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Color bleaching and oxygen diffusion in a niobium phosphate glass

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ABSTRACT

The color of niobium phosphate glasses ranges from clear to deep blue depending on their thermal history. In this study, a glass with the nominal composition (mole %) $23K_2O\cdot40Nb_2O_5\cdot37P_2O_5$ was treated in oxidizing and reducing atmospheres at temperatures around T_g (730 °C) and the color at room temperature was analyzed using optical spectroscopy. Electron spin resonance (ESR) spectroscopy shows that the blue color is associated with the presence of Nb^{4+} ions, which oxidize to Nb^{5+} in the clear glasses. Bleaching kinetics were determined from a series of heat treatments below T_g in flowing oxygen, and analyzed with an diffusion model that indicated an activation energy of 150 ± 31 kJ/mol.

1. Introduction

Niobium phosphate glasses are of interest for optical applications [1,2] and have been developed as hosts for radioactive wastes [3]. The color of niobium phosphate glasses varies from colorless [4,5] and yellowish [4] to dark blue [5], depending on the glass composition and preparation conditions. Chu et al. [5] observed that glasses from the $SrO–Nb_2O_5–P_2O_5$ system were blue when the P_2O_5/SrO ratio was greater than one, and colorless when the ratio was less than one. Tawarayama et al. [6] found that initially clear alkali tungsten-niobium phosphate glasses turned dark blue when heated at temperatures close to T_g in reducing atmospheres, then were bleached to a colorless on subsequent heat treatments in air. This bleaching effect was attributed to W oxidation, from W^{5+} to W^{6+}, occasioned by the diffusion of hydrogen (dissolved into the glass during the reducing heat treatment) out of the glass.

A glass with the nominal molar composition $23K_2O\cdot40Nb_2O_5\cdot37P_2O_5$ was developed to immobilize radioactive waste [3]. This glass possesses high chemical durability and stability against crystallization [7]. When melted in a microwave furnace at temperatures around 1200 °C, the resulting glass is yellowish, but when the same glass composition is melted at 1400 °C in a typical resistive element furnace, a dark blue glass results. The reduction of Nb^{5+} ions is believed to be the source of the blue color [8], although Möncke and Ehrt [9] report that photo-induced Nb^{4+} ions (d^1 configuration) could not be identified by optical or by ESR spectroscopy, appearing to disproportion rapidly into Nb^{5+} (d^0) and Nb^{3+} (d^2). Rakhimov [10] analyzed ESR spectra in terms of the reaction:

$$Nb^{4+}-O-Nb^{4+}\leftrightarrow Nb^{3+}-O-Nb^{5+}. \qquad (1)$$

And noted a shift towards the formation of Nb^{4+} pairs at lower temperatures.

In the present study, the $23K_2O\cdot40Nb_2O_5\cdot37P_2O_5$ glass has been prepared and the bleaching kinetics are described using optical spectroscopy with a model based on the diffusion of oxygen and its effect on the Nb^{4+}–Nb^{5+} redox reaction.

2. Experimental procedure

2.1. Glass preparation

A glass with the nominal molar composition $23K_2O\cdot40Nb_2O_5\cdot37P_2O_5$, designated Nb40, was obtained by mixing the appropriate amounts of K_2CO_3 (ALDRICH, 99.5%), Nb_2O_5 (APACHE CHEMICAL INC. 99.9%), and $NH_4H_2PO_4$ (ALFA AESAR, ACS 98%) and heating the batch in an Al_2O_3 crucible at 850 °C for one hour to decompose the raw materials, and then holding the melt for one hour at 1400 °C. Nitrogen gas was bubbled into the melt through an alumina tube to improve the glass homogeneity. The melt was poured onto a steel plate, and the glass was annealed at 730 °C for 30 min before being cooled to room temperature at 2 °C/min. The resulting glass was dark blue in the center and colorless along the edges, as shown in Fig. 1. The annealing temperature was $T_g = 730$ °C, as determined by differential thermal analysis (DTA 7, Perkin Elmer) of glass powders heated at 10 °C/min in an alumina crucible under flowing N_2. Glass compositions were

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Fig. 1. Nb40 glass after annealing in air at 730 °C for 30 min and cooling to room temperature at 2 °C/min.

determined using energy dispersive spectrometry (Helios NanoLab 600 FIB/FESEM); the average of five different spots on a sample is reported.

2.2. Thermal treatments under controlled atmospheres

The annealed glass was cut into $15 \times 15 \times 1 \mathrm{mm}^3$ sections, polished to a mirror finish on both large faces, and then subjected to various thermal treatments. Some samples were held under flowing O_2 at 730 °C for 12 h to produce a homogeneously colorless piece of glass. These samples were then exposed to different reducing conditions, either in a silica tube furnace with either flowing forming gas (99%N_2–1%H_2) or flowing N_2, or in a graphite furnace with flowing Ar or flowing N_2.

A second set of Nb40 samples were prepared to study the color bleaching kinetics. These samples were initially treated in the silica tube furnace at 730 °C for 12 h under flowing forming gas, then held in the same tube furnace under flowing O_2, for various times and at temperatures between 650 and 730 °C. Optical spectra (THERMO SCIENTIFIC, MODEL GENESIS 10uv) were collected at room temperature from the center of each of these samples.

