

## Crystal structure of low-pressure $\text{Ca}_2\text{AlSiO}_{5.5}$ defect perovskite

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$\text{CaSiO}_3$  perovskite could dissolve  $\text{Al}_2\text{O}_3$  component by forming oxygen vacancies.  $\text{Ca}_2\text{Al}_2\text{O}_5$  brownmillerite structure can be regarded as an endmember for this dissolution mechanism, as all Si are replaced with Al. As a result, 1/6 of the oxygens are removed, and half of the Al are in tetrahedral coordination. If this is the dominant mechanism for Al dissolution into  $\text{CaSiO}_3$  perovskite, the perovskite should contain oxygen vacancies, and physical properties such as elastic properties and transport properties would be significantly affected. For the intermediate composition of the  $\text{CaSiO}_3$ - $\text{Ca}_2\text{Al}_2\text{O}_5$  join,  $\text{Ca}_2\text{AlSiO}_{5.5}$  with a rhombohedral perovskite structure was reported (Fitz Gerald & Ringwood, 1991). Later, a lower-pressure form of this phase was also found (Blab et al., 2007). Both phases were regarded to have oxygen-deficient perovskite-related structures, and structural models were proposed (Blab et al., 2007). However, the crystal structures have not been determined to date. Recently, we have demonstrated that a combination of NMR and SDPD (structure determination from powder data) is very powerful technique to solve unknown crystal structures (Kanzaki et al., 2011). In this study, we have applied this technique to the low-pressure  $\text{Ca}_2\text{AlSiO}_{5.5}$  phase.

The low-pressure phase of  $\text{Ca}_2\text{AlSiO}_{5.5}$  was synthesized at 7 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 et al., 2011). Local structures around Si and Al were studied by <sup>29</sup>Si MAS NMR and <sup>27</sup>Al 3Q MAS NMR. The crystal structure was solved using real-space searching program FOX (Favre-Nicolin & Cerny, 2002). The number and coordination of sites for Al and Si obtained by NMR were utilized for FOX calculation. After the initial structure was obtained, the structure 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 8-fold superstructure. The space group was found to be  $C2/c$ . <sup>29</sup>Si MAS NMR spectrum revealed a single peak for tetrahedral Si. <sup>27</sup>Al 3Q MAS NMR spectrum revealed a single peak for octahedral Al. These results are in contrast to structure model proposed by Blab et al. (2007), in which both tetrahedral and octahedral Al and Si sites were assumed based on EELS spectra. Using NMR information as constraints, the crystal structure was successfully solved. The crystal structure of the phase is made of perovskite-like double-layer of  $\text{AlO}_6$  octahedra and double-layer of tetrahedral  $\text{SiO}_4$ , stacked alternatively in the [111] direction of cubic perovskite, forming 8-fold superstructure. Oxygen is deficient at the middle of the double-layer of  $\text{SiO}_4$ , and 1/3 of the oxygens are missing from this oxygen close packing layer. The remaining oxygens are moved to form tetrahedral sites. One notable feature of the structure is that each  $\text{SiO}_4$  tetrahedron has one non-bridging oxygen. This is in contrast to brownmillerite or perovskite structures, in which all oxygen are shared by two Al(Si). This new structure reveals another type of oxygen vacancy formation mode other than that of brownmillerite. Based on this structure, this phase is expected to have large anisotropic properties, such as higher compressibility in the c-direction.

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