SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBQUITOUS MINERALS AND MATERIALS

High-pressure behavior of thiospinel \( \text{CuCr}_2\text{S}_4 \)

MATTEO ALVARO\(^1,2,3,\ast\), FABRIZIO NESTOLA\(^4\), NANCY ROSS\(^5\), M. CHIARA DOMENEGHETTI\(^6\) AND LEONID REZNITSKY\(^7\)

\(^1\)Dipartimento di Geoscienze e Georisorse, Università degli Studi di Padova, Via G. Gradenigo 6, 35122 Padova, Italy
\(^2\)Department of Geosciences, Crystallography Lab, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24060, U.S.A.
\(^3\)Dipartimento di Scienze della Terra e dell’Ambiente, Università degli studi di Padova, Via A. Ferrata 1, 27100 Pavia, Italy
\(^4\)Institute of the Earth’s Crust, Siberian Branch, Russian Academy of Science, Lermontovsk str., 128, 664033 Irkutsk, Russia

ABSTRACT

This study reports for the first time the lattice parameters and the complete crystal structure evolution with increasing pressure for a thiospinel with composition \( \text{CuCr}_2\text{V}_6\text{S}_4 \) (space group \( \text{Fd} \text{Abm} \)) measured by single-crystal X-ray diffraction as a function of pressure up to 7 GPa. The \( P-V \) data are adequately described to a fourth-order Birch-Murnaghan equation of state with the following coefficients: \( V_0 = 947.8(6) \, \AA^3 \), \( K_T = 88(1) \), and \( \text{K}'' = 6.3(9), \text{K}'' = -1.1(4) \). This is the first time that the compressibility behavior of a spinel structure has been described by a fourth-order Birch-Murnaghan equation of state. The unit-cell volume shows a compression of about 6.3% over the entire pressure range investigated. The crystal structure evolution clearly indicates that the main compression mechanism is related to the compression of the \( \text{CuS}_4 \) tetrahedron, which is significantly greater than the \( \text{CrS}_4 \) octahedron. The tetrahedral volume decreases by 7.8% over the pressure range studied while the octahedral volume decreases by 5.5%. The change in the octahedral volume is accompanied by a decrease in the angular distortion of the \( \text{CrS}_4 \) octahedra.

Keywords: Thiospinel, high pressure, single-crystal X-ray diffraction

INTRODUCTION

\( \text{CuCr}_2\text{S}_4 \) belongs to the thiospinel group and crystallizes in the cubic spinel structure (space group \( \text{Fd} \text{Abm} \)). It is a normal spinel with \( \text{Cu}^{2+} \) occupying the tetrahedrally coordinated sites and the \( \text{Cr}^{3+} \) occupying the octahedrally coordinated sites. In the last decade, this class of compounds has attracted great interest because of their unusual optical, electrical, and magnetic properties (Berry et al. 2007; Dmitrieva et al. 2007; Haacke and Beagle 1968; Ito et al. 2003, 2006; Koroleva et al. 1991; Lotgering 1964; Masour et al. 2011; Nogues et al. 1979; Saha-Dasgupta et al. 2007; Samokhvalov et al. 1976a; Siberchicot 1993; Snyder et al. 2001; Tewari et al. 2010; Tressler and Stubican 1968; Zub 1983). Many phases belonging to the thiospinel group, with the same symmetry as \( \text{CuCr}_2\text{S}_4 \) (\( \text{Fd} \text{Abm} \)) have shown interesting structure-property changes under extreme high-temperature and high-pressure conditions. For example, it was demonstrated that some thiospinels undergo structural phase transitions at high pressure that are correlated changes in their magnetic properties (i.e., Garg et al. 2007; Ito et al. 2003; Nakamoto et al. 2005). It is, therefore, crucial to investigate the structural evolution of such important materials, which closely correlate with their unusual material properties.

In particular \( \text{CuCr}_2\text{S}_4 \) has always been considered to be a good candidate as a base material for the production of magneto-optical devices and as cathodes for Li-secondary batteries (Imanishi et al. 1993; Saha-Dasgupta et al. 2007). Because of its unique features involving magnetic phase transitions (i.e., higher ferromagnetic, metal-insulator, and semiconductor-metal phase transitions), \( \text{CuCr}_2\text{S}_4 \) has been investigated under low- and high-temperature conditions to better understand how resistivity, conductivity, and ferromagnetic properties are affected under non-ambient conditions (Albers and Rooymans 1965; Banus and Lavine 1969; Ito et al. 2003; Samokhvalov et al. 1976a, 1976b; Tressler et al. 1968). In this study, we present results of the elastic properties and crystal structure evolution of \( \text{CuCr}_2\text{S}_4 \) as a function of pressure to evaluate how chemical composition variations affect the high-pressure behavior in the thiospinel group.

EXPERIMENTAL METHODS

The natural crystal investigated in this study was selected from the same crystal batch studied by Reznitsky et al. (2011) who determined the following composition: \( (\text{Cu}_{0.95}\text{Fe}_{0.05})\text{Zn}_{0.1}\text{Al}_{1.9} \). \( (\text{Cr}_{0.9}\text{V}_{0.1}\text{As}_{0.05}) \text{S}_{4.0} \) (hereafter abbreviated as \( \text{CuCr}_2\text{V}_6\text{S}_4 \)). The crystal studied under high-pressure conditions (size \( 0.130 \times 0.090 \times 0.060 \, \text{mm} \)) was selected on the basis of its size, absence of twinning, and X-ray diffraction profiles. The crystal was loaded in an ETH-type diamond-anvil cell (DAC, Miletich et al. 2000) using a steel gasket (T301) pre-indented to a thickness of 90 \( \mu \text{m} \) and with a hole of 250 \( \mu \text{m} \) in diameter. A single crystal of quartz was used as an internal pressure measurement standard (Angel et al. 1997) and a 4:1 mixture of methanol:ethanol was used as pressure medium, which remains hydrostatic throughout the entire pressure range investigated (Angel et al. 2007). The unit-cell parameters were determined by single-crystal X-ray diffraction using a Huber four-circle diffractometer (monochromatized MoKα radiation) operating at 50 kV and 40 mA, automated by the SINGLE software (Angel and Finger 2011). The unit-cell parameters were measured at 13 different pressures.