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Electron Paramagnetic Resonance (EPR) studies on the photo-thermo ionization process of photo-thermo-refractive glasses

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ABSTRACT

Photo-thermo-refractive (PTR) glass is an optically transparent photosensitive sodium alumino silicate glass, containing NaF and KBr additives, along with cerium, silver, tin and antimony oxide dopants. UV-exposed regions of this glass produce NaF nanocrystals upon heating, giving rise to a permanent localized refractive index change. In this article we examine the initial stages of this crystallization process by continuous-wave and pulsed X-band electron paramagnetic resonance (EPR) spectroscopy. UV exposure of PTR glass produces unpaired electrons whose EPR spectrum is characterized by pronounced peak splitting arising from nuclear magnetic hyperfine interactions with spin-5/2 and spin-7/2 nuclei suggesting close proximity of the unpaired electrons with ^{121}Sb and ^{123}Sb nuclei. These results indicate that the Sb_2O_3 dopant plays a key role in the initial stages of the crystallization mechanism. Upon thermal annealing, leading to the crystallization of NaF, these species disappear, indicating their transient nature. A number of other unpaired electron species identified in the dopant free matrix appear to be unrelated to the crystallization process. These results clearly challenge the classical mechanism proposed decades ago to explain the complex crystallization process of PTR glass. Together with more recent results from optical spectroscopy they support the Nikonorov model involving (1) photoionization of Ce^{3+}, (2) transfer of this electron to Sb^{5+} species to create a Sb^{4+} species, (3) upon annealing electron transfer from Sb^{4+} to Ag^{+} ions, producing silver atoms, (4) coalescence of these species into Ag clusters, which (5) serve as nucleation catalysts for NaF nanocrystals.

1. Introduction

Photo-thermo refractive (PTR) glass is a photosensitive silicate glass whose optical properties can be modified in a controlled fashion by UV-exposure and subsequent annealing near the glass transition temperature, T_g. The chemical composition of a typical PTR glass is 15 Na_2O - 4 Al_2O_3 - 70 SiO_2 - 5 NaF - 5 ZnO - 1 KBr, with trace amounts (~0.01 mol.%) of the dopants Ce, Ag, Sb and Sn. By exposing glass samples to UV irradiation followed by adequate heat treatment, crystallization of NaF can be induced. Spatially patterned irradiation schemes afford glass-ceramics with periodically modulated indices of refraction, which are suitable for various photonic applications (generation of holograms, spectral and spatial filtering, and production of Bragg gratings) [1–4]. Devices of this kind are currently commercialized by a number of companies. The refractive index variations have been commonly postulated to arise from the formation of NaF nanocrystals in the UV-exposed areas of the sample upon annealing whose presence in the glass-ceramic has been detected by X-ray powder diffraction and solid state NMR [5]. For this reason many experimental studies have been devoted to elucidating the mechanism of NaF crystallization, dominantly using classical (macroscopic) examination methods [1–9]. However, it must be emphasized that there is – as of yet – only weak, indirect evidence linking the NaF crystals to the physical phenomenon of the refractive index variation. It is well-known that Ce^{3+} ions in glasses can be photo-ionized by UV irradiation and that the released electron can be trapped by an intrinsic defect or by an ion of a polyvalent element [10]. Initially it had been postulated that the main trapping mechanism is expected to be the formation of atomic Ag species, according to the reaction scheme [6–8]:

$$Ce^{3+} + Ag^{+} \rightarrow Ce^{4+} + Ag \quad (1)$$

Upon heating near the glass transition temperature, these Ag species are considered to form silver containing nanoparticles that serve as catalysts for the nucleation of NaF nanocrystals. The formation of these

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nanoparticles has been confirmed by a plasmon resonance broadband absorption centered at about 465 nm [11]. However, the special selective crystallization is known to proceed only in the presence the Sb and Sn dopants and the KBr additive, whose role in the crystallization process is not at all clear.

To obtain more specific structural information about the role of these dopants at the atomic level, suitable spectroscopic techniques are required. A wide range of optical spectroscopic studies have been carried out recently. For example Anne et al. studied the structure of cerium ions in PTR glass matrix [12]. They showed that even if the two absorption bands of Ce^{3+} and Ce^{4+} species are overlapped in the UV spectral region, their spectra can be decorrelated and decomposed into individual Gaussian bands (two for each type of ion). This study was then completed by Efimov et al. who studied the structure of the intrinsic absorption tail of glass matrix and impurities in UV [13] but also proposed a more complex and accurate model for the cerium absorption in UV range based on 3 elementary Gaussian bands for each ion [14]. Finally, additional optical spectroscopic work on silver ion exchanged PTR glass corroborated the suggestion that the photo-thermo-induced process mechanisms are more complex than that shown by Eq. (1) and that, similarly to polychromatic glasses [2], additional ions, such as antimony, may be involved in these photo-thermo-induced processes [15]. However, due to the overlap of the absorption bands of the active species (cerium, silver, antimony, glass matrix, impurities such as iron, color centers), the analysis of optical spectroscopic curves is a very challenging task and the results are subject to a large uncertainty.

