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High-pressure phase relations and calorimetry of perovskite-related materials with oxygen defects in the CaSiO3-CaAlO2.5 system

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Recently, the possibility of oxygen defects in $MgSiO_3$ perovskite due to Al substitution has been pointed out. Therefore, thermochemical information on oxygen defects in perovskite structure is needed. In the $CaSiO_3$-$CaAlO_{2.5}$ system, $CaSiO_3$ and $CaAlO_{2.5}$ endmembers have cubic perovskite and brownmillerite structures, respectively, which can be regarded as a perovskite structure with oxygen defects. Furthermore, in the intermediate composition of $Ca_2AlSiO_{5.5}$, it was reported by Fitz Gerald and Ringwood (1991) that rhombohedral perovskite structure with oxygen defects is stable at 16 GPa and 1700 C. In this study, high-pressure and high-temperature experiments were performed to investigate the high-pressure phase relations in the $Ca_2AlSiO_{5.5}$ composition. An unknown phase was found at pressure lower than 13 GPa. Drop solution calorimetry of the new phase, the rhombohedral perovskite-type $Ca_2AlSiO_{5.5}$ and the brownmillerite-type $CaAlO_{2.5}$ were made to determine their formation enthalpies. Obtained formation enthalpies are used to discuss the energetics of the phases.

A Kawai-type high-pressure apparatus at Gakushuin University was used in the high-pressure and high-temperature experiments. High-pressure phase relation experiments in the $Ca_2AlSiO_{5.5}$ system were performed at 7-23 GPa and 1200-1600 C. A starting material of $Ca_2AlSiO_{5.5}$ glass was held at desired conditions for one hour, and after quenching, samples were recovered to ambient conditions. The recovered samples were identified using a micro-focused X-ray diffractometer, a powder X-ray diffractometer and SEM-EDS.

Drop solution calorimetries of the rhombohedral perovskite-type $Ca_2AlSiO_{5.5}$, the new $Ca_2AlSiO_{5.5}$ phase and brownmillerite-type $CaAlO_{2.5}$ were performed using a Calvet-type high-temperature calorimeter at Gakushuin University. Powdered samples of 2-7 mg were compressed into pellet. The pellets were dropped from outside of calorimeter at 25 C to lead borate solvent in the calorimeter at 705 C. To dissolve the samples more quickly, a bubbling method with Ar gas was applied.

The results of high-pressure phase relation experiment indicate that the rhombohedral perovskite-type phase is stable in the pressure range of 13 to 23 GPa and that an unknown phase exists in the pressure range of 7 to 13 GPa at 1400 C. The XRD analysis of the unknown phase suggests that it has the crystal system of orthorhombic. The lattice parameters were determined to be a = 10.4460(5) A, b = 14.9195(7) A, c = 10.5550(4) A. The most likely space group of the phase is *Ima2*. The new phase will be called as orthorhombic $Ca_2AlSiO_{5.5}$ below. Simulation of the powder X-ray diffraction pattern suggested that basic structure of the orthorhombic $Ca_2AlSiO_{5.5}$ might be the same as that of ABO_3 perovskite, though a half of B sites might have not sixfold coordination but fourfold coordination.

From the results of drop-solution calorimetry, formation enthalpies (dH_f) of the rhombohedral perovskite-type $Ca_2AlSiO_{5.5}$, the orthorhombic $Ca_2AlSiO_{5.5}$ and the brownmillerite-type $CaAlO_{2.5}$ from oxides were determined as 51.8+-4.1, -32.4+-4.2 and 26.9+-2.8 kJ/mol, respectively. When those data are combined with the dH_f of cubic perovskite-type $CaSiO_3$ of 14.8+-4.4 kJ/mol by Kojitani et al. (2001), the dH_f of the rhombohedral perovskite-type $Ca_2AlSiO_{5.5}$ is smaller than that of the average of the $CaSiO_3$ perovskite and the brownmillerite-type $CaAlO_{2.5}$. The dH_f of the orthorhombic $Ca_2AlSiO_{5.5}$ is smaller than that of the rhombohedral $Ca_2AlSiO_{5.5}$. This is consistent with the stability field of the orthorhombic $Ca_2AlSiO_{5.5}$ at pressure lower than that of the rhombohedral $Ca_2AlSiO_{5.5}$.