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PARAFAC analysis of IBIL spectra from silver ion exchanged glasses

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ABSTRACT

In this work we present for the first time an application of PARALLEL FACTOR (PARAFAC) analysis to the investigation of Ion Beam Induced Luminescence (IBIL) spectra of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchanged silicate glasses, in order to check the possibility to obtain additional information on the formation of silver aggregates under ion irradiation by a proper statistical rearrangement of experimental spectra. We decomposed the data by PARAFAC taking into account both IBIL emission features and their evolution as a function of the time. Shape and trend under irradiation of the extracted components were correlated to silver concentration and aggregates in the investigated systems. Strength and weakness of this statistical approach applied to IBIL spectra recorded as a function of time were evidenced and discussed.

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1. Introduction

Ion exchange (IE) is a widely employed technique for the doping of amorphous or crystalline matrices and it is typically realized by dipping the substrate in a molten salt bath containing the desired metallic ions. Due to the chemical potential difference between the substrate surface and the fused salt bath, the metallic ions in the bath exchange with the alkali ion species of the glass. This process gives rise to a dopant diffusion profile whose shape and depth depend on the diffusion coefficients of the ions involved in the phenomenon, on the bath temperature, on the duration of the treatment, and on the salt composition.

In literature several papers were dedicated to the investigation of IE, since the first treatments for surface toughening of silicate glasses [1] and, subsequently, in the production of planar optical waveguides [2 and refs. therein, 3,4].

The most studied element in the production of silicate glasses optical waveguides is silver, whose high diffusivity and ionic polarizability allow to obtain, in relatively easy way, optical waveguides and integrated systems on glass substrates. $\text{Ag}^+ \leftrightarrow \text{Na}^+$ IE in alkali-silicate glasses has been also widely investigated for the realization of glass surfaces containing silver nanoaggregates [5,6]. The steps to the nucleation of silver nanoparticles involve the formation of luminescent polyions such as $\text{Ag}^+ - \text{Ag}^+$ dimers and $(\text{Ag}_3)^{2+}$ multimers, which has been identified as the seeds for the nucleation of metallic clusters [6–9]. Among the methods of inducing the formation of silver nanoparticles, ion

irradiation has been studied since 40 years [10 and refs. therein, 11–15]. Nonetheless, an accurate control of the particle nucleation and growth is still to be realized, owing to the lack of knowledge of the steps involving the defect formation, ion oxidation states and growth of the nucleation centres.

Ion Beam Induced Luminescence (IBIL) has been studied both as a method for the detection of luminescent species in inorganic compounds and as a technique for evaluating the radiation hardness of materials [16–21]. It is based on the detection of luminescence spectra induced by ion beam irradiation and on the analysis of their changes during irradiation due to the formation and aggregation of point defects. Recently, multivariate statistical methods like Principal Component Analysis (PCA) has been used in order to better exploit the evolution of IBIL spectra during irradiation or the identification of either sample types or luminescence components [22–24]. In particular, a work has been performed demonstrating the capability of PCA applied to IBIL to discriminate silver ion exchanged silicate glasses realized with different treatment conditions [25].

PARALLEL FACTOR analysis (PARAFAC) is used to decompose multi-way data arrays and to facilitate the identification and quantification of independent underlying signals, termed “components” [26]. In the last decade, this technique has been predominantly used to decompose fluorescence Excitation Emission Matrices (EEMs) into their underlying chemical components (e.g. [27–31]) and, to a less extent, to the data interpretation of other techniques: Gas Chromatography-Mass Spectrometry (GC-MS) [32], Nuclear Magnetic Resonance (NMR) [33], High Performance Liquid Chromatography (HPLC) [34], Electroencephalography (EEG) [35]. Briefly, PARAFAC is a multi-way method applicable to data arranged in three or higher order arrays (tensor)

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such as EEMs spectra (sample $\times I(\lambda_{\text{ex}}) \times I(\lambda_{\text{em}})$, were $I(\lambda_{\text{ex}})$ and $I(\lambda_{\text{em}})$ are the intensities at the excitation and emission wavelength, respectively), chromatographic data (sample \times elution time $\times m/z$ structure) or, for instance as in the present work, IBIL spectra (sample $\times I(\lambda_{\text{em}}) \times$ time).

In this paper, we present for the first time an application of PARAFAC statistical method for the analysis of IBIL spectra of $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchanged silicate glasses, in order to check the possibility to obtain additional information on spectral components occurring during ion irradiation. In particular, the aim is to follow trends of the luminescence features characteristic of silver ions and silver complexes during irradiation, in order to monitor the evolution of silver oxidation and aggregation states. We analyzed 21 glass samples obtained with different synthesis parameters (ion exchange bath composition, annealing temperature and duration time) and we applied PARAFAC to the 3D array of samples $\times I(\lambda_{\text{em}}) \times$ irradiation time, testing the capability of the method to evidence the characteristic emission bands. The results are commented and improvement approaches are suggested at the end of the work.

2. Materials and methods

Silver ion exchanged silicate glasses were realized on commercial soda-lime optical glass (SLG) slides with atomic % composition of 59.6 O, 23.9 Si, 10.1 Na, 2.6 Mg, 2.4 Ca, 0.7 Al, 0.5 K, 0.2 S + Ti + other elements in traces. Before the doping, the glass slides were prepared by a four-step cleaning process in an ultrasonic bath (deionized H_2O , trichloroethylene, acetone, isopropyl alcohol). IE was obtained by immersing the glass slides in a molten salt bath of $\text{AgNO}_3:\text{NaNO}_3$ at the temperature of 320 °C for 20 min. Two different silver molar concentrations were used in the bath mixture, namely 0.1% and 1%. Silver doped SLG slides were then cut into pieces and annealed in air at the temperature of 380 °C, 410 °C and 440 °C; for each temperature three different annealing times were explored: 1 h, 4 h and 16 h. The samples were labeled accordingly to their synthesis conditions: for instance, the sample named Low-410-4 was immersed in the molten salt bath with the lower content of silver nitride (0.1% mol), then annealed in air at $T = 410$ °C for 4 h. The samples labeled Low-RT and High-RT are the two as-exchanged glasses; the pristine soda-lime glass is named SLG.

