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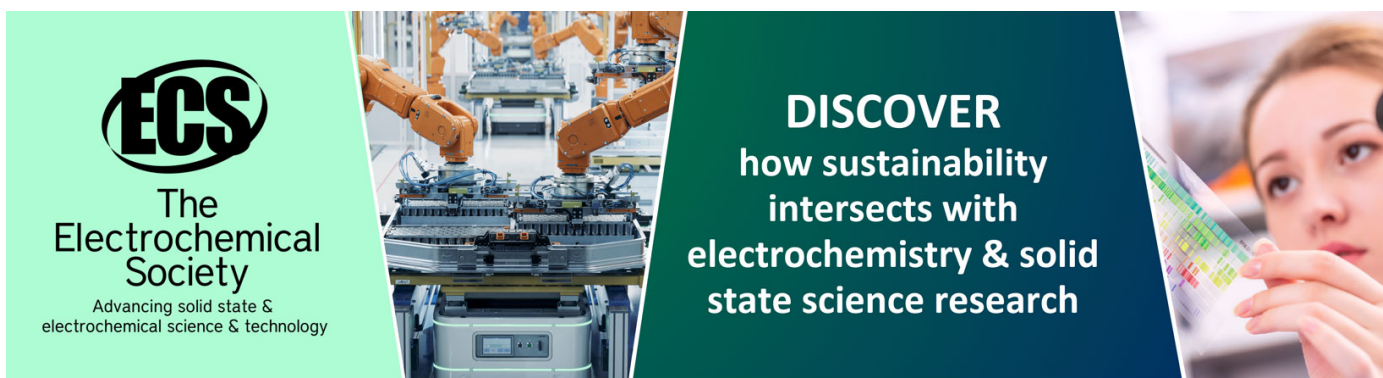
EPR studies of the oxyfluoride glass ceramics using Mn^{2+} as a paramagnetic probe

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EPR studies of the oxyfluoride glass ceramics using Mn^{2+} as a paramagnetic probe

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Abstract. In this work, we used Mn^{2+} as a dopant in the oxyfluoride glasses with various fluoride compounds. Electron paramagnetic resonance (EPR) measurements were carried out before and after a heat treatment of the material. In both cases, a well pronounced hyperfine (hf) structure of the EPR spectra characteristic to the Mn^{2+} ion have been observed. EPR measurements have also been studied for the separate fluoride counterparts of the oxyfluoride glasses. EPR spectra of the $\text{LaF}_3\text{:Mn}^{2+}$ and $\text{CaF}_2\text{:Mn}^{2+}$ powders show that Mn^{2+} ion has a strong superhyperfine (shf) interaction with surrounding fluorine nuclei, and this shf structure could be observed also in the heat treated glass samples.

1. Introduction

Nowadays oxyfluoride glass-ceramics materials are of great technological interest. Oxyfluoride glass ceramics consists of the glass matrix and the fluoride crystalline parts which are created by means of thermal treatment. Since this crystalline part of the material defines most of the crucial optical properties, it is very important to study crystallization processes in these materials. There is large number of papers reporting various optical properties of such materials mostly doped with rare-earth (RE) ions. For example, studies of the up-conversion luminescence of the RE ions show increase in luminescence intensity due to the crystallization [1–6]. However, these studies don't reveal direct information about surrounding environment of the impurity ion.

In this work we used electron paramagnetic resonance (EPR) as a structure sensitive method to investigate nearest coordination of the so-called paramagnetic probe – Mn^{2+} ion in this case – doped in the oxyfluoride glass-ceramics. Recently Mn^{2+} as a probe was studied in the fluorindate glasses [7] and $\text{CaF}_2\text{:Mn}^{2+}$ powder [8]. Although Mn^{2+} as a paramagnetic probe in crystals and glasses has been under detailed studies for a long time (see, for example [9–11] for $\text{CaF}_2\text{:Mn}^{2+}$ crystals and [12] for glasses), there are no reports on resolved superhyperfine structure of the EPR spectra of this ion in the disordered systems like powders and glasses.

