Structural study of ellenbergerite. Part I: Effects of high temperature

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Abstract: The thermal behaviour of ellenbergerite, a nesosilicate recently found in a high-pressure assemblage of the Dora-Maira massif, Western Alps, was studied between 20 and 754°C employing a microfurnace connected with a single-crystal diffractometer. The ellenbergerite chemical formula is \( [\text{Mg},(\text{Ti},\text{Zr}),\square\square_2\text{Mg}_6(\text{Al},\text{Mg})_6(\text{Si},\text{P})_8\text{O}_{28}(\text{OH})_{10}] \). Its hexagonal structure, space group \( P6_3 \), consists of single chains of face-sharing octahedra partially occupied by Mg and Ti or Zr and double chains consisting of couples of face-sharing octahedra occupied by Mg and Al linked by edges along the \( c \) axis. Isolated SiO\(_4\) tetrahedra interconnect the octahedral chains.

The lattice parameters measured at different temperatures increase according to the following equations:

\[
\frac{a}{a_0} = 1 + 5.50 \times 10^{-6} T + 3.46 \times 10^{-9} T^2
\]

\[
\frac{c}{c_0} = 1 + 7.94 \times 10^{-6} T + 4.65 \times 10^{-9} T^2
\]

\[
\frac{V}{V_0} = 1 + 1.86 \times 10^{-5} T + 1.20 \times 10^{-8} T^2
\]

where \( T \) is in °C.

The average coefficients of thermal expansion between 20 and 800°C are \( \bar{\alpha}_a = 8.2 \times 10^{-6} \text{°C}^{-1} \), \( \bar{\alpha}_c = 11.5 \times 10^{-6} \text{°C}^{-1} \) and \( \bar{\alpha}_V = 27.7 \times 10^{-6} \text{°C}^{-1} \).

The structure was refined at room conditions \( (R = 2.9\% \text{ for } 730 \text{ independent reflections}) \) and with data collected from crystals in the heating device at 20, 410 and 668°C \( (R = 3.3, 3.2 \text{ and } 3.5\% \text{ respectively, for } 355, 384 \text{ and } 363 \text{ independent reflections}) \).

The mean thermal expansion coefficient of the octahedron of the single chain is \( 3.09 \times 10^{-5} \text{°C}^{-1} \), whereas those of Mg and Al octahedra of the double chain are \( 2.99 \times 10^{-5} \) and \( 3.40 \times 10^{-5} \text{°C}^{-1} \), respectively. The temperature increases the off-centre shift of Mg and Al in the double chain, reducing the electrostatic repulsion, and does not produce centring of Ti in the single octahedral chain. No significant tetrahedral tilting is observed on heating. The irreversible weakening of the intensity of diffraction effects observed above 754°C, symptom of crystal damage, can be probably ascribed to loss of hydrogens.

Key-words: ellenbergerite, thermal expansion, high-temperature, crystal structure.

1. Introduction

Ellenbergerite is a silicate recently found as inclusions in pyrope from a phengite-quartzite layer of the Dora-Maira massif, Western Alps (Chopin, 1986; Chopin et al., 1986), where also coesite was found (Chopin, 1984). These rocks were formed under low-temperature, high-pressure conditions, about 700-800°C and 25-30 kbar, corresponding to geothermal gradients lower than 10°C/km.

Ellenbergerite, with the ideal formula \( [\text{Mg},(\text{Ti},\text{Zr}),\square\square_2\text{Mg}_6(\text{Al},\text{Mg})_6(\text{Si},\text{P})_8\text{O}_{28}(\text{OH})_{10}] \), is an orthosilicate (space group \( P6_3 \) or \( P6_3/mc \) for...