CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

Hexagonal Na$_{0.41}$[Na$_{0.125}$Mg$_{0.79}$Al$_{0.085}$]$_2$[Al$_{0.79}$Si$_{0.21}$]$_6$O$_{12}$ (NAL phase): Crystal structure refinement and elasticity†

MARTHA G. PAMATO$^{1,*}$, ALEXANDER KURNOSOV$^1$, TIZIANA BOFFA BALLARAN$^1$, DMYTRO M. TROTS$^1$, RAZVAN CARACAS$^2$ AND DANIEL J. FROST$^1$

$^1$Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
$^2$Laboratoire de Sciences de la Terre, Centre National de la Recherche Scientifique, Ecole Normale Supérieure de Lyon, 46 allée d’Italie, 69364 Lyon Cedex 07, France

ABSTRACT

At lower mantle conditions, subducted mid oceanic ridge basalts (MORB) will crystallize more than 20 vol% of an aluminum-rich phase, which is referred to generally as the new aluminum (NAL) phase. Given that a significant proportion of the lower mantle may be comprised of subducted crust, the NAL phase may contribute to the bulk elastic properties of the lower mantle. In this study we report for the first time the structure, Raman spectrum and elasticity of single crystals of Na$_{0.41}$[Na$_{0.125}$Mg$_{0.79}$Al$_{0.085}$]$_2$[Al$_{0.79}$Si$_{0.21}$]$_6$O$_{12}$ NAL phase, synthesized at 2260 °C and 20 GPa. The single-crystal structure refinement of NAL, which is consistent with the space group $P6_3/m$, reveals dynamic disorder of Na atoms along channels within the structure. The elastic tensor was experimentally determined at ambient conditions by Brillouin scattering spectroscopy. The elastic moduli obtained from the Voigt-Reuss-Hill approximation using the elastic constants determined in this study are $K_s = 206$ GPa and $\mu = 129$ GPa, whereas the isotropic compressional and shear sound velocities are $v_p = 9.9$ km/s and $v_s = 5.8$ km/s. The NAL phase is elastically anisotropic, displaying 13.9% compressional and shear wave anisotropy. Elastic constants as well as Raman active modes of NAL have also been calculated using density-functional theory and density-functional perturbation theory.

Keywords: NAL phase, Brillouin spectroscopy, single-crystal X-ray diffraction, lower mantle, elasticity

INTRODUCTION

As a consequence of plate tectonics, basaltic oceanic crust is subducted into the mantle. The subduction of oceanic lithosphere plays an important role in the dynamics of mantle convection and is believed to be responsible for the creation of lateral chemical heterogeneity in the mantle (Helffrich and Wood 2001). In this context, the high-pressure and -temperature metamorphic phases that recrystallize from basic rocks that form the oceanic crust are likely to be important components of the lower mantle and as such to influence its physical and chemical properties. Several high-pressure studies on MORB bulk compositions have shown that various Al-rich phases can form under lower mantle conditions (Irfune and Ringwood 1993; Kesson et al. 1994; Irfune et al. 1996; Akaogi et al. 1999; Miyajima et al. 1999, 2001). In particular, Irfune and Ringwood (1993) first reported the breakdown of majorite garnet to an assemblage of Mg-perovskite, Ca-perovskite, and a separate aluminous phase at pressure and temperature conditions of the lower mantle. This so-called new Al phase or NAL has a hexagonal crystal structure and can contain several different cations, such as Na, K, Ca, Mg, and Fe (Akaogi et al. 1999; Miura et al. 2000; Gasparik et al. 2000; Miyajima et al. 1999, 2001). NAL is therefore likely to be the main host for alkali elements in oceanic crust that has been subducted to ~600–1300 km (Miyajima et al. 2001). Due to the extremely long timescale required for the chemical equilibration of subducted crustal heterogeneities in the lower mantle (Holzapfel et al. 2005), it has also been proposed that the bulk of the mantle might be a mechanical mixture between a depleted mantle residue and subducted crustal components (Xu et al. 2008). In this case, NAL is likely to form a major part of the basal part of the crustal component.

Recently, Walter et al. (2011) described sublithospheric diamonds hosting composite multiphase inclusions with compositions encompassing phase assemblages expected to crystallize from basic crustal material under lower-mantle conditions. In particular, Walter et al. (2011) suggested that some of these inclusions were present as the NAL phase at lower mantle conditions, giving further support for the existence of this phase in the Earth’s lower mantle. The elastic properties of NAL, hence, may influence the bulk elastic properties of the lower mantle.

NAL phases crystallizing in MORB compositions display complex solid solutions and have the general formula XY$_2$Z$_6$O$_{12}$ where X represents a large monovalent or divalent cation (Ca$^{2+}$, K$^+$, Na$^+$), Y a middle-sized cation (Mg$^{2+}$, Fe$^{2+}$, or Fe$^{3+}$), and Z a small cation (Al$^{3+}$ and Si$^{4+}$).

To date several studies have been conducted on the structure, stability, and compression of NAL phases both in complex and simplified systems (Gasparik et al. 2000; Miura et al. 2000; Ko-