

**MIXED VALENCE COMPOUND MELONJOSEPHITE $\text{Ca}_2\text{Fe}^{2+}_2\text{Fe}^{3+}_2(\text{PO}_4)_4(\text{OH})_2$:
STRUCTURE AND ^{57}Fe MÖSSBAUER SPECTROSCOPY**

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Melonjosephite was described first in [1] and its structure determined later on in [2]. However, no anisotropic refinement has so far been given and the valence state of iron is undefined, even if it was stated that ferric and ferrous iron are distributed among the two octahedral M sites. For a complete characterisation of the compound studied, we have used (i) sample material from the type locality Angarf-Sud [1] and (ii) synthetic crystals grown in a hydrothermal experiment (600°C, 0.4 GPa, NNO solid state buffer). Temperature dependent X-ray diffraction (80 K – 300 K) and ^{57}Fe Mössbauer spectroscopic (80 K – 500 K) investigations were performed in order to shed more light on this complex iron phosphate.

Melonjosephite shows *Pbam* symmetry, lattice parameters $a = 9.537(1)$ Å, $b = 10.839(1)$ Å, $c = 6.374(1)$ Å, $Z = 4$. A prominent feature of the structure is a linear chain of edge-sharing M1 octahedra aligned parallel the *c*-axis. Within this chain the average Fe(1)-O bond length is 2.076(2) Å. The octahedra are highly distorted in terms of the quadratic octahedral angle variance (OAV = 68.4°). An interesting feature are alternating short (2.968(1) Å) and long (3.406(1) Å) Fe-Fe interatomic distances within the infinite chain. Symmetry equivalent M(1)-site chains are cross-linked along the *a*-axis by edge-sharing dimers of $\text{Fe}(2)\text{O}_6(\text{OH})_2$ composition. The two Fe(2) octahedra, forming the dimer, exhibit an average Fe(2)-O bond length of 2.056(2) Å, the polyhedral distortion of this M(2) site is by far smaller than the one of the M(1) site. The interatomic Fe-Fe distance within the dimer is 3.220(1) Å. At both sites the average Fe-O bond lengths suggest a mixed occupation with Fe^{2+} and Fe^{3+} .

This assumption is proofed by the ^{57}Fe Mössbauer spectrum collected at 80 K. Four different subspectra, two for Fe^{2+} and two for Fe^{3+} , have to be used to adequately model the experimental spectrum at low temperature (80 K). Relative area ratios show that (i) about half of the iron is in the trivalent state and that (ii) Fe^{2+} and Fe^{3+} are equally distributed among both sites. At temperatures $T > 250$ K additional resonance absorption appears, which without doubt has to be ascribed to thermally induced fast electron hopping between Fe^{2+} and Fe^{3+} . The spectral signatures of this $\text{Fe}^{“2.5+”}$ becomes very evident at temperatures above 400 K where single peaks develop instead of broad absorption shoulders.

References

- [1] FRANSOLET, A.-M. (1973): Bull. Soc. Fr. Mineral. Cristallogr., 1973, 135 - 142.
- [2] KAMPF, A.R., MOORE, P.B. (1977): Am. Mineral. 62, 60 - 66.