

**Discovery and structural characterization of zolenskyite, FeCr₂S₄, in the
Muonionalusta meteorite: Advancing micron-scale mineralogy in planetary
science**

Luca Bindi^{1,*}, Dan Holtstam²

¹Dipartimento di Scienze della Terra, Università degli Studi di Firenze, via La Pira 4,
I-50121 Firenze, Italy

²Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-
10405 Stockholm, Sweden

*luca.bindi@unifi.it

Abstract

Here we present the first single-crystal X-ray diffraction analysis of zolenskyite, a chromium-bearing sulfide mineral (FeCr₂S₄) and newly identified polymorph of daubréelite, discovered in the Muonionalusta meteorite, a well-characterized IVA iron meteorite. Zolenskyite occurs as rare micron-scale grains closely associated with daubréelite and stishovite, within a troilite matrix. Chemical analysis confirms a pure, homogeneous FeCr₂S₄ composition. The crystal structure was refined in the monoclinic *C2/m* space group, revealing a framework of face-sharing octahedra, consistent with a cation-deficient NiAs-type structure, distinct from the spinel-type structure of daubréelite. Zolenskyite forms under high-pressure (>7 GPa) and high-temperature (>1000 K) conditions, likely through solid-state transformation from daubréelite during shock events. The serendipitous recognition of zolenskyite emphasizes the value of careful micron-scale mineralogical investigations in revealing transient or metastable phases that record otherwise inaccessible

physicochemical conditions. These findings contribute to understanding the thermal and shock history of meteorite parent bodies and the stability of Fe–Cr sulfides in extraterrestrial environments.

Keywords: zolenskyite; daubréelite; FeCr₂S₄; Muonionalusta; iron meteorite; shock metamorphism; crystal structure; thiospinel; nickeline derivative structure; X-ray diffraction; micron-scale mineralogical studies.

Introduction

The study of extraterrestrial minerals provides critical insights into the physicochemical conditions that prevailed during the early history of the Solar System. Among these, sulfide minerals play a significant role to shed light on thermal metamorphism, redox conditions, and differentiation processes within planetary bodies (e.g., Brett and Bell, 1969; Fleet, 2006). One among such minerals, zolenskyite, a chromium-bearing sulfide that represents a polymorph of FeCr₂S₄ after daubréelite, has recently been discovered in the Indarch meteorite (EH chondrite), but its crystal structure has not been conclusively determined (Ma and Rubin, 2022). This work presents the first single-crystal X-ray diffraction analysis of zolenskyite, identified for the first time in the Muonionalusta meteorite. Muonionalusta is classified as an octahedrite belonging to group IVA, which represents approximately 8% of all known iron meteorites. Its primary mineral composition – with the metal fraction containing about 9 wt.% nickel and 0.4 wt.% cobalt (Hidaka *et al.*, 2019) – has been thoroughly documented in earlier studies (Buchwald, 1975; Holtstam *et al.*, 2003; Ahlgren *et al.*, 2016). The Muonionalusta meteoroid is believed to have been ejected from its parent body roughly 400 million years ago during a high-energy impact event (Blichert-Toft *et al.*, 2010). It entered Earth's atmosphere, likely during the Middle

Pleistocene, fragmented during atmospheric entry, and dispersed across a wide region (Lagerbäck and Wickman, 1997).

Zolenskyite is part of a broader group of sulfides that includes rare and metastable phases often formed under non-equilibrium conditions, such as shock or rapid cooling, commonly encountered in meteoritic environments (e.g., Leroux *et al.*, 2008; Miyahara *et al.*, 2021). Its occurrence in the Muonionalusta meteorite is particularly notable due to the meteorite's history of high-temperature processes, followed by slow cooling and multiple shock events (Yang *et al.*, 2010). The presence and characteristics of zolenskyite in this context can thus provide important clues regarding the metamorphic and impact history of its parent body.

The structural determination of zolenskyite is essential not only for mineralogical classification but also for understanding the conditions of its formation and stability. Previous studies have relied primarily on electron-backscatter diffraction, limiting the accuracy of atomic positional data (Ma and Rubin, 2022). By applying single-crystal X-ray diffraction techniques, we here provide a precise and unambiguous characterization of this mineral, contributing significantly to the mineralogical dataset of meteoritic sulfides.

