Mechanochemical Synthesis of Doped Apatite-type Lanthanum Silicates

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Apatite type lanthanum silicates (ATLS) attract an interest as a new class of solid electrolytes possessing a high oxide-ion conductivity at intermediate temperatures as well as catalysts for oxidative coupling. These materials are tolerant to a broad range of dopants that provides a possibility of conductivity control. Recently the synthesis of undoped apatite-type silicates by mechanically milling constituent oxides at room temperature has been reported. Our later studies have shown that both undoped ATLS and ones doped with Al and Fe on the Si sites can be prepared at room temperature via the mechanochemical synthesis (MCS) using high power planetary ball mills that allows the milling time to be significantly decreased. In this paper, our results on mechanochemical synthesis of ATLS are summarized.

The effect of the dopant type, its parent compound nature and amount of water on the Al and Fe-doped ATLS formation as well as possible phenomenological models of mechanism of apatite-type silicates synthesis are considered. As lanthanum and silicon sources, the La_2O_3 and $SiO_2 \cdot nH_2O$ have been taken. As dopant precursors, Fe- and Al-oxides and hydroxides, $Fe(HCOO)_3$, SiO_2 impregnated with nitrates have been taken. The apatite formation in the course of milling is studied by XRD, TEM, ^{29}Si and ^{27}Al MAS NMR, IR and UV-Vis spectroscopy.[1-5]

The key role of intermediate $La(OH)_3$ formation, acid-base reactions and double-contact generation in the many-component mixtures due to aluminum or ferrosilicate formation for the rapid MCS of doped ATLS is shown. The doped ATLS formation via the topotactic mechanism was observed in the case of mixtures containing $Al(OH)_3$ and SiO_2 impregnated with nitrates. The water presence favours fast passing of acid-base reactions, however a large quantity of water may lead to ATLS formation via the activated mixture amorphization.

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