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Solid solution along the synthetic $LiAlSi_2O_6$-$LiFeSi_2O_6$ (spodumene-ferri-spodumene) join: A general picture of solid solutions, bond lengths, lattice strains, steric effects, symmetries, and chemical compositions of Li clinopyroxenes

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ABSTRACT

Seven clinopyroxene compositions along the join $^{M2}Li^{M1}Al^{T}Si_2O_6$ (spodumene) to $^{M2}Li^{M1}Fe^{3+T}Si_2O_6$ (ferri-spodumene) were synthesized at 2 GPa, 800 °C under highly oxidizing conditions (using H_2O_2 fluid) in an end-loaded piston cylinder. In addition, the $LiFe^{3+}Si_2O_6$ composition was also synthesized under the intrinsically reducing conditions in a piston cylinder, to check the effect of f_{O_2} on iron speciation. The run products were characterized by field emission scanning electron microscope (FE-SEM), Rietveld refinements on XRPD synchrotron data, and space groups were assigned using SAED-TEM patterns. Run products are composed mainly of lithium clinopyroxene (Li-Cpx), plus minor amounts of hematite (magnetite under reducing condition) and corundum, as independently detected by image analysis (area%) and Rietveld refinements (wt%); moreover, Rietveld results were used to derive cell parameters, M1-site occupancy (Al vs. Fe^{3+}), atomic positions, and average bond lengths of all these Li-Cpx indexed in the *C*2/*c* space groups according to SAED-TEM.

Li-Cpx with Al and Fe^{3+} amounts close to 50:50 are actually slightly richer in Al apfu than nominal; the $LiFe^{3+}Si_2O_6$ grown under very oxidized and reducing conditions have very similar cell parameters, indicating that f_{O_2} is unable to induce a significant incorporation of Fe^{2+} in these Li-Cpx. The replacement of Al with Fe^{3+} induces a linear (%) increase of the cell edges following $b > a > c$, whereas β is roughly constant and the cell volume increases linearly. Furthermore, the substitution of Al with Fe^{3+} only weakly affects the T-O average length (<1%), whereas M2-O and M1-O bonds increase linearly of 2.3 and 5.0%, respectively.

These new experimental data have been compared with other available on Li-, Na-, and Ca-Cpx, i.e., $^{M2}(Li,Na,Ca,Mg,Fe^{2+})^{M1}(Mg,Fe^{2+}Al,Ni,Cr,Ga,V,Fe^{3+},Mn,Sc,In)^{T}Si_2O_6$, to model lattice strain, bond lengths, steric effects, and phase transitions behaviors. The replacement of Al with progressively larger cations in $LiM^{3+}Si_2O_6$ Cpx (M^{3+}: Ni, Cr, Ga, V, Fe^{3+}, Ti, Sc, and In) results in a linear increase following $V > b > a > c$, whereas β is roughly constant except for Ti-end-member and $P2_1/c$ compositions. Lattice strains induced by *X*, *T*, and *P* for Li-Cpx in the *C*2/*c* stability field show that when the M1 site is progressively filled with a large cation, ε_1 axis ($\varepsilon_1 > \varepsilon_2 > \varepsilon_3$) increases along *b*, whereas ε_2 and ε_3 are nearly parallel to *a* and at about 30° from *c*. Conversely, *T* will provoke a similar enlargement of ε_1 and ε_2 along *b* and *a* edges, respectively, whereas ε_3 is again oriented at about 30° from *c*; the increasing of *P* will instead shorten all strain tensor components (ε_1, ε_2, and ε_3) with a similar percentage amount; notably, high-*P* is the only stress that induces a strain component to be almost parallel to *c* edge. Moreover, finite lattice strains and orientation in *C*2/*c* $LiMe^{3+}Si_2O_6$ Li-Cpx induced by Me^{3+}: Al-Fe^{3+}, Fe^{3+}-Sc, Sc-In are slightly different, with ε_1 invariably lying along *b*; conversely, Li-Na cation substitution is completely different with the highest and lowest deformations on the *ac* plane and ε_2 along *b*; ε_3 vector is negative and oriented at about 30° from T-chains. The ideal replacement of Al with larger cations up to In in Li-Cpx induces the M1-O, M2-O, and T-O average bond lengths to increase by 10.6, 4.3, and <0.5%. Steric effects in $Li^{M1}Me^{3+}Si_2O_6$ and $Na^{M1}Me^{3+}Si_2O_6$ Cpx are significant and very similar, whereas several other Me^{1+} and Me^{2+} substitutions in Cpx at both the M1 and M2 site, keeping fixed the other site, display less or even the absence of steric effects. Our new data also better elucidate relationships between Li-Cpx composition, symmetry at room and non-ambient conditions and T_c. The aggregate cation radii at the M1 site does not exclusively control the stability of *C*2/*c* and $P2_1/c$ polymorphs; instead valence electrons can profoundly favor the stabilization of a polymorph.

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Finally, Li can be easily and accurately detected (0.1/0.2 apfu) in natural clinopyroxenes by cell parameters, especially using the β angle.

Keywords: Lithium, clinopyroxenes, solid solutions, bond lengths, lattice strains, steric effects