Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical and Experimental Investigation of Al^{3+} Ion-Suppressed Phase-Separation Structures in Rare-Earth-Doped High-Phosphorus Silica Glasses

He-He Dong[a,b], Jin-Jun Ren[a], Ying-Gang Chen[a,b], Fan Wang[a], Dan-Ping Chen[a], Lu Deng[a], Chong-Yun Shao[a], Shi-Kai Wang*[a], Chun-Lei Yu**[a,c] and Li-Li Hu***[a,c]

[a] *Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China*

[b] *Centre of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

[c] *Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, People's Republic of China*

Correspondence: woshiwsk@163.com, sdycllcy@163.com, hulili@siom.ac.cn

Experiment Details

Synthesis of Glasses: Er-Yb co-doped high-phosphorus silica-based glasses were prepared using a modified sol-gel method combined with high-temperature melting and molding technology. Tetraethyl orthosilicate (TEOS), C_2H_5OH, P, and Al sources were used as precursors, and deionized water was added to sustain the hydrolysis reaction. The names of the samples and their corresponding raw materials are listed in **Table S1**. Al^{3+} or Al^{3+} and P^{5+} randomly entered the Si–O matrix during the sol-gel process. Heat treatment was performed at 1000 °C for 5 h to decompose hydroxyl groups and organics in the gel. The flow rate of O_2 was set to 50 L/h. After heat treatment, the xerogel was ball-milled into micron-sized glass powder and melted in a vacuum furnace at 1700 ~ 1800 °C for 1 h to obtain silica glass of high optical quality.

Table S1. Names and raw materials of glasses.

Name	Si source	P source	Al source	Er source	Yb source
EYP10	TEOS	P_2O_5	-	$ErCl_3·6H_2O$	$YbCl_3·6H_2O$
EYPA10	TEOS	P_2O_5	$AlCl_3·6H_2O$	$ErCl_3·6H_2O$	$YbCl_3·6H_2O$

Characterization of Glasses: Glass rods were cut into 2mm thick pieces of glass and polished for the physical and spectroscopic property tests. To investigate the doping homogeneity, the distributions of P, Si, Er, and Yb were characterized using an electron probe microanalyzer (Shimadzu, 1720 H). The P^{5+}, Al^{3+}, Yb^{3+}, and Er^{3+} ion contents were determined using a Thermo iCAP 6300 radial-view inductively coupled plasma optical emission spectrometer. The density and refractive index of the EYP10 and EYPA10 glasses at 633 nm were measured by using Archimedes' principle (error: ±0.005 g/cm^3) and the waveguide prism coupling method (error: ±0.0005). The absorption spectra of the EYP10 and EYPA10 glasses were recorded by using a Lambda 950 ultraviolet–visible–near-infrared spectrophotometer (Perkin Elmer). An FLS 920 spectrofluorometer (Edinburgh) was used to detect the photoluminescence spectra and fluorescence decay curves of Yb^{3+} ions and Er^{3+} ions.

An X 'Pert PRO (Netherlands) diffractometer was used to analyze the glass. HRTEM (Tecnai G2, FEI) equipped with EDS was used to evaluate the morphology and size distribution of the nanocrystals in the samples. The HRTEM imaging detector was targeted at backscattered electrons, and the counting time resulting from EDS was approximately 180 s. The Raman spectra were recorded by using Raman spectroscopy (Horiba) with a 633-nm He–Ne laser. All the nuclear magnetic resonance (NMR) experiments were conducted by using a Bruker spectrometer (Avance III HD 500 MHz, 11.7 T). The ^{27}Al magic angle spinning (MAS) NMR spectra were recorded at a resonance frequency of 130.3 MHz, using a 4-mm probe operating at a rotor spinning rate of 12 kHz, a 10° liquid pulse of 0.56 μs, and a relaxation delay of 2 s. The ^{31}P MAS NMR experiments were conducted at 202.44 MHz, using a 4-mm probe operating at a rotor spinning rate of 12 kHz, a 90° pulse of 2.5 μs, and a relaxation delay of 40 s. ^{31}P constant-time double quantum-based dipolar recoupling effects nuclear alignment reduction (CT-DQ-DRENAR) experiments were conducted with a 2.5-mm probe and a rotor frequency of 25 kHz. A 90° pulse length of 4.3 μs and a relaxation delay of 10 s were set with a loop value of 2. ^{27}Al{^{31}P}-compensated rotational-echo double resonance experiments were conducted using a 4-mm probe operating at a rotor frequency of 12 kHz. Two-dimensional hyperfine sublevel correlation electron paramagnetic resonance (EPR) spectroscopy images of each sample were obtained using an E580 pulse EPR detector (Bruker) at a test temperature of 4 K.

