Alacranite, As₈S₉: structural study of the holotype and re-assignment of the original chemical formula

PAOLA BONAZZI,1,* LUCA BINDI,1,2 VALENTINA POPOVA,3 GIOVANNI PRATESI,1,2 AND SILVIO MENCHETTI1

1Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4, Firenze, Italy
2Museo di Storia Naturale, sez. di Mineralogia e Litologia, Università degli Studi di Firenze, via La Pira 4, Firenze, Italy
3Institute for Mineralogy, Urals Branch of RAS, Chelyabinsk district, Miass 456317, Russian Federation

ABSTRACT

Alacranite from the type locality (Uzon caldera, Kamchatka, Russian Federation) was submitted for structural analysis. A single crystal was selected and the following lattice parameters were determined: a = 9.942(4), b = 9.601(2), c = 9.178(3) Å, β = 101.94(3)°, V = 857.1 (5) Å³. The crystal structure was solved in the P2/c space group using direct methods and refined to R = 6.79% for 472 observed reflections. The structure of alacranite consists of an ordered sequence of As₂S₄ and As₄S₅ cage-like molecules, with a molecular packing closely resembling that found in the β-As₄S₅ phase. Both As-As and As-S intramolecular distances are in the range usually observed for covalent bonds.

The structural model confirms the chemical formula As₂S₄ for alacranite, and accounts for differences in the unit-cell parameters of alacranite compared to those of the natural analogue of β-As₄S₅. This latter mineral, therefore, should receive a new name.

INTRODUCTION

Alacranite, As₈S₉, was first found by Popova et al. (1986) at the Uzon caldera (Kamchatka, Russian Federation). Due to the similarity of its XRD powder pattern, these authors assumed the mineral to be identical to the species occurring in the Ag-As-Sb vein deposit at Alacràn (Chile) and described by Clark (1970) as a natural high-temperature As₂S₅ phase. For this reason, the mineral was named alacranite. However, the lattice parameters of alacranite resemble barely those of the natural β-phase from Alacràn (Clark 1970) and those of synthetic β-As₂S₅ (Porter and Sheldrick 1972; Bonazzi et al. 1996). In particular, alacranite exhibits a greater unit-cell volume, in keeping with the different chemical composition. Due to the low diffraction quality of alacranite crystals, the crystal structure remained unsolved; however, single crystal X-ray rotation photographs indicated space group P2/c, while synthetic β-As₂S₅ crystallizes in space group C2/c (Porter and Sheldrick 1972). The mineral and name were approved by the NMMN-IMA Commission (Hawthorne et al. 1988) for a species having chemical formula As₂S₄ and space group C2/c in the recently published Mineralogical Tables (Strunz and Nickel 2001) as well as in The American Mineralogist crystal structure database (Downs and Hall-Wallace 2003).

More recently, Bonazzi et al. (2003) studied non-stoichiometric sulfide minerals from the Katerina mine (Czech Republic) with chemical compositions ranging continuously from As₂S₄ to As₂S₅ and observed a gradual change of the translation lattice symmetry from C to P, together with a linear increase of unit-cell volume as a function of the S content.

From the results of their structural study, Bonazzi et al. (2003) also found that the non-stoichiometric As₂S₅–As₂S₄ compounds crystallize as disordered mixtures of As₂S₄ and As₂S₅ molecules packed in the same way as in the β-As₂S₅ phase. Because the As₂S₅ stoichiometry (alacranite s.s.) seems to be the upper limit of the compositional range, the non-stoichiometric sulfides from Katerina mine were assumed to consist of both As₂S₄(C2/c) and As₂S₅(P2/c) microdomains. This hypothesis explains the observed gradual change of the translation symmetry along the series. On this basis, one can speculate that the alacranite structure consists of an ordered sequence of As₂S₅ and As₂S₄ molecules.

In order to check this hypothesis, a crystal of the original sample from the Uzon caldera was examined from the structural point of view.

EXPERIMENTAL AND STRUCTURE SOLUTION

Several crystals of the alacranite holotype (preserved at the Institute for Mineralogy, Urals Branch of RAS, Chelyabinsk district, Miass 456317, Russian Federation, catalogue number U-2) were mounted on an Enraf-Nonius CAD4 single-crystal diffractometer and examined with graphite-monochromatized MoKα radiation. Most were found to be composed of multiple crystallites. A single crystal (approximately 30 × 60 × 120 mm) of relatively high diffraction quality was selected for the structural study.

Unit-cell dimensions (reported in Table 1 together with data from the litera-