



# Statistical structure analysis of GeO<sub>2</sub> modified Yb<sup>3+</sup>: Phosphate glasses based on Raman and FTIR study



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## ABSTRACT

Structural modification of conventional Yb<sup>3+</sup> doped phosphate glass by GeO<sub>2</sub> was shown to significantly improve both thermal and spectroscopic properties, namely, transition temperature, coefficient of thermal expansion, effective line width, Stark splitting, and fluorescence lifetime. Raman and IR spectroscopic techniques, in conjunction with a statistical analysis method, were used to determine plausible network structure units, or “genes”, which had significant effects on the properties, specifically the distributions of tetrahedron units (<sup>14</sup>Ge-O-<sup>14</sup>Ge, <sup>14</sup>Ge-O-P, P-O-P) and octahedron units (<sup>6</sup>Ge-O-<sup>6</sup>Ge) in the GeO<sub>2</sub>-containing glasses. The use of statistical approach enabled us to build linear mathematic functions of network structure units – property relationships, or models, and the model predictions were closely matched with the measured values. The outcome demonstrates that statistically derived results from Raman and/or IR spectra can be used to aid glass design, achieving target properties.

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## 1. Introduction

Yb<sup>3+</sup> doped laser glasses perform a broad range of applications in femtosecond, high power solid-state lasers and amplifiers because of their higher Yb<sup>3+</sup> doping ability, smoother gain shape, larger size and better optical quality than Yb<sup>3+</sup> doped crystals [1]. Phosphate glass is believed to be a good Yb<sup>3+</sup> host material with many advantages, such as long lifetime, large emission cross section, good glass forming ability and thermal stability, etc. [2,3]. However, Yb<sup>3+</sup> exhibits relatively narrow Stark splitting in conventional phosphate glasses and in turn, realization of high power Yb<sup>3+</sup> laser becomes difficult. According to our previous study, Yb<sup>3+</sup> Stark splitting, crystal field parameter as well as the degree of Yb<sup>3+</sup> asymmetry were the highest in germanate glass among commonly used laser glass systems. A series of Yb<sup>3+</sup>: phosphate glasses modified by introducing a second glass network former, GeO<sub>2</sub>, (up to 20 mol%) was studied in this work. Results demonstrated that GeO<sub>2</sub>-induced structural modification improved the performance of phosphate glass greatly, including Stark splitting, spectroscopic properties, and thermal stability.

Raman and Fourier transform infra-red (IR) are complementary spectroscopic techniques for studying glass structures and the related evolution as functions of compositions, which can reveal and explain the related property changes [6–8]. In this work, GeO<sub>2</sub>-induced network variations of the host phosphate glass were firstly investigated by using both Raman and IR techniques. By performing following procedures, i.e., spectrum deconvolution or curve fitting and assignments of the structure vibrational bands that match with literature, we were able to identify plausible structure units, or “genes” of the host glass network as a function of GeO<sub>2</sub>, which will be detailed next. Statistical composition – property models have been successfully adopted in designing glass compositions of different systems for target properties [10–12]. To the best of our knowledge, a spectroscopy based statistical structure – property model approach has not been reported in literature, except for statistical analysis of relationship between Raman spectroscopy derived glass structure and glass compositions [13]. In this study, both Raman and IR derived glass structure units were used to establish statistical structure – property correlations or models. Predictions by the Raman and IR models were shown to closely match with the measured values. The newly proposed approach can potentially offer benefits for researchers to search for new glass compositions that can simultaneously meet property requirements key to Yb<sup>3+</sup> emission performance, i.e., fluorescence lifetime ( $\tau_f$ ), effective bandwidth ( $\Delta\lambda_{\text{eff}}$ ), and emission cross section ( $\sigma_{\text{emi}}$ ) as

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well as other glass properties. Because of the page limitation, actual procedures used for model development were not included and will be detailed elsewhere in near future.

