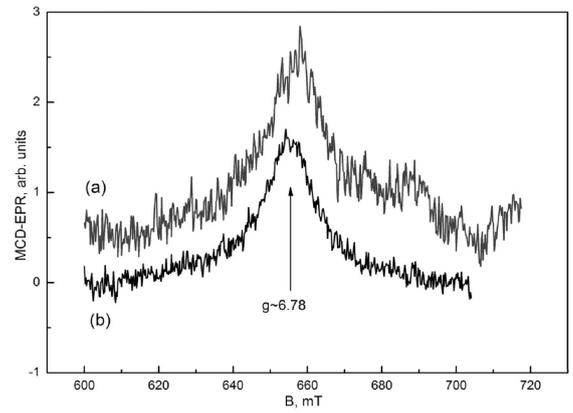


Fig. 2. MCD-EPR spectrum of the Er-doped glass-ceramics sample, measured at two different MCD bands — 377 nm (a) and 521 nm (b) at $T = 1.5$ K and at the microwave frequency 62 GHz. The magnetic field dependent background has been subtracted. The resonance at $g \approx 6.78$ corresponds to the cubic Er^{3+} in CaF_2 crystallites.

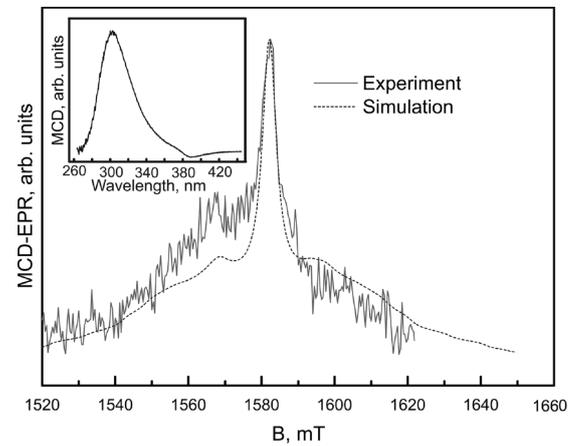


Fig. 3. MCD-EPR spectrum of the Gd^{3+} -doped glass ceramics sample measured at the 44.2 GHz microwave frequency. The spectrum could be well simulated with the EPR parameters of the cubic Gd^{3+} in the CaF_2 crystallites (for more details see [8]). Inset shows the corresponding MCD spectrum of the glass-ceramics, measured at $T = 4.2$ K and $B = 1$ T.

in the CaF_2 crystallites. The experimental MCD-EPR spectrum of the Fig. 3 has been successfully simulated with the EPR parameters of the cubic Gd^{3+} centre in CaF_2 [11]. In the initial Gd-doped glass-ceramics no MCD-EPR signals of the cubic Gd^{3+} could be observed. The embedding of the Gd^{3+} in the cubic symmetry has been observed also in the SrF_2 crystallites (not shown), however, the other symmetry environments are present as well [12].

For the Mn-doped oxyfluoride glass-ceramics, the temperature dependence of the MCD spectra shows the paramagnetic behaviour only at wavelengths above 360 nm (Fig. 4).

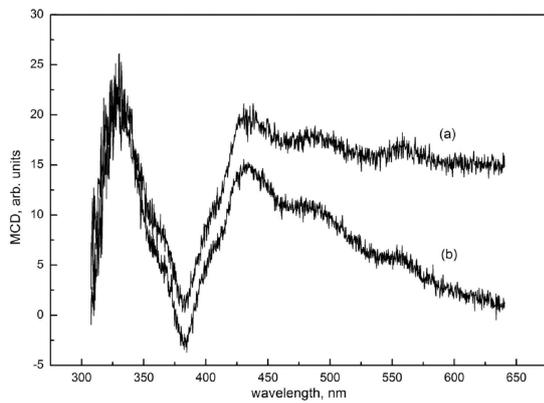


Fig. 4. MCD spectrum of the Mn-doped glass-ceramics, measured at $B = 2$ T and temperature 1.5 K (a) and 4.2 K (b).

