INTRODUCTION

The system CaO–MgO–Al2O3–SiO2 (CMAS) can be conveniently utilized as a model for studying deep-sitting rocks. Extensive experimental data collected on this system within a broad pressure range provide insight into much of the petrology of processes occurring at significant depths. However, an intrinsic disadvantage of this approach is that the studied systems contained no alkalis, first and foremost, Na. Although Na-bearing systems have been experimentally studied in certain model systems (Gasparik, 1989, 1992, 1996; Ono and Yasuda, 1996; Gasparik and Litvin, 1997; Bobrov et al., 1989a, 1989b), the physicochemical behavior of sodic components of minerals in magmatic processes at mantle temperatures and pressures is still largely uncertain. At the same time, Na contents in some mantle rocks are high enough (Ringwood, 1991), which pertains first of all to eclogites, and hence, experimental study of multicomponent systems of composition close to these rocks facilitates more accurate reproduction of deep-sitting mineral assemblages and sheds light onto compositional traits and structure of deep Earth’s levels. In this context, it is undoubtedly important that garnet bearing elevated Na and Si concentrations was found in practically all kimberlite provinces worldwide (Moore and Gurney, 1985; Sobolev et al., 1987; Wang et al., 2000; Stachel, 2001; Davies et al., 2004; Harte and Cayzer, 2007; Shatsky et al., 2010). According to experimental data (Akaogi and Akimoto, 1977; Irifune, 1987), diamond with inclusions of such majorite garnet crystallized under pressures of 7.5–16 GPa. Lately we examined simple Na-bearing systems within broad temperature and pressure ranges (Bobrov et al., 2008a, 2008b, 2009, 2012; Dymshits et al., 2013) in relation to the problem of the genesis of Na-bearing majorite garnet. Regrettfully, the data obtained in the course of these studies are still not fully applicable to studying naturally occurring mineral assemblages. High enough Ca concentrations in natural garnet found as inclusions in diamond, first of all in eclogite associations, can likely provide valuable information on their genesis and the accommodation Na in the garnet. A first-priority task in this study is the analysis of individual components of the garnets, because mixing in these series of solid solutions is complicated, and their study requires specialized skills. Studies of garnet end members, such as pyrope and grossular, and their binary solid solutions has provided extensive data on their equilibrium relations, including their thermodynamic and crystal-chemical relations (see, for example, Irifune and Ohtani, 1986; Geiger, 1999; Butvina et al., 2001).

Phase Relations in the System \((\text{Mg, Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}\text{Na}_2\text{MgSi}_5\text{O}_{12}\) at 7.0 and 8.5 GPa and 1400–1900°C

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Abstract—The \(\text{CaO–MgO–Al}_2\text{O}_3–\text{SiO}_2–\text{Na}_2\text{O}\) multicomponent system was experimentally studied at 7.0 and 8.5 GPa using an anvil-with-hole toroidal high-pressure apparatus to examine two binary joins: pyrope–grossular and grossular–Na-majorite. These and literature data were employed to simulate the liquidus surface of the pyrope–grossular–Na-majorite system. The liquidus surface of garnet of predominantly pyrope composition is dominant in the diagram, and the garnet contains much of the \(\text{Na}_2\text{MgSi}_5\text{O}_{12}\) end member. Melting was observed in this region at temperatures above 1900°C, and the solidus of the system occurs at temperatures below 1550°C. The pyrope–grossular system shows a miscibility gap at 50–65 mol % of the pyrope component and two series of garnet solid solutions. The dominant phase at grossular and Na-majorite mixing is pyroxene, and garnet crystallizes within a fairly narrow field in the grossular-rich region. All garnets synthesized in the systems have elevated Si and Na concentrations and belong to the majorite series, for which a uniform mechanism of isomorphism \((\text{Mg, Ca}) + \text{Al} = \text{Si} + \text{Na}\) was proved.

Keywords: pyrope, sodic majorite, grossular, experiment, phase relations, mantle

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All thermodynamic parameters have been reliably determined for practically all solid solutions with complete (or near-ideal) mixing of their components. Inasmuch as the nonideality of mixing strongly depends on differences in the isomorphic cations, the most interesting and nonideal solutions are those of pyrope Mg3Al2Si3O12 and grossular Ca3Al2Si3O12. Addition of the empirical end member Na3MgSi5O12, which makes it possible to characterize the behavior of minor components, to this system provides an insight into isomorphism on the sites M1 of the garnet structure.

