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A XAS study of low phonon glass-ceramics

A. Czajka[1]*, T. Strączek[1], K. Gąska[1], D.A. Zając[1], Cz. Kapusta[1] and M. Środa[2]

[1]*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Department of Solid State Physics, al. A. Mickiewicza 30, 30-059 Kraków, Poland*
[2]*AGH University of Science and Technology, Faculty of Material Science and Ceramics, al. A. Mickiewicza 30, 30-059 Kraków, Poland*

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*e-mail: Agnieszka.Czajka@fis.agh.edu.pl

Introduction

Luminescent materials are used in optical devices such as optical converters or solid state lasers. A novel class of such material consist rare earth containing oxide-fluoride glass-ceramics. They combine excellent optical properties of fluoride with the corresponding chemical and thermal parameters of the oxide phase. Rare earth ions act as optically active impurities there. To diminish the impact of phonon relaxation processes on the luminescent decay, optically active rare earth centers should be located in the structure of low-energy phonons, such as e.g. heavy metal fluorides, which reveal the lowest energies of phonons. Thereby, low phonon fluoride phase, which reduces the likelihood of non-radiative decays. This allows getting a higher luminescence efficiency and longer lifetime of excited states.

Applications of the rare earth ions in the active optical centers are linked to the specific electronic structure of lanthanides. The high refraction is related to the large number of electron shells completely filled in the lanthanide ion. This significantly increases the electron density of the medium where are lanthanides, and thereby also its polarization susceptibility.

Lanthanide ions in solids have discrete absorption and emission lines associated with the change of the resultant orbital moment and spin moment of the electron of the 4f subshell. Electronic transitions taking place on this subshell lead to the emission of radiation in the spectral range from near infrared to the near ultraviolet.

Luminescent lanthanide bands are very narrow and have almost linear character. As in the case of electronic absorption spectra, the energy shift of a band depends to a small extent on the structure of the atomic/ionic environment.

Glass-ceramics are glassy materials in which a partial crystallization was induced by means of ceramization in order to achieve particular properties. Such a material consists of a glass matrix containing crystallites of various sizes dispersed in it. The use of glass-ceramics in optoelectronics has been made possible owing to the development of thermal processing and controlled crystallization of the amorphous structure. Choosing an appropriate route of thermal treatment it is possible to obtain glass-ceramics with various degrees of transparency. In practice, the glass-ceramic materials are transparent when the size of crystallites formed is an order of magnitude smaller than the wavelengths of visible light, which correspond to the crystallite diameter less than 100 nm.

Experimental

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 Spectropy (XAS) study has been carried out 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 probing depth of the TEY signal varies from a few nanometers at the energy of 500 eV to tens of nanometers at energies above 1000 eV.

Results and discussion

The F:K edge TEY spectra in the XANES range are presented in Fig.1.

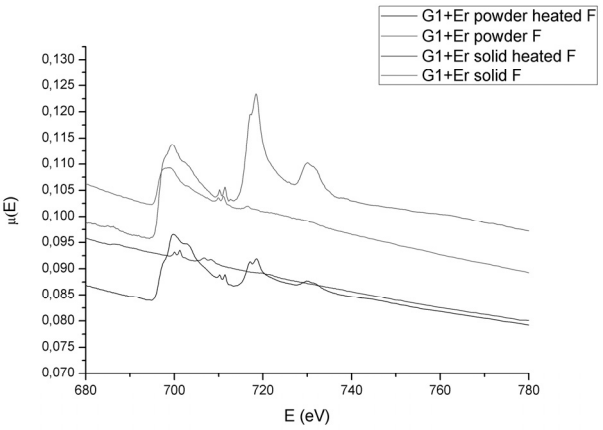

Figure 1. XAS spectra for the F:K edge of the samples studied.

This figure shows unnormalized spectra for glass G1 before and after ceramization (heat treatment). It is worth noting that the heat treated solid glass shows a much lower intensity of the fluorine spectrum than the other samples, whchich can be attributed to a sublimation of fluorine from the surface layer of a few nanometers. This does not occur for the glass powder.

Except for the main edge at about 700 eV additional peaks appear at the energies of 20 eV and 30 eV higher, which are attributed to two-electron excitations. Their intensity relatively to the main edge is the strongest for the powder glass and decreases with annealing. For the solid glass it is barely visible.

