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Bi(III)-containing lanthanum germanium apatite-type oxide ion conductors and their structure-property relationships

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Oxide ion conductors are used in a wide variety of applications, including oxygen sensors and separation membranes, but are undergoing significant study for their use in solid oxide fuel cells (SOFCs), which allow for the direct conversion of chemical to electrical energy. Apatite-type silicates and germanates, $\text{La}_{9.33+x}(\text{TO}_4)_6\text{O}_{2+3x/2}$ (T = Si, Ge), have exhibited high oxide ion conductivities, potentially allowing for their use in SOFCs.

Apatite-type compounds have the general formula, $[\text{Al}_4][\text{AlI}_6][\text{TO}_4]_6\text{X}_{2\pm\delta}$, (A = alkaline or rare earth metal, or Pb; T = Ge, Si, P, V; X = O, OH, halides) and can be thought of as comprised of a framework of $\text{Al}_4(\text{TO}_4)_6$ with flexible cavities containing AlI_6X_2 units. The structures of apatite-type materials are primarily hexagonal, with the remainder being monoclinic, with several triclinic examples known. The origin of the triclinic structure is thought to be partly due to the size differences between the units comprising the framework and those within the cavities. The inclusion of interstitial oxide ions have been shown to promote the triclinic distortion, potentially caused by further expansion of the framework.

Three novel Bi(III)-containing lanthanum germanium apatite compounds ($\text{Bi}_2\text{La}_8[(\text{GeO}_4)_6\text{]O}_3$, $\text{Bi}_4\text{Ca}_4\text{La}_2[(\text{VO}_4)_2(\text{GeO}_4)_4]\text{O}_2$, and $\text{Bi}_4\text{Ca}_2\text{La}_4[(\text{GeO}_4)_6]\text{O}_2$) were synthesised by a solid state synthetic method, before undergoing AC impedance spectroscopy experiments to study their electrical properties. The $\text{Bi}_2\text{La}_8[(\text{GeO}_4)_6\text{]O}_3$ compound has been identified as being the first bismuth containing apatite with a triclinic structure, whilst the Bi₄-containing compounds possess hexagonal structures. All samples show high levels of conductivity, with the triclinic sample possessing higher conductivity values than the hexagonal samples at high temperature.

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