

Rietveld refinement of post-perovskite-type CaRuO_3

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Recently, Murakami et al. (2004) reported that MgSiO_3 perovskite transforms at 125 GPa and 2200 C to a post-perovskite phase which has the same structure as CaIrO_3 . Since the phase transition conditions are consistent with those for a seismic wave velocity discontinuity at D' layer, many researchers have been interested in the perovskite - post-perovskite phase transition. However, details on the phase transition have not been cleared yet due to the phase stability field higher than 100 GPa and unquenchable nature of the post-perovskite phase to ambient conditions. Comparative crystal chemical approach using analogue materials which show the phase transition at lower pressure than that in MgSiO_3 may be useful to know physical properties and phase transition mechanism for the perovskite - post-perovskite transition. Although it is known that CaIrO_3 , MgGeO_3 , MnGeO_3 , NaMgF_3 show the perovskite - post-perovskite phase transition, all post-perovskite phases of these compounds except for CaIrO_3 are unquenchable to ambient conditions. Therefore, it has been needed to find further compounds with the post-perovskite structure. In this study, a new high-pressure phase of CaRuO_3 was found by high-pressure and high-temperature experiments. As the new high-pressure phase of CaRuO_3 showed considerably similar X-ray diffraction (XRD) pattern to that of CaIrO_3 post-perovskite, we performed the Rietveld refinement of the new phase.

The high-pressure and high-temperature experiments were made using a Kawai-type high-pressure apparatus at Gakushuin University with tungsten carbide anvils (truncation size of 2.5 mm). CaRuO_3 perovskite for a starting material was prepared as follows. Reagent grade CaCO_3 and RuO_2 were mixed in mol ratio of 1:1, then compressed into a pellet. The mixture was heated at 1150 C for 14 hours in air. The new high-pressure phase of CaRuO_3 was synthesized by heating the starting material of CaRuO_3 perovskite at 23 GPa and 950 C for 1 hour. A powder XRD profile of the recovered sample was measured using Rigaku RINT2500V (Cr K α , 45 kV, 250 mA). A 2 theta range and a step size of the XRD measurement were 20-140 degree and 0.02 degree, respectively. To decrease the effect of a preferred orientation, powdered sample was scattered on a quartz plate on which thin layer of spray glue was stuck. RIETAN-2000 was used for the Rietveld refinement. The crystal structure of CaIrO_3 post-perovskite was applied to a model.

The final R_{wp} factor of 8.1% indicates that the crystal structure of the new high-pressure phase of CaRuO_3 can be regarded as the post-perovskite. Lattice parameters were determined to be $a = 3.1150(1)$ A, $b = 9.8268(1)$ A, $c = 7.2963(1)$ A. An average Ca-O distance of 2.436 A for CaRuO_3 post-perovskite is the same as that for CaIrO_3 post-perovskite (2.445 A) within the scattering. An average Ru-O distance in CaRuO_3 post-perovskite (2.008 A) is about 0.01 A smaller than that of an average Ir-O distance in CaIrO_3 (2.024 A). This fact shows good agreement with that the ionic radius of six-coordinated Ru^{4+} is about 0.01 A smaller than that of Ir^{4+} . Bond angles in CaRuO_3 post-perovskite are relatively close to those in CaIrO_3 post-perovskite.