## 2. Experimental

A glass composition (in mol%) 60P<sub>2</sub>O<sub>5</sub>-7.5Al<sub>2</sub>O<sub>3</sub>-15K<sub>2</sub>O-17.5BaO was used as a baseline phosphate glass, labeled as P. Compositions of glass P were diluted by adding 2, 10, and 20 mol% GeO<sub>2</sub>, separately, and the modified glasses were labeled as PG1, PG2 and PG3. The four glasses were also doped with 1 mol% Yb<sub>2</sub>O<sub>3</sub>. In sample preparation, 300 g of batch per composition was first melted in a high purity silica crucible, during which a special dehydration procedure was used. After initial melting, the melt was poured into a platinum crucible for fining and homogenizing at the same temperature, during which the crucible was covered by a platinum lid to reduce volatilization. The final homogenized melt was cast into a preheated steel mold for annealing at a preset temperature. Each annealed glass was cut and polished to the size of 20 mm × 10 mm × 1 mm for subsequent property measurements.

Glass transition temperature (T<sub>g</sub>) was measured by Netzsch STA449/C differential scanning calorimeter (DSC) at a heating rate of 10 °C/min. Glass density (ρ) was determined using Archimedes method in distilled water. Coefficient of thermal expansion (CTE) was recorded by NETZSCH DIL 402 PC thermal dilatometer. Raman spectra were acquired with Renishaw InVia Raman spectrometer and Infra-red (IR) absorption spectra of powder samples, by KBr method, were obtained by Thermo Nicolet NEXU FT-IR spectrophotometer. For IR measurements, the mass ratio of glass powder to KBr was kept constant. All of the above measurements were carried out at room temperature.

Deconvolution of Raman and IR spectra was done by using GRAMS/32 software (Galactic Industries Corp); the curve-fitting methodology is based on the nonlinear least-squares Levenberg-Marquardt method for fitting overlapping bands. Mysen et al. [9] recommended the curve-fitting by minimizing overall χ<sup>2</sup> values defined as:

$$\chi^2 = \frac{1}{(n-f)} \sum_{i=1}^n \left( \frac{I_{i(m)} - I_{i(c)}}{R_{MSN}} \right)^2$$

where *n* is the number of data points in the fitted region, *f* is the total number of bands and baseline function parameters estimated from the Raman data (*n*-*f* is the number of “residual” degrees of freedom for the fit), *I*<sub>*i*(*m*)</sub> and *I*<sub>*i*(*c*)</sub> are the measured and calculated Raman (or IR) intensity values for the *i*-th data point, respectively, and *R*<sub>*MSN*</sub> is the estimated root-mean-squared noise in the measured data over the fitted region of the Raman (or IR) spectrum, obtained by subtracting a smooth fit of the data from the raw data. The Levenberg-Marquardt algorithm iteratively adjusts parameters for each peak to minimize the χ<sup>2</sup> value.

## 3. Results and discussion

### 3.1. Properties of the glasses

Table 1 summarizes spectroscopic, thermal, and physical properties of P and PG glasses. Stark splitting was derived from the absorption and emission spectra described elsewhere [4,5]. GeO<sub>2</sub> introduction significantly enhanced spectroscopic and thermal properties of phosphate glass, whereas glass density generally increased except for the PG1 glass with 2 mol% GeO<sub>2</sub> addition.

Specifically, modification of phosphate glass network by a second network former, GeO<sub>2</sub>, resulted in improvements on thermal

properties, i.e., lowering CTE by up to 22% and increasing T<sub>g</sub> by up to 127 °C, pending on GeO<sub>2</sub> concentration. Significant improvements were also achieved for the glass spectroscopic properties as more GeO<sub>2</sub> were added; Δλ<sub>eff</sub>, τ<sub>f</sub>, and Stark splitting were increased by as much as 5.92 nm, 0.52 ms, and 188 cm<sup>-1</sup>, respectively. At the same time, a stable σ<sub>emi</sub> was obtained. Undoubtedly, all of the observed improvements came from the introduction of GeO<sub>2</sub>. The related structural changes by Raman and IR spectroscopic analysis will be discussed later.

