

## Mössbauer analysis of silicate $\text{Li}_2\text{FeSiO}_4$ and delithiated $\text{Li}_{2-x}\text{FeSiO}_4$ ( $x = 0.66$ ) compounds

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Lithium iron silicate compounds of  $\text{Li}_2\text{FeSiO}_4$  and partially delithiated  $\text{Li}_{2-x}\text{FeSiO}_4$  ( $x = 0.66$ ) were synthesized by vacuum-sealed solid-state and chemical delithiation reactions, and their magnetic properties were characterized based on Mössbauer analysis. Crystal structures of both  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_{2-x}\text{FeSiO}_4$  ( $x = 0.66$ ) compounds are found to be  $\gamma_s$ -type ( $P2_1/n$ ) monoclinic structures with difference in the lattice parameters due to lithium delithiation. Mössbauer spectrum of  $\text{Li}_2\text{FeSiO}_4$  below  $T_{N1} = 20$  K exhibits eight Lorentzians of  $\text{Fe}^{2+}$  with antiferromagnetic ordering. However, the spectrum of intermediate  $\text{Li}_{2-x}\text{FeSiO}_4$  ( $x = 0.66$ ) compound shows the appearance of magnetically ordered  $\text{Fe}^{3+}$  sextet below  $T_{N2} = 28$  K. The temperature-dependent isomer shift of  $\text{Li}_{2-x}\text{FeSiO}_4$  indicates the coexistence of nonequivalent  $\text{Fe}^{2+}/\text{Fe}^{3+}$  valence states with the partial oxidation of  $\text{FeO}_4$ , enhanced by the lithium ion deficiency. Also, we have observed a considerable change in electric quadrupole interaction between  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions in  $\text{Li}_{2-x}\text{FeSiO}_4$ , when compared to that of  $\text{Li}_2\text{FeSiO}_4$ , due to the different lattice and valence electron contributions, being originated from crystalline and valence transitions caused by the lithiation/delithiation process. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4799153>]