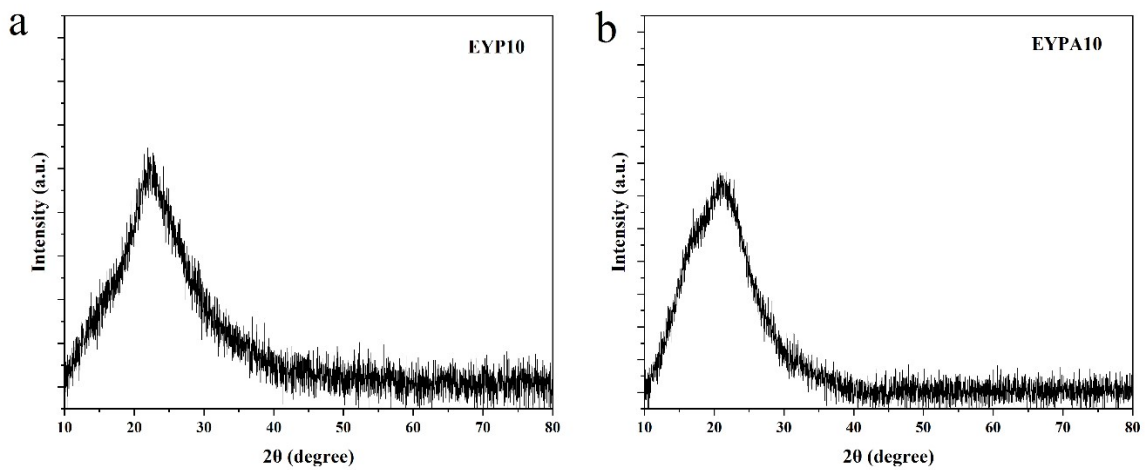

Figure S1 XRD data of dry gel particles of (a) EYP10 glass and (b) EYPA10 glass.

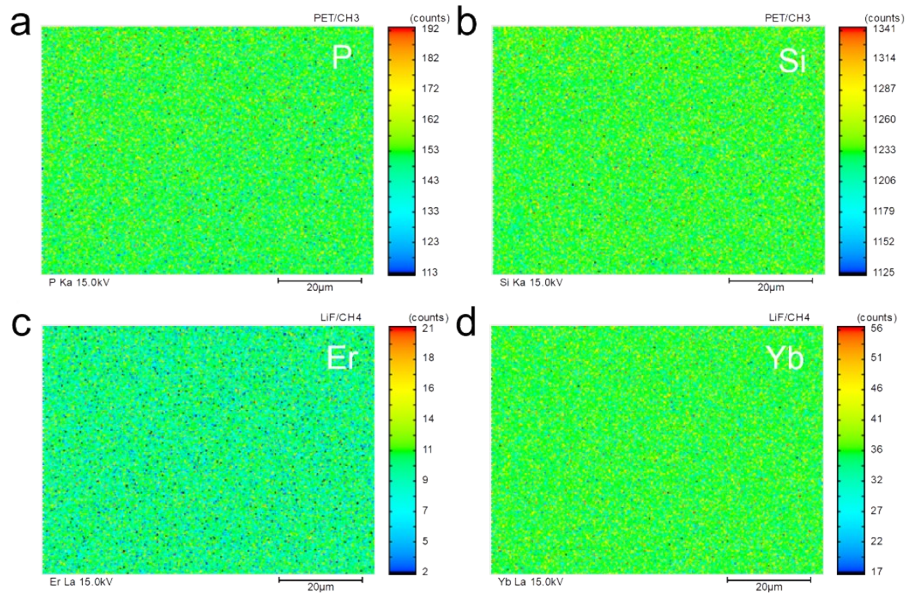

Figure S2 Cross-sectional electron probe microanalysis mapping of (a) element P, (b) element Si, (c) element Er, and (d) element P in EYP10 glass.

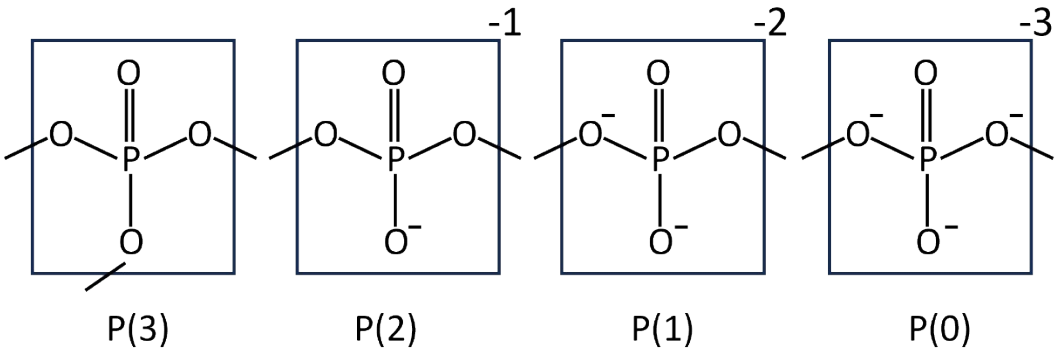

Figure S3 Schematic structure of different P(n) units.