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Comparison of hardness variation of ion irradiated borosilicate glasses with different projected ranges

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ABSTRACT

Borosilicate glass has potential application for vitrification of high-level radioactive waste, which attracts extensive interest in studying its radiation durability. In this study, sodium borosilicate glass samples were irradiated with 4 MeV Kr^{17+} ion, 5 MeV Xe^{26+} ion and 0.3 MeV P^{+} ion, respectively. The hardness of irradiated borosilicate glass samples was measured with nanoindentation in continuous stiffness mode and quasi continuous stiffness mode, separately. Extrapolation method, mean value method, squared extrapolation method and selected point method are used to obtain hardness of irradiated glass and a comparison among these four methods is conducted. The extrapolation method is suggested to analyze the hardness of ion irradiated glass. With increasing irradiation dose, the values of hardness for samples irradiated with Kr, Xe and P ions dropped and then saturated at 0.02 dpa. Besides, both the maximum variations and decay constants for three kinds of ions with different energies are similar indicates the similarity behind the hardness variation in glasses after irradiation. Furthermore, the hardness variation of low energy P ion irradiated samples whose range is much smaller than those of high energy Kr and Xe ions, has the same trend as that of Kr and Xe ions. It suggested that electronic energy loss did not play a significant role in hardness decrease for irradiation of low energy ions.

1. Introduction

Borosilicate glass is usually used to deal with high-level radioactive waste (HLW) for its good performance, e.g., thermal conductivity, mechanical resistance and chemical durability [1,2]. To simulate the circumstance of HLW in process of geological disposal, studies on irradiation effects of borosilicate glass have been carried out extensively [3–15]. In Sun et al.'s work, phase separation induced by electron irradiation in a sodium borosilicate glass was investigated in-situ by analytical electron microscopy to simulate the beta radiation [3]. Mir et al. studied defect recovery and damage reduction in borosilicate glass irradiated with alpha particles and gold ions [4]. Meanwhile, to investigate the properties of borosilicate glasses, many characterization methods are conducted. Ollier et al. explored the para-magnetic defects concentration in glass irradiated with electron via electron paramagnetic resonance spectroscopy [5]. Sebastian Wegner et al. employed ex situ Magic Angle Spinning (MAS) Nuclear Magnetic Resonance spectroscopy (NMR) and dipolar MAS NMR to study microscopic aspects of phase separation in fast-quenched and annealed borosilicate glass samples [6]. Furthermore, characterization methods including Raman spectroscopy, Transmission Electron Microscope, Scanning Electron Microscope, etc., were used as well for identifying molecular structure, studying microstructure of materials, observing the surface morphology of samples, etc. [7–11]. In addition, a series of work on irradiation effects of borosilicate glasses were carried out by Wang et al. [12–15].

After irradiation, not only the micro-properties, for instance, the properties mentioned above change, but also macro-properties including hardness, modulus, etc. would vary actually. Hardness decrease in glasses after irradiation has been presented in many experiments [16,17]. The reason for this was suggested to be the glass network breakdown. Peng et al. suggested that nuclear energy loss played a dominant role for impact of 4 MeV Kr ions on borosilicate glass [18,19]. Meanwhile, Peuget et al. illustrated that electronic energy loss also worked for impact of swift heavy ion and recovery effect may happen in part of the glasses due to the irradiation with He ions [20,21]. The threshold of energy was achieved in their work. They proposed that swift heavy ions with high electronic energy loss ($\geq$ 4 keV/nm) result in

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significant modifications whereas light ions with low electronic energy loss (≤ 1 keV/nm) result in only mild damage formation. In Peng et al.'s work [19], energy loss of incident ion in the glass was below the threshold energy loss with which ion track would be formed. Besides, the electronic energy loss is 1.2 keV/nm. Thus, it is suggested that the lower limit of low electronic energy loss of ions resulting in mild damage formation could increase to 1.2 keV/nm.

Furthermore, the measurement of hardness of irradiated borosilicate glass is related to the projected ion range and thus can be affected by the data analysis method. To calculate the hardness variation induced by ions with different projected ranges, several methods were applied to analyze the original data obtained by nanoindentation. Currently, mean value method is widely accepted. Peng et al. applied extrapolation method to analyze the hardness and modulus of borosilicate glass samples [19].

In addition, two other analysis methods: squared extrapolation method and selected point method are employed and the corresponding results were exhibited below. The squared extrapolation were proposed by Kasada to evaluated the hardness of alloy irradiated with ions [22]. By comparing results of the two methods along with that of mean value method and extrapolation method, the difference of those four methods were studied and the extrapolation method was suggested in this paper.

2. Experimental setup

The compositions of borosilicate glass samples investigated in this work (NBS1) in weight percent are 58.2%, 16.8% and 25.0% for SiO_2, B_2O_3 and Na_2O, respectively. The samples were melted and stirred for 4 h at 1200 °C. After 24-h-annealing at 500 °C in order to remove residual stresses, the samples were cut into the size of 10 mm × 10 mm × 1 mm and then were optically polished on both the sides.

