AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†
The structure of crystals, glasses, and melts along the CaO-Al2O3 join: Results from Raman, Al L- and K-edge X-ray absorption, and 27Al NMR spectroscopy

DANIEL R. NEUVILLE,1,* GRANT S. HENDERSON,2 LAURENT CORMIER,3 AND DOMINIQUE MASSIOT4

1CNRS-IPGP, Géochimie et Cosmochimie, Physique des Minéraux et des Magmas, 4 place Jussieu, 75005 Paris, France
2Department of Geology, University of Toronto, Toronto M5S 3B1, Canada
3IMPMC, CNRS UMR 7590, 140 rue de Lourmel, 75015 Paris, France
4CNRS-CERMHTI UPR3079 and Université d’Orléans, 1D av. Recherche Scientifique, 45071 Orléans, France

ABSTRACT

Calcium aluminate glasses are important materials where Al2O3 is the only network former. Aluminum in crystals or glasses between CaO and Al2O3 can have different environments as a function of the CaO/Al2O3 ratio. Using X-ray absorption at the Al K- and L-edges, Raman and 27Al NMR spectroscopies, we have determined the structural surroundings of Al in glasses, crystals, and melts in this binary system. Aluminum is in octahedral coordination at high-Al2O3 content (>80 mol%) and essentially in fourfold coordination with 4 bridging O atoms (BOs) at Al2O3 contents between 30 and 75 mol%. At around 25 mol% Al2O3, Al is in tetrahedral coordination with two BOs. The presence of higher-coordinated species at high-Al2O3 contents and their absence at low Al2O3 imply different viscous flow mechanisms for high- and low-concentration Al2O3 networks.

Keywords: Aluminate, crystal, glasses, melts, Raman, NMR, XANES

INTRODUCTION

The CaO-Al2O3 (CA) system is important in geochemical and material sciences (Geiger et al. 1988). Crystalline phases in this system occur as calcium-aluminum inclusions (CAIs) in chondritic meteorites (Hofmeister et al. 2004) and are also important in the glass-ceramic (Strukel et al. 2009) and cement industries (Oliveira et al. 2009). CA mineral phases are highly refractory materials that can also form glasses in the compositional region between CaAl2O4 (1:1 CaO:Al2O3) and Ca3Al2O6 (3:1 CaO:Al2O3). Calcium aluminate glasses are interesting from a fundamental glass structure point of view because aluminum is the only network former incorporated into the network. In addition, glasses within this compositional range are of technological interest because of their infrared (IR) transmission (ultralow optical losses) and mechanical properties (Highby et al. 1990; Wallenberger et al. 2004). Calcium aluminates are also the base of the CaO-Al2O3-SiO2 (CAS) ternary system, which is important for geological applications.

The crystal structures of the CA phases (Fig. 1) show great variation in their local aluminum and calcium environments. Aluminum tetrahedra may be Q1 or Q2 species (Q* indicates tetrahedral sites with n bridging O atoms) while Ca may exist in six-, seven- eight-, or ninefold coordination, often with one or more coordination geometries within a single-crystal phase. The structure of CaAl2O4 (CA) is tridymite-like with six-membered rings of AlO4 tetrahedra (Fig. 1a). Calcium atoms occupy cavities within the fully polymerized AlO4 network. However, there are three Ca sites, two with Ca in octahedral coordination and a third with Ca bonded to 9 O atoms. The Al2O3 tetrahedra are all fully interconnected (Q1) (Hörkner and Muller-Buschbaum 1976). CaAl2O4 (CA2) has a feldspar-like structure (Fig. 1b). The calcium atoms occupy large cavities within the interconnected AlO4 tetrahedra and are in sevenfold coordination. The Al2O3 tetrahedra are all Q species although one of the O atoms forms an “oxygen tricluster” by being bound to three AlO4 tetrahedra (Goodwin and Lindop 1970; Iuga et al. 2005). The structure of Ca3Al2O6 (C3A) consists of puckered six-membered rings of Al2O3 tetrahedra forming Q2 species (Fig. 1c). Each ring consists of two types of slightly distorted AlO4 tetrahedra that alternate around the ring. The Ca atoms occupy holes between the rings in different sites. Three sites contain Ca in sixfold coordination and one each in seven-, eight-, and ninefold coordination (Mondal and Jeffery 1975).

Two other crystalline phases that lie along the CaO-Al2O3 join are CaAl12O19 (CA6) that naturally occurs as the mineral hibonite and Ca2Al3O5 (C12A7) that occurs naturally as mayenite. The structure of CA6 has been refined by Utsunomiya et al. (1988) and that of C12A7 by Boysen et al. (2007). CA6 is a hexagonal layer structure isostructural with magnetoplumbite (cf. Moore et al. 1989) with the Al atoms distributed over three crystallographically independent octahedral sites, one tetrahedral site, and one trigonal bipyramidal site (Fig. 1d). Of the three