

Localisation of iron in the structure of natural sinhalites

Weber, Sven-Ulf¹ Grodzicki, Michael¹ Redhammer, Günther¹ Lottermoser, Werner¹ Topa, Dan¹ Tippelt, Gerold¹ Amthauer, Georg¹

¹ Universität Salzburg, Fachbereich Materialforschung und Physik, Abteilung Mineralogie, A-5020 Salzburg

Natural sinhalite single crystals from Ratnapura District, Sri Lanka, and from Hamburg, Sussex, New Jersey, USA, were studied in order to determine the oxidation state and location of iron in the unit cell.

Microprobe measurements of the specimens were performed with high-grid resolution yielding the chemical composition $\text{Al}_{0.99}\text{Mg}_{0.93}\text{Fe}_{0.06}\text{B}_{1.03}\text{O}_4$ for the Ratnapura sinhalite and $\text{Al}_{0.99}\text{Mg}_{0.96}\text{Fe}_{0.03}\text{B}_{1.02}\text{O}_4$ for the Hamburg sinhalite. The crystals appear to be homogeneous.

Single-crystal data for both specimens were collected on a BRUKER SMART APEX 3-axes CCD-diffractometer and were refined assuming the experimentally determined chemical composition, space group $Pnma$, $Z=4$, and the initial fractional coordinates from Fang and Newnham (1965) assuming partial substitution of Mg by Fe. According to the results of the refinement the untwinned sinhalites have a slightly distorted hexagonal close-packed structure of oxygen atoms with Al^{3+} and Mg^{2+} occupying the octahedral and B^{3+} occupying the tetrahedral interstices of sinhalite, respectively. Al^{3+} occupies the smaller M1 position with point symmetry $\bar{3}2$, while Mg and Fe occupy the M2-site with point symmetry m . Both, the microprobe measurements and structure refinements reveal that iron substitutes for Mg^{2+} .

The ^{57}Fe Mössbauer spectra at RT exhibit two asymmetric lines, and are, thus, fitted with two different doublets. The isomer shift and quadrupole splitting values of both doublets are common for Fe^{2+} in a moderately distorted six-fold coordination. Hence, Fe^{2+} might be attributed to both octahedral sites with some preference for the larger M2 position following from the refined site occupancy of about 68% and 71% of the whole iron content, respectively. The Mössbauer spectrum does not exhibit any evidence for the presence of tetrahedrally coordinated Fe^{2+} or of Fe^{3+} in the sinhalite structure.

Electronic structure calculations in local spin-density approximation based on the crystallographic data yield hyperfine parameter for Fe^{2+} at the M2 position that are consistent with the experimental data. Calculated spectroscopic data for Fe^{2+} at the M1-site, however, are at variance with the Mössbauer- and NIR-measurements, as well as with the observed high-spin state. If, therefore, the M1-site is occupied with Fe^{2+} , at all, this must be accompanied by considerable expansion of the octahedron.

Acknowledgement: The authors thank H Bank, Idar-Oberstein, for providing the sinhalite samples. The support of the Austrian Fund for Scientific Research (FWF) under the grant number P18329-N20 is gratefully acknowledged.

Fang JH, Newnham RE (1965) The structure of sinhalite. *Min Mag* 35:196-199

Abs. No. **498**
Meeting: **DMG 2008**
submitted by: **Weber, Sven-Ulf**
email: **sven.weber@sbg.ac.at**
date: **2008-06-02**
Req. presentation: **Poster**
Req. session: **S08**