Moreover, the recognition and structural resolution of μm -sized phases such as zolenskyite underscore the growing importance of micron-scale mineralogy in planetary science. Submicron-sized mineral inclusions often record high-resolution signatures of physicochemical processes that are otherwise undetectable in bulk analyses (e.g., Xu *et al.*, 2017). Such studies do not only expand our mineralogical knowledge but also aid in a better reconstruction of the formation environments of meteorites and their parent bodies.

This paper reports the occurrence, description, and crystal structure of zolenskyite from the Muonionalusta meteorite. The findings provide new constraints on the formation conditions of Fe–Cr sulfides in iron meteorites and highlight the value of high-resolution mineralogical analysis in decoding planetary processes.

Occurrence of zolenskyite in Muonionalusta

Zolenskyite occurrence in Muonionalusta is very rare. It occurs in μm -sized grains closely associated with daubréelite (the other FeCr_2S_4 polymorph) in a troilite matrix (Fig. 1). Zolenskyite was found in the Muonionalusta sample originally studied by Holtstam *et al.* (2003), from the collections of the Swedish Museum of Natural History, catalogue no. GEO-NRM 20020049. These authors identified stishovite (pseudomorph after tridymite), chromite, hisingerite and schreibersite by means of a combination of micron-Raman spectroscopy and X-ray powder diffraction.

Chemical Composition

The chemical composition of zolenskyite was qualitatively analyzed with energy-dispersive microanalysis (EDS, Fig. 2) with a ZEISS EVO 15-MA scanning electron microscope equipped with microanalysis EDS system Oxford UltimMax 40 (Oxford Instruments, UK). SEM-EDS X-ray maps and analyses were performed with an acceleration voltage of 15 kV and nominal beam current of 0.7 nA, acquiring spectra for 20 seconds live time. The analyses (4 spot analyses) did not show the presence of elements ($Z > 9$) other than Fe, Cr, and S (Fig. 2b) and indicate a chemically homogeneous mineral within analytical uncertainties of our measurements. X-ray compositional maps were also collected from a large area (Fig. 2a). The derived empirical formula for zolenskyite is close to pure FeCr_2S_4 .

X-ray single-crystal diffraction

A small zolenskyite fragment ($0.02 \times 0.02 \times 0.01 \text{ mm}^3$ in size) from Muonionalusta (Fig. 1) was extracted from the polished section under a reflected light microscope and mounted on a $5 \text{ }\mu\text{m}$ diameter carbon fiber, which was, in turn, attached to a glass rod. The fragment consists of crystalline zolenskyite [unit-cell parameters: $a = 12.8345(11)$, $b = 3.4359(3)$, $c = 5.9345(5) \text{ }\text{\AA}$, $\beta = 116.832(6)^\circ$, $V = 233.52(4) \text{ }\text{\AA}^3$ and $Z = 2$; space group $C2/m$] associated to minor, fine-grained polycrystalline troilite. Single-crystal X-ray diffraction intensity data of zolenskyite were collected with a Bruker D8 Venture Photon 100 CMOS equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation (Table 1). The detector-to-crystal distance was 5 cm. Data were collected using ω and ϕ scan modes, in 0.5° slices, with an exposure time of 20 s per frame. The data were corrected for Lorentz and polarization factors and absorption using the software package *APEX3* (Bruker, 2023). A total of 633 unique reflections was collected. Given the similarity in unit-cell values and space groups, the structure was refined starting from the atomic coordinates reported for the $C2/m$ CrNb_2Se_4 - Cr_3S_4 -type structure of synthetic FeCr_2S_4 (Tressler *et al.*, 1968), using the program SHELXL-2018 (Sheldrick, 2015). The site occupancy factor at the cation sites was allowed to vary [Fe (and Cr) vs. structural vacancy for the two octahedral sites] using scattering curves for neutral atoms taken from the *International Tables for Crystallography* (Wilson, 1992) but was found to be 26 and 24 e^- for the Fe and Cr positions, respectively. It was then fixed in the subsequent refinement cycles. At the last stage, with anisotropic displacement parameters for all the atoms, the structure was refined to $R1 = 0.0206$ using 633 independent reflections.

Atomic coordinates are given in Table 2. Selected bond distances are shown in Table 3. A Crystallographic Information File (CIF) is deposited.

