

# Solid solution along the synthetic $\text{LiAlSi}_2\text{O}_6$ - $\text{LiFeSi}_2\text{O}_6$ (spodumene-ferri-spodumene) join: A general picture of solid solutions, bond lengths, lattice strains, steric effects, symmetries, and chemical compositions of Li clinopyroxenes

GIANLUCA IEZZI<sup>1,2,\*</sup>, GEOFFREY D. BROMILEY<sup>3</sup>, ANDREA CAVALLO<sup>2,4</sup>, PARTHA P. DAS<sup>5,6,7</sup>, FOTINI KARAVASSILI<sup>5</sup>, IRENE MARGIOLAKI<sup>5</sup>, ANDREW A. STEWART<sup>8</sup>, MARIO TRIBAUDINO<sup>9</sup>, AND JONATHAN P. WRIGHT<sup>10</sup>

<sup>1</sup>Dipartimento di Ingegneria & Geologia, Università G. d'Annunzio, via Dei Vestini 30, I-66100 Chieti, Italy

<sup>2</sup>INGV-Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy

<sup>3</sup>School of GeoSciences and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, U.K.

<sup>4</sup>Laboratorio Tecnologico Multidisciplinare di Grosseto (CERTEMA), (GR), Italy

<sup>5</sup>Department of Biology, University of Patras, Patras, Greece

<sup>6</sup>NanoMEGAS SPRL, Brussels, Belgium

<sup>7</sup>Electron Crystallography Solutions, Madrid, Spain

<sup>8</sup>Department of Physics and Energy, University of Limerick, Ireland

<sup>9</sup>Dipartimento di Fisica e Scienze della Terra, Università di Parma, Italy

<sup>10</sup>ESRF, Grenoble, France

## ABSTRACT

Seven clinopyroxene compositions along the join  $^{\text{M2}}\text{Li}^{\text{M1}}\text{Al}^{\text{T}}\text{Si}_2\text{O}_6$  (spodumene) to  $^{\text{M2}}\text{Li}^{\text{M1}}\text{Fe}^{3+\text{T}}\text{Si}_2\text{O}_6$  (ferri-spodumene) were synthesized at 2 GPa, 800 °C under highly oxidizing conditions (using  $\text{H}_2\text{O}_2$  fluid) in an end-loaded piston cylinder. In addition, the  $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$  composition was also synthesized under the intrinsically reducing conditions in a piston cylinder, to check the effect of  $f_{\text{O}_2}$  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.  $\text{Fe}^{3+}$ ), atomic positions, and average bond lengths of all these Li-Cpx indexed in the  $C2/c$  space groups according to SAED-TEM.

Li-Cpx with Al and  $\text{Fe}^{3+}$  amounts close to 50:50 are actually slightly richer in Al apfu than nominal; the  $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$  grown under very oxidized and reducing conditions have very similar cell parameters, indicating that  $f_{\text{O}_2}$  is unable to induce a significant incorporation of  $\text{Fe}^{2+}$  in these Li-Cpx. The replacement of Al with  $\text{Fe}^{3+}$  induces a linear (%) increase of the cell edges following  $b > a > c$ , whereas  $\beta$  is roughly constant and the cell volume increases linearly. Furthermore, the substitution of Al with  $\text{Fe}^{3+}$  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.,  $^{\text{M2}}(\text{Li,Na,Ca,Mg,Fe}^{2+})^{\text{M1}}(\text{Mg,Fe}^{2+}\text{Al,Ni,Cr,Ga,V,Fe}^{3+},\text{Mn,Sc,In})^{\text{T}}\text{Si}_2\text{O}_6$ , to model lattice strain, bond lengths, steric effects, and phase transitions behaviors. The replacement of Al with progressively larger cations in  $\text{LiM}^{3+}\text{Si}_2\text{O}_6$  Cpx ( $\text{M}^{3+}$ : Ni, Cr, Ga, V,  $\text{Fe}^{3+}$ , Ti, Sc, and In) results in a linear increase following  $V > b > a > c$ , whereas  $\beta$  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  $C2/c$  stability field show that when the M1 site is progressively filled with a large cation,  $\epsilon_1$  axis ( $\epsilon_1 > \epsilon_2 > \epsilon_3$ ) increases along  $b$ , whereas  $\epsilon_2$  and  $\epsilon_3$  are nearly parallel to  $a$  and at about 30° from  $c$ . Conversely,  $T$  will provoke a similar enlargement of  $\epsilon_1$  and  $\epsilon_2$  along  $b$  and  $a$  edges, respectively, whereas  $\epsilon_3$  is again oriented at about 30° from  $c$ ; the increasing of  $P$  will instead shorten all strain tensor components ( $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$ ) 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  $C2/c$   $\text{LiMe}^{3+}\text{Si}_2\text{O}_6$  Li-Cpx induced by  $\text{Me}^{3+}$ : Al- $\text{Fe}^{3+}$ ,  $\text{Fe}^{3+}$ -Sc, Sc-In are slightly different, with  $\epsilon_1$  invariably lying along  $b$ ; conversely, Li-Na cation substitution is completely different with the highest and lowest deformations on the  $ac$  plane and  $\epsilon_2$  along  $b$ ;  $\epsilon_3$  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  $\text{Li}^{\text{M1}}\text{Me}^{3+}\text{Si}_2\text{O}_6$  and  $\text{Na}^{\text{M1}}\text{Me}^{3+}\text{Si}_2\text{O}_6$  Cpx are significant and very similar, whereas several other  $\text{Me}^{1+}$  and  $\text{Me}^{2+}$  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  $C2/c$  and  $P2_1/c$  polymorphs; instead valence electrons can profoundly favor the stabilization of a polymorph.

\* E-mail: gianluca.iezzi@unich.it

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

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