

Structure Investigation of Pure and Cr Doped Li_3VO_4

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Li_3VO_4 finds applications in the fields of optics, electrochemistry (ionic conduction) and electronics. The RT β II form is orthorhombic (S.G. $\text{Pmn}2_1$) with LiO_4 tetrahedra larger and more distorted than VO_4 ones; empty sites exist allowing the Li^+ cation migration. Other polymorphs were revealed by increasing temperature up to the melting point. Our study deals with the effect of chromium doping (up to 10% of the V-cationic fraction) on the structure of Li_3VO_4 . The structural investigation was carried out by means of XRD, μ -Raman, EPR and ^7Li and ^{51}V MAS-NMR. To study the thermal stability of the solid solutions also HT XRD measurements were performed. XRD and μ -Raman analyses point out that Cr ions can easily substitute on the cationic sites of Li_3VO_4 without evidence of impurity phases. The host crystal structure does not depend on Cr-doping, neither at RT nor at HT. The EPR spectra put into evidence the presence of Cr^{3+} and Cr^{5+} . The combined analysis of EPR and ^7Li and ^{51}V MAS-NMR signals allows us to detect that Cr^{5+} and Cr^{3+} substitute on V^{5+} and Li^+ site respectively. The Cr^{3+} presence on Li site is also compatible with Rietveld refinements and Raman results: such substitution requires vacancies formation on Li sublattice, so increasing the ionic conductivity of the material as demonstrated also by our impedance spectroscopy and thermoelectric power measurements.

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