Results and Discussion

Crystal-chemical remarks

FeCr_2S_4 can crystallize in two distinct structural forms – one adopting the thiospinel structure and the other based on a nickeline-type (NiAs-derived) structure – each exhibiting quantitatively different crystallographic, electronic, and magnetic properties that reflect their underlying atomic arrangements. In the thiospinel structure, the mineral daubréelite, FeCr_2S_4 crystallizes in the cubic system with space group $Fd-3m$, exhibiting a lattice parameter typically around 9.97 Å (Lundqvist, 1943). In this configuration, Fe^{2+} occupies the tetrahedral (8a) sites while Cr^{3+} resides on the octahedral (16d) sites, leading to a well-ordered distribution of cations. The sulfur anions form a close-packed face-centered cubic sublattice, creating a three-dimensional network of Fe–S–Cr super-exchange paths.

By contrast, in the NiAs-type derivative structure, FeCr_2S_4 can show two distinct arrangements: (i) the classic hexagonal structure in which the cations and vacancies are disordered; (ii) the monoclinic structure in which A^{2+} ions and vacancies occupy the same plane, and the B^{3+} ions occupy filled alternate planes. Zolenskyite crystallizes in this second type with the structure made up of face-sharing octahedra (Fig. 3).

The NiAs-derived phase often displays semimetallic or metallic conductivity due to increased cation–anion–cation orbital overlap and reduced cation ordering, resulting in diminished electronic localization (Motizuki *et al.*, 1986). Magnetically, this phase may exhibit weaker long-range order or different transition behaviour, often lacking the well-defined ferrimagnetic transition seen in the spinel form. The effective magnetic moments in the NiAs-type structure can be significantly reduced

due to itinerant behaviour or spin compensation effects, and the magnetic susceptibility typically shows a more Pauli-like response.

From a thermodynamic standpoint, the thiospinel structure is the stable equilibrium phase under ambient pressure and moderate temperatures, while the NiAs-type derivative is generally metastable or stabilized only under non-ambient conditions, such as pressures above 5 GPa or through rapid quenching techniques. The energy difference between these phases is subtle – estimated in DFT calculations to be within tens of meV per formula unit – making the relative stability sensitive to factors like stoichiometry, strain, or defect chemistry (e.g. Amiel *et al.*, 2011).

Zolenskyite is the Fe-analogue of brezinaite (ideally Cr_3S_4) or the Cr-analog of heideite (FeTi_2S_4).

Origin

Shock conditions estimated for the Muonionalusta meteorite are in the P range 13–40 GPa and T range 1200–1300 K (Jain and Lipschutz, 1970; Buchwald, 1975). Experiments show that daubréelite can convert into zolenskyite at high pressures and relatively low temperatures (e.g., 5.5 GPa, 520 °C; 3 GPa, 200 °C; Tressler *et al.*, 1968). On the basis of the coexistence of zolenskyite with stishovite (Fig. 1), we suggest that zolenskyite crystallized by solid state transformation from daubréelite at a temperature > 1000 K and pressure \geq 7 GPa.

Implications

The micron-scale mineralogy studies of meteorites carry profound implications for understanding planetary processes across the solar system. The studies of high-pressure minerals can help to shed light on high-temperature events, shock metamorphism, and aqueous alteration that occurred during the early formation and

evolution of planetary bodies. Micron and submicron-sized minerals, indeed, often preserve conditions that are otherwise lost at larger scales, enabling the reconstruction of thermal histories, chemical exchanges, and dynamic processes within asteroids and protoplanets. Furthermore, micron-scale mineralogical analyses can reveal the presence of exotic or transient phases, offering clues about the environments in which these materials formed.

Although zolenskyite in shock veins may be due to kinetic factors as a metastable crystallization due to rapid cooling during decompression from the peak shock pressures experienced by the meteorite, new theoretical and experimental studies of the stability of thiospinel-related structures are clearly needed.

Acknowledgments

The paper benefited by the official reviews made by Pete Leverett and two anonymous reviewers. This study was conducted within the Space It Up project funded by the Italian Space Agency, ASI, and the Ministry of University and Research, MUR, under contract n. 2024-5-E.0-CUP n. I53D24000060005.

Competing interests: The authors declare none.

