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# Mixture experimental design applied to gallium-rich $GaO_{3/2}$-$GeO_2$-$NaO_{1/2}$ glasses

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ABSTRACT

A mixture-design method was used as a multivariate data analysis tool to investigate properties of gallate glasses in the $GaO_{3/2}$–$GeO_2$–$NaO_{1/2}$ system. The objective was to design compositions having gallium oxide as the main component of the glass expected for further applications like wave guided transmission in the near- and mid-infrared optical domain. Accordingly to this tool a set of glass compositions were defined in a constrained domain of the ternary glass system rich in gallium oxide and prepared by the traditional melt-quenching technique. Sample density, refractive index, multiphonon cut-off wavelength as well as thermal characteristics were measured as representative multiple responses and a linear model fitting those physical properties *vs* glass composition was established. The obtained model allows to predict and optimize the different responses for any composition in the studied domain and a better understanding of the influence of each glass component on its physical properties. This study demonstrates that gallium-richest compositions lead to an increase in the polarizability and contribute to a slight enlargement of the transmission window which are the primary conditions requested for intended applications. Complementary structural investigation allows to confirm the influence of the component content in the glass composition revealed by the model.



## 1. Introduction

The demand for adapted glass compositions implemented in optical applications is continuously rising in the near and mid-infrared (up to 5 μm) where most of the molecules present a fingerprint absorption (harmonic vibrations). Silicate, phosphate and aluminate glasses have been widely investigated for NIR applications [1] but little attention has been devoted to gallate glass matrices, which are potentially excellent candidates. Some studies on binary and ternary gallium oxide containing glasses have been reported in the literature [2–14] but only a few present a gallium oxide rich content.

From a structural point of view, gallium is expected to act like aluminum in the vitreous oxide network. When the latter is introduced to an alkali-silica glass system, $Si^{4+}$ ions can be substituted by $Al^{3+}$ ions, which are then compensated by alkali ions, thus reducing the number of non-bridging oxygens (NBOs) [15,16]. Regarding optical properties, gallate glasses are expected to exhibit a wider transparency window in the middle infrared compared to classical oxide glasses [10,17,18,15], such as borates, phosphates or silicates, because of the higher atomic weight of gallium. Also they exhibit significant polarizability and hyperpolarizability which makes them promising materials for nonlinear optical properties [17]. Their low phonon energy (~850 $cm^{-1}$ for germanogallate glasses, ~675 $cm^{-1}$ for some alkali-earth-gallate glasses [13,19]) makes them of interest for hosting rare-earth ions in luminescent and laser materials [20]. From the foregoing gallate-based glasses would offer an excellent compromise for mid-infrared transmission applications with the required thermal stability and mechanical resistance for fiber waveguide shaping [21]. Recently, studies on optical waveguiding with gallophosphate glasses have been reported by Vangheluwe et al. [22] but none with compositions rich in gallium oxide. Most of the previous investigations conducted on germanogallate glass systems, which are expected to fulfill these properties, have been focused on the germanium oxide ($GeO_2$) rich portion of the glass system [5,8,10,18,20,23–29].

On the contrary this study will focus on the investigation of gallium-rich glass compositions belonging to the sodo-germanogallate ternary system with the perspective of applications in the mid-infrared range (3 to 5 μm). For this purpose, a first modelling of the glass properties (thermal stability toward crystallization, IR transmission, linear refractive indices and density) is explored with the mixture design technique in the gallium oxide rich system. In our knowledge, this represent the first study in the literature with this system which does not permit an

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effective use of properties calculations features from a glass property database as the SciGlass information system [30]. Properties linear modelling of the measured properties is expected to predict the influence of each component in the studied domain. Complementary structural investigations will be conducted using Raman and $^{71}$Ga NMR spectroscopy to confirm, precise and support the model predictions.

## 2. Experimental details

### 2.1. Glass preparation

Here, the used components for the ternary composition studied system are $GaO_{3/2}$, $GeO_2$ and $NaO_{1/2}$ which are more relevant to highlight the role of each cation. Glasses in the $GaO_{3/2}$-$GeO_2$-$NaO_{1/2}$ system were then prepared by traditional melt-casting technique from gallium oxide $Ga_2O_3$ (99.99%), germanium oxide $GeO_2$ (99.99%) and sodium carbonate $Na_2CO_3$ (99.95%). The weighed and mixed powders were pre-sintered at 950 °C for 1 h and then melted in platinum crucible in ambient atmosphere for 30 min at 1300–1550 °C depending on the compositions. The melted glasses were poured on a stainless steel mold preheated at 40 °C below the glass transition temperature and annealed for 6 h at the same temperature before being slowly cooled to room temperature. All the obtained glasses were colorless, transparent and bubble-free. The glass samples were finally cut and polished on both parallel faces for optical characterization.

