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XAS study of oxide-fluoride glass-ceramics

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The materials studied represent a novel class of rare earth containing oxide-fluoride glass-ceramics exhibiting luminescent properties. Such materials are candidates for applications in optical devices such as converters or solid state lasers.. They combine excellent optical properties of fluorides with good chemical and thermal parameters of the oxide phase. Rare earth ions act as optically active centers there. To reduce the impact of phonon relaxation processes on the luminescent decay, optically active rare earth centers should be located in the low-energy phonons environment, such as e.g. in heavy metal fluorides. This allows getting a higher luminescence efficiency and longer lifetimes of excited states.

In order to achieve particular properties e.g. for applications in optoelectronics, partial crystallization is induced. The material obtained consists of a glass matrix containing crystallites of various sizes dispersed in it. Choosing the appropriate route of thermal treatment it is possible to obtain glass-ceramics with the crystallite size less than 100 nm, i.e. much less than the optical wavelength, when they are transparent.

For the study two types of oxide-fluoride glasses have been used: glass G1 doped with erbium and G2 glass doped with europium. X-ray Absorption Spectroscopy (XAS) measurements have been performed in the Helmholtz-Zentrum Berlin at a bending magnet beamline of the synchrotron radiation storage ring BESSY II. The spectra were recorded in the total electron yield (TEY) and partial fluorescence yield (PFY) modes at room temperature. The energy range covering the areas of O:K, F:K, Na:K, Eu:M, Gd:M, ErM, and Al:K have been scanned.

The O:K edge TEY spectra of the G1+Er samples in the XANES range are presented in Fig.1.

Except for the main edge at about 540 eV additional peaks appear at the energies of 60 eV and 80 eV higher, which are assigned to two-electron excitations involving metal atom neighbours. They are not observed for the unnanealed glass.

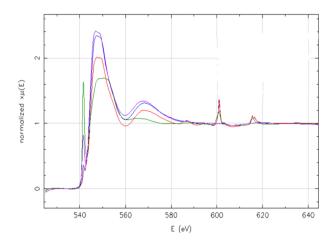


Figure 1. XAS spectra for the O:K edge of the of the G1+Er samples.

A similar behaviour is observed for the F:K edge. The effect is attributed to a modification of the local atomic environments at the surfaces and fluorine escape upon annealing.

Figure 2 illustrates the TEY spectrum at the M5 and M4 edges of erbium in the G1+Er powder glass before and after annealing,.

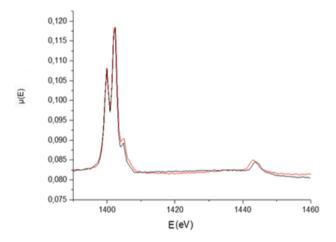


Figure 2. XAS spectra for Er edges M4, M5 for the G1+Er powder sample before (red) and after (black) annealing.

For powdered samples a significant shift of the M4 edge white line corresponding to the final states 4f5/2 to higher energies is observed, which mean they stronger bonding energy in the annealed sample.

The effects are analysed and discussed in terms of modifications of local atomic neighborhoods on annealing (ceramization) and differences in electronic interactions between fluoride and oxide environments.