References

- Ahlgren, K., Wasson, J.T. and Haack, H. (2016) Chemical and structural features of Muonionalusta and other IVA iron meteorites: Evidence for complex parent-body history. *Geochimica et Cosmochimica Acta*, **188**, 245–259.
- Amiel, Y., Rozenberg, G. Kh., Nissim, N., Milner, A., Pasternak, M.P., Hanfland, M. and Taylor, R.D. (2011) Intricate relationship between pressure-induced electronic and structural transformations in FeCr₂S₄. *Physical Review B*, **84**, 224114.

- Blichert-Toft J., Moynier F., Lee C.T.A., Telouk P. and Albarède F. (2010) The early formation of the IVA iron meteorite parent body. *Earth and Planetary Science Letters*, **296**, 469–480.
- Brett, R. and Bell, P.M. (1969) Sulfide phase equilibria in meteoritic materials. *Geochimica et Cosmochimica Acta*, **33**, 1135–1151.
- Bruker (2023) APEX5 software suite. *Bruker AXS Inc.*, Madison, Wisconsin, USA.
- Buchwald V.F. (1975) *Handbook of iron meteorites. Their history, distribution, composition and structure*. University of California Press, Berkeley, 1426 pp.
- Fleet, M.E. (2006) *Phase equilibria of sulfide minerals*. Mineralogical Association of Canada Short Course Series.
- Hidaka Y., Shirai N., Yamaguchi A. and Ebihara M. (2019) Siderophile element characteristics of acapulcoite–lodranites and winonaite: Implications for the early differentiation processes of their parent bodies. *Meteoritics & Planetary Science*, **54**, 1153–1166.
- Holtstam, D., Broman, C., Söderhielm, J. and Zetterqvist, A. (2003) First discovery of stishovite in an iron meteorite. *Meteoritics & Planetary Science*, **38**, 1579–1583.
- Jain A.V. and Lipschutz M.E. (1970) On preferred disorder and the shock history of chemical group IVA meteorites. *Geochimica et Cosmochimica Acta*, **34**, 883–892.
- Lagerbäck R. and Wickman F.E. (1997) A new iron meteorite from Muonionalusta, northernmost Sweden. *GFF*, **119**, 193–198.
- Leroux, H., Cuvillier, P. and Zanda, B. (2008) A TEM study of high-pressure phases in the Tenham chondrite: Clues to shock conditions. *Geochimica et Cosmochimica Acta*, **72**, 5471–5482.

- Lundqvist, D. (1943) Crystal structure of daubréelite. *Arkiv för Kemi, Mineralogi och Geologi*, **17B**, 1–4.
- Ma, C. and Rubin, A.E. (2022) Zolenskyite, FeCr_2S_4 , a new sulfide mineral from the Indarch meteorite. *American Mineralogist*, **107**, 1030–1033.
- Miyahara, M., Tomioka, N. and Bindi, L. (2021) Natural and experimental high-pressure, shock-produced terrestrial and extraterrestrial materials. *Progress in Earth and Planetary Science*, **8**, 59.
- Motizuki, K., Katoh K. and Yanase, A. (1986) Electronic band structures of NiAs-type compounds. I. Nonmagnetic state. *Journal of Physics C: Solid State Physics*, **19**, 495.
- Sheldrick, G.M. (2015) Structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.
- Tressler R.E., Hummel, F.A. and Stubican, V.S. (1968) Pressure-temperature study of sulfospinel. *Journal of the American Ceramic Society*, **51**, 648–651.
- Wilson, A.J.C. (1992) International Tables for Crystallography. Volume C: Mathematical, Physical and Chemical Tables. *Kluwer Academic Publishers*, Amsterdam.
- Xu, H., Wang, J. and Liu, X. (2017) Nanomineralogy of meteorites: Unveiling the nanoscale record of solar system processes. *American Mineralogist*, **102**, 520–536.
- Yang, J., Goldstein, J.I. and Scott, E.R.D. (2010) Metallographic cooling rates and origin of IVA iron meteorites. *Geochimica et Cosmochimica Acta*, **74**, 4493–4506.

Figure Captions

Figure 1. SEM-BSE image of a portion of the studied Muonionalusta sample. All the phases have been labelled.

