

m22.p04

Raman and IR spectroscopic study of nano-crystalline calcium silicate hydrates of type C-S-H(I)

B. Gasharova¹), K. Garbev²), M. Bornefeld¹), L. Black³), P. Stemmermann²)

1) Institute for Synchrotron Radiation / ANKA, Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, D-76021 Karlsruhe, Germany 2) Institute for Technical Chemistry-TAB, Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, D-76021 Karlsruhe, Germany, 3) MERI, Sheffield Hallam University, Sheffield, S1 1WB, England

Keywords: C-S-H, Raman and IR spectroscopy, structure

Nano-crystalline calcium silicate hydrates (C-S-H gels) are formed upon hydration of Ca_3SiO_5 and $\beta\text{-Ca}_2\text{SiO}_4$, and are therefore the primary hydration products of Portland cements. Raman and IR spectra of a series of mechanochemically prepared C-S-H samples of type C-S-H(1) with Ca/Si ratios ranging from 0.4 to 1.5 reveal changes in structure dependent upon Ca/Si ratio. Finite silicate chains (Q^2) dominate the structures of the samples at Ca/Si ratios 0.4-1.0, the spectra showing characteristic symmetrical stretching bands between 1010 and 1020 cm^{-1} (R) and asymmetrical stretching around 965 cm^{-1} (IR), with Q^3 units present at Ca/Si \leq 0.75 (~1080 cm^{-1} (R)). Q^2 units give rise to an intense symmetrical bending vibration (SB) at ~670 cm^{-1} (R). Single chains of type "Dreierketten" may be regarded as composed of two paired Si tetrahedra (Si_p) interconnected by an additional bridging tetrahedron (Si_{br}). There is a very good correlation between the $\text{Si}_p\text{-O-Si}_p$ angles of crystalline phases composed of single silicate chains such as 14Å tobermorite, jennite, foshagite and wollastonite, and the SB (Q^2) vibrational frequency in their Raman spectra [1]. Following this we estimate the $\text{Si}_p\text{-O-Si}_p$ angles in our C-S-H(I) phases as being ~140°, which implies a closer relationship of C-S-H(I) phases to 14Å tobermorite than to jennite.

When the samples are measured in air, the Raman and IR spectra show carbonate bands arising from surface carbonation. The $\nu_1[\text{CO}_3]$ bands obscure the SS band of Q^3 units at about 1080 cm^{-1} (R), which is clearly seen in fresh samples analyzed in closed capillaries. At Ca/Si > 1.00, dimers (Q^1) are the main building unit of the silicate anionic structure (Raman bands at 890 cm^{-1} , IR band at 945 cm^{-1}). In these samples portlandite is also observed. The similarity of the silicate contribution to the spectra (R and IR) of the samples with Ca/Si = 1.33 and 1.50, and their differing portlandite contents, suggests a similar limit of incorporation of Ca into the C-S-H(I) structure in both phases, which lies under Ca/Si=1.33. In these phases we observe increased ordering of Ca-bonded OH groups. The same trend of increased ordering of the Ca environment is also seen in the development of the intensity and FWHM of the Ca-O band at 332 cm^{-1} (R), 255 cm^{-1} (IR) which is consistent with observations in the Ca2p XPS spectra [2].

[1] K. Garbev, PhD Thesis, Univ. of Heidelberg, Germany (2004).

[2] L. Black, K. Garbev, G. Beuchle, P. Stemmermann, D. Schild. Submitted to *Cement and Concrete Research*.

m22.p05

Radiospectroscopy of vein quartz of the subpolar ural deposits

E.N. Kotova

Institute of geology, Pervomajskaya str., 54, 167982, Syktyvkar, Russia.
E-mail: enkotova@geo.komisc.ru

Keywords: spectroscopy, quartz, mineral physics

The vein quartz and mountain crystal used as raw material for synthesis of monocrystals and melting of glass is characterized by a wide variety of the constitution and properties. The main task of the research is estimation of the contents of the structural impurity-related paramagnetic centers in basic industrial and potentially industrial quartz types of some Subpolar Ural deposits. This investigation is of interest as for the analysis of mineralogenesis conditions as for an estimation of quality of quartz raw materials. Researches were made using electron spin resonance (ESR) data on defects connected with isomorphous incorporation of Al- and Ge- ions into the lattice of vein quartz. ESR spectra of Al- and Ge-centres of the powder preparations of quartz were recorded with the radiospectrometer SE/X 2547 (RadioPAN, Poland) at 77 K and 300 K.

The carried out research has shown variety of the basic industrial types of vein quartz and mountain crystal under the contents paramagnetic aluminum and germanium centers. The increase of average values and of variations ranges of these centers concentrations from earlier primarily fine-grained vein quartz generation to later smoky and smoky-citrine quartz generations is stated. The positive correlation between the Al- and Ge-centers contents in quartz of various types was established. The received data on the contents of structural impurity in quartz characterize the quality of the Subpolar Ural quartz as raw material for melting of glass. Primarily fine-grained and granulated vein quartz, which widely advanced in the Subpolar Ural provinces, is regarded as less structural impured and potentially perspective.

The investigation was made within the financial support of the grant of the President of the Russian Federation (MK-1044.2005.5).