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Investigations on the photoluminescence spectra and its defect-related nature for the ultraviolet transmitting fluoride-containing phosphate-based glasses

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ABSTRACT

Two types of fluoride-containing phosphate-based glasses were prepared under the reducing and ambient air atmosphere, respectively. And the interrelation between the micro-defects and luminescence for these glasses was investigated by studying their absorption, photoluminescence emission (PL) and excitation (PLE) spectra as well as electron spin resonance (ESR) spectra. The emission spectra under the excitation at 351 nm and the excitation spectra by monitoring the emission wavelength at 433 nm, 454 nm, 505 nm, 645 nm and 780 nm, together with the absorption spectra of these two types of glasses were investigated through Gaussian peak fitting method. Their photoluminescence spectra exhibit a general character with a broadband emission at around 430 nm and a minor band at around 645 nm. The photoluminescence excitation spectra and absorption spectra indicate that the Gaussian peak fitting of the emission spectra with the maximum at about 433, 455, 505 and 645 nm, respectively, are closely associated with phosphate-related oxygen hole center defects and fluorine-related color centers. In addition, the emission and excitation spectra of the glass samples after the thermal treatment process in hydrogen atmosphere manifest that the reducing conditions promote the formation of phosphate-related oxygen hole center defects, oxygen related hole center defects and fluorine-related non-paramagnetic color centers as well as PO_4^{3-} defects, while decrease the concentration level of Fe^{3+} and PO_3^{2-} defects. The investigations on the glasses' photoluminescence properties and their changes with the glass melting and thermal treatment atmosphere will promote the further development in preparation technology of the fluoride-containing phosphate-based glasses.

1. Introduction

Phosphate based optical glasses and fluoride-phosphate optical glasses have attracted a great deal of interest due to their excellent properties, including but not limited to tunable melt viscosity and glass forming ability, relatively lower refractive together with low non-linear refractive indices, high transparency from the ultraviolet to the infrared region of the optical spectra, negative temperature coefficient of refractive index and also adjustable thermo-optical coefficient from negative to zero, which make them an attractive candidate for high-performance optics and laser technology [1–4]. With the increasing demands of high-performance UV transmitting materials to be applied for lens system in UV microlithography equipments, excimer laser systems and other special UV optics, from several decades ago till nowadays, the investigations [5–14] on the optical performance, detailed structure-property relations of various fluoride-phosphate and other phosphate-based glasses have never stopped in the pursuit of developing new types of fluoride-containing phosphate-based glasses. The effects of intrinsic defects, extrinsic impurity ions, the irradiations of UV-lamp, excimer lasers, X-ray and Gamma-ray, etc., have been widely studied in order to explore the related defect formation mechanism and the applicability of these phosphate-based glass materials.

UV transmission materials with high resistance to laser-induced damage, high UV transmission, and less fluorescence influence of materials have attracted more and more increasing attention in recent years [15–17]. To achieve a higher UV transmission, it is necessary to minimize the Fe^{3+} content in the glasses. One way is to use the ultra-high purity raw materials with low iron content, another, to reduce Fe^{3+} into Fe^{2+} through a reducing glass melting conditions [13,18–20].

Photoluminescence (PL) spectrum is regarded to be an effective method to investigate the intrinsic and extrinsic defects in all kinds of optical materials. And for these low fluorescent materials with no

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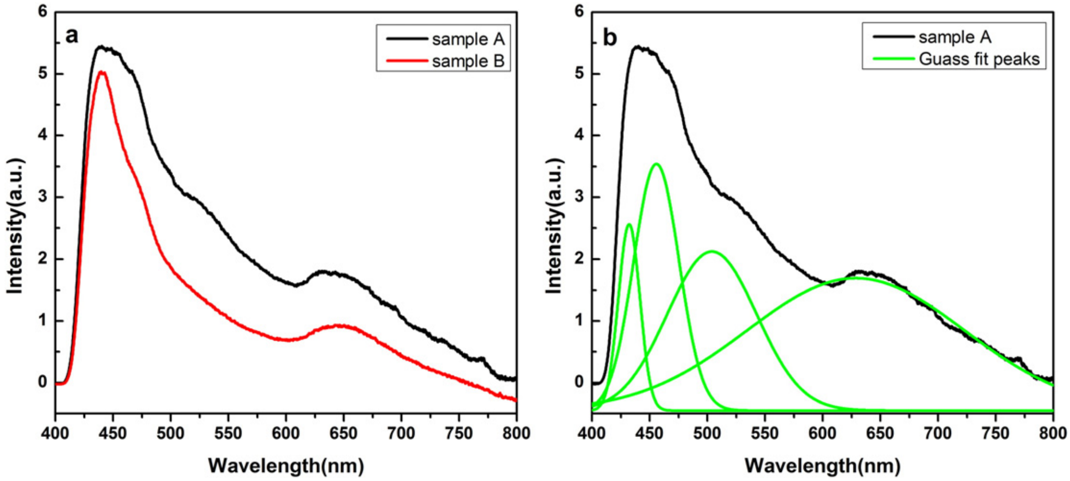