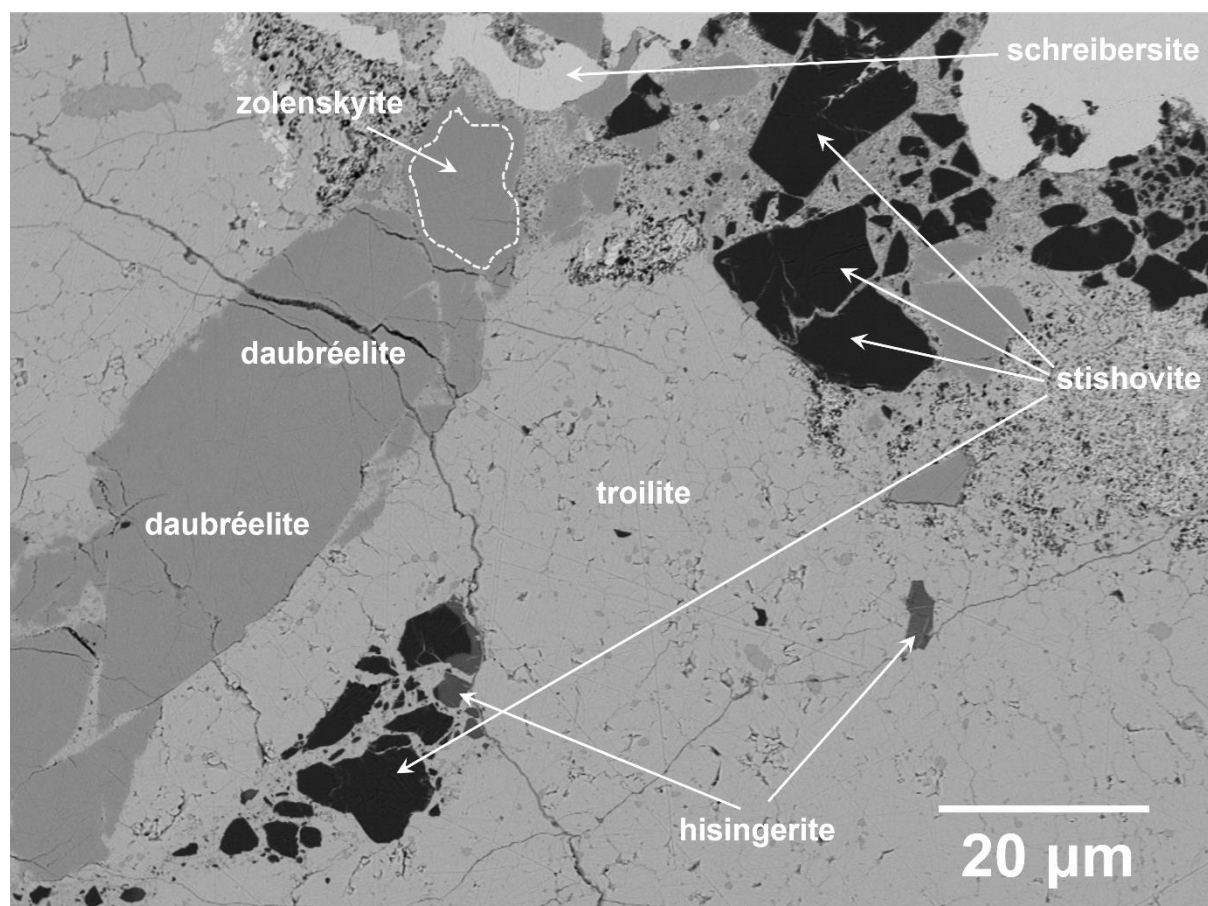


Figure 2. X-ray compositional map of the studied sample (top) together with an EDS spectrum of region composed by daubréelite/zolenskyite (bottom).

