CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

In situ observation of the pyroxene-majorite transition in Na$_2$MgSi$_2$O$_{12}$ using synchrotron radiation and Raman spectroscopy of Na-majorite†

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ABSTRACT

In situ X-ray diffraction study of the pyroxene to majorite transition in Na$_2$MgSi$_2$O$_{12}$ was carried out in Kawai-type high-pressure apparatus coupled with synchrotron radiation. The phase boundary between Na-pyroxene and Na-majorite was determined over the temperature interval of 1073–1973 K and was described by a linear equation $P$ (GPa) = 12.39 + 0.0018×$T$ (K). The Clapeyron slope (dP/dT) determined in this study is similar to the one predicted by computer simulations (Vinograd et al. 2011) but smoother than the one obtained by quenched experiments (Dymshtis et al. 2010). The presence of sodium in the system lowers the pressure of pyroxene-to-majorite transformation. For the first time Na-majorite was characterized using Raman spectroscopy. Raman peaks of Na-majorite are broader than pyrope due to the substitution of Mg$^{2+}$ for Na$^+$ at the X site. Both Si-O symmetric stretching ($A_{1g}$-$v_1$) and O-Si-O symmetric bending ($A_{1g}$-$v_3$) modes of Na-majorite are significantly shifted to higher frequencies relative to corresponding bands of pyrope. In contrast the $A_{1g}$-$R$ (SiO$_4$) mode of Na-majorite (342 cm$^{-1}$) displays a lower frequency than that of pyrope (365 cm$^{-1}$). Our results enable further understanding of the mechanisms responsible for phase transformations in the Earth’s transition zone and lower mantle.

Keywords: Na-pyroxene, Na-majorite, phase transition, in situ experiment, diamond, mantle

INTRODUCTION

An important mechanism for phase transformation of silicate minerals in the Earth’s mantle is the change of Si coordination from four (tetrahedral) to six (octahedral) with an increase in pressure. The particular interest of this change is the formation of mixed-coordination phases with Si substitution cations in the octahedral position. Pyroxene with the composition of Na(Mg$_{2.9}$Si$_{1.1}$)SiO$_4$ (Na-px) was first obtained by Angel et al. (1988) and contained Si in tetrahedral and octahedral positions. A high-pressure analog of Na-px with a denser structure was originally proposed by Gasparik (1989) as Na-majorite (Na-maj), [Na$_2$MgSi$_4$(SiO$_4$)$_3$].

Garnets with significant sodium concentration (>1 wt% Na$_2$O) have been found as inclusions in diamonds and mantle xenoliths in many locations worldwide (e.g., Kiseeva et al. 2013; Shatskii et al. 2010; Sobolev et al. 1991, 2004; Sobolev and Lavrent’ev, 1971; Stachel 2001). Rarely found in peridotite paragenesis, Na-rich garnets are quite common for eclogitic assemblage (Fig. 1). Figure 1 shows a clear correlation between Na and Si contents in eclogitic garnets, which is the evidence of Na-major incorporation into the garnet structure. Sobolev and Lavrent’ev (1971) first supposed that pressure controls Na admixture in the dodecahedral positions of garnet, and that Na in dodecahedral sites is connected to a silicon excess in octahedral site. Later, this pressure dependence was confirmed experimentally in model and natural eclogitic systems (Bobrov et al. 2009; Dymshits et al. 2013; Hirose and Fei 2002; Litasov and Ohtani 2005; Okamoto and Maruyama 2004). Therefore, revealed pressure dependence of Na-major content in garnet may be taken into account in the calculation of geobarometers for sodium-bearing garnet assemblages.

Increasing interest in Na-maj and Na-px is related to a growing number of reports of sodium-bearing mineral inclusions from a “super-deep” diamonds (e.g., Harte and Hudson 2013; Plá Cid et al. 2014). An unusual mineral inclusion with garnet structure and composition [16 mol% Na-majorite (Maj) Mg$_{2.9}$Si$_{1.1}$O$_{12}$] was found in diamond from Lianoning province, China (Gasparik and Hutchison 2000; Wang and Sueno 1996). First attempts to estimate the pressure of this inclusion on the basis of pyroxene–majorite transition was made by Gasparik and Hutchison (2000). According to their experiment, pyroxene with such composition transforms into garnet at a minimum pressure of 16.5 GPa and temperature of 1923 K that corresponds to mantle transition zone (MTZ). Recently, Plá Cid et al. (2014) found unusual mineral inclusion containing 40 mol% Na-majorite in the diamond from Juina province, Brazil. The formation pressure of such alkali-rich inclusion can be estimated based on

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