A new cubic perovskite in PbGeO$_3$ at high pressures

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**ABSTRACT**

A new cubic perovskite polymorph of PbGeO$_3$ (Phase II) was synthesized by laser heating in the diamond-anvil cell (DAC) at the pressure of 36 GPa. Fitting the Birch-Murnaghan equation of state against its observed $P-V$ data yields a bulk modulus $K'_0$ of 196(6) GPa and the volume $V'_0$ of 56.70(13) Å$^3$ when $K'_0$ is assumed being 4. After the pressure is released, the PbGeO$_3$ Phase II changes gradually into an amorphous phase, which contains mainly fourfold-coordinated germanium. It indicates that the PbGeO$_3$ Phase II with a GeO$_6$ octahedron framework transforms to a GeO$_4$ tetrahedron network during the amorphization. The existence of PbGeO$_3$ cubic perovskite Phase II at high pressures indicates that the polarized character of the Pb$^{2+}$ ion induced by its fs lone pair electrons would be totally reduced in the environment of major silicate perovskites inside the lower mantle, and thus the Pb atom would substitute the Ca atom to enter the CaSiO$_3$ perovskite.

**Keywords:** Lead germanate, cubic perovskite, high pressure, amorphization

**INTRODUCTION**

The ABO$_3$ perovskite-structured oxides have been extensively investigated in geosciences, physics, chemistry, and material sciences. Many novel phase transitions in perovskite compounds have been thus discovered. For instance, the cubic PbCrO$_3$ perovskite (Phase I) transforms reversibly to another cubic perovskite (Phase II) with a 9.8% volume collapse at the pressure of ~1.6 GPa (Xiao et al. 2010); the multiferroic material of PbVO$_3$, which crystallizes in the polarized tetragonal perovskite ($P4mm$) structure at ambient conditions, changes reversibly to a cubic perovskite with >10% volume collapse at about 2 GPa (Belik et al. 2005); BiCoO$_3$ has the same polarized structure as PbVO$_3$ at ambient conditions but transforms to the orthorhombic perovskite ($Pnma$) with a 13% volume reduction at 3–4 GPa, which is induced by the high-spin to low-spin electronic transition in Co$^{3+}$ cation and the complete suppression of the polarized character in the Bi$^{3+}$ cation (Oka et al. 2010). Silicate perovskites are the primary mineral components in the Earth’s lower mantle (Kesson et al. 1998; Wood 2000). Whether those novel phase transitions could appear in silicate perovskites or not is thus an intriguing topic in mineral crystal chemistry and mantle mineralogy. The Ge-O and Si-O bonds exhibit the similar covalent nature, and germanides and silicates appear to have similar structural characteristics and physical, chemical properties (Gibbs et al. 1998), therefore, germanates are considered as an analogs of silicates in high-pressure research.

PbGeO$_3$ crystallizes in the monoclinic pyroxenoid structure ($P2_1/n$, $Z = 12$) at ambient conditions. The lattice parameters are $a = 11.469$, $b = 7.236$, $c = 12.555$ Å, $\beta = 113^\circ18'$, and $V = 956.96$ Å$^3$ (Nozik et al. 1979). It is the same structure as the natural mineral of alamosite (PbSiO$_3$) (Boucher and Peacor 1968). In the structure, the dominant feature is that a chain of the silicon (or germanium)-oxygen tetrahedra extends parallel to [100] and each chain has a lattice-translation repeat of 12 tetrahedral (Boucher and Peacor 1968). In addition, there is also a PbGeO$_3$ amorphous state (PbGeO$_3$ glass; labeled as Phase A1 below) when its melt is quenched at ambient pressure (Tomasi et al. 2005). At higher temperatures, the PbGeO$_3$ glass (Phase A1) transforms into an intermediate metastable crystalline modification at a temperature of about 430 °C and further to the stable monoclinic structure at about 570 °C (Tomasi et al. 2002). The structural details of this intermediate metastable modification remain unknown although it can be indexed as a hexagonal unit cell (Yamaguchi et al. 1985).

The investigation of pressure effects on structural behaviors of PbGeO$_3$ is scarce. When the intermediate hexagonal metastable modification of PbGeO$_3$ discussed above is compressed at room temperature, it undergoes an amorphization at 12–18 GPa with the coordination of Ge changing from 4 to 6 (Oelker et al. 2009). When the pressure is released, the high-pressure amorphous phase of PbGeO$_3$ transforms to a low-pressure amorphous phase with the sixfold coordination of Ge atoms reverting to fourfold, and the micro-structure of this decompressed amorphous material

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