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SOME ASPECTS OF REAL STRUCTURE AND THERMAL DECOMPOSITION OF K_2SiF_6

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Infrared, Raman and chemical studies have been carried out on hexafluorosilicates especially K_2SiF_6. There are some special features in the spectra which indicate that the real structure of K_2SiF_6 differs from the other hexafluorosilicates. Preliminary investigations indicate that siloxan bridges like those in fluorosiloxanes or oxofluorosilicates are formed due to replacement of fluorine by oxygen. K_2SiF_6 which is precipitated in alkaline solution contains in addition another type of siloxan bridges and silanol groups. It's assumed that silanol groups can be formed from substitution of fluorine by hydroxyl groups. In contrast Na_2SiF_6 is hydrolysed to SiO_2 and NaF in alkaline solution. IR spectra of K_2SiF_6 prepared in the normal way in acidic solution show protons to be present. Thermal decomposition between 673 and 773 K is dominated by hydrolysis reactions at open atmosphere. Two steps of hydrolysis are distinguished: At first SiO_2 and K_3SiF_7 are formed due to chemisorption of H_2O on K_2SiF_6. Then hydrolysis of K_3SiF_7 to potassium silicates begins only, when decomposition of K_2SiF_6 complete. Desorption processes and thermal dissociation of the surface layers are observed between 373 and 523 K. These processes are drastically changed by the conditions of precipitation. Thermal dissociation of the bulk according $3\ K_2SiF_6 \longrightarrow 2\ K_3SiF_7 + SiF_4$ is observed at 793 K. With rising potassium excess, K_3SiF_7 is formed at lower temperatures close to 523 K. The liberation of SiF_4 is discontinuous.