MS13-1-7 Solid solutions in the system Li_4GeO_4-Li_2CaGeO_4
#MS13-1-7

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Abstract
LISICON, $Li_{14}Zn(GeO_4)_4$ is one of the solid solutions with general formula $Li_{2+2x}Zn_{1-x}GeO_4$ (-0.36 < x < 0.87). These solid solutions are derivatives of the stoichiometric compound Li_2ZnGeO_4 where Zn^{2+} is substituted by Li^+. These compounds are isostructural to Li_3PO_4 with crystal structure based on $[Li_nZn_m(GeO4)_p]$ framework and an "interstitial" loosely bonded Li^+. This unique arrangement predetermines ionic conductivity of the mentioned compounds. Li_2GeO_4 has been also tested as a laser and phosphor matrix, semiconductor and biosensor. It was reported that Mg, Co, Fe, Ni, Cd also form solid solutions isostructural to Li_3PO_4, and the substitution of Ge by Si, V, P is also acceptable. The general formula for these solid solutions is defined as $Li_{2+2x}\textbf{Me1}_{1-x}\textbf{Me2}O_4$, where **Me1** is divalent cation and **Me2** form a $(\textbf{Me2}O_4)^{4-}$ anion.
Here we report for first time the synthesis of solid solutions in the system Li_4GeO_4-Li_2CaGeO_4. As Ca^{2+} has a larger ionic radius than Zn^{2+} and the mentioned before cations, it could be expected that the framework "voids" in $Li_{2+2x}Ca_{1-x}GeO4$ will be larger, influencing the ionic conductivity and the luminescence properties. Compositions of $Li_{2+2x}Ca_{1-x}GeO_4$ with **x**=0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0 were prepared by conventional solid state reactions. The desired quantities of Li_2CO_3 (99,9), $CaCO_3$ (99,9), GeO_2(99,999) were mixed, milled and heated at 800°C for 3 h. The decarbonized samples were milled again and heated at 1050°C for 6h. The resulting powders were studied using XRD, DSC-TG analyses. Two phase regions were defined between Li_2CaGeO_4 (x=0) and Li_4GeO_4 (x=1,0). For 1050°C these regions are as follow: for **x** between 0 and 0.1 crystalizes $Li_{2+2x}Ca_{1-x}GeO_4$ solid solutions owing tetragonal Li_2CaGeO_4 structure type; for **x** between 0.1 and 0.7 a mixture of $Li_{2+2x}Ca_{1-x}GeO_4$ solid solutions with Li_2CaGeO_4 tetragonal and orthorhombic type structures; for **x** between 0,7 and 0,9 solid solutions of $Li_{2+2x}Ca_{1-x}GeO_4$ with orthorhombic Li_2CaGeO_4 type structure; and finally for **x** above 0.9 solid solutions with Li_4GeO_4 type structure. X-ray powder analyses for selected compositions (SiO_2 was used as an internal standard) are represented on the Figure 1. The studied samples were compared with the PDF data of the basic Li_2CaGeO_4 tetragonal and orthorhombic structures.
An interesting result is the presence of wide region of crystallization of $Li2+2xCa1-x GeO4$ solid solutions with two different structures. It would be important to look for relations between this phenomenon and the ionic conductivity of the obtained mixtures. It is also notable that in the orthorhombic $Li2+2xMe21-xGeO4$ phase the Me2 atoms are tetrahedrally coordinated. Such coordination is very unusual for Ca ion and it is important it to be confirmed for orthorhombic $Li2+2xCa1-xGeO4$ single crystal sample.

X-ray powder data for selected compositions