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Spectroscopic investigation of gamma radiation-induced coloration in silicate glass for nuclear applications

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ABSTRACT

Silicate glass irradiated by γ-rays was investigated in this study using spectroscopic analyses which included ultraviolet–visible (UV–Vis) absorption, electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR). The phenomenon of coloration on γ-ray-irradiated silicate glass was analyzed and the effect of annealing on the silicate coloration was also investigated. The results revealed that the coloration originates from the creation of hole-centers (*HC*) caused by radiation. The shade of the coloration highly correlates to the amount of these *HC*-related defects but can be reversed by thermal annealing. The variation in coloration is an effective predictive factor in understanding radiation damage on silicate glass. Therefore, this study is relevant in the development of radiation detectors using silicate material as well as in the permanent disposal of high-level nuclear waste in glass form.

1. Introduction

Silicate glass materials with disordered structure are widely used in various optical applications such as communication fibers due to their transparency in the mid-infrared range. Also, silicates can be utilized in both ultraviolet (UV) optics and high-power pulsed laser optics. On the other hand, silicate glass is a potential candidate as a matrix for high-level nuclear waste storage since it possesses high chemical, mechanical, thermal and radiation stability [1]. Due to its potential application in high-level nuclear waste disposition, it is of significant importance to investigate its radiation-induced effects. Some research studies have suggested that radiation damage may lead to the formation of defect centers in silicate glass materials used in high-level nuclear waste matrices, such as voids or disorders accompanied by volume variation, phase separation or radiation bombardment [2–5]. In order to comprehend the mechanisms of defect formation and recovery, radiation-induced defects in silicate glass materials need to be identified and studied. In 1968, Weeks and Bray [6] investigated gamma-irradiated phosphate glass materials using an electron paramagnetic resonance (EPR) spectrometer and clarified the formation mechanisms of oxygen vacancies. Griscom [7] has been conducting a longitudinal EPR analysis of irradiated glass materials. Another research study concerning radiation damage induced by X-ray irradiation has been conducted by Camara et al. [8,9]. Bogomolova et al. [10] have also studied gamma radiation-induced paramagnetic species in fluoride glass materials at room temperature and liquid-nitrogen temperature. Furthermore, a variety of glass materials of different compositions have been extensively analyzed in order to develop applications for radiation detectors [11,12]. In fact, the visible coloration resulting from the defects induced by radiation damage or the so called "color centers" is the most apparent characteristic change in part of glass materials in response to radiation exposure [13]. In recent decade, the effects of alpha decay accumulation in nuclear glasses have been investigated in detail by Peuget et al., indicating that the accumulation of alpha decay leads to the macroscopic property changes and helium build-up in nuclear glasses [14]. Boizot et al. have also found that the beta irradiation causes the structural damage of nuclear waste glasses which is induced by the defect formation and molecular oxygen dissolution [15–17]. Thus it can be expected that different mechanisms of radiation-induced damage would be involved in a mixed radiation field consisting of alpha, beta, and gamma rays in nuclear waste glasses. For this reason, the objective of this study is to conduct a spectroscopic investigation of defect-induced coloration on silicate glass materials via gamma irradiation. A predictive model involving the evolution of microscopic radiation-induced

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defects in silicate glass materials, which is expected to be useful in searching for possible glass materials for the long-term disposal of high-level nuclear waste, is also well established.

2. Experiment

2 mm-thick glass sheets in 2.0 cm × 1.0 cm size were used to conduct the γ-ray irradiation experiments. The glass samples were silicate comprised primarily of sodium, magnesium, calcium, and aluminum, as noted in Table 1. In order to clearly demonstrate the radiation-induced coloration of silicate glass, the glass balls of about 5-cm diameter with the same composition as the glass sheets were also employed to simultaneously perform the γ-ray irradiation. These specimens were inspected using inductively coupled plasma mass spectrometry (ICP-MS). A Perkin Elmer SCIEX ELAN 5000 spectrometer with a detection limit of ~0.01 ppb was used to identify the elements comprising the glass sheets. A Co-60 gamma source with a radioactivity of 29,000 Curie was utilized to irradiate the specimens at a dosage rate of 1.404 kGy/h at room temperature. The irradiated doses were 0.19, 0.4, 1.4, 4.5, and 20 kGy. Following γ-ray irradiation, the samples were annealed in a furnace at various annealing temperatures and for various durations. Subsequently, several spectroscopic analyses including ultraviolet–visible (UV–Vis) absorption, EPR, and nuclear magnetic resonance (NMR) were employed to analyze property variations in the γ-ray-irradiated silicate glass specimens and to better comprehend coloration phenomena. The UV–Vis absorption spectra were measured using a HITACHI U-4100 spectrophotometer at room temperature and that ranged between 300 and 800 nm in wavelength. The EPR analysis was implemented using a BRUKER ELEXSYS E-580 spectrometer at room temperature. The microwave frequency and microwave power were 9.8 GHz and 15 mW respectively, while the sweep width was 100 G during the experiment. A BRUKER AVANCE III 400 spectrometer was utilized to conduct an NMR analysis at room temperature. The superconductive magnetic field and nuclear magnetic resonance frequency were 9.4 T and 400 MHz respectively. The spectra were fitted by Gaussian curves whose fitting parameters are given in Refs. 20,21.

