



Enhanced NIR emission from nanocrystalline LaF₃:Ho³⁺ germanate glass ceramics for E-band optical amplification

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ABSTRACT

Nanocrystalline LaF₃ germanate glass ceramics were prepared and used as host for optically active Ho³⁺ ions. LaF₃ crystallites precipitate by internal nucleation with sizes in the range of 7–17 nm. During crystallization, Ho³⁺ is incorporated into the fluoride lattice on La³⁺ sites, leading to reduced probability of multiphonon relaxation and, hence, significantly enhanced emissions within 1300–1440 and 1400–1550 nm wavelength range. Excited state absorption spectra, stimulated emission spectra and spectral gain coefficients of the (⁵S₂, ⁵F₄) → ⁵I₅ transition indicate suitability of the material for E-band optical amplification.

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1. Introduction

Continuously increasing demand for data transmission capacity of optical communication systems has been stimulating an ongoing search for fiber optical amplifiers which operate within the low-loss transmission window of OH-free silica fiber (1.2–1.7 μm) [1]. Ideally, this would be achieved by a material with broadband luminescence in the relevant spectral range, which has been demonstrated for doping with various transition and heavy metal ions such as Ni²⁺ [2,3] and various Bi-species [4]. At present, however, despite their much lower emission bandwidth, rare earth ions remain the dopant-of-choice because of superior emission cross-section and/or lifetime. Pr³⁺-doped fiber amplifiers (PDFA, 1.3 μm) and Tm³⁺-doped fiber amplifiers (T DFA, 1.4 μm) have been developed as additions to the commercially available Er³⁺-doped fiber amplifier (EDFA, C-(1530–1565 nm) and L-(1565–1625 nm) bands) [5,6]. For complete exploitation of the silica transmission window, however, also the E-(1360–1460 nm) and U-(1625–1675 nm) bands must be covered. For this purpose, Ho³⁺ has been considered as a promising active ion for its (⁵S₂, ⁵F₄) → ⁵I₅ and ⁵I₅ → ⁵I₇ radiative transitions [7–9]. Owing to the narrow gap between the fluorescing level and the next lower-lying level, these emissions can only be achieved in hosts with low phonon energy such as fluoride, selenide and chalcogenide glass systems [7,8]. From the point of view of real-world applicability, however, the poor chemical and mechanical properties of these

matrix candidates remain a critical issue. So far, only oxyfluoride glass ceramics (GC) [10–13] which combine the low phonon energy of a crystalline fluoride lattice with the high chemical and mechanical stability of oxide glasses appear to overcome this problem. Recently, transparent Ho³⁺-doped oxyfluoride GC have been reported as potential material for optical amplifiers operating at 0.75 and 1.2 μm [14,15].

In the present paper, we are considering precipitation of LaF₃ nanocrystallites which act as host for Ho³⁺ dopant in a matrix of germanate glass. Compared to silicate GC, gallate or bismuthate matrices, this provides even lower phonon energy [16,17] as well as lower melting temperature of the glass and, hence, more easy processing. The spectroscopic properties of the Ho³⁺ center are examined with particular attention to the emission bands and gain coefficients at 1.37 and 1.45 μm.

2. Experiments

GC samples were prepared by thermal precipitation of LaF₃ crystallites from precursor glasses (PG) with nominal molar composition of (50-x)GeO₂-22Al₂O₃-13LaF₃-15LiF-xHoF₃ (denoted as PGH_x) (x = 0, 0.05, 0.1, 0.2, 0.4, and 0.8). For that, batched of properly mixed raw materials (analytical grade) were melted in covered corundum crucibles at 1350 °C for 1 h. The melts were then quenched on a preheated stainless steel plate and subsequently annealed at 450 °C for 2 h to remove residual stress. Transformation into visually transparent GC was conducted via a heat-treatment at 560 °C for 8 h (samples denoted as GCH_x). Differential scanning calorimetry (DSC) was carried out on ground glass (PGH0.8) at a heating rate of 10 K/min to evaluate the characteristic temperatures of glass transformation and crystallization onset. For microstructural analyses, X-ray powder diffractometer (X'Pert PROX, Cu Kα) and transmission electron microscopy (TEM, JEM-2010) were employed. The density (ρ = 4.07 g/cm³) of GCH0.4 was measured by the Archimedes method. The refractive index was obtained using a Metricon 2010 prism cou-