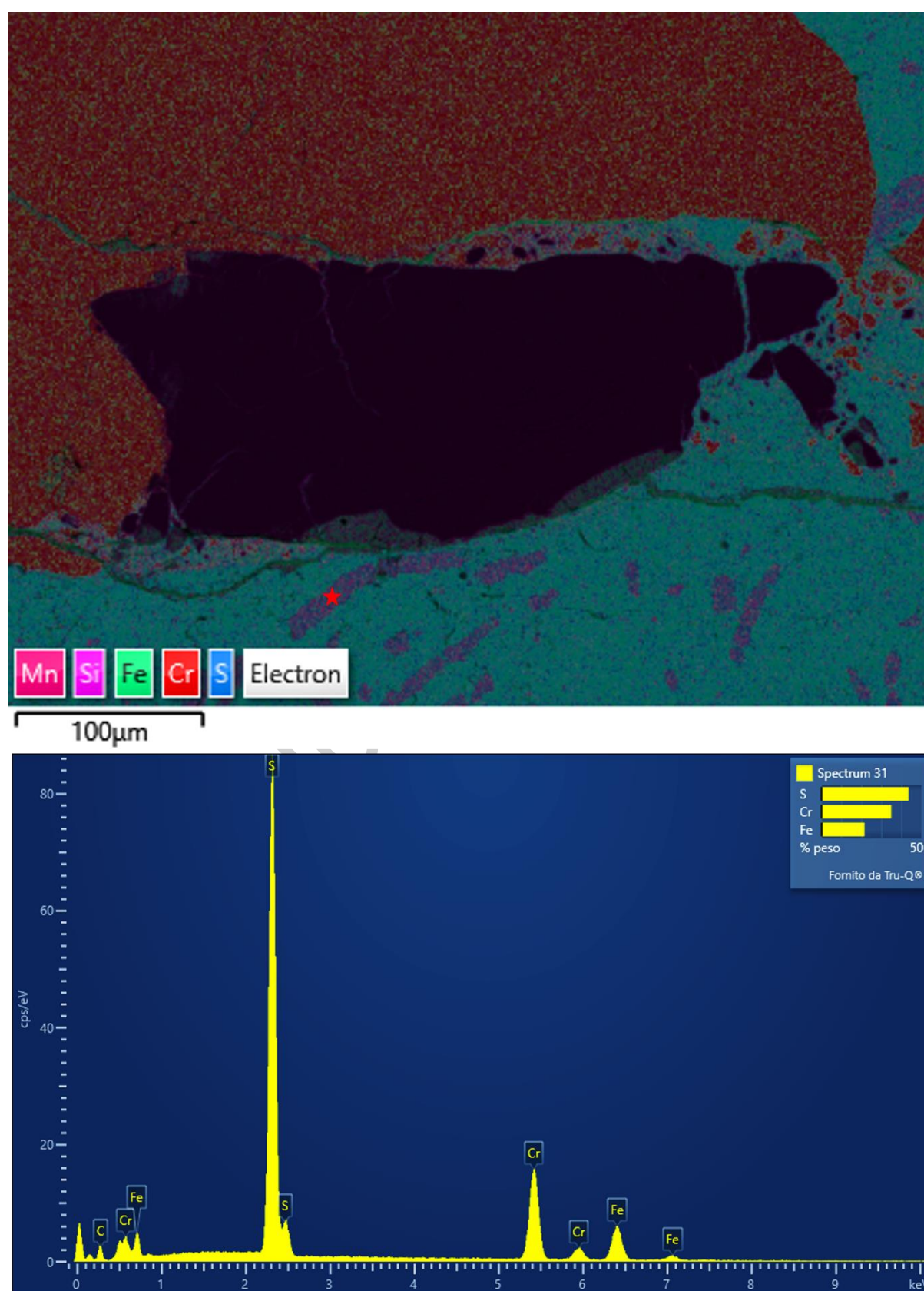


Figure 3. The crystal structure of zolenskyite. Yellow and grey octahedra refer to Fe and Cr atoms, respectively. Sulfur atoms are given as yellow circles. The unit-cell and the orientation of the structure is given.

