

Synthesis of Na-bearing majorite in the system $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Na}_2\text{MgSi}_5\text{O}_{12}$ at 11-20 GPa: solid solutions and structural features

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Currently various ultrahigh-pressure minerals are described as inclusions in diamonds [e.g. *Stachel*, 2001]. The proof of their truly deep origin often appears problematic because of decompressional structural transformations. Experimental researches available for today, and also complex analysis of the Earth's mantle P–T conditions allow to establish the whole series of the phase transitions and chemical reactions in the conditions of the asthenosphere (> 200 km) and a transition zone (410–660 km). Ultrahigh-pressure minerals, such as MgSiO with ilmenite and perovskite structures, CaSiO_3 with perovskite structure, magnesio-wustite (ferropericlasite), and majoritic garnet. One characteristic feature of this mineral is silicon excess (over 3 pfu) and an isomorphous sodium admixture that allows to carry them to Na-bearing majoritic garnets.

The present experimental researches were aimed on reception of the every possible data about garnet phase $\text{Na}_2\text{MgSi}_5\text{O}_{12}$ (NaMaj): an establishment of pyroxene/garnet phase transition boundaries in P–T coordinates, definition of structural features in the pure state and in solid solutions with a pyrope (Prp), and also solubility studying in modeling systems Prp–NaMaj. Experiments were performed in the Tohoku University (Sendai, Japan) at $P = 11\text{--}20$ GPa and $T = 1500\text{--}2100^\circ\text{C}$ on high-pressure Kawai-type apparatus, where cell assemblage with the sample was compressed by eight cubic anvils truncated with triangular faces. Single-crystal shooting of samples was spent with a Bruker-Enraf MACH3 diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation. The small crystals were in addition studied with use an Oxford Diffraction Xcalibur 3 diffractometer fitted with a Sapphire 2 CCD detector.

Crystals of a Na-pyroxene and Na-majorite and the fields of their stability were received during experiments at 13-19 GPa [*Dymshits et al.*, 2010]. The phase boundary is described by the equation P (GPa) = $0.0050(2) \cdot T + 7.5(4)$. Detailed studying of Na-majorite by single-crystal X-ray diffraction has allowed to establish that Na-majorite is tetragonal, space group $I4_1/acd$, with lattice parameters $a = 11.3966(6)$, $c = 11.3369(5)$ Å, $V = 1472.5(1)$ Å³ [*Bindi et al.*, 2011].

Structures of the garnets with compositions between Na-majorite and pyrope (NaMaj₂₀, NaMaj₄₀, NaMaj₅₀, NaMaj₆₀ и NaMaj₈₀) were also investigated using a Bruker-Enraf MACH3 single-crystal diffractometer. The results have shown that the increase of NaMaj in starting material leads to gradual reduction of lattice parameter and then to change from cubic to tetragonal at maintenance of NaMaj more than 80 %. It is interesting to notice that similar transformation was observed for pyrope-majorite that is visually presented in Fig. 1 [*Parise et al.*, 1996].

Experimental study at 11-20 GPa of the start composition 50 mol.% NaMaj has been spent for demonstrating a tendency of sodium increase in garnet with pressure. Run conditions got out counting upon liquidus crystallization of garnets close to solid that allows receiving the greatest Na concentration. Pyroxene of enstatite-jadeite composition was also found among the run products together with garnet and stishovite at pressures of 11-15 GPa. At pressures over 16 GPa the pyroxene has not been established in run products, and the quantity of stishovite also was the lowest (no more than 5-7%). Garnets with the maximal Na_2O content (>5 wt.%) reached at the assumed solidus of the system and forms subidiomorphic crystals in a small amount of

quenched melt (<5%) (Fig. 2). Small phenocrysts (5-10 μm) of sodium rich solid solution with $Na(Mg_xSi_xAl_{1-2x})SiO_4$ ($0 < x < 0.5$) and MgO content no more 3.8 wt.% together with Grt in are formed with decrease of temperature in run products. This phase, apparently, corresponds $NaAlSiO_4$ (with calcioferrite structure) with a various impurity of $MgAl_2O_4$ component.