Despite the fact that several of the postulated species involved in the proposed reaction mechanisms (Ce^{3+}, atomic silver and small $Ag_n^{(n-1)+}$ clusters, Sb^{5+} species trapping an electron) carry unpaired electrons, to the present date no studies by electron paramagnetic resonance (EPR) have been carried out on this system. In this contribution we present, for the first time, results from continuous-wave and pulsed EPR spectroscopic measurements in order to characterize the mechanisms of photo-thermo-induced ionization that precede the crystallization process and the appearance of desired localized refractive index change. By varying their dopant compositions we have identified the various types of paramagnetic species formed during this process and characterized them according to their spin Hamiltonian parameters. Furthermore the observation (or absence) of nuclear magnetic hyperfine couplings in the EPR spectra can provide evidence for (or against) the involvement of the various different dopants in the ionization and nucleation process. Our results offer new evidence for the key role of the antimony oxide dopant in PTR glasses.

2. Experimental

2.1. Sample preparation and characterization

Table I summarizes the samples investigated in the present study. Samples were prepared according to previously published protocols [4]. The powdered starting materials Na_2CO_3, Al_2O_3, SiO_2, NaF, ZnO, KBr, Ce_2O_3, Ag_2O, Sb_2O_3, and SnO_2 were melted at 1450 °C for 120 min in a platinum crucible (typical batch size 500 g), and subsequently cooled to room temperature at a rate of 0.1 K/s. Light exposure was done using either a Xenon lamp or a He-Cd laser (wavelength 325 nm) under the conditions specified in Table 1. Table 2 summarizes the glass composition of samples B5 and B6, according to chemical analysis. Samples B1 and B2 have the same base compositions, but were prepared without the dopants Ce_2O_3, Ag_2O, Sb_2O_3, and SnO_2 while in the samples B3 and B4 Ag_2O was the sole dopant species present. X-ray powder diffraction confirmed that all the untreated samples were amorphous, as expected. Following this preparation step, some samples were annealed at 450 °C for 2 h, to induce nucleation of silver clusters and NaF.

Table 1
Compositions and treatment of the samples under study.

Sample	Dopant composition	Light exposure
B1	None	None
B2	None	20 min, Xe lamp [16]
B3	Ag_2O	None
B4	Ag_2O	20 min, Xe lamp [16]
B5	Ce_2O_3, Ag_2O, Sb_2O_3, SnO_2	None
B6	Ce_2O_3, Ag_2O, Sb_2O_3, SnO_2	He-Cd laser (325 nm), 10 J/cm^2 [17]

2.2. EPR spectroscopy

Continuous wave and pulsed EPR experiments were carried out in an E-580 BRUKER ELEXIS X-band EPR spectrometer operating at a microwave frequency around 9.5 GHz. The temperature was controlled by continuous flow liquid helium cryostats ESR-900 (cw) and CF-935 (pulsed) and PID controller from Oxford Instruments ITC503. CW measurements were performed at 30 K and pulsed experiments at 10 K. All samples were broken into small pieces to fit the bottom of a 3 mm inner diameter quartz tube used as a sample holder. The echo-detected field-sweep absorption spectra, EDFS, were recorded using a two-pulse echo sequence (π/2)-τ-(π)-τ-echo with a typical π/2 pulse width of 8 ns and repetition time of 2 ms. The pulse spacing, τ, was set long enough to suppress modulation effects and the integrated echo intensities were measured as a function of the magnetic field strength over the range of 0.1–12.1 kG. Spectral simulations were done by the function "*pepper*" of the software package EasySpin® implemented in MATLAB (MathWorks, Inc) [18]. The simulations consider the static spin Hamiltonian for electron-nucleus spin pairs in the solid state, given by

$$\mathcal{H} = \beta_e \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \sum_j \boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I}_j, \quad (2)$$

where the summation extends over the nuclear species considered in the simulation. In this expression the symmetric tensor $\boldsymbol{g}$, with its principal values g_{xx}, g_{yy} and g_{zz}, describes the anisotropic interaction of the electron spins $\boldsymbol{S}$ with the external magnetic field $\boldsymbol{H}$, while the tensor $\boldsymbol{A}$ describes the anisotropic magnetic hyperfine interaction between the electron spins and the nuclear spins $\boldsymbol{I}$ present. In the case of glassy systems we find a distribution the principal values for g and A, therefore, strain parameters were used to represent the disorder found in glasses. These strain parameters characterize Gaussian distribution functions of the g- and the A- parameters, resulting in field-dependent (g-strain) and field-independent (A-strain) line-broadening effects in the spectra [18]. Euler angles describing the orientation of g- and A-tensors relative to the molecular frame are considered all zero (coincident tensors). Table 3 summarizes the lineshape components and their corresponding Hamiltonian parameters.

Table 2
Precise chemical composition of the PTR glasses B5 and B6, according to chemical analysis.

NPTR glass composition	Wt.%	Mol.%
SiO_2	68.5	71.127
Al_2O_3	4.8	2.924
Na_2O	12.9	12.987
ZnO	6.6	5.100
NaF	4.3	6.362
KBr	2.8	1.457
Ag_2O	0.02	0.0062
CeO_2	0.02	0.0072
Sb_2O_3	0.10	0.021
SnO_2	0.02	0.0082
		Mol. weight
		62.4