Samples were irradiated with three kinds of ions to different fluences at room temperature, separately. Irradiations with 4 MeV Kr^{17+} ion and 5 MeV Xe^{26+} ion were carried out at the 320 kV Platform for Multi-Discipline Research with Highly Charged Ions, Institute of Modern Physics in Lanzhou. Irradiation with 0.3 MeV P^+ ion was performed at key laboratory of beam technology and material modification of ministry of education in Beijing Normal University. To obtain specific fluence, beam fluxes were from 40 nA/cm^2 to 1.3 μA/cm^2 for all the ions. The irradiation parameters including specific irradiation doses for different ions are showed in Table 1. Projected ranges of various ions in glass were estimated by SRIM 2008 program [23]. The corresponding elastic interaction region is two times the selected regions, which was suggested by Peuget [24]. The irradiation dose in the unit of displacement per atom (dpa) is defined by Eq. (1), which is modified from the corresponding equation in [19]:

$$Dose = \frac{\Phi \cdot V \cdot S}{N} \tag{1}$$

where Φ is the fluence in ions/cm^2, S is unit area in cm^2 and V which is calculated by SRIM 2008 program is the number of vacancies produced by one ion in a layer whose thickness is two times of the maximum of fitting depth (or two times of the selected point's depth with selected point method) [23]. The N is the number of total atoms in the layer.

Nano-indentation measurement was carried out to measure the hardness change of borosilicate glass samples after irradiation.

The detailed information of continuous stiffness measurements (CSM) was introduced by Joslin and Oliver [25], in whose work nanohardness was defined as Eq. (2):

$$H = \frac{P}{A} \tag{2}$$

where H is the measured hardness, P is the load applied on the indenter, and A is the projected contact area between a sample and the indenter.

Relative variation of hardness, v_H, is introduced to evaluate the change of hardness. v_H was defined as Eq. (3):

Table 1
Experimental details of performed irradiations.

Ion	Energy (MeV)	Range (μm)	Fluence (Ions/cm^2)	Dose (dpa)	
				Other three methods[a]	QCSM method[b]
Kr^{17+}	4	2.4	3.0×10^{11}	2.05×10^{-4}	1.67×10^{-4}
			3.0×10^{12}	2.05×10^{-3}	1.67×10^{-3}
			6.0×10^{12}	4.10×10^{-3}	3.34×10^{-3}
			1.0×10^{13}	6.83×10^{-3}	5.57×10^{-3}
			3.0×10^{13}	2.05×10^{-2}	1.67×10^{-2}
			1.0×10^{14}	6.83×10^{-2}	5.57×10^{-2}
			5.0×10^{14}	3.41×10^{-1}	2.78×10^{-1}
Xe^{26+}	5	2.0	6.1×10^{11}	8.35×10^{-4}	–
			1.8×10^{12}	2.47×10^{-3}	–
			3.6×10^{12}	5.03×10^{-3}	–
			6.1×10^{12}	8.35×10^{-3}	–
			1.8×10^{13}	2.47×10^{-2}	–
			6.1×10^{13}	8.35×10^{-2}	–
			3.0×10^{14}	4.18×10^{-1}	–
			6.1×10^{14}	8.35×10^{-1}	–
P^+	0.3	0.4	4.0×10^{11}	2.26×10^{-4}	–
			1.4×10^{12}	7.95×10^{-4}	–
			4.0×10^{12}	2.26×10^{-3}	–
			8.0×10^{12}	4.52×10^{-3}	–
			1.4×10^{13}	7.95×10^{-3}	–
			4.0×10^{13}	2.26×10^{-2}	–
			1.4×10^{14}	7.95×10^{-2}	–
			7.0×10^{14}	3.94×10^{-1}	–

[a] Mean value method, extrapolation method and squared extrapolation method.
[b] Selected point method at 550 ± 12 nm.

$$v_H = -\frac{H - H_{un}}{H_{un}} \times 100\% \tag{3}$$

where H is the measured hardness after irradiation and H_{un} is the hardness of pristine sample.

A MTS G200 Nano-Indenter device using CSM mode was used to measure the mechanical property of the samples irradiated with Kr, Xe and P ions at Suzhou Institute of Nano-tech and Nano-bionics. The maximum penetration depth was fixed at 2000 nm for the samples irradiated by Kr and Xe ions. The tests were conducted at night to reduce the measuring uncertainty from environment factors such as temperature fluctuation and vibration. The maximum load is 500 mN. Considering the surface roughness of samples and the effect of indenter tip radius, at least the first 50 nm original data were ignored. Analyzing methods with this mode included mean value method, extrapolation method and squared extrapolation method.

At the same time, Quasi-Continuous Stiffness Measurement (QCSM) was used to measure the hardness of the samples irradiated with Kr ion at Helmholtz-Zentrum Dresden-Rossendorf. The applied equipment is a Universal Nanomechanical Tester UNAT (ASMEC/Zwick) equipped with a Berkovich indenter. An average curve and the corresponding uncertainty were obtained from five indents performed on one sample. The definition of hardness is the same as Eq. (2) with this mode and that of hardness variation is the same as Eq. (3). Selected point method was used to analyze the hardness data with this test mode.

3. Results and discussion

Fig. 1 displays the typical measured hardness curve of NBS1 as a function of penetration depth by using CSM mode. The solid line presents hardness curve of sample without irradiation. The dashed, dashed-dotted and short dotted lines are data of samples irradiated with Kr, Xe and P ions at the fluences of 5×10^{14}, 6.1×10^{14} and 7×10^{14} ions/cm^2, respectively.

The method of mean value means choosing the average value of the selected penetration region as the unified value of the region. From Fig. 1, it's easy to find that different results will be obtained if different