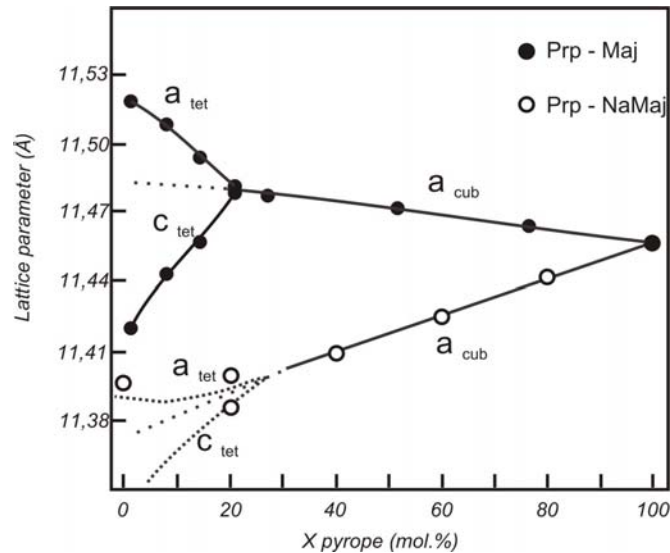


Fig. 1. Lattice parameters in dependence of garnets composition.

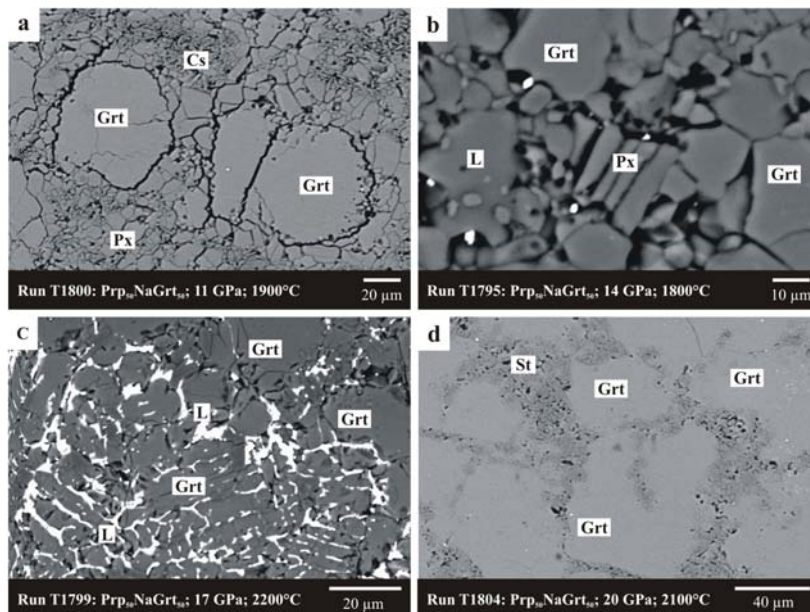


Fig. 2. BSE images of the samples obtained in experiments on the $Prp_{50}-Na\text{-majorite}_{50}$.

As a result of the experiments Na-bearing majorite garnets were synthesized in a wide range of temperatures and pressures, and natural increase of sodium, silicon and, as consequence, concentration of sodium majorite in garnets with pressure was observed (Fig. 3)