Garnet has a cubic structure, and its space group (Ia3d) does not allow for strong long-range cation ordering because of the limited number of types of independent crystallographic sites (dodecahedral, octahedral, and tetrahedral). Thereby any ordering in the garnet structure should decrease its symmetry. It is interesting to estimate mixing of multicomponent solutions involving cations of different enough ionic radii on the site M1, to which pyrope—grossular mixing corresponds.

When studying the multicomponent system pyrope—grossular—Na-majorite, we have examined binary boundary joins at 7 GPa, with much attention paid to studying pyrope—grossular solid solutions and calculating the topography of the liquidus surface in the triple system. We have also synthesized garnet containing much Na for certain compositions at 8.5 GPa.

### EXPERIMENTAL METHOD

Our experiments were conducted at pressures of 7.0 and 8.5 GPa and temperatures of 1400–1900°C at the Institute of Experimental Mineralogy, Russian Academy of Sciences, in Chernogolovka, Moscow oblast, in NL-13T anvil with hole toroidal high-pressure apparatus, which is a modification of the Bridgman-type anvil assembly (Litvin, 1991). The outer diameter of the solid-state cell (made of lithographic limestone, whose dominant component is CaCO3) was 30 mm. The cell housed a graphite heater 6 mm in diameter and 7.2 mm in height. The heater had a hole 2 × 2 mm in its central part, into which experimental material was placed; after the experiment, the sample volume was reduced to approximately 1 mm³. To ensure higher chemical inertness of the cell and optimize temperature and pressure stability within the synthesis cell, we made use of a sleeve manufactured of pressed mixture of powdered periclase and boron nitride (MgO : BN = 3 : 1). Preparatory to the experiments, we had carried out a set of calibrating experiments in order to optimize the accuracy of temperature (±20°C) and pressure (±0.1 GPa) control within the reaction volume (Bobrov et al., 2008b).

The starting materials were stoichiometric gels of the silicates, which had been prepared by the method (Hamilton and Henderson, 1968). The gels had been mixed in desired proportions, homogenized in mortars in the presence of ethanol, carefully dried, placed into the cell housing the heater, and heated in the high-pressure apparatus to desired temperature under a pressure of 7.0 or 8.5 GPa. After the experimental runs, the samples were quenched by shutting off the power and gradually depressurized. Each of the experimental samples was first examined under a binocular and was then divided into a number of portions, one of which was placed in an epoxy pellet and polished. The samples were then closely examined at the Laboratory of Local Methods of Matter Study at the Geological Faculty of the Moscow State University, using a JEOL JSM-6480LV scanning electron microscope equipped with an analytical setup with a composite scheme of microprobe analysis, incorporating an INCA-Energy 350 (ATW window) energy-dispersive and an INCA-wave 500 four-crystal (LiF200, TAP, PET, and LSM-80N crystals) wave-dispersive spectrometer. The raw data were processed with the SEM Control User Interface, version 7.11 professional software. All synthetic phases were texturally—structurally and chemically homogeneous, and this was confirmed by the consistency of analyses in the central and marginal portions of the grains. This, in turn, led us to conclude that equilibrium was reached in the experimental runs. The presence of melt among the experimental products was inferred from the occurrence of quench aggregates of pyroxene, coesite, and (to a lesser degree) garnet. Its composition was analyzed by scanning over an area of 10 × 10 µm.

### EXPERIMENTAL RESULTS

**Pyrope—Grossular Boundary Join**

The conditions and results of our experiments in the pyrope—grossular system at 7.0 GPa are summarized in Table 1. The chemistries of the phases synthesized in the experiments varied with temperature and with the composition of the starting materials (Table 2). The pyroxene was identified only qualitatively because of the small sizes of its grains in the synthesized aggregates and, hence, difficulties of their analysis. Our experimental data obtained on the system at temperatures of 1900–1500°C confirm the occurrence of two solid solution series of dominantly pyrope and grossular composition. A miscibility gap was detected within the range of 50–65 mol % of the pyrope component.

**Pyrope** melts incongruently in the system at 1960°C (Irifune and Ohtani, 1986) and has a fairly broad stability field as a liquidus phase. As the temperature was decreased, pyroxene started crystallizing together with garnet. The presence of spinel among the products of run 1682 may be explained by a decrease in the Mg solubility in the garnet solid solution and transition to its own phase. No spinel has been identified in the products of any other of our experiments, which calls for further study of the system near the solidus. Up to a temperature of 1650°C, garnet of pyrope composition occurs in equilibrium with clinopyroxene (Fig. 1).