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NETWORK-FORMING OXIDES FOR DESIGNING FUNCTIONAL MATERIALS

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Abstract

Flexible networks of typical network-forming oxides (SiO_2, GeO_2, B_2O_3, P_2O_5) are at the heart of many glassy materials with functional properties. Controlling the network structure and its relation to a system's mechanical-, physical-, and chemical-properties is a direction for manufacturing new materials through the principle of rational design. This method can be applied to design nuclear wastes storage-, and ion conducting-, bioactive-materials.

1. Introduction

Multicomponent oxides based on typical network-forming oxides (SiO_2, GeO_2, B_2O_3, P_2O_5) have been studied extensively by different techniques within last decades. Experiment and simulation results [1-8] showed that structure of silicate and borosilicate glasses has appropriate mechanical-, physical-, and chemical-properties to immobilize and isolate nuclear wastes from the biosphere. As alkali oxides (alkaline-earth oxides) are added into borosilicate glass, some properties of the glass system (melting temperature, electrical conductivity, thermal

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conductivity, thermal expansion coefficient ...) will be improved and the $[NBO]^-$ bonds (non-bridging oxygen) are also generated in network structure.

In nuclear waste glasses, the elements in nuclear waste tend to bind to the $[NBO]^-$ and form the bonds: R–NBO–T, R'–NBO–T, RE–NBO–T and An–NBO–T (T is Si, B; R and R' are the alkali and alkaline-earth metals, RE is the rare earth elements, An is the elements in actinide series). Capability of nuclear waste immobilization in the glass network will increase as $[NBO]^-$ concentration increases. Research results in [1, 9-11] show that $[NBO]^-$ bonds and $[BO_4]^-$, $[AlO_4]^-$ units will be generated in the glass network structure as Na_2O is added to B_2O_3-SiO_2, Al_2O_3-B_2O_3-SiO_2. At low Na_2O concentration, Na^+ cations tend to be close to the $[BO_4]^-$, $[AlO_4]^-$ units and they have role of charge-balance. Conversely, at higher Na_2O concentrations, the Na^+ cations tend to be closer to the $[NBO]^-$ and they act as the network-modifier. The molecular dynamics simulations in [12, 13] showed that in RE-bearing silicate glasses, the RE^{3+} cations are surrounded by $[NBO]^-$ whereas the alkali cations are surrounded by both $[NBO]^-$ and BO. For the SiO_2, Al_2O_3-RE_2O_3 system (RE = La, Ce, Nd ...), study results showed that SiO_2, Al_2O_3-RE_2O_3 glass has the structural characteristics and good properties for immobilization of trivalent actinides (Pu^{3+}, Am^{3+}, Cm^{3+}) [14-18]. Specifically, in the borosilicate glasses containing the actinides, the $An^{3,4+}$ cations can be connected to Si^{4+} via $[NBO]^-$ and the alkali cations provide complementary bond valence on the $An^{3,4+}$–NBO–Si^{4+} bonds [19–23]. EXAFS spectra of Nd showed that the Nd–O–Nd bond does not exist in the structure of sodium silicate containing 4.33 mol% Nd_2O_3. However, in the Nd-doped silica, the experiment results show the existence of Nd–O–Nd bonds with the

Nd–Nd distance of 3.80Å [24, 25]. Calculation results by using Greaves' model showed that in Nd_2O_3-containing alkali-silicate glasses, Nd^{3+} cations are located in regions rich in both Na^+ and $[NBO]^-$ (see Figure 18 in work [31]). The Nd^{3+} cations are connected to Si^{4+} in the network via $[NBO]^-$ and the Nd–O–Si bond angle is about 180°. Because Nd^{3+} cations have higher field strength than Na^+, the addition of Nd_2O_3 into silicate glass will improve the durability of glass. However, studies relate to the role of Nd^{3+} in silicate and borosilicate glass are still relatively limited [26–31]. Zirconium (Zr) is also an important component in nuclear waste glasses. For zirconium-bearing aluminosilicate glasses, EXAFS and XANES spectra showed that the coordination number of Zr is 6 or 7, the Zr-O bond distance is 2.15 ± 0.02Å [32, 33]. Meanwhile, for silicate glasses [31, 34, 35], it showed that the Zr-O bond distance is about 2.07-2.10Å. Addition of ZrO_2 into silicate glass will increase the chemical durability of the silicate glass. The present of Zr–O–Si bonds in the structure will improve the mechanical property of the glass. However, the increase of zirconium content will lead to increasing the surface area (the increase of zirconium content will prevent closure of the porosity), leading to increasing chemical corrosion. The mechanism of forming closed pores is an interesting issue that is being studied recently [36, 37]. In multicomponent oxide glasses containing two or more alkali metal cations (Na, K, Li, Cs ...), physical properties such as electrical conductivity, thermal conductivity, diffusion coefficient, molar volume, glass phase-transition temperature Tg, and thermal expansion coefficient can be nonlinearly with regard to ratio of alkali atoms. Nature of this phenomenon is due to the MAE effect (Mixed Alkali Effect). One of the causes of the MAE (that associated with ion-conduction) is that during ionic conduction the transfer energy between different kind of alkali ions (for example, between K^+ and Na^+) is much higher than that between the same kind (between Na^+ and Na^+ or between K^+ and K^+). Many researches about structure of glass systems (both theoretical and

empirical) have been performed to elucidate this phenomenon, such as molecular dynamics simulations [38], X-ray scattering and Raman spectroscopy [39], Nuclear magnetic resonance (NMR) [40]. Analyzing the local structure of alkali metal atoms in silicate glass containing Na and Cs [41, 42] and borate containing Na and Cs [40] by NMR method showed that the coordination number of Na^+ and Cs^+ cations decrease as the mixing ratio $Cs^+/(Na^+ + Cs^+)$ increases, and this may be one of the causes of the MAE effect. In glass systems containing two or more glass-forming elements, the MAE effect associated with transport properties has been confirmed.

Bioactive materials based on network-forming oxides have different families with different composition. Some classes of bioactive glass systems, like bioglass (45S5), are now being used as bone grafting material. 445S5 bioactive glass is composed of SiO_2 (46.1 mol%), CaO (26.9 mol%), Na_2O (24.4 mol%), and P_2O_5 (2.6 mol%) [43]. The higher affinity of modifier Na and Ca cations for coordinating phosphate rather than silicate, together with the formation of P-O-Si linkages. This increases polymerization of the silicate network with increasing P_2O_5 content. The number of bridging oxygen atoms (BO) are responsible for the network connectivity because these bridging oxygen atoms join the two neighboring polyhedra. BO can be utilized to assess the bioactivity, surface reactivity and solubility of a glass. A decreased BO shows that the glass has low Tg but higher solubility and higher reactivity and vice versa. Therefore, BO is a key tool for designing new materials with desired functional properties [44, 45].

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