THE $C2/C$ - $P2_1/C$ PHASE TRANSITION WITHIN THE SYNTHETIC CLINOPYROXENE-SERIES $NaFeGe_2O_6$ - $LiFeGe_2O_6$

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The mineral group of the pyroxenes is known to exhibit several phase transitions as a function of temperature and pressure. At ambient conditions, the most frequent occurring structure is the high temperature HT-$C2/c$ structure, which transforms to $P2_1/c$ at low temperatures or at high pressures. This was described e.g. by REDHAMMER & ROTH (2004) for $LiM^{3+}Si_2O_6$ clinopyroxenes, showing transition temperatures between 210 and 340 K. The analogue $LiM^{3+}Ge_2O_6$ compounds display $P2_1/c$ symmetry at room temperature and transform to $C2/c$ symmetry at much higher temperatures. $LiFeGe_2O_6$ shows a $P2_1/c$ to HT $C2/c$ transition at 789 K, thus shifted by more than 500 K (REDHAMMER et al., 2010). The germanium analogue to aegirine, $NaFeGe_2O_6$, exhibit $C2/c$ symmetry at room temperature (REDHAMMER et al., 2011), thus a transition from $C2/c$ to $P2_1/c$ symmetry within the $(Na_{1-x}Li_x)FeGe_2O_6$ solid solution series is to be expected.

The synthetic samples show $C2/c$ symmetry up to a composition of $Na_{0.5}Li_{0.5}FeGe_2O_6$, for higher Li-contents, the $P2_1/c$ symmetry is observed. Using single crystal X-ray diffraction and thermal analysis a T-X phase diagram of the stability of the corresponding symmetries was established (see Figure). The unit cell volume decreases with increasing Li - content, at the phase transition composition a discontinuity and a change in slope is observed. Such discontinuities are valid for all lattice parameters a, b, c and the monoclinic angle; additionally average as well as individual bond lengths for Li-O, Fe-O and Ge-O are subject of smooth variations with Li-content, with more or less pronounced discontinuities at the phase transition. Evident e.g. is the variation of the O3-O3-O3 bridging angle of tetrahedral chains: it decreases from 185 ° to 174 ° with increasing Li-content, at the phase transition two independent chains arise in the $P2_1/c$ phase with kinking angles of 199 ° and 155 ° For the composition of $Na_{0.6}Li_{0.4}Ge_2O_6$ and $Na_{0.7}Li_{0.3}Ge_2O_6$ low temperature in situ X-ray diffraction experiments were done to follow the $C2/c$ - $P2_1/c$ phase transition also as a function of temperature.

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