

## INFRARED AND RAMAN SPECTROSCOPIC STUDY ON GYROLITE-GROUP MINERALS

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Gyrolite,  $\text{Ca}_{16}[\text{Si}_8\text{O}_{20}]_3(\text{OH})_8 \cdot 14\text{H}_2\text{O}$ , is a member of the large family of the calcium-silicate-hydrate (C-S-H) phases, which are of great importance in cement chemistry. It occurs in hydrothermally-treated cement systems with low CaO/SiO<sub>2</sub>-ratios.

The mechanisms of incorporation of Zn and the reaction of the crystal structure of synthetic Ca-gyrolite upon heating in air at temperatures greater than 400 °C were investigated.

After our X-ray analysis Zn substitutes Ca in the so-called X octahedral layer consisting of isolated octahedra. The maximum substitution corresponds to  $\text{Zn}/(\text{Zn}+\text{Ca}) = 1/6$ . In this case the X layer is fully occupied by Zn:  $\text{Zn}_3\text{Ca}_4[\text{Si}_8\text{O}_{20}]_3\text{O}_2(\text{OH})_6 \cdot 14\text{H}_2\text{O}$ . Results from infrared spectroscopic investigations of a series of Zn substituted gyrolites between  $\text{Zn}/(\text{Zn}+\text{Ca}) = 0$  up to 1/6 will be presented. Incorporation of Zn causes a disorder in the positions of the OH groups pointing towards the X octahedral layer as shown by the disappearing of a well defined OH stretching band at 3615 cm<sup>-1</sup> characteristic for the pure Ca-gyrolite and the broadening of the main OH stretching band at 3638 cm<sup>-1</sup>. The two crystallographically different positions of H<sub>2</sub>O molecules (coordinating Ca and free water molecules) are reflected in the two bending bands at about 1633 and 1670 cm<sup>-1</sup>. Increasing Zn content changes the crystallographical environment of the water molecules shown by the “smearing” of the bending bands. In the case of a fully occupied X octahedral layer by Zn, the former free water molecules coordinate Zn octahedra. Correspondingly to that the higher frequency bending peak disappears. The intensity of the asymmetrical Q<sup>3</sup> Ca<sub>X</sub> – O – Si<sub>2</sub> bond stretching at about 1134 cm<sup>-1</sup> decreases relatively to the intensity of the 1148 cm<sup>-1</sup> peak with increasing Zn doping.

Synthetic Ca-gyrolite (consisting of single silicate sheets) transforms to a truscottite-like phase (single + double silicate sheets) upon heating at 400-600 °C in air as evidenced by XRD, IR and Raman spectroscopy. The trigger for the gyrolite – truscottite phase transition is the loss of the water molecules at 400 °C. There exists a correlation in the IR spectra between the decrease in the intensity of the main H<sub>2</sub>O bending band at 1633 cm<sup>-1</sup>, the disappearance of the shoulders at 1595 and 1666 cm<sup>-1</sup>, and the appearance of two additional OH stretching bands at about 3697 and 3740 cm<sup>-1</sup> after heating at 400 °C. We suppose that the new OH groups giving rise to the higher frequency bands at 3697 cm<sup>-1</sup>, appearing also in the Raman spectra are coordinated only by one Ca atom in the interstices of the truscottite-like structure. The FIR spectra of gyrolite heated at 400 and 500 °C support the idea that the main changes in the Ca structure occur during the gyrolite – truscottite phase transition at 400 °C. These are related to the transformation of two of the water molecules coordinating Ca<sub>X</sub> cations into OH groups thus provoking the breakdown of the Ca X-sheet. At the same time, two S<sub>2</sub> silicate sheets condense forming new 180° Si-O-Si bonds and giving rise to new symmetrical and asymmetrical Si-O-Si (Q<sup>4</sup>) stretching bands at about 806 and 1253 cm<sup>-1</sup> (IR) and 1182 cm<sup>-1</sup> (Raman).