### 3.2. Structures of phosphate and germanate glasses

Phosphate glass can be characterized by its mole ratio of [O]/[P] as follows. Vitreous P<sub>2</sub>O<sub>5</sub> glass with [O]/[P] of 2.5 represents ultraphosphate chemistry, i.e., three bridging oxygen (BO or P-O-P) atoms and one double bonded terminal oxygen (P=O); the network mostly consists of P<sup>(3)</sup> units, where the superscript represents the number of BOs per PO<sub>4</sub> tetrahedral unit. Metaphosphate glass (chain of PO<sub>3</sub><sup>-</sup>) with [O]/[P] of 3.0, besides P<sup>(3)</sup> units, also contains P<sup>(2)</sup> units, i.e., 2BOs and 2 non-bridging oxygen (NBO) atoms per PO<sub>4</sub> tetrahedral unit. Pyrophosphate glass (P<sub>2</sub>O<sub>7</sub><sup>2-</sup>) with [O]/[P] of 3.5, new structure units of P<sup>(1)</sup> are also present, i.e., 1 BO and 3 NBOs per PO<sub>4</sub> tetrahedral unit. Orthophosphate glass (PO<sub>4</sub><sup>3-</sup>) with [O]/[P] ratio of 4.0 consists primarily isolated P<sup>(0)</sup> units, i.e., 4 NBOs per PO<sub>4</sub> tetrahedral unit. Speciation of phosphate glass follows either 2P<sup>(*n*)</sup> + M<sub>2</sub>O (MO) ↔ 2P<sup>(*n*-1)</sup> (*n* is the number of BO atoms per PO<sub>4</sub> tetrahedron unit) or 2P<sup>(*n*)</sup> ↔ P<sup>(*n*-1)</sup> + P<sup>(*n*+1)</sup>, depending on the charge (*q*) of M<sup>*q*+</sup> cations, ratio of [M<sup>*q*+</sup>]/[P], and [O]/[P] 15.

To ascribe specific polyhedron linkages of O-Ge-O, a left superscript, <sup>[4]</sup>Ge or <sup>[6]</sup>Ge, was used to distinguish 4-fold and 6-fold coordinated Ge with O. Structure of GeO<sub>2</sub> glass resembles SiO<sub>2</sub> glass [16,17] and speciation reactions of the germanate glasses were detailed elsewhere [18]. For xNa<sub>2</sub>O-(1-x)GeO<sub>2</sub> glass, as an example, the reaction, GeO<sub>4/2</sub> + Na<sub>2</sub>O = (GeO<sub>6/2</sub>)<sup>2-</sup> + 2Na<sup>+</sup>, was proposed when *x* or Na<sub>2</sub>O was lower, no greater than 15 mol%. In this case, the 6-fold coordinated GeO<sub>6</sub> units, or <sup>[6]</sup>Ge-O-<sup>[6]</sup>Ge, were created without or with little NBO19. However, other studies pointed out the existence of GeO<sub>5</sub> or <sup>[5]</sup>Ge-O-<sup>[5]</sup>Ge units instead [20]. With higher Na<sub>2</sub>O present, the reaction, GeO<sub>4/2</sub> + Na<sub>2</sub>O = GeO<sub>3/2</sub>O<sup>-</sup> + 2Na<sup>+</sup>, was proposed, creating NBOs. For the latter, with sufficiently higher Na<sub>2</sub>O, the 4-fold coordinated GeO<sub>4</sub> units or <sup>[4]</sup>Ge-O-<sup>[4]</sup>Ge were stable; its speciation reaction resembles silicates. Both of the speciation reaction models are still controversial although higher coordination of Ge-O in germanate glass has been identified from several spectroscopic studies20.

In our study, the baseline glass P has a composition of metaphosphate according to its [O]/[P]. With 2 mol% GeO<sub>2</sub> addition, the PG1 glass with [O]/[P] close to 3.0 should contained both P<sup>(2)</sup> and P<sup>(3)</sup> units (each PO<sub>4</sub> tetrahedron unit contains 2 and 3 BOs, respectively) as expected for a metaphosphate glass. In addition, the ratio of [K + Ba + Yb]/[P] was 0.55 (or 0.56 on an oxide basis). Hence, P<sup>(1)</sup> units in the P and PG glasses with [O]/[P] of 3.0–3.3 are expected to be very little, plus isolated P<sup>(0)</sup> units should be absent for Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> metaphosphate composition with 0–50 mol% GeO<sub>2</sub>21. Because only GeO<sub>2</sub> was introduced to the phosphate network, it is reasonable to postulate that GeO<sub>2</sub> in the network existed in a form of either isolated Ge-O-Ge moiety or more or less randomly and uniformly connected with the P-O-P network, in which P-O-Ge bonds might take place [21–23] All of the annealed glasses (P, PG1, PG2, and PG3) exhibited a high transparency, proving an evidence on the absence of micro-scale phase separation in the glasses. In addition, relative to glass P, T<sub>g</sub> increased and CTE decreased continuously with the addition of GeO<sub>2</sub> for the PG glasses. Combining the above findings, it is reasonable to believe

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