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pler, obtaining a value of $n = 1.655$ at a wavelength of $\lambda = 0.633 \mu\text{m}$ (GCH0.4). Ultra-violet (UV) to near infrared (NIR) absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer with a spectral resolution of 1 nm. Optical excitation and emission spectra were obtained with a resolution of 1 nm on an Edinburgh Instruments FLS920 spectrofluorometer equipped with a 450 W Xenon lamp (Xe900) as the excitation source. Decay curves of the fluorescence signals were recorded using the same set-up with a μF900 microsecond flashlamp as excitation source. All optical measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows exemplary DSC curves of PG0 and PG0.8. The sharp exothermic peak at 648°C (PGH0.8) is attributed to precipitation of crystalline LaF_3 (as confirmed by XRD, to be discussed in the following). The calorimetric glass transition temperature T_g is found at 568°C . Noteworthy, no significant differences can be detected between PGH0 and PCH0.8. The latter indicates that Ho^{3+} doping does, at least within the considered range of dopant concentration, not affect nucleation and crystal growth in the employed glass system. To ascertain the origin of the exothermic crystallization peak, bulk PGH0 was subjected to thermal treatment at 650°C for 3 h. During this procedure, the sample changes from transparent to translucent appearance. XRD analyses were performed on glass samples before and after thermal treatment to evaluate the nature of crystalline phase(s). As shown in Fig. 2(a), no diffraction peaks can be detected in PG, confirming its glassy state. After heat treatment (GCH0), intense diffraction peaks occur. These can readily be assigned to hexagonal LaF_3 phase (JCPDS Card No. 01-076-1500). The temperature of the crystallization peak as observed by DSC results from relatively fast heating. For prolonged isothermal annealing (i.e., extrapolation of the heating rate to 0 K/min), notable crystallization occurs already at significantly lower temperature. Here, we identified a temperature of 560°C as a suitable trade-off for controlled crystal precipitation (e.g. 560°C for 8 h, Fig. 2). TEM combined with selected area electron diffraction (SAED, Fig. 2(b)–(c)) reveals crystallite sizes of about 7–17 nm, consistent with XRD. These LaF_3 crystallites are densely and homogeneously distributed within the glass matrix. The diffraction peaks exhibit a slight shift towards higher angles for GCH0.8 as compared to GCH0, inset of Fig. 2(a). This is ascribed to lattice contraction caused by the substitution of La^{3+} (1.32 Å) ions by Ho^{3+} (0.89 Å) ions and taken as first evidence for the incorporation of Ho^{3+} into the crystalline lattice of LaF_3 . Fig. 3 illustrates the absorption cross section of Ho^{3+} in GC samples as calculated from the absorption spectrum, $\sigma_a(\lambda) = \frac{2.303 \log(I_0/I)}{Nl}$ (where N is the concentration of Ho^{3+} , l and $\log(I_0/I)$ represent thickness and absorbance of sample, respectively) [18]. All absorption bands appear similar in position and shape to those of corresponding Ho^{3+} -doped silicate GC [16]. The absorption bands are assigned to the intra-4f transitions of

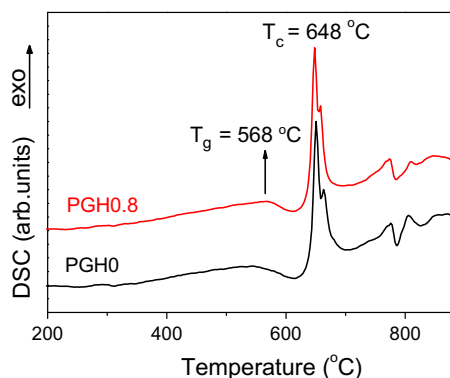


Fig. 1. DSC traces of PG samples recorded at a heating rate of 10 K/min: PGH0: blank sample; PGH0.8: Ho^{3+} dopant concentration of 0.8 mol %.