Fig. 1. (a) Photoluminescence spectra of the glass samples A (melted under the reducing atmosphere) and B (melted under ambient air atmosphere) under the excitation at 351 nm. (b) The photoluminescence spectrum of sample A with Gaussian peak fittings.

intentional doping of luminescent ions, the analytical emission intensity level significantly offers potential for the characterization of high quality material for the next generation [21]. D. Ehrt et al., have done extensive work on the PL in the UV–VIS region [4] and photo-ionization of polyvalent ions in fluoride-phosphate, meta-phosphate and boron-silicate glasses [22]. Especially, A. Engel et al. [23] investigated the quality control of multi-component phosphate optical glass emission spectra under excitation at 365 nm and found that the intensity level of emission spectra of the optical glasses gets a shape closer to CaF_2 crystal. Researches indicated that the emission bands have several maxima at about 435, 485, 525, 575 and 670 nm, which are closely dependent on the glass composition [23]. Nevertheless, it isn't clear. More recently, we have just reported a new series of ultraviolet transmitting fluoride-containing phosphate-based glasses with high pulse laser-induced damage thresholds (LIDTs), and proposed that the distinct laser-induced fluorescence phenomenon with a character of eye-

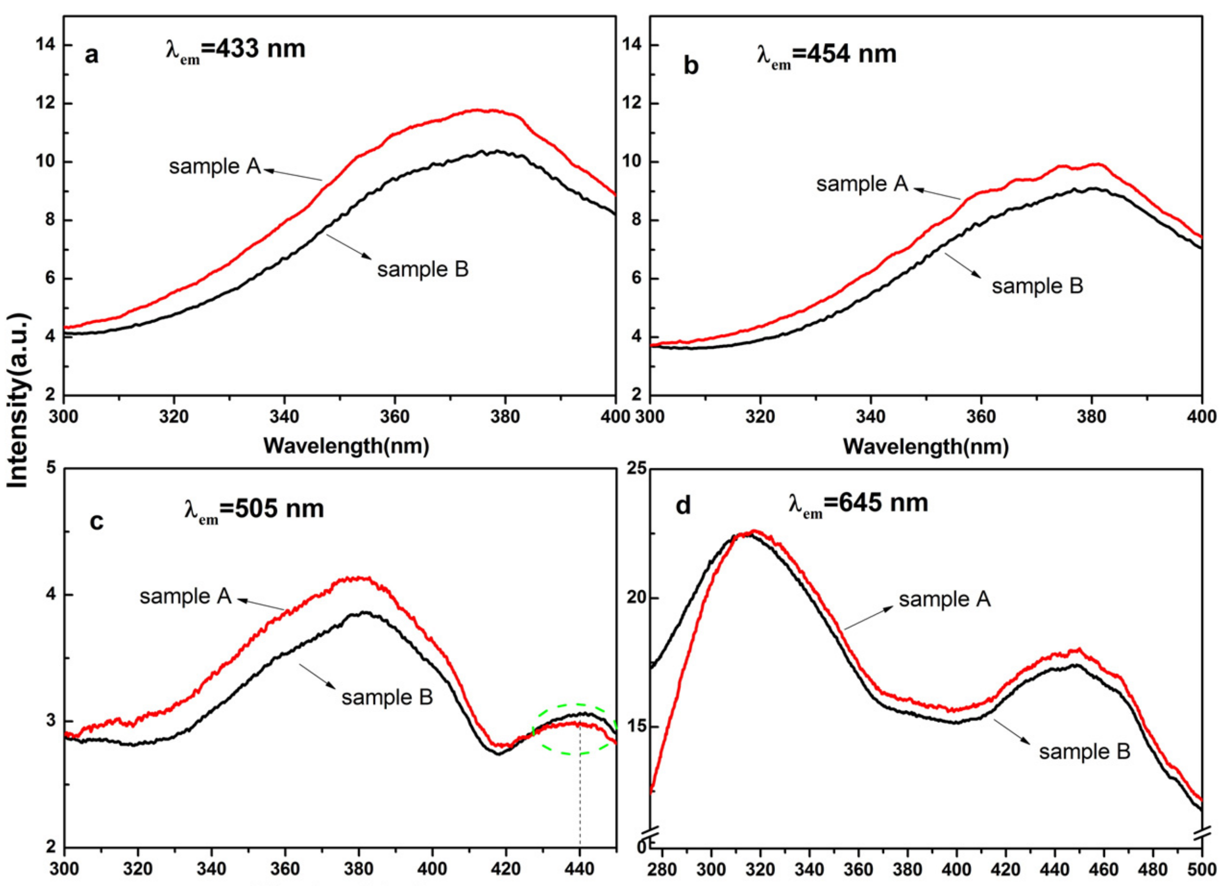

Fig. 2. Excitation spectra of the glass samples A (melted under the reducing atmosphere) and B (melted under ambient air atmosphere) under monitoring at 433 nm (a), 455 nm (b), 505 nm (c) and 645 nm (d), respectively.