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Cation order-disorder in Fe-bearing pyrope and grossular garnets: A ^{27}Al and ^{29}Si MAS NMR and ^{57}Fe Mössbauer spectroscopy study

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Abstract

A suite of Fe-bearing natural and synthetic grossular-rich [$(Ca,Fe)_3(Al,Fe)_2Si_3O_{12}$] and pyrope-rich [$(Mg,Fe)_3Al_2Si_3O_{12}$] garnets were investigated using ^{27}Al and ^{29}Si MAS NMR and ^{57}Fe Mössbauer spectroscopy. This was done to study the state of cation order-disorder in garnet solid solutions by analyzing paramagnetically shifted resonances in high-resolution NMR spectra. The Mössbauer spectra, along with electron microprobe results, give the concentrations of Fe^{2+} and Fe^{3+} and their site occupancies, even in grossular samples with very low concentrations of Fe. MAS NMR spectra were collected on Fe^{2+}-bearing grossular- and pyrope-rich garnets with up to 25 mol% almandine component and on other Fe^{3+}-bearing grossular samples with up to 9 mol% andradite component. Despite peak broadening and signal loss, structural information was even obtained from garnet with relatively high Fe contents (25 mol% almandine component). Paramagnetically shifted NMR peaks, related to the presence of Fe^{2+}, were observed in grossular samples and are similar in nature to those reported previously for natural, relatively low-Fe^{2+} pyrope garnets by Stebbins and Kelsey (2009). Additional NMR peaks appear as the concentration of Fe^{2+} increases, reflecting an increase in the average number of neighboring Fe^{2+} cations around AlO_6 and SiO_4 groups. These newly observed peaks hold potential to provide information concerning the presence or absence of short-range ordering in certain Fe-bearing silicate garnets. The effect of Fe^{3+} on the MAS NMR spectra of garnet appears to be less pronounced, because it does not produce any observable paramagnetically shifted resonances.

Keywords: NMR spectroscopy, Mössbauer spectroscopy, pyrope, grossular, almandine, garnet, paramagnetic shifts, short-range order