

## MECHANOCHEMICAL SYNTHESIS AND ION TRANSPORT PROPERTIES OF $\text{Pb}_{0.75}\text{M}_{0.20}\text{K}_{0.05}\text{F}_{1.95}$ (M = Ca, Sr, Ba) SOLID ELECTROLYTES

Synthesis of new nanostructured superionic conductors with high fluoride-ion mobility is an urgent scientific issue, and these materials have good prospects for practical applications in alternative energy, chemical sensors, optics and other fields. Mechanochemical synthesis as a green modern method for production of nanomaterials has recognized advantages in terms of energy, time and resource efficiency, and it is very suitable for synthesis of multicomponent fluoride materials, which can avoid negative effects caused by high-temperature synthesis, such as fluoride pyrohydrolysis reactions. Fluorite-structured fluorides ( $\beta\text{-PbF}_2$ ,  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ ) is widely used in solid fluoride ion electrolytes, doping them with heterovalent metals can effectively improve the ionic conductivity of materials. Based on  $\beta\text{-PbF}_2$  is possible to obtain strongly nonstoichiometric solid solutions with high isomorphic capacity by replacing lead ions with almost any homo- and heterovalent cations. The purpose of this work is to synthesize highly conductive solid electrolytes  $\text{Pb}_{0.75}\text{M}_{0.20}\text{K}_{0.05}\text{F}_{1.95}$  (M = Ca, Sr, Ba) by using mechanochemical synthesis and study their ion transport properties.

Mechanochemical synthesis of solid electrolytes  $\text{Pb}_{0.75}\text{M}_{0.20}\text{K}_{0.05}\text{F}_{1.95}$  (M = Ca, Sr, Ba) was performed by using the PM100 Retsch planetary ball mill. The phase composition, structure and morphology of the obtained materials were characterized using modern analytical techniques, such as X-ray phase analysis, scanning electron microscopy, transmission electron microscopy and thermal analysis. Temperature dependence of conductivity and activation energy of the prepared solid electrolytes were studied using impedance spectroscopy. The conductivity of solid electrolyte  $\beta\text{-Pb}_{0.75}\text{Sr}_{0.20}\text{K}_{0.05}\text{F}_{1.95}$  obtained by using mechanochemical synthesis is  $4.70 \times 10^{-4}$  S/cm at room temperature. The conductivity of solid electrolyte  $\beta\text{-Pb}_{0.75}\text{Ca}_{0.20}\text{K}_{0.05}\text{F}_{1.95}$  obtained after annealing at  $350^\circ\text{C}$  is  $1.46 \times 10^{-3}$  S/cm at room temperature, which is more than ten thousand times higher than the conductivity of  $\beta\text{-PbF}_2$ , and it is one of the best fluoride-ion conductors available. According to the obtained data, it is shown the fundamental possibility to obtain new superionic conductors with high fluoride-ion mobility in the  $\text{PbF}_2\text{-MF}_2\text{-KF}$  (M = Ca, Sr, Ba) system, which can be used in solid-state electrochemical devices.

*Keywords:* mechanochemical synthesis, ion transport, fluoride-ion solid electrolyte.

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