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Report:

The crystal structure of garnets is characterised by the presence of different cation sites, among which triangular dodecahedra XO_8, consisting of eight oxygens which coordinate bivalent cations (mainly Mg, Ca, Fe^{2+}, Mn). Since most of garnets are multicomponent solutions of different end members, the dodecahedral site is usually shared by different cationic species, such as Fe^{2+} and Mn in the join Almandine-Spessartine studied in the present work.. The study of the local environment of the cations occupying the dodecahedral site and the amount of static and/or dynamic disorder is of particular importance since it provides information on the possible deviations from the ideality of the garnet solid-solutions, suggested by the analysis of their thermodynamic data (Ganguly & Saxena, 1981; Berman, 1990; Geiger & Feenstra, 1997).

The present report deals with the XAFS study of the local environment of Fe^{2+} and Mn, sharing the dodecahedral site a in a series of garnets, belonging to the Almandine-Spessartine join, with different Fe-Mn content: Alm100, Alm75Sp25, Alm50Sp50, Alm25Sp75, Sp100. The Mn and Fe K edges (6450eV and 7112 eV, respectively) XAFS spectra were collected in transmission mode for all the samples and for the standard compounds (MnO_2 and Fe_2O_3). In order to get information on the dynamic disorder, the experiments were performed on each

sample at different temperatures: 77, 100, 200, 273, 373 e 450 K. The Mn and Fe EXAFS data collected at 77K of all the samples were analysed using the standard background subtraction and and Fourier filtering, whereas the determination of the structural parameters has been carried out through FEFFIT (FUSE package) (Ravel, 1998). The same analysis, still in progress, has been performed on Mn edge of pure spessartine Sp100 at different temperatures in order to compare it with the results obtained at the Fe edge on pure almandine Alm100 (Quartieri et al. 1997).

Table 1 reports the results of the XAFS analysis at the Fe K-edge relative to the first peak of the FT at three different temperatures. The bond distances remain essentially unchanged over the measured Fe^{2+} concentrations at all temperatures. At each temperature the XAFS DW factor relative to the longer Fe(2)-O distance (σ^2_2) is larger than the one relative to the shorter Fe(1)-O bond (σ^2_1). Moreover, as already observed for almandine (Quartieri et al. 1997), σ^2_2 has a larger T-dependence than σ^2_1, which remains, in comparison, almost constant over the measured temperature range. These results suggest that the local structural environment of Fe is almost independent on the composition of the solid solution and confirm that the dynamic disorder in the X-site cation is strongly anisotropic in all the join.

Table 1 Results of the XAFS analysis at three different temperatures (Fe K edge)

77K	$\sigma^2_{(Fe(1)-O)} (\text{Å}^2)$	$\sigma^2_{(Fe(2)-O)} (\text{Å}^2)$	$R_{(Fe(1)-O)} (\text{Å})$	$R_{(Fe(2)-O)} (\text{Å})$
Alm	0.006(1)	0.013(3)	2.213(8)	2.347(22)
Sp25	0.007(1)	0.010(4)	2.212(5)	2.334(22)
Sp50	0.008(1)	0.009(3)	2.209(9)	2.332(18)
Sp75	0.009(2)	0.008(5)	2.206(9)	2.334(24)
RT	$\sigma^2_{(Fe(1)-O)} (\text{Å}^2)$	$\sigma^2_{(Fe(2)-O)} (\text{Å}^2)$	$R_{(Fe(1)-O)} (\text{Å})$	$R_{(Fe(2)-O)} (\text{Å})$
Alm	0.009(1)	0.017(3)	2.214(8)	2.352(22)
Sp25	0.009(2)	0.018(4)	2.217(12)	2.344(22)
Sp50	0.009(1)	0.019(3)	2.215(9)	2.346(18)
Sp75	0.009(2)	0.019(5)	2.219(13)	2.343(24)
473 K	$\sigma^2_{(Fe(1)-O)} (\text{Å}^2)$	$\sigma^2_{(Fe(2)-O)} (\text{Å}^2)$	$R_{(Fe(1)-O)} (\text{Å})$	$R_{(Fe(2)-O)} (\text{Å})$
Alm	0.008(1)	0.023(3)	2.213(8)	2.364(19)
Sp25	0.009(1)	0.022(4)	2.210(8)	2.365(19)
Sp50	0.008(1)	0.021(2)	2.214(5)	2.370(12)
Sp75	0.012(2)	0.022(5)	2.212(13)	2.353(30)

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