

⁵⁴Fe³⁺-O distance in synthetic kimzeyite garnet

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In natural kimzeyite garnet and in its synthetics analogues trivalent Fe is known to be located in the tetrahedral site substituting for silicon and/or Al [1,2,3,4]. Fe ionic radius is much larger than that of Al and Si in tetrahedral coordination; thus Fe substitution for Si and/or Al accounts for a large increase in both the kimzeyite cell volume and <T-O> distance. However, as Fe and Si (and eventually Al) are located in symmetry equivalent sites, X-ray diffraction (XRD) cannot provide a direct measure of the Fe-O distance. As ⁵⁴Fe³⁺-O distances are not commonly reported in minerals, a synthetic sample has been studied by powder XRD and X-ray Absorption Spectroscopy (XAS) in order to get information on both the average structure and on the local environment around Fe tetrahedron.

Synthetic kimzeyite analogue has been prepared by mixing stoichiometric amounts of reagent grade oxides and holding the reagents at 1250° C for 36 hours. The products consist of Ca₃Zr₂[Fe₂SiO₁₂] kimzeyite garnet and minor CaZrO₂ (<5 wt%). Powder XRD spectra have been collected by means of a Philips PW1830 diffractometer equipped with a graphite monochromatised Cu K_α X-ray tube, whereas Fe K-edge XAS spectra have been collected in fluorescence mode at the GILDA beamline of the ESRF storage ring using a Si (311) monochromator. Structural refinement and EXAFS data analysis have been carried out by means of the GSAS code and GNXAS package respectively. Preliminary theoretical XANES spectra have been calculated by means of the MXAN code.

The garnet cell parameter (a₀=12.625 ± 0.001 Å) is consistent with those found in the literature for a synthetic sample of similar composition [2]. Also interatomic distances (<Ca-O>=2.507 Å, Zr-O=2.105 Å, <T-O>=1.773 Å) are reasonably consistent with those of natural samples when taking into account chemical differences of the samples examined. The tetrahedral T-O distance is unusually long compared with garnets where tetrahedra are occupied solely by Si due to the large Fe content of this site.

XANES data display a pre-edge peak whose intensity and energy position are consistent with the presence of trivalent Fe in tetrahedral coordination. The EXAFS derived <Fe-O> distance (=1.85 ± 0.02 Å) is consistent with extrapolation from literature data for garnets having different tetrahedral Fe occupancies (assuming full occupancy of the tetrahedral site by Fe³⁺), and is also in agreement with previous literature data on ⁵⁴Fe³⁺ in tetraferriphlogopite (Fe-O=1.86 ± 0.02 Å [5]) and in a phonolite glass (Fe-O=1.85 ± 0.01 Å [6]). Further Rietveld structural refinement were performed assuming a splitting of the oxygen position, resulting in two sites (with occupancies 2/3 and 1/3) at 1.845 and 1.610 Å respectively from the tetrahedral cation.

References:

- [1] Milton, C., Ingram B.L., Blade, L.V. (1961) *American Mineralogist*, 46, 533-548.
- [2] Ito, J. & Frondel, C. (1967) *American Mineralogist* 52, 773-781.
- [3] Munno, R., Rossi, G., Tadini, C., A. (1980): *American Mineralogist*, 65, 188-191.
- [4] Schingaro, E., Scordari, F., Capitanio, F., Parodi, G., Smith, D.C., Mottana, A. (2001) *European Journal of Mineralogy*, 13, 749-759.
- [5] G. Giuli, E. Paris, M.F. Brigatti, Z. Wu, A. Mottana, A. Marcelli, G. Cibin (2001), *European Journal of Mineralogy*, 13, 1099-1108.
- [6] G. Giuli, E. Paris, K.U. Hess, D.B. Dingwell, M.R. Cicconi, S.G. Eckhout, K.T. Fehr, P. Valenti (2011), *American Mineralogist*, 96, 631-636.