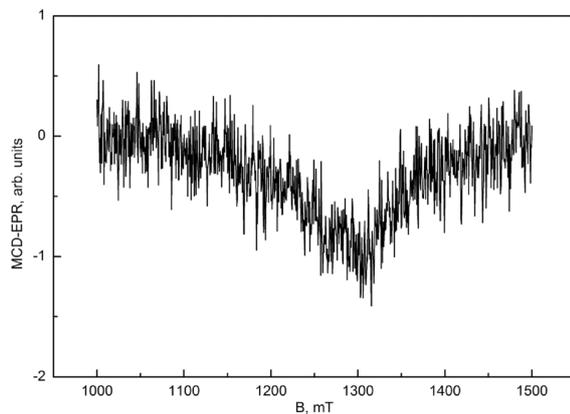


Fig. 5. MCD-EPR spectrum of the Mn-doped glass-ceramics sample, measured at temperature 1.5 K in the 430 nm MCD band, with the microwave frequency of 35 GHz. The magnetic field dependent background is subtracted.

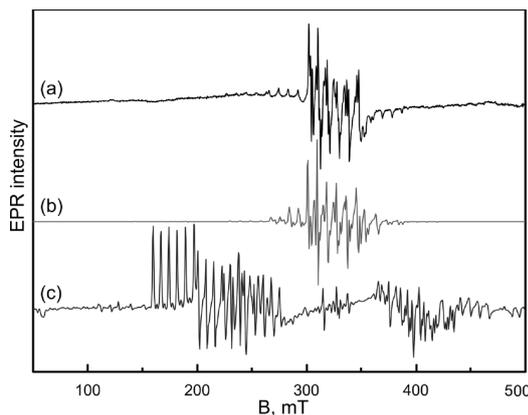


Fig. 6. EPR spectrum of the Mn-doped YAP ceramics sample (the same as in [9]) measured at the temperature 77 K and microwave frequency of 9.14 GHz. (a) Experimental spectrum, (b) and (c) are simulated spectra with the Mn^{2+} (b) and Mn^{4+} (c) EPR parameters from [14].

At the wavelength of 430 nm, where the temperature dependence is more or less pronounced, the broad MCD-EPR band could be observed (Fig. 4).

The broad MCD-EPR resonance at $g \approx 2$ coincides with the range of the Mn^{2+} EPR spectrum in the SrF_2 crystallites [13]. No such resonances have been observed for the corresponding Mn-doped oxyfluoride glass.

The correlation between the optical spectra and paramagnetic centres is an actual task also for ceramic samples, for example, Mn-doped YAP, investigated with the optical methods in [9]. Due to the opacity of these ceramics, the MCD techniques could not be applied directly to the ceramics. On the other hand, these YAP:Mn ceramics show the luminescence of at least two luminescence centres, namely Mn^{2+} and Mn^{4+} [9]. Our recent EPR spectra contain the resonances of the Mn^{2+} centres as shown in Fig. 6 (curve a).

The spectrum was compared with the simulations of the Mn^{2+} and Mn^{4+} centres from Rakhimov et al. [14]. It is evident that the EPR of the sample IK6 show only EPR lines from the Mn^{2+} ions, however, in Ref. [9], both the luminescence bands of the Mn^{2+} and Mn^{4+} have been observed.

The correlation of the Mn^{2+} and Mn^{4+} luminescence and corresponding EPR bands would be proved by the methods of the optically detected EPR in the future, on crystalline or half-transparent samples.

4. Conclusions

For the Er^{3+} doped oxyfluoride glass-ceramics, the MCD-EPR in the 377 nm and 521 nm MCD bands reveals the resonance line at $g = 6.78$. This resonance corresponds to the Er^{3+} centre in the cubic symmetry vicinity of the CaF_2 crystallites in these glass ceramics, similarly to the previously observed cubic Gd^{3+} centres in oxyfluoride glass-ceramics with CaF_2 crystallites. Therefore, in small CaF_2 crystallites (with the size of few tens of nm) in the oxyfluoride glass-ceramics, the investigated trivalent rare earth ions prefer to embed in the cubic symmetry environment.

For the Mn-doped YAP ceramics, the direct estimation of the correlation between the optical spectra and paramagnetic centres is hindered due to their non-transparency. The PM centres could be detected through their EPR spectra and then compared to the luminescence bands of these ceramics.

Acknowledgments

The financial support of the Latvian-Ukrainian Joint Research Project (No LV-UA/2016/1 in Latvia and No M/78-2016 in Ukraine) is acknowledged.

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