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Changes in the crystal structure of tsaregorodtsevite $[N(CH_3)_4][Si_2(Si_{0.5}Al_{0.5})O_6]_2$ on heating

Barbara L. Sherriff,[1] Elena V. Sokolova,[2] Janice Cramer,[1] Gerald Kunath-Fandrei,[3] Christian Jäger,[3] and Leonid A. Pautov[4]

[1]Department of Geological Sciences, University of Manitoba, Canada R3T 2N2
[2]Department of Crystallography, Faculty of Geology, Moscow State University, Moscow 119899, Russia
[3]Institut für Optik und Quantenelektronik, Friedrich-Schiller Universität, Max-Wien Platz 1, D-07743 Jena, Germany
[4]Mineralogical Museum, Il'men Natural Reserve, Miass 456301, Russia

Abstract

Tsaregorodtsevite $[N(CH_3)_4][Si_2(Si_{0.5}Al_{0.5})O_6]_2$ is a unique feldspathoid with a tetramethylammonium (TMA^+) organic cation in an ordered, sodalite-like framework of orthorhombic symmetry (*I*222) with a = 8.984(3), b = 8.937(2), and c = 8.927(2) Å. Here, ^{13}C cross polarization MAS and ^1H MAS NMR spectra give direct evidence that the organic material in the cavities in tsaregorodtsevite is TMA^+. The ^{27}Al and ^{29}Si MAS NMR spectra, and XRD data show that the framework is well ordered with Si in the T1 and T2 sites and both Si and Al in the T3 site. Upon heating, the colorless tsaregorodtsevite crystals change color becoming yellow, then brown, and finally black. In this study ^1H, ^{13}C, ^{27}Al, and ^{29}Si MAS NMR, powder XRD, and electron microprobe analyses are used to investigate the structural changes in tsaregorodtsevite on heating. The cell dimensions and T-O bond lengths decrease, and there are two phase changes. At 690 °C, the TMA^+ molecule breaks down to form aromatic rings and acidic groups, possibly including benzene and the pyridinium ion, with ammonia and other gases produced. The Al-Si framework changes slightly to give a less well-ordered tetragonal structure (I422), with a = 8.925(1), c = 8.908(1) Å, and a small amount of Al enters a separate phase. After heating at 970 °C, the organic material has further broken down with little C and H visible by NMR spectroscopy. The Al-Si framework forms at least two new phases: one with a cubic crystalline structure (I432) with a = 8.817(3) Å, and an amorphous aluminosilicate phase. There is a small residue of the initial structure even after heating for one hour at over 900 °C.