

Crystal chemistry of oxygen deficient calcium aluminum silicate perovskites

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In last JPGU meeting (SIT41-03), we reported the crystal structure of a low-pressure $\text{Ca}_2\text{AlSiO}_{5.5}$ oxygen deficient perovskite phase. In this presentation, we further report the crystal structure of low-pressure $\text{Ca}_2\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{5.6}$ phase, another oxygen deficient phase along the CaSiO_3 - $\text{Ca}_2\text{Al}_2\text{O}_5$ join (Blab et al, 2007).

The $\text{Ca}_2\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{5.6}$ phase was synthesized at 11 GPa and 1500 °C for 2H using a multi-anvil high-pressure device. Powder X-ray diffraction pattern for structural analysis was measured at BL19B2 of SPring-8 (for details, see Kanzaki and Xue, 2012). Local structures around Si and Al were studied by ²⁹Si MAS NMR and ²⁷Al 3Q MAS NMR. The crystal structure was solved using real-space searching program FOX (Favre-Nicolin & Cerny, 2002). The number of sites and oxygen coordination numbers for Al and Si obtained by NMR were utilized for FOX calculations. After the structure was solved, it was refined using Rietveld method (RIETAN-FP; Izumi & Momma, 2007).

Powder X-ray diffraction pattern of the phase is essentially identical to those reported by previous studies, and the obtained lattice parameters are consistent with those of Blab et al. (2007) with a 10-fold superstructure. The space group was found to be C2/c. ²⁹Si MAS NMR spectrum revealed two peaks due to a tetrahedral and an octahedral Si site. ²⁷Al 3Q MAS NMR spectrum revealed a single peak for octahedral Al. Using this information as well as the structure of low-pressure $\text{Ca}_2\text{AlSiO}_{5.5}$ as guide, the crystal structure was successfully solved.

The crystal structure of the $\text{Ca}_2\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{5.6}$ phase is made of triple-layers of perovskite-like octahedral $\text{AlO}_6/\text{SiO}_6$ and double-layers of tetrahedral SiO_4 , which are stacked alternatively in the [111] direction of cubic perovskite, forming a 10-fold superstructure. The triple-layers consist of a middle SiO_6 octahedral layer sandwiched by two AlO_6 octahedral layers. This structure can be obtained by inserting an octahedral Si layer in between the two AlO_6 octahedral layers of the structure for the low-pressure $\text{Ca}_2\text{AlSiO}_{5.5}$ phase. The double-layers of SiO_4 in both phases are similar, having deficient oxygens at the middle, with one non-bridging oxygen for each SiO_4 tetrahedron. This is in contrast to brownmillerite or perovskite structures, in which all oxygen are shared by two Al(Si).

Since $\text{Ca}_2\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{5.6}$ and $\text{Ca}_2\text{AlSiO}_{5.5}$ phases have triple and double octahedral layers, respectively, we could speculate another structure with a single octahedral layer. Such a phase in fact does exist as an ambient pressure phase ($\text{BaCa}_2\text{MgSi}_2\text{O}_8$), although the octahedral layer is made of MgO_6 (Park et al., 2011). This structure is a variant of merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$). This suggests that merwinite can also be regarded as a perovskite-related structure. The present study thus revealed that there is a series of oxygen deficient perovskite structures with different numbers of octahedral layers. These phases revealed another type of oxygen deficient local structure that is different from the well-known brownmillerite-type and involves non-bridging oxygens. It might be realized in Al- or Fe^{3+} -containing calcium perovskite solid solutions.

This study was partly conducted during Misasa International Student Intern Program 2012 (S.N.).

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Keywords: silicate perovskite, oxygen defect, high pressure phase, crystal structure, NMR, $\text{Ca}_2\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{5.6}$