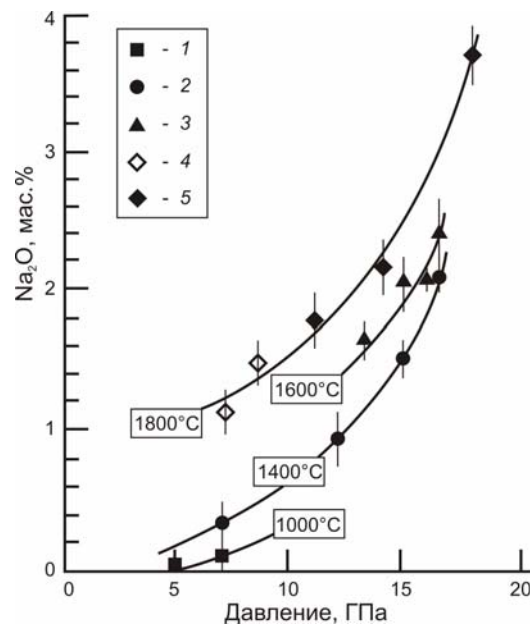


Fig. 3. Variation of Na_2O content in garnets, synthesized at different temperatures and pressures in eclogite system [Okamoto, Maruyama, 1998] (1), MORB [Ono, Yasuda, 1996] (2, 3), modeling system pyrope– $Na_2MgSi_5O_{12}$ (our data) at 7.0 and 8.5 ГПа [Bobrov et al., 2008b] (4) and 11–20 ГПа (5). An accuracy of pressure measurement is indicated by horizontal bars.

Presence of a pyroxene (one more Na-bearing phase) at a number of experiments complicates noted tendency of the garnet liquidus crystallization and leads to change of distribution coefficient of sodium between the garnet and liquid. Nevertheless, from results of experiences follows, that solubility of Na-component in garnet in the studied system at least up to 40 mol%, that is in a good agreement with forsterite-jadeite system (Table 1; Fig. 4) [Gasparik, Litvin, 1997].

Essential solubility of Na-majorite in the pyrope, and also finds of natural garnets with significant concentration of Na (> 1 мас. % Na_2O) allows to consider that Na-bearing majoritic garnet can be an important potential sodium concentrator in the lower parts of the upper mantle and transition zone. The successful synthesis of the $Na_2MgSi_5O_{12}$ end-member and its structural characterization is of key importance, because the study of its thermodynamic constants combined with the data of computer modeling provide new constraints on thermobarometry of majorite garnet assemblages.

Table 1. Composition of garnets in the system $Mg_3Al_2Si_3O_{12}-Na_2MgSi_5O_{12}$

Run	T1800	T1795	ES-243	T1796	T1804
P, ГПа	11	14	15	18	20
SiO ₂	49.33	49.81	54.86	54.72	56.66
Al ₂ O ₃	19.31	20.93	15.67	17.03	14.57
MgO	28.57	27.93	27.07	24.83	23.52
Na ₂ O	1.8	2.19	3.72	4.60	5.71
Total	99.01	100.86	101.33	100.00	100.46
Formula units per 12 O					
Si	3.343	3.315	3.630	3.628	3.785
Al	1.542	1.641	1.222	1.330	1.147
Mg	2.884	2.768	2.668	2.452	2.340
Na	0.236	0.282	0.477	0.591	0.739
Total	8.005	8.006	7.997	8.002	8.011

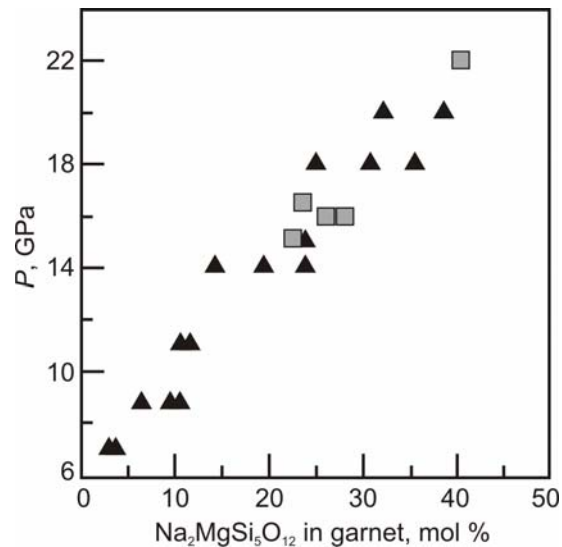


Fig. 4. Solubility of $Na_2MgSi_5O_{12}$ in garnet with pressure in the system Prp_{50} – Na -majorite₅₀ (triangles) in comparison to the data [Gasparik, Litvin, 1997] (squares).

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