

## The crystal structure of low melanophlogite

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### ABSTRACT

The crystal structure of the low temperature form of natural melanophlogite,  $46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$  ( $\text{M}^{14} = \text{N}_2, \text{CO}_2$ ;  $\text{M}^{12} = \text{CH}_4, \text{N}_2$ ), 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  $\text{SiO}_4$  tetrahedra forming large internal voids represented by distorted tetrakaidecahedra and pentagonododecahedra, which accommodate  $\text{CO}_2$  or  $\text{N}_2$  and  $\text{CH}_4$  or  $\text{N}_2$  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  $171^\circ$  with a mean value of  $159.4(3)^\circ$ . The thermal vibrations of Si are nearly isotropic with amplitudes approximately equal to the average mean square displacement of  $0.0119(4)$  Å<sup>2</sup>. 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.