### 2.2. Characterization techniques

#### 2.2.1. Physico-chemical and optical response measurements

Two physico-chemical experimental responses, density and thermal stability, are studied here. The density of the glass, ρ, is related to composition and structural evolution, as well as the thermal stability against crystallization, corresponding to the difference, ΔT, between the onset temperature of crystallization and the glass transition temperature. The latter must be as large as possible (≥100–120 °C) to facilitate any future technological transfer. Two optical parameters are also studied: the IR cut-off wavelength, which is crucial for mid-infrared applications, and the refractive index, n, which is expected to be the signature of high third-order optical susceptibilities which can be involved in higher level applications like Raman gain or frequency mixing [31,32].

Confirmation of nominal glass stoichiometry was verified with a deviation of ±2 mol% by using Electron Probe Micro Analysis on a VG Microlab 310F apparatus. The glass transition temperature, $T_g$, and the onset temperature of crystallization, $T_x$, were determined by differential scanning calorimetric (DSC), using a Netzsch DSC Pegasus 404F3 apparatus on glass pieces in Pt pans at a heating rate of 10 °C/min and with a precision of ±2 °C. The glass density was determined at room temperature by the Archimedes' method with an Alfa-Mirage MD-300S densimeter using deionized water as immersion liquid. The measurement precision was estimated to be ±0.01 g/cm$^3$.

The infrared transmission spectra were recorded on glass samples of about 2 mm thickness on a FTIR Perkin Elmer Frontier spectrometer. The linear refractive index was measured by employing the M-lines prism coupling technique (using a Metricon 2010) at 532 nm with an accuracy of ±0.005.

#### 2.2.2. Complementary structural characterization

The Raman spectra were obtained using a Horiba Jobin-Yvon LabRAM HR800 micro-Raman spectrometer equipped with a 532 nm laser.

$^{71}$Ga magic-angle spinning NMR spectra were recorded in a magnetic field of 21.1 T using a Bruker Avance II 900 MHz spectrometer at the Canadian National Ultrahigh-field NMR Facility for Solids (Ottawa, Ontario). Samples were ground to a fine powder, packed into 1.3 mm (outer diameter) rotors and spun at 60 kHz. Single-pulse excitation with a 15 degree tip angle was used to acquire 8000 transients, separated by an optimized relaxation delay of 5 s. The chemical shift reference was 1 M $Ga_2(SO_4)_3$ (aq) at 0ppm. Spectra were fit using a Czjzek model in the software package dmfit [33], which allows parameter distributions suitable for network-forming oxide glasses [34].

## 3. Design of experiments: glass composition study in the $GaO_{3/2}$-$GeO_2$-$NaO_{1/2}$ system

### 3.1. Definition of the experimental domain

The realization of an optimized design of experiments provides a maximum of information with a minimum of experiments. Within the context of the selection of compositions belonging to the ternary $GaO_{3/2}$-$GeO_2$-$NaO_{1/2}$ system, designing experiments consists in polynomial modelling of the properties of interest defined in terms of responses of the system as a function of the composition. Here, the cationic molar percentages of $GaO_{3/2}$, $GeO_2$ and $NaO_{1/2}$ are noted xGa; xGe; xNa respectively.

In a first step, a preliminary exploratory experiment was performed using the selected preparation method to reach a first piece of information and permit the definition of the domain of study. In this case, the central point in the ternary diagram (domain of compositions) where xGa = xGe = xNa = 33.3% was prepared and characterized (composition N°2 in Fig. 1, Table 1 and Table 2). In order to define our experimental domain, the range of variations of the xGa, xGe and xNa compositions and the relational constraints between variables were fixed [35]. The sum of xGa, xGe and xNa, *i.e.* of all the oxides percentages, must equal to 100%. The gallium oxide $GaO_{3/2}$ content was selected to be larger than that of germanium oxide $GeO_2$, to focus on rich-gallate glasses and investigate the role played by the gallium cation as a main constituent of the glass network. This leads to the following constraints equations:

$$xGa + xGe + xNa = 100\ \text{mol\%}$$

$$xGa \geq xGe$$

The range of variation for each parameter xGa, xGe and xNa was fixed around 10 mol% to stay in the homogeneous glass-forming region and to build up a linear model of the experimental responses:

$$GaO_{3/2}(\text{mol\%}): \quad 33 \leq xGa \leq 44$$

$$GeO_2(\text{mol\%}): \quad 24 \leq xGe \leq 34$$

$$NaO_{1/2}(\text{mol\%}): \quad 29 \leq xNa \leq 38$$

These ranges of variations were chosen so as to inscribe the domain of study inside a reduced equilateral triangle moved from the central preliminary test to the richest part of gallium oxide in the ternary diagram. The reduced triangle and domain of composition are depicted in the diagram presented in Fig. 1.

### 3.2. Determination and quality of the design of experiments

The optimal design of glass compositions was obtained by using the 'optimal-D' criterion of optimization from the "Design Expert®" version 8 software [36]. Eight experiments, *i.e.* glass compositions, were selected, including the exploratory point. Adjustments were necessary for some compositions which proved to be outside the glass-forming region after preparation, using the conditions described above. In order to construct the model, compositions rich in information and showing glass-forming ability were therefore provided by the software. The final compositions are given in Table 1 and are represented in the ternary diagram shown in Fig. 1. Note that we are considering cationic

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