THE P21/C - C2/C PHASE TRANSITION IN KANOITE $MnMgSi_2O_6$; A SINGLE CRYSTAL X-RAY AND OPTICAL STUDY.

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Kanoite is a P21/c clinopyroxene with ideally $MnMgSi_2O_6$ composition. The structure of natural kanoite crystals was recently refined by GNOS et al. (1996) and the sample 6005 was also used for this high temperature study.

Kanoite was found to undergo a phase transition from P21/c to C2/c. The goal of this study was to investigate the structures and optical properties of low and high kanoite as a function of temperature. The lattice constants and the cell volume show considerable deviations from linearity. Above ca. 225°C c and a increase dramatically while b decreases slightly and reaches its absolute minimum at 240°C, representing the P–C transition. The intensities of the h+k odd reflections (forbidden in C2/c) remained sharp until they disappeared at 240 ± 10°C. The sharpness of h+k odd reflections indicates a large domain size (>100 nm). After equilibrating 2 days at 300°C, the transition temperature was found to increase slightly.

The structural data refined at 200°C and 270°C were used to model optical properties based on the point dipol model (ABBOTT, in press). The optical data for synthetic kanoite end-member were measured at RT: c^Z: 40°; $2V_z$: 54.5°; n(α): 1.699; n(β): 1.702; n(γ): 1.724 and used to calculate electronic polarizabilities. The optimised values are: α(Mg)= 0.48 Å^3, α(Mn)= 0.37 Å^3, α(Si)= 0.19 Å^3, $a(O_{non\ bridging})$= 1.40 Å3, $a(O_{bridging})$= 1.43 Å^3. The ratio of polarizabilities for M1/M2 was found to be linearly correlated to the ratio of M1/M2 ionic radii in clinopyroxenes. Calculation of optical properties for high temperature kanoite shows, that birefringence is increasing with temperature in low kanoite and even more obviously during the P-C-transition.

Heating a thin section on a fluid inclusion microscope, this increase of retardation was experimentally confirmed. A dramatic increase of retardation reflects the phase transition in agreement with the single-crystal X-ray data (figure). A two phase field was found over a temperature range of approx. 20°C.

In P21/c clinopyroxenes two symmetry independent tetrahedral chains are distinguished. In low kanoite the A chain is slightly S-rotated (O3A–O3A'–O3A"= 171.5° at 25°C and 173.3° at 200°C) while the O-rotated B chain is relatively kinked (O3B–O3B'–O3B"= 153.9 at 25°C and 157.2° at 200°C). In high kanoite the angles are equivalent in both chains (175.4° at 270°C) and O-rotated. The M2 position of low kanoite is coordinated by seven O atoms (5+2) while it is six-coordinated (4+2) in high kanoite. M2 is much stronger distorted than the M1-polyhedron. During the P21/c–C2/c-transition the average of the six shortest M2-O lengths decreases and there is no expansion in M1O6.

Strongly anisotropic and temperature dependent motion is observed for the bridging O3-position indicating a dynamic disorder of the O3–O3–O3 angle in high kanoite.

The data show that the structures of low (P21/c) and high kanoite (C2/c) are isotypic with the P21/c and C2/c modifications found in pigeonite and clinohypersthene. The transition temperature of 220°C is the lowest observed in clinopyroxenes and confirms a very low activation energy.

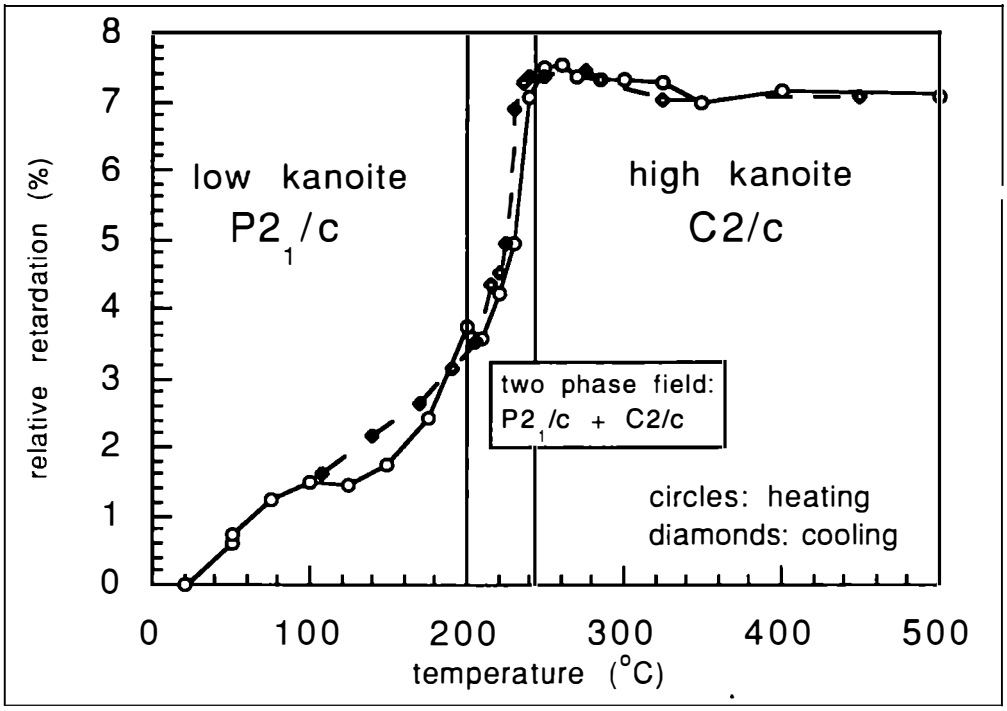

Figure:
relative retardation vs. temperature of kanoite, sample 6005

ABBOTT, R.N. (in press): Optical properties of C2/c pyroxenes: a point-dipole explanation. Submitted to the Canadian Mineralogist.

GNOS, E., ARMBRUSTER, T., NYFELER, D. (1996): Kanoite, donpeacorite and tirodite: Mn-Mg-silicates from a manganiferous quartzite in the United Arab Emirates. - Eur. J. Mineral., 8, 251-261.