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The crystal structure of low melanophlogite

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ABSTRACT

The crystal structure of the low temperature form of natural melanophlogite, $46SiO_2 \cdot 6M^{14} \cdot 2M^{12}$ ($M^{14} = N_2$, CO_2; $M^{12} = CH_4$, N_2), was determined using single-crystal X-ray diffraction data at room temperature. The structure is tetragonal with space group $P4_2/nbc$ and unit cell $a = 26.818(2)$ and $c = 13.365(1)$ Å, which is the $(2 \times 2 \times 1)$ superstructure of high-temperature cubic melanophlogite and includes four formula units. The structure with 335 variable parameters including anisotropic temperature factors (or atomic displacement factors) was refined to $R = 0.0288$ for 2706 observed reflections. The main silica framework consists of nearly regular SiO_4 tetrahedra forming large internal voids represented by distorted tetrakaidecahedra and pentagondodecahedra, which accommodate CO_2 or N_2 and CH_4 or N_2 guest molecules, respectively.

This low temperature form is a displacive variant of the cubic high-temperature form. The mean bond length is 1.588(4) Å for Si-O, and the bond angles for Si-O-Si are distributed over a large range from about 145 to 171° with a mean value of 159.4(3)°. The thermal vibrations of Si are nearly isotropic with amplitudes approximately equal to the average mean square displacement of 0.0119(4) Å^2. The thermal vibrations of the O atoms are highly anisotropic with a wide range of mean square displacements. There is a positive correlation between the Si-O-Si bond angles and the mean-square displacements of the O atoms.