AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Structure of Mg- and Mg/Ca aluminosilicate glasses: $^{27}$Al NMR and Raman spectroscopy investigations

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ABSTRACT

The structure and properties of glasses and melts in the MgO-Al$_2$O$_3$-SiO$_2$ (MAS) and CaO-MgO-Al$_2$O$_3$-SiO$_2$ (CMAS) systems play an important role in Earth and material sciences. Aluminum has a crucial influence in these systems, and its environment is still questioned. In this paper, we present new results using Raman spectroscopy and $^{27}$Al nuclear magnetic resonance on MAS and CMAS glasses. We propose an Al/Si tetrahedral distribution in the glass network in different Q$^n$ species for silicon and essentially in Q$^1$ and Q$^2$Al for aluminum. For the CMAS glasses, an increase of Q$^1$Al and Q$^2$Al is clearly visible as a function of the increase of Mg/Ca ratio in the (Ca,Mg)$_2$Al$_2$Si$_2$O$_8$ (garnet) and (Ca,Mg)Al$_2$Si$_2$O$_8$ (anorthite) glass compositions. In the MAS system, the proportion of Q$^1$Al and Q$^2$Al increases with decreasing SiO$_2$ and, similarly with calcium aluminosilicate glasses, the maximum of Q$^1$Al is located in the center of the ternary system.

Keywords: Aluminosilicate, glasses, NMR, Raman

INTRODUCTION

The traditional structural model of covalent oxide glasses and melts relies upon the distinction between network forming (Si, Al) and network modifying (alkali, alkaline-earth) cations. Among the former, aluminum and silicon are the two most abundant in natural magmatic liquids. Although Si is always in tetrahedral coordination in normal pressure conditions, Al can adopt various coordination numbers implying different structural roles. A systematic study of the aluminum environment is therefore necessary to the understanding of the structure of silicate glasses and melts that influences macroscopic properties (i.e., viscosity, density, diffusivity, entropy, etc.). Due to its peculiar structural role, Al exerts a profound influence on physical properties of naturally occurring silicate melts (see for example Day and Rindone 1962, an early reference). For instance, the measurements of Rossin et al. (1964) and Riebling (1964, 1966) have shown that the viscosity strongly depends upon the Al$_2$O$_3$ concentration in a more complex way than the SiO$_2$ content. The density is not as sensitive a function of the structure as the viscosity, but a nonlinear compositional dependence of the density has been discussed (Bottinga et al. 1982). Early studies have referred to the dual structural role of aluminum that can act either as a network former, substituting to silicon in tetrahedral positions, or as a network modifier, similar to alkaline or alkaline-earth cations, disrupting the tetrahedral network (Bottinga and Weill 1972).

For Al$^{3+}$, which has an intermediate charge and radius, it is generally assumed that association with “charge balancing” cations (e.g., Mg$^{2+}$, Ca$^{2+}$ = X) stabilizes aluminum in tetrahedral coordination (Taylor and Brown 1979). Therefore, addition of aluminum to a depolymerized silicate melt removes metal cations from network modifying roles until no more non-bridging O (NBO) atoms remain. If all Al atoms are incorporated in this way, NBO/T falls to zero when the molar ratio XO/Al$_2$O$_3$ = 1 (the “charge balanced join” corresponding to tectosilicate glasses) (see Seifert et al. 1982; Neuville and Mysen 1996). If further Al is added to the SiO$_2$-Al$_2$O$_3$ compositions, the “excess” Al enters in fivefold, Q$^1$Al, or sixfold, Q$^2$Al, coordination (Risbud et al. 1987; Poe et al. 1992; Toplis et al. 2000; Sen and Youngman 2004). Quantification of the abundance of these species in peraluminous CaO-Al$_2$O$_3$-SiO$_2$ (CAS) glasses shows a strong preference for the formation of Q$^2$Al (Sen and Youngman 2004; Neuville et al. 2004a, 2006).

This Q$^2$Al species was also observed in peralkaline and tectosilicate CAS glasses where its presence was not expected, based on stoichiometric considerations (Neuville et al. 2004a, 2006, 2007, 2008). The presence and amount of Q$^2$Al for the anorthite glass composition (CaAl$_2$Si$_2$O$_8$) correlates with the content of NBO determined by Stebbins and Xue (1997). This Q$^2$Al can explain the observed viscosity or glass transition temperature variation observed on aluminosilicate melts (Neuville et al., in preparation) without the use of oxygen tricluster (i.e., an oxygen