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Glass powder doping of nanocrystal-doped fibres – Challenges and results

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ABSTRACT

Incorporating new optical materials as nanocrystals into glass fibres for new functionalities has recently become a hot research topic. Our team (funded by the European FET Open project NCLAS) investigates the introduction of nanoscale laser crystallites into the core of optical fibres using the glass powder doping method. Active Y_2O_3:Pr^{3+} nanocrystals (NCs) were prepared via different synthesis methods, and structurally and spectroscopically characterized. After modification of technological parameters, the optimised NCs have been proposed as a luminescence centres to embed into germanate and silicate glass hosts. Glasses were analysed in terms of optical (transmission, refractive index matching to NCs) and thermal (thermal stability, viscosity, thermal expansion coefficient) parameters. Crystallisation issues during fibre drawing were particularly investigated. In a first step, glass powder-NCs mixing techniques and fibre preform preparation were developed. It was shown that temperature cycle profiles including dwell time and heating/cooling ramp rates influenced the glass-NCs properties and can lead to glass crystallisation or NCs dissolution. The sintering investigations pointed out the melting temperature limits to preserve active NCs in the glasses. In germanate glasses, Y_2O_3:Pr^{3+} dissolution was noticed at 800°C. In the case of the silicate glass compositions these regions vary from 700°C to 1050°C. The results allowed to select optical fibre drawing conditions performed by the powder-in-tube method. Their distribution uniformity is not yet sufficient, requiring further optimisation of the drawing kinetics.

Keywords: optical fibres, glass powder doping, nanoparticles, nanocrystals, fluorescence, rare-earth ions

1. INTRODUCTION

Optical fibres have been instrumental in establishing the internet and have also revolutionized laser materials processing using fibre lasers. Even fibre sensors have become an important topic, despite silica not offering a wealth of physical effects for detection. It also concerns the limited transmission range to 2.2μm and the phonon energy value of 1100 cm^{-1}. Shifting the edge of infrared absorption requires suggestions for other glass compositions that usually do not contain silica, such as fluoride, chalcogenide, telluride or germanate [1, 2]. However, this causes a significant reduction in the glass parameters required in the optical fibre technique, such as thermal stability and an increased tendency to crystallization and, consequently, an increase in attenuation and a reduced mechanical weakness [3].

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In turn, the modification of the phonon energy of the active dopant can be considered both as a modification of the matrix or the introduction of the low-phonon active crystals. The classical active glass-ceramics methods include the controlled thermal treatment and the sol-gel method that enable the introduction of a crystalline phase [4]. Other more fibre-oriented methods are direct crystal doping, initial fibre preform preparation by glass powder doping and crystal doping using MCVD method [5, 6, 7]. It should be emphasized that none of the mentioned ones are privileged from the point of view of the active glass-nanocrystals optical fibres development for laser applications. In anticipation of a breakthrough in this area, new hybrid glass-crystalline materials for obtaining fibre lasers and broadband sources are currently proposed. Thus, incorporating new optical materials as NCs into fibres for new functionalities has recently become a hot research topic [8]. Our team (funded by the European FET Open project NCLAS) investigates the introduction of nanoscale laser crystallites into the core of optical fibres using the glass powder doping method as describes elsewhere [8].

In this paper, the research on introduction of Y_2O_3:Pr^{3+} nanocrystals into multicomponent glasses is proposed. The problem of incompatibility of the composition of germanate and other glasses in the preparation of the glass-nanocrystal composites is discussed. It occurred that drawing germanate glass-ceramics optical fibres lead to crystallization effects in the core. However, in silicate fibre some NCs survived the fibre drawing process. Further work will be carried out on the optimization of the drawing kinetics for obtaining an active crystalline phase in the glass matrix.

2. EXPERIMENTAL

Cubic Pr^{3+}-doped Y_2O_3 NCs were prepared via Pechini synthesis methods, and structurally and spectroscopically characterized [9]. Among all these methods, the best results in terms of size, aggregation, reproducibility, scale-up and luminescence properties were obtained for solvothermal and homogeneous precipitation routes. After modification of different parameters, the best luminescence performances (photoluminescence intensity and lifetime) were observed for 0.2%mol Pr^{3+}.

