Phase separation and crystallization strategies to enhance the lumininescence of silver and rare earth doped muliti-phase glass and glass-ceramics

Xusheng Qiao*[1], Junjie Zhao[1], Xiaotong Chen[1], Xiuxia Xu[1], Ronghua Ma[1], Jincheng Du[2], and Xianping Fan[1]

[1]Zhejiang University – 866 Yuhangtang Road * Hangzhou * Zhejiang Province * 310058 * P. R. China, China

[2]University of North Texas (UNT) – P.O. Box 311277 Denton, Texas 76203-1277, United States

Abstract

Sub-nanometer noble metal quantum-clusters, such as [Agm]n+, are emerging as an attractive luminescent specie to develop new types of biosensor applications, optoelectronic devices, chemical sensing and optical recording media. However, metal nanoclusters tend to aggregate irreversibly so as to reduce the surface energy. An organic or inorganic scaffold is thus indispensably to be employed as stabilizing ligands to [Agm]n+. The reported maximum PL QY of organically stabilized [Agm]n+ is 64 %, while that of inorganically stabilized has been up to 96.7%. It is easy to form mono-dispersed and heavily-doped [Agm]n+ active quantum clusters in some inorganic glass due to the stabilization role of network tetrahedra, such as [BO4], [AlO4] and [ZnO4].

Trivalent rare earth ions (Ln3+) are also typical luminescent centers, but 4f-4f transition dominated PL of rare earths are usually parity-forbidden and suffer from their weak absorption and low efficient emission. On the contrary, [Agm]n+ possess parity-allowed molecule-like PL transition with broad band width and high QYs. Mutually, codoping [Agm]n+ and rare earths in an identical glass host should be a good strategy to mutually reinforce the spectroscopic performance of materials. However, energy transfers (ETs) between [Agm]n+ and Ln3+ will lead to a significant PL quenching. We thus propose to suppress such ET processes by means of typical behaviors of inorganic glass, which are phase separation and crystallization.

Here we prepared a series of glass-ceramics simultaneously containing [Agm]n+-enriched borate nano-glassy-phases, Ln3+-doped fluoride nano-crystalline phases, and residual silicate glass phases. On the one hand, the borate glass phase separation and fluoride nano-crystals are well isolated by the residual silicate glass phase. There is no mutual interference between [Agm]n+ and Ln3+, ETs are well suppressed and QYs are greatly enhanced. The enhancement of QYs are as high as about 2 times than the precursor glasses. On the other hand, aggregation degree and charge quantity of [Agm]n+ in the glasses could be well controlled to tailor the PL band via solubility and charge compensation strategies. It is further interpreted through a TDDFT simulation with B3LYP and LANL2DZ basis sets.

Keywords: [Agm]n+ quantum cluster, Rare earth, Glass ceramics, Luminescence, phase separation, crystallization

*Speaker