



Relaxation of anisotropic alkali metaphosphate glass

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ABSTRACT

The anisotropic glass of 12.5Li₂O-12.5Na₂O-12.5K₂O-12.5Cs₂O-50P₂O₅ (mol%) shows significant shrinkage during relaxation to an isotropic structure. To clarify the relaxation mechanism, the change in storage modulus (E') and structure for isotropic and anisotropic glasses was investigated in temperatures ranging from room temperature to above the glass transition temperature (T_g). The E' for the isotropic glass gradually decreased with increasing temperature. On the other hand, the anisotropic glass showed a marked decrease in the E' even below T_g , then increased, reaching the minimum around T_g , and finally reached the value of the isotropic glass. Raman spectra for the anisotropic glass with increasing temperature showed that the bond strength between alkali cations and non-bridging oxygen, of some local structures in oriented -P-O-P- chains, rapidly weakened. These changes were accompanied by a decrease in O⁻-P-O⁻ bond angle below T_g . Additionally, the number of these local structures increased with increasing temperature. This structural change led to deformation in the oriented chain and loss of directionality. The change became significant above T_g , and the highly oriented structure could not be maintained. This unique relaxation in the direction of the oriented chain produced the noticeable shrinkage of the anisotropic glass.

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1. Introduction

Glass is generally isotropic, but it is known to develop anisotropy when stressed above the glass transition temperature (T_g) and then cooled to room temperature (RT) [1–4]. Properties and relaxation behavior for anisotropic glasses are reported [1,3,4]. It has recently been shown that a mixed alkali metaphosphate glass of 12.5Li₂O-12.5Na₂O-12.5K₂O-12.5Cs₂O-50P₂O₅ (mol%, LNKCP), which is primarily composed of one-dimensional -P-O-P- chains, displays a large birefringence (i.e., a significant anisotropy) due to the highly oriented -P-O-P- chains [5]. The birefringence was much higher than for anisotropic oxide glasses previously reported. The anisotropic LNKCP glass shows significant shrinkage, during relaxation from the anisotropic to isotropic structure, owing to entropy relaxation around T_g [5]. In this study, the change of dynamic mechanical properties and structures for both anisotropic and isotropic glasses was investigated in the range from RT to above T_g , to clarify the unique relaxation mechanism for the LNKCP anisotropic glass.

2. Experimental

The LNKCP metaphosphate glass was prepared by melting a mixture of LiPO₃, NaPO₃, KPO₃, Cs₂CO₃, and NH₄H₂PO₄ in a 95% Pt-5%Au crucible at 1000 °C for 1 h.

An isotropic LNKCP glass (IG) fiber was prepared by quickly drawing up a silica rod inserted into the glass melt. To prepare an anisotropic LNKCP glass (AG) fiber, the as-drawn IG fiber was elongated under an initial nominal tensile stress of 5 MPa at 230 °C for about 10 min and then cooled rapidly from 230 °C to RT.

Birefringence (Δn) of the fibers was determined from phase retardation measured with a polarization microscope using a quartz wedge and a de Sénarmont compensator.

The T_g of the fibers was measured by differential thermal analysis using a thermal analyzer (TG/DTA 6300, Seiko Instrument Inc.) at a heating rate of 10 °C min⁻¹. The T_g for the IG and AG was 209 and 207 °C, respectively.

The temperature dependence of storage moduli (E') and loss factors ($\tan\delta$) were evaluated by dynamic mechanical analysis (DMA) using a dynamic viscoelastic analyzer (DVA-200, IT Keisoku Seigyo, Japan) at 10 Hz with a longitudinal dynamic tensile strain of 0.01%. Glass fibers with a diameter of 300–340 μm and length of 1.3 mm were heated from RT to 250 °C at a rate of 5 °C min⁻¹.

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