Germanate glasses (BGG) as well as commercial glass hosts of the lanthanum heavy flint and silicates were analysed in terms of the typical criterions in optical fibre technology including optical (transmission - TAUI25/1060, refractive index - n_d) and thermal (vitrification temp. - T_g, viscosity - T7.6, thermal expansion coefficient - alpha 20/300) parameters (Table 1). Differential Scanning Calorimetry (DSC) measurements were performed on a Setaram LabSys model. For several glasses with the refractive index matching to the NCs 1.93 (Y_2O_3:Pr^{3+}) the potential crystallisation during fibre drawing was investigated. In order to show our technological approach, the BGG and Schott (N-LASF46B, AR-glass) glasses were discussed. Various glass hosts present different compositions which allow to analyse their influence on NCs dissolution.

Table 1. Optical and thermal glass properties.

Glass	n_d	TAUI25 /1060	T_g	T7.6	alpha 20/300
BGG (BaO-Ga_2O_3-GeO_2)	1.7345	0.993	618	680	9.24
N-LASF46B (Schott)	1.9036	0.996	611	703	7.10
AR-glass® (Schott)	1.5140	0.997	525	720	9.10

In the first step, glass powder-NCs mixing techniques and pellet preparation were developed. The uniform NC distribution was confirmed by the fluorescence mapping. Mixed materials were sintered at different heating rates using induction and conventional furnaces under air atmosphere. It was shown that temperature cycle profiles including dwell time and heating/cooling ramp rates influenced the glass-NCs properties and can lead to glass crystallisation or NC dissolution. Luminescence measurements were performed using FLSP920 spectrofluorometer (Edinburgh Inst.), a 488 nm line of an Ar^+-Kr^+ with a T64000 spectrometer (Horiba-Jobin-Yvon) or a Raman spectrometer (WITec Alpha 300M). The last two systems were equipped with confocal microscopes with the possibility of mapping the sintered glass-NCs materials and optical fibre core cross-sections. Optical fibres were drawn using conventional towers equipped with electric and induction furnaces (depending on the drawing temperature).

3. RESULTS AND DISCUSSION

The research results contain cognitive aspects concerning the powder preparation techniques, their luminescent properties after the sintering process and their influence on the production of optical fibres. They will be discussed with examples of selected glasses to illustrate certain fabrication issues. The glass powders were analysed by the DSC technique before and after grinding, and also after homogenization with the nanocrystals. It has been found that additional surface and volume crystallization may occur due to the dissolving $Y_2O_3:Pr^{3+}$ nanocrystals. Thermal analysis showed no changes of BGG and AR-glass, however in N-LASF46B glass additional crystallization bands (780 °C, 905 °C) were observed which resulted in crystallisation during fibre drawing (Fig. 1).

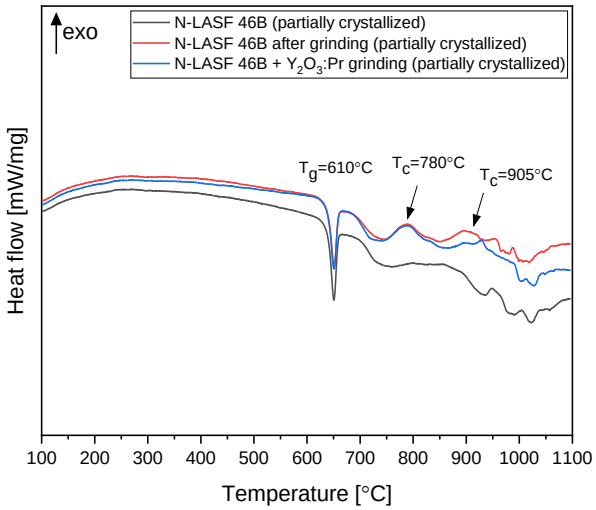

Figure 1. DSC analysis of N-LASF46B parent glass, after grinding and mixing with $Y_2O_3:Pr^{3+}$ NCs.