2.3. FTIR and ESR spectroscopies

Fourier transform infrared (FTIR) spectra were collected in transmission using a THERMO NICOLET, MODEL NEXUS 670 spectrometer, from Nb40 samples that had been exposed to both reducing and oxidizing environments. Electron spin resonance spectra were collected using a BRUKER EMX spectrometer operating in the X-band at 150 K, using liquid N_2. Operating parameters included modulation amplitude of 3 G, microwave power of 1.968 to 1.970 mW at 20 dB attenuation, and a ~100 kHz modulation frequency. The spectra were collected with powdered samples placed in an ESR-transparent quartz glass tube.

3. Results

Table 1 shows the nominal glass composition and that measured by EDS. For these analyses, the relative cation concentrations were determined and converted to the most stable respective oxides. Some Al_2O_3 was detected in the glass, transferred from the Al_2O_3 crucible and/or the Al_2O_3 bubbler tube used during melting.

Table 1
Nominal and analyzed compositions of the Nb40 glass.

Compound	Nominal (mol%)	Measured (mol%)
Al_2O_3	–	2.8 ± 0.3
K_2O	23.0	23.6 ± 0.5
P_2O_5	37.0	34.7 ± 0.3
Nb_2O_5	40.0	38.9 ± 1.0

Fig. 2 shows samples of Nb40 glass after 12 h at 730 °C under flowing O_2 (left) and after the same time and temperature, but under flowing forming gas (right). The dark blue color of the reduced sample was also created when initially colorless glasses were heated for 12 h at 730 °C in the graphite furnace with both nitrogen and argon atmospheres.

Fig. 3 shows the ESR spectra for these same four samples. The three blue glasses each possess ESR lineshapes which match those measured in previous studies of systems containing niobium [10]. Given such close agreement, ESR results obtained for the niobium phosphate glasses studied here presumably are due to Nb^{4+} ions occurring in binuclear pairs, as proposed by Rakhimov et al., [10]. Their proposed model is based on careful fitting of experimental ESR data and interpretation of those fits. Such fits also strongly suggest that only one type of Nb^{4+} binuclear pair occurs, due to the fact that experimental data can be predicted only for a single set of spin Hamiltonian parameters consistent with a pair of Nb^{4+} ions.

The model further predicts a shift in equilibrium from Nb^{3+}–O–Nb^{5+} binuclear pairs to Nb^{4+}–O–Nb^{4+} pairs as temperatures are lowered from room temperature. This shift is indicated by large increases in ESR signal intensities at temperatures below 300 K; moreover, these increases cannot be explained or predicted by simple Curie law behavior. The present work reveals similar increases, thus confirming the previous experiments and providing additional evidence for temperature-driven formation of Nb^{4+}–O–Nb^{4+} binuclear pairs.

Overall, the present ESR experiments reveal substantially enhanced signal intensities in blue Nb40 glasses in comparison with colorless ones. These spectra are interpreted as evidence for the presence of ESR-sensitive Nb^{4+} ions, occurring in binuclear pairs. Generation of an increased fraction of Nb^{4+}–O–Nb^{4+} pairs (versus Nb^{3+}–O–Nb^{5+} pairs) at lower temperatures is confirmed here in blue Nb40 samples. The near absence of ESR signals in the colorless glass suggests that Nb^{4+} ions are almost nonexistent even at temperatures down to ~150 K.

Fig. 4 shows the optical spectra collected from Nb40 samples that were initially blue (after heat treatments in forming gas), then bleached at 730 °C in flowing O_2 for different times. With increasing time in oxygen, the broad absorption band with maximum at around 800 nm decreases in intensity.

Fig. 5 shows the FTIR spectra collected from of an Nb40 sample initially reduced in forming gas (blue in color), then heat-treated at 710 °C in flowing oxygen for different times (until colorless). The broad absorption peak centered near 2900 cm^{-1} has been assigned to hydroxyl ions in a phosphate network [11]. There is no evidence in these spectra, or in those collected from other samples, that the change in glass color is correlated with any measurable change in the residual hydroxyls in the glass.

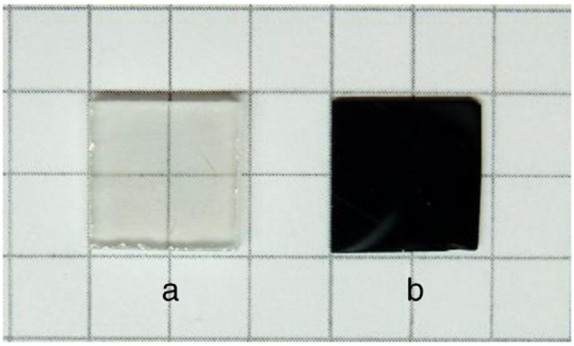

Fig. 2. Nb40 glass (a) after thermal treatment at 730 °C for 12 h under flowing O_2, and (b) after an additional treatment at 730 °C for 12 h under forming gas.