2. Experimental

Two types of oxyfluoride glasses containing different fluoride counterparts were synthesized at the Institute of Solid State Physics, University of Latvia. The preparation of the samples was done using common melting-quenching techniques [1–3]. The composition (in mol%) of the oxyfluoride glass

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containing LaF_3 was $40\text{SiO}_2\text{-}25\text{Al}_2\text{O}_3\text{-}19\text{Na}_2\text{CO}_3\text{-}3\text{NaF-}9\text{LaF}_3\text{-}0.5\text{ErF}_3\text{-}0.5\text{MnF}_2$. The composition of the glass containing CaF_2 was $45\text{SiO}_2\text{-}25\text{Al}_2\text{O}_3\text{-}5\text{Na}_2\text{CO}_3\text{-}10\text{NaF-}15\text{CaF}_2\text{-}0.2\text{MnF}_2$. The $\text{LaF}_3\text{:Mn}^{2+}$ and $\text{CaF}_2\text{:Mn}^{2+}$ powders were synthesized by means of the wet chemistry. Produced glass samples further were thermally treated at various temperatures (750°C , 800°C , and 850°C) for one hour. The CaF_2 powder was heated for 30 minutes at 650°C . All EPR measurements were done at liquid nitrogen temperature (77K). We used standard X band EPR spectrometer with microwave frequency $\sim 9.1\text{ GHz}$. Formation of the crystalline phases was controlled by X-ray powder diffraction techniques (XRD).

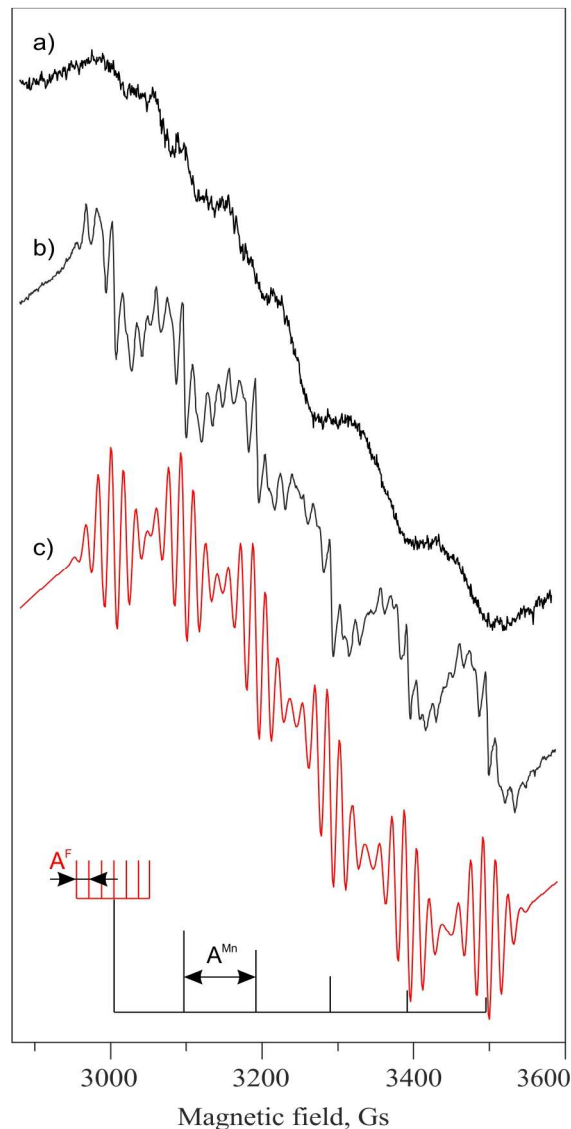


Figure 1. EPR spectra of Mn^{2+} ion: a) in the glass and glass-ceramics containing LaF_3 , b) in the $\text{LaF}_3\text{:Mn}^{2+}$ powder, c) theoretically calculated LaF_3 powder spectrum.