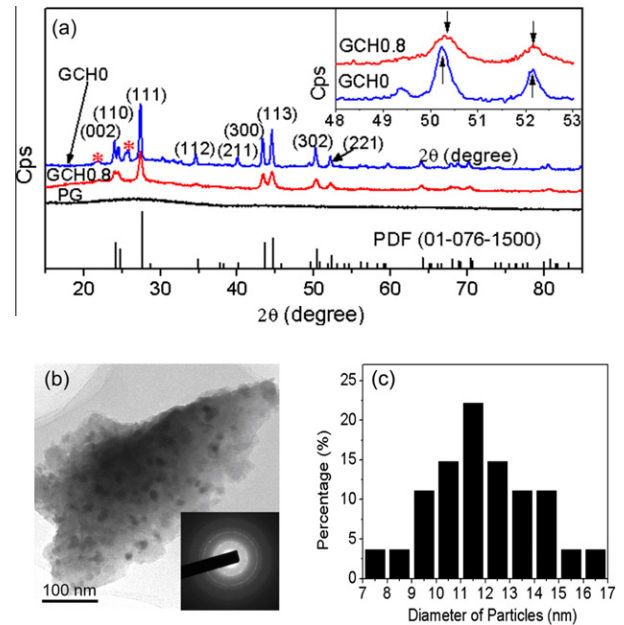


Fig. 2. (a) XRD patterns of PG, Ho^{3+} -doped (GCH0.8) and Ho^{3+} -free GC (GCH0) heat-treated at 560°C for 8 h and 650°C for 3 h, respectively. Inset in (a) zoom at the intermediate angular scattering range of GCH0.8 and GCH0. (b) TEM bright field image and corresponding selected area electron diffraction pattern (inset) of GC. (c) Computed size distribution of LaF_3 nanocrystals in the micrograph of (b).

Ho^{3+} from the ground state to different excited states as indexed in the figure. The peak values for $^5\text{I}_8 \rightarrow ^5\text{G}_6$, $^5\text{F}_1$ (452 nm), $^5\text{I}_8 \rightarrow ^5\text{F}_4$, $^5\text{S}_2$ (537 nm) and $^5\text{I}_8 \rightarrow ^5\text{F}_5$ (640 nm) transitions are 3.26×10^{-20} , 1.06×10^{-20} and $0.73 \times 10^{-20} \text{cm}^2$, respectively. Judd–Ofelt (J–O) [19,20] parameters ($\Omega_{2,4,6}$) were calculated from the absorption spectrum of GCH0.4, obtaining values of 4.12×10^{-20} , 2.74×10^{-20} and $1.8 \times 10^{-20} \text{cm}^2$ by least-square fitting. The results for GCH0.1 sample are quite similar, with $\Omega_2 = 4.21 \times 10^{-20}$, $\Omega_4 = 2.59 \times 10^{-20}$, and $1.8 \times 10^{-20} \text{cm}^2$, respectively. The small-scale variations of J–O parameters Ω_λ ($\lambda = 2,4,6$) with varying doping concentration have been obtained, which allow us to ignore the effect of dopant concentration on spectra parameters estimated from Ω_λ , such as radiative transitions probabilities and emission cross sections. This assumption is possible especially for the $(^5\text{F}_4, ^5\text{S}_2) \rightarrow ^5\text{I}_5$ and $^5\text{F}_5 \rightarrow ^5\text{I}_6$ transitions since the corresponding reduced matrix elements $\|U^{(2)}\|$ and $\|U^{(4)}\|$ are much smaller than $\|U^{(6)}\|$. In this case, the parameter Ω_6 would play a dominant role in such spectra parameters, whereas the small-scale variations of $\Omega_{2,4}$ might cause little influence on the re-

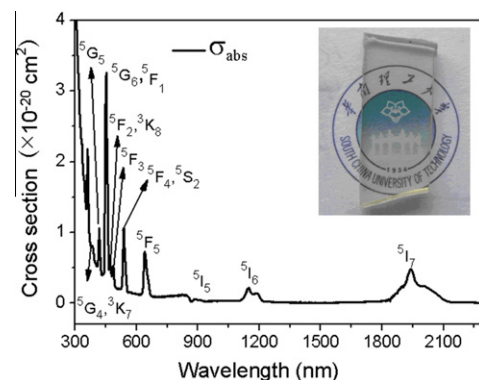


Fig. 3. Absorption cross section of Ho^{3+} in GCH0.4. The inset shows an exemplary photograph of this sample.

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