The sintering investigations gave a first indication on the melting temperature limits to preserve NCs in the glasses. In the case of BGG samples with $Y_2O_3:Pr^{3+}$ NCs, the sintering process was performed in the range from room temperature to 1000°C. It has been observed that at the temperature of 800°C the characteristic Pr^{3+} emission in Y_2O_3 NCs (Fig. 2a) changed dramatically, indicating that NCs were already dissolved in the glass matrix. The measured luminescence of Pr^{3+} ions showed in the range of 600nm - 670nm ($^1D_2 \rightarrow {}^3H_4$) a broad spectrum characteristic of an amorphous environment (Fig. 2b) and in contrast to the initial Y_2O_3 crystal surrounding (Fig. 2a). Additionally, during the fibre drawing crystallisation in the core appeared.

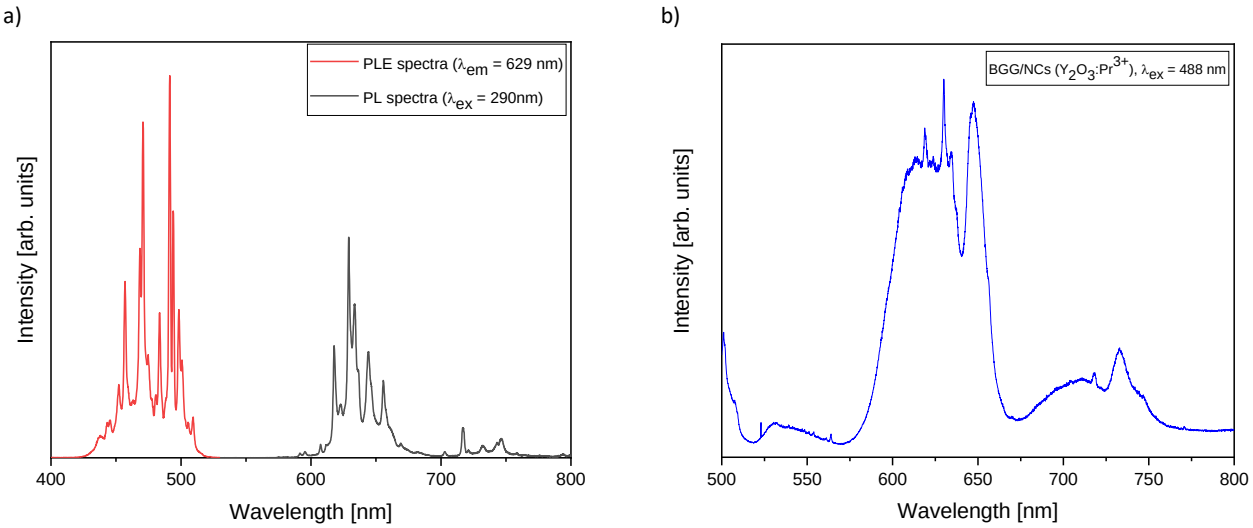

Figure 2. Luminescence (PL) and excitation spectra (PLE) of $Y_2O_3:Pr^{3+}$ NCs (a);
PL of BGG/$Y_2O_3:Pr^{3+}$ sintered material at 800 °C, (λ_{ex} = 488 nm) (b)

Besides the matrix glasses N-LASF46B (crystallisation issues) and BGG (NCs dissolution issues), other glasses have been investigated as well. For example, silicate AR-glass (Schott) was used as the NCs dissolution rates appeared to be much slower than in the other glasses. In Fig. 3a there is the luminescence of the AR-glass-NCs composite sintered at 800 °C. It has been found that incorporation of the $Y_2O_3:Pr^{3+}$ NCs into the silica-based glass is also challenging (comparing to NCs emission at Fig. 2a) but partially possible when fast heating-cooling ramp is optimised during fibre drawing. This is shown in the Fig. 3b where surviving $Y_2O_3:Pr^{3+}$ NCs were detected.

