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OH ABSORPTION IN FLUORIDE GLASSES

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Hydroxyl absorption in fluoride glasses is considerably different from the one in silicate glasses. By the hydration in saturated steam at a high temperature, the weight of fluoride glasses decreases, while the one of silicate glasses increases. This phenomenon in fluoride glasses can be expressed by the following pyrohydrolysis process,

$$MF_{x(glass)} + yH_2O_{(vapor)} \longrightarrow MF_{x-y}(OH)_{y(glass)} + yHF_{(vapor)} \qquad (I)$$

(-2g equivalent per F^- and OH^- substitution)

and, in practice, HF evolution can be recognized in the course of the pyrohydrolysis. In IR spectra of hydrated silicate glasses, the absorptions of 6.1 μm by H-O-H bending, 4.2 - 3.6 μm by hydrogen bonding of SiOH---OSi, and 2.7 - 2.8 μm by H-O-H or SiO-H stretching can be observed(1). On the other hand, in fluoride glasses, only one absorption at 2.9 μm is observed, and the absorption by molecular water at 6.2 μm can be observed as a very weak absorption only at the final stage of long hydration. This means that, in the fluoride glasses, almost all hydroxyls exist as M-OH and not as molecular water. This can be explained as that the glass matrix of fluoride is easily attacked by H_2O, while the one of silicate is relatively stable, and therefore H_2O exists much more stably in silicates than in fluoride glasses. In addition, since the peak position of 2.9 μm band in fluoride glasses is in the lower energy region, M-OH seems to be forming weak hydrogen bonding with the surrounding F^- as M-OH---FM. The situation around the hydroxyls influences the absorptivity of the hydroxyls, in general.

The authors estimated molar extinction coefficients, ε, for OH in various fluoride glasses systematically by measuring the intensity change of OH absorption band during heating the glass under steam, which corresponds to the concentration of OH as indicated by equation (I). The values for OH in fluoride glasses are smaller than the one of pure silica(~ 90 l/mol•cm)(2) and are in the same range for multicomponent silicate glasses(~ 20 l/mol•cm)(3). For the system of ZrF_4, the values ε are the smallest and fall in the range of 8 to 20 l/mol•cm. The values ε for the other system of ZnF_2, AlF_3 or ThF_4 are relatively higher and they fall in the range of 21 to 38 l/mol•cm.

1 R.F. Bartholomew, et al., J. Am. Ceram. Soc., 63(1980)481.
2 J.P. Williams, et al., Ceram. Bull., 55(1976)524.
3 J.E. Shelby, et al., J. Am. Ceram. Soc., 65(1982)C-59.