

Hexagonal perovskites in barium silicate

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Silicate perovskites in ASiO_3 have been widely surveyed as the key materials in the Earth's interior. Especially, both Mg^{2+} and Ca^{2+} bearing silicate perovskites attract lots of attention for their possible abundance in the lower mantle. In such silicate perovskites, only cubic and orthorhombic forms have been recognized for a long time except for a minor tetragonal modification of CaSiO_3 perovskite (Shim et al. 2002). Recently, the presence of hexagonal perovskite (6H- BaTiO_3 type) was confirmed in strontium silicates at 35 GPa (Yusa et al. 2005). On the crystallographic aspect, the symmetry of such perovskites is associated with the ionic radii of divalent cations. The tolerance factor, $t = (r_A + r_O) / \sqrt{2}(r_{\text{Si}} + r_O)$, where r denotes the ionic radii of each element, has been viewed as such a indicator. The cubic structure in perovskite (e.g. CaSiO_3 : $t=0.99$) exhibits the value close to 1.0. In case of the hexagonal perovskite in SrSiO_3 , the value ($t=1.04$) is greater than unity. In the present study, we note the high tolerance factor ($t=1.11$) of BaSiO_3 to explore the systematics of phase sequence in ASiO_3 . It is known that both CaSiO_3 and SrSiO_3 perovskite can not be recovered at ambient pressure due to amorphisation during decompression. Hence, we tried to conduct in-situ x-ray diffraction experiments under high pressure to examine the high-pressure phase of BaSiO_3 .

The high P, T experiments have been done at BL-10XU (SPring-8) using a symmetrical diamond anvil cell (DAC) combined with Nd:YLF laser. The angle dispersed x-ray diffraction (30 keV) was detected by an imaging plate and x-ray CCD camera. The starting sample of BaSiO_3 was prepared from an equimolar mixture of BaCO_3 and SiO_2 using an electrical furnace at 1623 K for 18 hrs. The structure is identified as a structure of high-temperature BaGeO_3 type structure. The sample mixed with a small amount of platinum was compressed without pressure medium in the DAC. After compression to 32 GPa, the sample was heated at 1500 - 1700 K by the laser. The diffraction patterns drastically changed after heating and then the pressure dropped by 10 %. All diffraction peaks can be assigned by a hexagonal perovskite which exhibits 9R periodicity with a space group of $R\bar{3}m$. Further laser heating experiment was carried out at 52 GPa. The diffraction pattern changed once again, and then 6H perovskite ($P63/mmc$) was identified under high pressure, which is the same structure as found in SrSiO_3 . Any other transformation was not observed by laser heating experiments up to 75 GPa. Both 9R and 6H perovskites decomposed to amorphous during decompression to ambient pressure as dose SrSiO_3 hexagonal perovskite. The structural difference of 9R and 6H perovskites is explained by the periodicity of face-sharing SiO_6 octahedron. In the direction of c axis, 9R perovskite exhibits $(\text{chh})_3$; whereas, 6H perovskite exhibits $(\text{cch})_2$ sequence, where c and h correspond to corner- and face-sharing octahedral, respectively. The fact suggests that the large divalent cation of barium can be incorporate into 9R perovskite structure with increasing the number of face-sharing octahedra even at comparable pressure to stabilize 6H perovskite structure in SrSiO_3 .