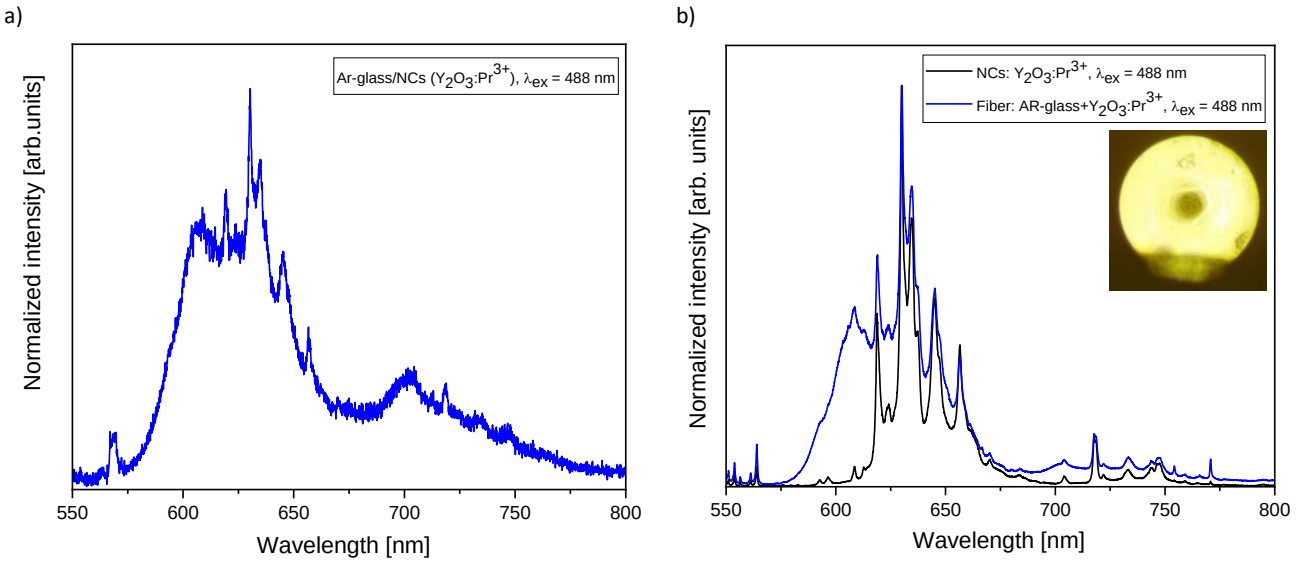

Figure 3. Luminescence of AR-glass/$Y_2O_3:Pr^{3+}$ sintered material at 800 °C (a) and optical fibre core: AR-glass/$Y_2O_3:Pr^{3+}$, cladding: AR-glass (b), optical fibre (diameter 150 μm) cross-section (inset)

We have found that in principal the survival of the NCs can be obtained in the optical fibres under a strict control of glass-NCs composition and drawing parameters. The discovered temperature cycle profiles are in the range of optical fibre drawing towers, however, an extensive (in comparison to a standard drawing process) optimisation of the drawing parameters (preform feeding, length of the heating zone) has to be performed to improve consistency. The planned optimisation the drawing kinetics in relation to a core pre-sintering process it is based on the promising results of the optical fibres, among the AR-glass/$Y_2O_3:Pr^{3+}$/AR-glass optical fibre. An alternative solution is to apply a core-shell $Y_2O_3:Pr^{3+}@SiO_2$ nanoparticles, e.g. using SiO_2 layer to prevent NCs dissolution during glass fibre formation and luminescence quenching. Further research on the development of glass-NCs active hybrid optical fibres will include above techniques.

4. CONCLUSIONS

Incorporating new optical materials as nanocrystals into glass fibres for new functionalities has been discussed. The powder doping method was applied as a potential technique to obtain hybrid active NC/glass optical fibres. The several stages from $Y_2O_3:Pr^{3+}$ nanocrystals, glass powder synthesis through sintering and fibre drawing showed that it is a complex technological process which requires special attention and individual approach with regard to the core material preparation. Optimised $Y_2O_3:Pr^{3+}$ NCs have been embed into germanate, lanthanum heavy flint and silicate glass hosts. There are two important challenges: crystallisation of the matrix glass and the dissolution of the active NCs. The former appeared in N-LASF46B and BGG glasses during sintering and fibre drawing, but was resolved in other glasses. The latter issue ($Y_2O_3:Pr^{3+}$ nanocrystals dissolution) is a common problem appearing almost irrespective of the glass composition. However, in an NC-doped AR-glass fibre, the survival of $Y_2O_3:Pr^{3+}$ nanocrystals was observed. The results allowed to select optical fibre drawing conditions performed by the powder-in-tube method. Their distribution uniformity is not yet sufficient, requiring further optimisation of the drawing kinetics or protective shell application.

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