IBIL measurements were performed at the AN2000 accelerator of INFN Laboratori Nazionali di Legnaro, Italy. Samples were irradiated with a 2.0 MeV H^+ ion beam, with a current density of about $1.6 \mu\text{A} \times \text{cm}^{-2}$ on an area of $3 \times 2 \text{ mm}^2$. Full spectra (from 199 nm to 997 nm) were collected during irradiation by an UV graded silica fibre (600 μm of diameter) aligned in front of the sample and recorded by an Ocean Optics QE 65000 spectrometer. Every single spectrum was acquired with 1 s of integration time and for each sample 200 spectra were collected, corresponding to 200 s of irradiation time. The total irradiation charge was measured with a Faraday cup, which was the scattering chamber itself. The beam cross section was measured from the spot on a paper target. Spectra were normalized on the spot area and on the charge collected within 1 s. So, the intensities at each wavelength were expressed as counts $\times \text{C}^{-1} \times \text{cm}^{-2}$. Then, the original dimensions of the tensor to characterize with PARAFAC analysis are: 21 samples, 1044 wavelengths (number of detector channels), 200 spectra.

Referring to IBIL spectra, PARAFAC analysis was used by decomposing the original three-way dataset (X_{ijk}), given by samples $\times I(\lambda_{\text{em}}) \times$ time into a set of trilinear terms ($a_{if} \times b_{jf} \times c_{kf}$) and a residual array (e_{ijk}) as shown in Eq. (1):

$$X_{ijk} = \sum_{f=1}^F \alpha_{if} b_{jf} c_{kf} + e_{ijk} \quad (1)$$

where X_{ijk} are the spectral intensities corresponding to the i th sample at the j th wavelength at the k th time, and e_{ijk} is the residual representing the variability not accounted by the model characterized by F components. So, each component is characterized by: i) an array \mathbf{I}_f of a -values

(scores), one for each sample; ii) an array \mathbf{J}_f of b -values, one for each emission wavelength; iii) an array \mathbf{K}_f of c -values, one for each time. In this paper the F components have the following interpretations: the vectors \mathbf{J}_f are a scaled estimate of the emission spectrum of the f th spectral component; the vectors \mathbf{K}_f are a scaled estimate of the intensity decreasing rate of the f th spectral component; the parameter a_{if} is directly proportional to the yield of the f th spectral component in sample i . For further details about the theoretical description of PARAFAC the reader is referred to earlier references [26,36–39].

The numerical procedure for the PARAFAC analysis was performed with Matlab R2013a; specifically by using drEEM (version 0.1.0) and N-way (version 3.20) toolboxes and following the indications of the tutorial Appendix A of Murphy et al. [26] properly adapted to the peculiarities of the IBIL spectra. In fact, the IBIL data were elaborated with toolboxes specifically designed for spectral correction and PARAFAC analysis of EEMs spectra. Initially, several tests were performed with the original dataset in order to identify the optimal components number. Results showed that scores of some components are strongly correlated, indicating that the overall spectral absolute intensities is the dominant effect in the dataset. So, the dataset was normalized to unit norm as described in Appendix A of Murphy et al. [26] in order to reduce the intensity related collinearity and to allow to low intensity spectral features to take part of the model. Actually, the study is focused on the detection of the differences in spectral shape among different samples rather than on the study of the absolute luminescence yield.

Subsequently, nine models characterized by components number ranging between 2 and 10 were calculated. Best results were obtained with three components model characterized by explained variance of 99.7%. This option has been identified considering, as described in [26]: i) the consistency of the shape components with physical phenomenon studied, ii) the effect on model fit of adding more components, expressed as the lowering of squared residual values with the increase of the number of components iii) the stability of the solutions of twenty models (calculated with the same number of components) initialized using different random starting vectors, iv) the decrease of the core consistency values with the increase of the number of components, v) the randomness of residual patterns of each sample, vi) the results of the split half analysis and validation tests.

Before the abovementioned normalization the following data were excluded from the dataset: i) the first spectra ($t = 1$ s) of each sample due to its highest leverage value; ii) intensities wavelengths lower than 250 nm and higher than 950 nm due to their noisy patterns; iii) samples High-440-4 and High-440-16 due to their high leverage values probably related to their atypical shape - if compared to the other samples - for wavelengths higher than 500 nm (reason and impact of this samples exclusion are discussed below). Then, the dimensions of the tensor characterized with PARAFAC analysis are: 19 samples, 916 wavelength, 199 spectra.

The robustness of the overall model has been checked with split half analysis and the following validation tests (alternating split style, four splits, six combinations, three tests - $\text{S}_4\text{C}_6\text{T}_3$), for further details refer to [26] and references therein. Incidentally, with 21 samples the model characterized by four components shows the best results. However, $\text{S}_4\text{C}_6\text{T}_3$ does not validate the overall model because in one test one component of the overall model does not find any match. This is probably due to the low dimension of the dataset and - more noticeably - to the marked shape difference of IBIL spectra between the two mentioned samples (excluded in the validate model discussed in the following) and the others.

3. Results

Fig. 1 shows the spectra of each sample acquired after 10 s of IBIL analyses, that is after 10 s of irradiation time. Note that the two samples excluded in the PARAFAC analysis are in the lower part of the chart.

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