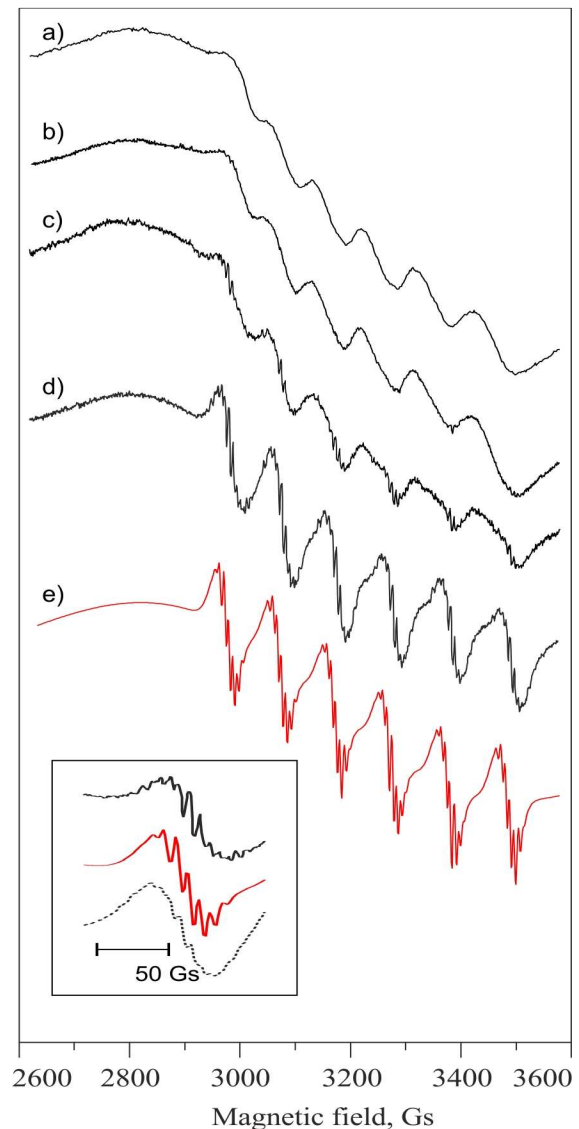


Figure 2. EPR spectra of the Mn^{2+} ion in the oxyfluoride glass ceramics containing CaF_2 crystallites: a) untreated glass, b) thermally treated glass at 750°C , c) at 800°C , d) at 850°C , e) theoretically calculated spectrum. The inset shows a detailed shf structure of the first Mn^{2+} hf line in the heat treated oxyfluoride (curve d), calculated spectra (curve e) and a powder spectrum (dotted curve).

3. Results and discussion

The characteristic EPR spectra of the Mn^{2+} ion were observed in all studied materials. Two features are common in all of the EPR spectra (see Figure 1 and Figure 2). At first, it is a broad envelope of the width about 800 Gs. This background signal is attributed to a distribution of the anisotropic fine structure parameters [7]. At second, six broad hyperfine lines at $g \sim 2$ – characteristic to Mn^{2+} ($I=5/2$) hfs which are superimposed on the broad background.

For glass-ceramics samples containing LaF_3 after a heat treatment no changes in the structure and intensity of the spectrum were observed. This indicates that there are some limitations for the Mn^{2+} to substitute the La^{3+} ion in the LaF_3 crystalline structure. As the most probable, there is unavailable charge compensation. Moreover, ErF_3 was one of the fluoride components and Er^{3+} ion has more potential to incorporate in the LaF_3 structure, since it doesn't need any charge compensation. However EPR spectra of erbium could not be observed at 77 K.

The EPR spectra of the non-treated $\text{LaF}_3:\text{Mn}^{2+}$ powder is shown in the Figure 1b. A well resolved additional superhyperfine splitting from the surrounding fluorine atoms is clearly visible. Each manganese hyperfine line has been split into additional 7 superhyperfine lines. Such structure could be created by equivalent 6 surrounding fluorine atoms what is characteristic configuration for octahedral crystalline structures. For the simulations of the EPR spectra we used Easyspin Matlab package [13]. Calculated spectrum for such model is shown in Figure 1c. All hyperfine and superhyperfine structure lines are in good coincidence with the experimental curves. Neglecting the fine structure interaction, the EPR spectrum of the electron ($S=1/2$, $g \sim 2.000$) with the hf interaction of the Mn^{2+} ($A^{\text{Mn}} = 275$ MHz) and superhyperfine interaction with six equivalent fluorine nuclei ($I^{\text{F}}=1/2$, $A^{\text{F}}=45$ MHz, $i=6$) could be described with the following spin-hamiltonian (SH):

$$H = Sg\beta B + SA^{\text{Mn}}I^{\text{Mn}} + \sum_i SA_i^{\text{F}}I_i^{\text{F}}$$

Although calculated spectrum agrees well with the experimental results we can't say that Mn^{2+} locates directly in the LaF_3 structure since in that case there should be 11 fluorine neighbors [6] which should result in more complex EPR spectrum. Detailed XRD analysis should be done here to clarify crystalline structures in this powder.

