Atom disorder and structural transitions in melanophlogite and tridymite

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Melanophlogite (MEP) is a mineral having composition 23SiO2.M12.3M14, where M12 denotes entagondodecahedral and M14 tetrakaidecahedral voids. MEP shows an alpha-beta structuraql transition at about 65 degree C. Among tridymite (TM) phases of silica, the monoclinic series belongs to space group Aa at room temperature (denoted usually as MC), and transforms to an orthorhombic phase in P212121 at about 105 degree C. The phase transition mechanisms in MEP and TM are reviewed based on recently published structural data(1, 2). The unit-cell parameters and mean-square displacements (MSD) of O atoms of monoclinic tridymite (MC) show only weak temperature dependences, but abruptly change to those of an orthorhombic phase, OP. On the other hand, the c-dimension and MSDs of O atoms in the low-temperature tetragonal phase (alpha) of MEP more steeply increase at higher temperatures up to those of the cubic high-temperature phase (beta).

The extremely large MSDs of O atoms in OP tridymite and beta-MEP, tetrahedrally coordinated to Si atoms with ordinary magnitudes of MSDs, arise from its disorder, probably orientational disorder of the corner-linked SiO4 units. However, the different temperature dependences noted above reflect the difference in the mechanisms of the respective transformations from MC to OP in tridymite and from alpha to beta in MEP. The disorder in beta-MEP is considered to occur involving 12 domains of alpha-MEP, and a similar, but partial disorder already occurs in alpha-MEP and becomes increasingly significant with increasing temperature. On the other hand, the O atom disorder in OP may occur between two potential energy minima, corresponding to two orientations of SiO4. It is important to note that the distortion of such SiO4 frameworks is not identified with that of MC, and no sign of disorder was indicated at all temperatures for MC. In conclusion, the alpha-to-beta transformation in MEP, appeared to be of the second order or tricritical one, is driven by increasing disorder of multiple domains of alpha-MEP with increasing temperature, whereas, in the MC-to-OP transformation, ordered MC suddenly changes to a disordered state over two orientations; the probable domain structures are of other than MC. In the present study, it is also argued that the near-to-second order or tricritical nature of phase transition in some minerals is resulted from temperature-dependent effects of disordering motions over multi-wells of potential energies, that is boosted by low-frequency phonon modes through coupling, if both the motions are symmetrically compatible with each other.

1)T. Hirose et al., J. Miner. Petrolo. Sci. 100, 55-69, 2005. 2) T. Nakagawa et al., J. Miner. Petrolo. Sci. 100, 247-259, 2005.