Figure 2 illustrates the spectrum of the samples G1+Er glass before and after heat treatment (ceramization), at the M_5 and M_4 edges of gadolinium.

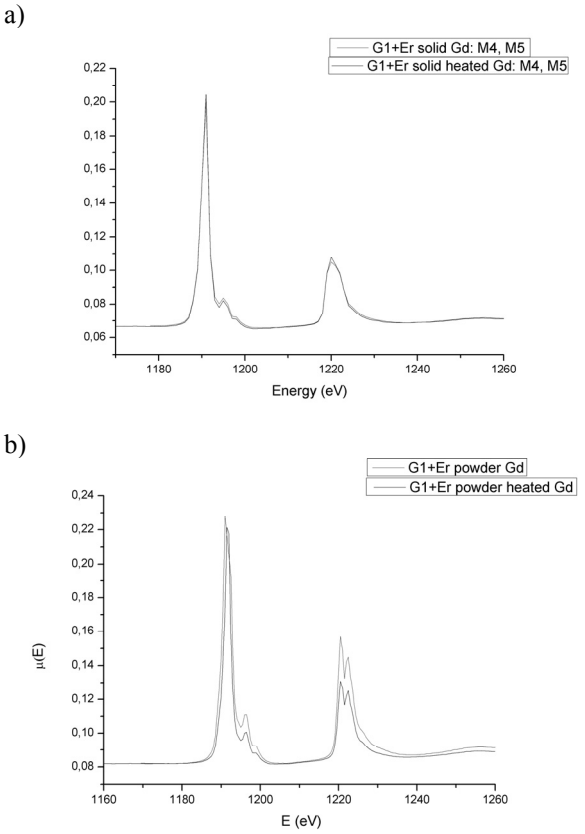

Figure 2. XAS spectra for Gd edges M_4, M_5 for a) solid glass sample, and b) the powder sample.

For solid glass samples before and after ceramization the spectra coincide. For powdered samples significant splitting of the M_4 edge white line corresponding to the final states $4f_{5/2}$ is observed. Also its intensity is considerably larger for the untreated powder. The effect can tentatively be attributed to a greater sensitivity of these states to the surface state, i.e. ceramized or untreated.

For solid glasses the thermal conductivity has been measured down to 4 K in order to check for a possible appearance of the "crystalline peak" at low temperatures after ceramization. A Thermal Transport option of the PPMS (Physical Property Measurement System) set-up was used.

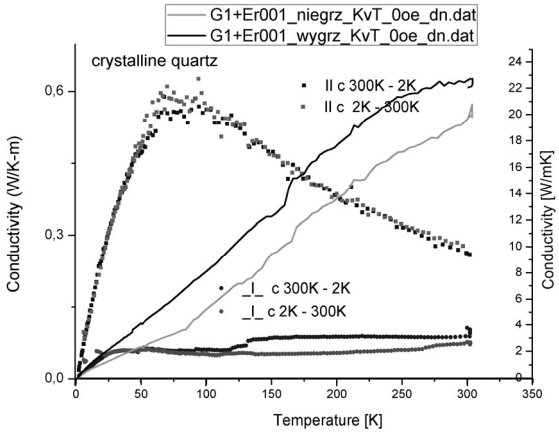

Figure 3. The temperature dependence of the thermal conductivity of the G1-Er glass "as prepared" (green line) and ceramized (black line), left side scale. The data on a quartz single crystal for the heat flux along the c-axis and perpendicular to it are also shown for a comparison, right side scale.

The thermal conductivity increases slightly after heating, but "crystalline peak" does not appear, which means that crystallization takes place to a minimal extent or at regions of nanometric size, smaller than the mean free path of phonons, which is of a few nanometers in such materials.

Conclusions

In the study we could observe the two-electron effects at the F:K edge, dependent on the type of material and its thermal treatment. Also the Gd $4f_{5/2}$ states were found to be sensitive to it. Crystallization caused by ceramization crystallization occurs at a minimal extent or at regions of nanometric size. The observed loss of fluorine from nanometric surface layer on ceramization is an important information for preparation of the optical elements using such a technological route.

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