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Study of the $La_{1/2+1/2x}Li_{1/2-1/2x}Ti_{1-x}Al_xO_3$ ($0 \leq x \leq 1$) solid solution. A new example of percolative system in fast ion conductors

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Abstract

The synthesis by solid state reaction of new fast ion conductors with perovskite structure was carried out. The crystal structure and electric properties of the $La_{1/2+1/2x}Li_{1/2-1/2x}Ti_{1-x}Al_xO_3$ ($0 \leq x \leq 1$) solid solution were investigated by powder X-ray diffraction and impedance spectroscopy. All compositions of the $La_{1/2}Li_{1/2}TiO_3$-$LaAlO_3$ system, exhibited a single cubic perovskite structure ($a_c \approx 3.87$-3.79 Å; SG *Pm-3m*). The progressive decrease in the unit cell parameters agrees with the lower ionic radii of Al^{3+} in relation to Ti^{4+}, which are allocated in the same octahedra. An upward deviation from the lineal ideal solid solution behaviour described by Vegard's law was observed and it was tentatively associated with a volume excess created by solid dilution of ~~maximum of disorder on distribution of cations involved in the solid solution as a consequence of the~~ non-isovalent cations ~~nature of the solid solution~~. Structural features were deduced from Rietveld analysis of XRD patterns. $Ti(Al)O_6$ octahedra are regular and La/vacancies are randomly distributed in A-site of the perovskite. The conductivity decreased almost four orders of magnitude with the Li content. This important decrease on the conductivity was attributed to the charge carrier (Li^+) decrease and the blockade of the perovskite conduction pathways by La ions, according to a three dimensional percolative process. In consequence we present here a new example of percolative system of ionic conductors and the results confirm the important role played by effective vacant A-sites, $n_{eff} = [Li] + n_A$, on Li conductivity of this fast ion conductors family with perovskite structure.

Keywords: X-ray diffraction; Ionic conduction; Solid-State Electrolyte; Li-Batteries; Percolative phenomena.