3. Results and discussion

Changes in coloration induced by γ-ray irradiation were demonstrated using silicate balls (see the photographs in Fig. 1). As can be seen in Fig. 1, the unirradiated, the 0.19 kGy-irradiated, and the 0.4 kGy-irradiated silicates are depicted from left to right in the upper row, while the 1.4 kGy-irradiated, the 4.5 kGy-irradiated, and the 20 kGy-irradiated silicates are shown from right to the left in the bottom row. It can be seen that the transparent silicate glass materials turn a yellowish-orange color following γ-ray irradiation. Moreover, the color became darker with increasing doses of radiation. Specifically, the irradiated samples with doses of 0.4, 1.4, and 4.5 kGy were selected for performing spectroscopic analysis and for making comparisons. Fig. 2(a) shows the UV–Vis spectra of the irradiated samples as a function of irradiated dose. As can be seen, there is a broad absorption peak located in the 360–540 nm range which largely corresponds to the wavelength of blue-violet light in the UV–Vis spectrum. A shoulder next to the peak reveals weak absorption in the other wavelength ranges. The wide range absorption band is caused by radiation-induced defects which can be roughly categorized into two types of hole centers, HC_1 and HC_2. The molecular structure of the former can be represented as $\equiv Si{-}O^{\cdot}\cdots Me^{+}$ which signifies an oxygen-dangling bond near a metal ion. The latter, also called *NBOHC* (nonbridging oxygen hole center), is actually identical to HC_1 but without any metal ions ($\equiv Si{-}O^{\cdot}$) [18,19]. As indicated by Zatsepin et al. [19], absorption bands located around 2.0 eV (~620 nm) and 2.75 eV (~450 nm), as shown in Fig. 2(a), can be assigned to *NBOHC* and HC_1 ($\equiv Si{-}O^{\cdot}\cdots Na^{+}$), respectively. Defects related to other minor metals also contribute to absorption, but the proportions are much lower. According to the color wheel, this result is reasonable since the color of the irradiated silicate balls shown in Fig. 1 is complementary to that of the light absorbed in the spectrum in Fig. 2(a). It is also worth noting that the amount of absorption increases as the radiation dosage increases. Fig. 2(b)–(d) show the spectra of the irradiated samples with the three doses annealed at various temperatures ranging from 100 to 200 °C for 15 min. As can be seen, absorption intensity is gradually reduced as annealing temperature increases in all three cases, implying that the colorized silicate glass can revert to transparent state following thermal treatment. In other words, the defects induced by γ-ray irradiation can be reversed via annealing. In order to evaluate the thermally-activated defect recovery process, the relationship between light absorption and annealing temperature can be fitted by the Arrhenius' equation given as Eq. (1):

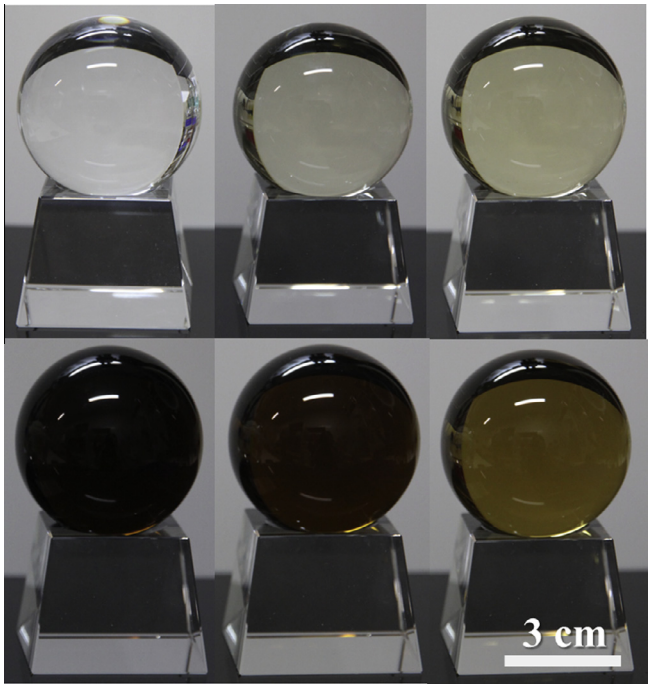

Fig. 1. Silicate balls irradiated by 0, 0.19, 0.4 (upper row, left to right), 1.4, 4.5, and 20 (lower row, right to left) kGy γ-ray.

Table 1
ICP-MS results of silicate glass adopted in this study.

Element	Mass (g/mole)	Concentration (ppb)
Li	7	1.8
Be	9	–
B	11	–
Na	23	11,000
Mg	24	3300
Al	27	1200
Si	29	110,000
P	31	4.6
S	34	–
K	39	1.2
Ca	43	2400
Sc	45	1.8
Ti	47	–
V	51	1.1
Cr	53	2.2