Similar situation was observed in the oxyfluoride glass containing CaF_2 crystallites. The EPR spectrum of the pure glass material is shown in Figure 2a. It consists of six manganese hyperfine structure lines superimposed on the broad envelope. However, a thermal treatment of the samples causes interesting changes in the spectrum. After heating of the sample, another group of manganese sextet has been observed. It is slightly shifted towards higher field (smaller g -factor) with additional shf splitting of every Mn^{2+} hf line into 9 components with binomially distributed intensities. Obviously, there are two Mn^{2+} centres: one in the glass matrix and other in the CaF_2 crystalline phase. The hf structure constant A^{Mn} and a g -factor differs from that of the manganese in the glass matrix. As could be seen from the spectra in Figure 2, heating produces more intense shf splitting. This could be explained by the increase of the crystallites and increased manganese contamination in the CaF_2 crystalline phase. Theoretical calculations for both centres were done using previous SH with parameters $g_1 = 2.000$, $g_2 = 2.005$, $A^{\text{Mn}} = 285$ MHz and $A^{\text{F}} = 21.5$ MHz also taking into account shf interaction with 8 fluorine nuclei. This describes the well known situation of Mn^{2+} impurity in the CaF_2 crystals [9-11] where it resides in the Ca^{2+} cubic site and the shf interaction is clearly resolved in the EPR spectra. However, it is also stated that this structure should be obscured in the disordered structures [7, 8, 12].

For clarifying the situation comparison of the EPR spectrum of the glass ceramics containing CaF_2 with the EPR spectrum of the $\text{CaF}_2:\text{Mn}^{2+}$ powder was done. It's spectrum also shows six broad manganese hfs lines. Untreated samples show barely resolvable superhyperfine structure. The heat treatment increases intensity of the superhyperfine structure spectra of the fluorine atoms what could be explained by more intense Mn^{2+} incorporation in the CaF_2 structure (see the inset in Figure 2). It should be mentioned that CaF_2 powder spectrum lacks broad envelope which was common in the LaF_3

glass, glass ceramics and powder, as well as CaF_2 glass and glass ceramics. As could be seen from the inset in the Figure 2, all shf structure lines are clearly resolved in the glass-ceramics and in the CaF_2 powder and are also in agreement with the calculated spectrum.

4. Conclusions

In the oxyfluoride glass ceramics with LaF_3 crystallites manganese doesn't reside in the La sites – most of the Mn^{2+} remain embeded in the glass.

In the oxyfluoride glass with CaF_2 manganese occupies the cubic Ca site and has SHF interaction with 8 nearest fluorine atoms.

The intensity of the HF and SHF spectra of the Mn^{2+} in the glass ceramics containing CaF_2 rises with the increase of the heat treatment temperature.

Acknowledgements

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References

- [1] Mortier M, Bensalah A, Dantelle G, Patriarhe G and Vivien D 2007 *Opt. Mater.* **29** 1263–70
- [2] Chen D, Wang Y, Yu Y, Ma E and Hu Z 2005 *J. Phys.: Condens. Matter* **17** 6545–57
- [3] Sarakovskis A, Dimitrocenko L, Misnevs A, Rogulis U and Springis M 2007 *J. Phys.: Conf. Ser.* **93** 012041
- [4] Kusatsugu M, Kanno M, Honma T and Komatsu T 2008 *J. Solid State Chem.* **181** 1176–83
- [5] Chen D, Wang Y, Yu Y, Ma E, Bao F, Hu Z and Cheng Y 2006 *Mater. Chem. Phys.* **95** 264–9
- [6] Zhang X, Hayakawa T and Nogami M 2009 *IOP Conf. Ser.: Mater. Sci. Eng.* **1** 012021
- [7] Franco R W A, Lima J F, Magon C J, Donoso J P and Messaddeq Y 2006 *J. Non-Cryst. Sol.* **352** 3414–22
- [8] Danilkin M, Lust A, Kerikmae M, Seeman V, Mandar H and Must M 2006 *Rad. Meas.* **41** 677–681
- [9] Low W 1957 *Phys. Rev.* **105** 793–800
- [10] Baker J M, Bleaney B and Hayes W 1958 *Proc. Roy. Soc.* **A247** 141
- [11] Lay F M and Nolle A W 1967 *Phys. Rev.* **163** 266
- [12] Bogomolova L D and Krasilnikova N A 1995 *Glass. Phys. Chem.* **21** 303
- [13] Stoll S and Schweiger A 2005 *J. Magn. Res.* **177** 390