OPTICAL PROPERTIES AND LOCAL STRUCTURES OF Tm$^{3+}$ IONS IN F CO-DOPED LEAD-GERMANATE GLASSES

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Rare-earth doped optical fibres have received considerable attention in recent years due to the enhanced performance that optically pumped fibre devices can give over bulk glass devices. For many years, however, fabrication of low loss rare-earth doped fibres has been confined to silica-related glasses (lately fluoride-based ZBLAN glass fibres have become available, but their weak mechanical strength and poor chemical durability are problematic in practice). This has caused considerable problem in developing future important fibre devices such as 1.3 $\mu$m optical amplifiers and long or short wavelength fibre lasers. It is thus absolutely essential that the range of rare-earth doped glasses that can be made into fibre structures is extended, particularly into lower phonon-energy glasses, combining possibly the best properties of both silica (low-loss, high strength etc.) and fluoride-based glasses (low non-radiative relaxation rate, etc.).

With this regard, we have reported the preparation and characterisation of Tm$^{3+}$-doped lead-germanate based glasses and fibres [1]. This has lead to the realization of a new class of rare-earth doped, low loss, high strength optical fibres suitable for fibre device applications [2], as well as a record low loss planar-waveguide made by using ion-implantation [3]. In this paper we report the optical and thermal properties of the Tm$^{3+}$ and F co-doped lead-germanate glasses, the local structures of Tm$^{3+}$ ions, and their influence on the spectral properties of Tm$^{3+}$ in the glasses. The glasses were made by using either PbF$_2$, ZnF$_2$ or BaF$_2$ as a substitute for PbO, ZnO or BaO, respectively, in the original lead-germanate glass composition reported in [1]. All glasses were 0.2 wt% Tm$_2$O$_3$ doped. It was found that the thermal stability was well kept in all glasses with fluoride concentration up to 10 mol%. A maximum of only 15 $^\circ$C less in glass transition temperature (Tg) was measured by DTA with respect to the fluorine free initial lead-germanate glass. The refractive indices of the glasses decreased as the fluoride content increased. These properties made the selection of core/clad glasses for fibre fabrication with great ease. The local structures of Tm$^{3+}$ ions in these fluoride co-doped lead-germanate glasses were analyzed using our early proposed "crystal-chemistry model" [4]. The results were in agreement with measured spectral properties of Tm$^{3+}$ in the glasses. We observed an increased fluorescent lifetime from Tm$^{3+}$ $^3$F$_4$ level with increased fluorine content in the glass. Detailed Raman spectra for the glasses were also studied.

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