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Raman spectroscopy in Ca,Co pyroxenes: a model for structure and composition in silicates

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Pyroxenes are among the most abundant major rock-forming minerals. They have a relatively simple structure allowing a wide range of chemical substitutions. The silicate chain provides a simple structural feature to model the effect of deformation in silicates, and the polyhedra that build up the pyroxene structure show different degrees of flexibility, so that the effects of chemical substitution on different cation polyhedra can be ascertained.

One of the most intriguing features in pyroxenes is the substitution of smaller cations onto the M2 polyhedron, which in $C2/c$ pyroxenes generally hosts a larger cation like Na or Ca. An example is given by the series diopside - enstatite ($CaMgSi_2O_6$- $Mg_2Si_2O_6$). Along this series the substitution of Ca by Mg promotes the formation of a miscibility gap (the basis for the two pyroxene thermometry) and, at hypersolvus conditions, gives rise to a phase transition between $C2/c$ and $P2_1/c$ pyroxenes.

Raman spectra of the diopside - enstatite series show a one-mode behaviour, and changes in peak positions are related with structural features, like tetrahedral chain kinking angles and average bond lengths (Tribaudino *et al.*, 2012). Here we will examine the results of the companion series $CaCoSi_2O_6$- $Co_2Si_2O_6$. In this series the replacement of Ca by Co, with cation radius similar to that of Mg (0.745 vs 0.72 Å), is expected to result in a similar change structure to the replacement of Ca by Mg, although owing to significantly different masses the effect in Raman spectrum has to be verified.

A series of samples with compositions between $CaCoSi_2O_6$ and $Co_2Si_2O_6$ were synthesized at P=3 GPa and T=1200˚C - 1350˚C using a piston-cylinder apparatus. Additional synthesis experiments were performed in order to obtain single crystals of composition $Ca_{0.8}Co_{1.2}Si_2O_6$, $Ca_{0.6}Co_{1.4}Si_2O_6$ and $Ca_{0.4}Co_{1.6}Si_2O_6$, which were then studied by single crystal XRD. Raman spectra were obtained from all the samples. As expected, changes in the atomic structure were close to those found for the Ca-Mg substitution in the M2 site. The Raman spectrum in Ca,Co pyroxenes is also similar to that of Ca,Mg ones; a significant change in the peak position *vs* composition was observed at the composition $Ca_{0.4}Co_{1.6}Si_2O_6$, for peaks between 300 and 500 cm^{-1} and at the composition $Ca_{0.2}Co_{1.8}Si_2O_6$ for the peaks at 660 and 1000 cm^{-1}. These changes were related to the transition from C to P lattice. However, splitting of the 660 cm^{-1} peak previously ascribed to the presence of symmetrically distinct chains in $P2_1/c$ pyroxenes, was not found, as has been note in clinoferrosilite ($Fe_2Si_2O_6$). A comparison of changes of peak position with composition in Raman spectra of Ca,Co and Ca,Mg pyroxenes also shows a different trend. For instance, the peak at 1010 cm^{-1}, which does not change for Ca-Mg substitution, shifts by as much as 20 cm^{-1} between $CaCoSi_2O_6$ and $Co_2Si_2O_6$. The effect of similar structural changes in chain kinking and polyhedral deformation on Raman peak positions is also different, although qualitatively similar.

This point is discussed in terms of the interplay between the effect of mass and structure changes on the Raman spectra. Careful analysis has yet to be performed to separate the two effects, also taking into account the fact that the modes often involve contributions from several atoms in the structure.

Tribaudino M., Mantovani L., Bersani D. and Lottici P.P. (in press) *Raman Spectroscopy of (Ca,Mg)$MgSi_2O_6$clinopyroxenes*, American Mineralogist.