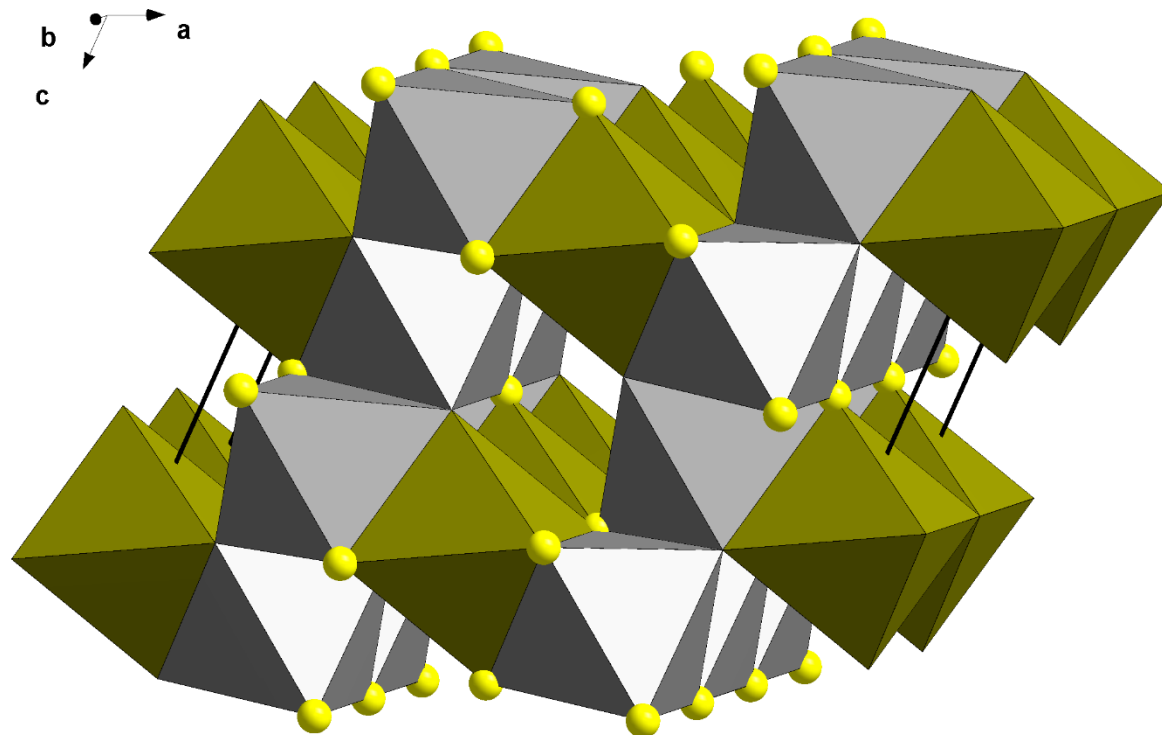


Table 1. Data and experimental details for the selected zolenskyite crystal.

Crystal data	
Formula	FeCr ₂ S ₄
Crystal size (mm)	0.02 × 0.02 × 0.01
Form	block
Colour	black
Crystal system	monoclinic
Space group	<i>C2/m</i> (#12)
<i>a</i> (Å)	12.8345(11)
<i>b</i> (Å)	3.4359(3)
<i>c</i> (Å)	5.9345(5)
β (°)	116.832(6)
<i>V</i> (Å ³)	233.52(4)
<i>Z</i>	2
Data collection	
Instrument	Bruker D8 Venture
Radiation type	MoK α (λ = 0.71073)
Temperature (K)	293(3)
Detector to sample distance (cm)	5
Number of frames	854
Measuring time (s)	20
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.865
Absorption correction	multi-scan
Collected reflections	2156
Unique reflections	633
Reflections with $F_o > 4\sigma(F_o)$	431
R_{int}	0.0256

Refinement

Refinement	Full-matrix least squares on F^2
Final R_1 [$F_o > 4\sigma(F_o)$]	0.0176
Final R_1 (all data)	0.0206
Final WR	0.0861
Number refined parameters	23
GoF	1.271
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	0.40 (at 1.52 \AA from S1)
$\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	-0.51 (at 0.79 \AA from Cr)

$$R_{\text{int}} = (n/n-1)^{1/2} [F_o^2 - F_o(\text{mean})^2] / \sum F_o^2$$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \quad wR_2 = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \right\}^{1/2}$$

$$Goof = \left\{ \sum [w(F_o^2 - F_c^2)^2] / (n-p) \right\}^{1/2} \quad \text{where } n = \text{no. of reflections, } p = \text{no. of refined parameters}$$

Table 2. Atoms, fractional atomic coordinates, and equivalent isotropic displacement parameters (\AA^2) for the selected zolenskyite crystal.

Atom	x/a	y/b	z/c	U_{eq}
Fe	0	0	0	0.04483(17)
Cr	0.74115(4)	0	0.69181(9)	0.04187(16)
S1	0.63884(8)	0	0.9779(2)	0.0564(2)
S2	0.88906(9)	0	0.55072(19)	0.0546(2)

Table 3. Selected bond-distances (in \AA) for cations in the analysed zolenskyite crystal.

Fe-S2 ($\times 2$)	2.3894(10)
Fe-S1 ($\times 4$)	2.5208(8)
<Fe-S>	2.477
Cr-S2 ($\times 2$)	2.3758(8)
Cr-S2	2.3958(12)
Cr-S1 ($\times 2$)	2.5378(8)
Cr-S1	2.5727(12)
<Cr-S>	2.466