

Original paper

Alfredcasparite, $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$, a new mineral from the Caspar quarry, Bellerberg volcano, Germany, and new data on wesselsite, $\text{SrCuSi}_4\text{O}_{10}$

Rafał JUROSZEK^{1*}, Krystian PRUSIK², Christof SCHÄFER³

¹ Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland; rafal.juroszek@us.edu.pl

² Institute of Materials Engineering, University of Silesia, 75 Pułku Piechoty 1A, 41-500 Chorzów, Poland

³ Gustav Stresemann-Strasse 34, D-74257, Untereisesheim, Germany

*Corresponding author



The new mineral alfredcasparite, ideally $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$, is a Sr-analogue of fresnoite $\text{Ba}_2\text{TiO}(\text{Si}_2\text{O}_7)$. It is an accessory phase, which was found in a silicate xenolith within the tephritic lava from the Caspar quarry, Bellerberg volcano, Germany. Usually, alfredcasparite occurs together with potentially new mineral $(\text{Sr}_2\text{Na})\text{Ti}(\text{Si}_2\text{Fe})\text{Si}_2\text{O}_{14}$, in small cracks in the K-feldspar (sanidine)–quartz–pyroxene (aegirine–diopside)–matrix, and wollastonite. In the type material, alfredcasparite rarely forms flattened crystals up to 30 μm in diameter; more common are irregular grains which do not exceed 15 μm in size. Alfredcasparite is colourless, transparent, and has a vitreous lustre and white streak. It is brittle with an irregular fracture and exhibits good cleavage on (001). The calculated density equals $3.950\text{ g}\cdot\text{cm}^{-3}$ and the Mohs hardness is $\sim 3\text{--}4$. Optically, alfredcasparite is uniaxial and non-pleochroic under transmitted light ($n_{\text{mean}} = 1.823$). The empirical formula calculated based on 8 O atom per formula unit (pfu) is $(\text{Sr}_{1.54}\text{Ba}_{0.29}\text{Ca}_{0.10}\text{Na}_{0.03}\text{K}_{0.03})_{\Sigma 1.99}(\text{Ti}_{0.94}\text{Fe}_{0.04}\text{Mg}_{0.03})_{\Sigma 1.01}(\text{Si}_{2.04}\text{Al}_{0.01})_{\Sigma 2.05}\text{O}_8$, which leads to the ideal end-member formula $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$. According to the electron back-scattered diffraction (EBSD) pattern, tetragonal alfredcasparite fit to the using structural model of synthetic $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$ with the following parameters: space group $P4bm$, $a = 8.32\text{ \AA}$, $c = 5.02\text{ \AA}$, $V = 347.77\text{ \AA}^3$, $Z = 2$. The crystal structure consists of layers composed of corner-sharing TiO_3 square-base pyramids and Si_2O_7 disilicate units, with interstices occupied by Sr^{2+} cations. The Raman spectrum of alfredcasparite is characterised by a sharp and intense Raman band at 863 cm^{-1} with lower-intensity shoulder bands at ~ 850 and 874 cm^{-1} , which have a complex nature and are assigned to both symmetric stretching SiO_3 vibrations of the disilicate group $(\text{Si}_2\text{O}_7)^{6-}$ and Ti–O vibrations in the square pyramid $(\text{TiO}_3)^{6-}$. The authors assume that alfredcasparite forms as an effect of residual melt crystallisation enriched in incompatible elements like Ba, Sr, Ti, or P at a temperature around 1000°C . In addition, based on chemical EPMA and Raman spectroscopy investigations, the second world occurrence of wesselsite, $\text{SrCuSi}_4\text{O}_{10}$, was confirmed in the same xenolith. Chemical analyses resulted in the empirical formula (based on 10 O pfu) $(\text{Sr}_{0.67}\text{Ba}_{0.28}\text{Ca}_{0.04}\text{Na}_{0.01}\text{K}_{0.01})_{\Sigma 1.01}(\text{Cu}_{0.93}\text{Mg}_{0.04}\text{Fe}_{0.02})_{\Sigma 0.99}\text{Si}_{4.01}\text{O}_{10}$. Furthermore, the Raman spectrum of natural wesselsite was obtained and described in detail for the first time, in relation to its crystal structure.

Keywords: alfredcasparite, new mineral, Caspar Quarry, Bellerberg volcano, xenolith, wesselsite

Received: 6 February 2024; **accepted:** 20 August 2024; **handling editor:** J. Cempírek

The online version of this article (doi: 10.3190/jgeosci.394) contains electronic supplementary material.

1. Introduction

Alfredcasparite, ideally $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$, is a new accessory mineral found in a silicate xenolith within the tephritic lava from the Caspar quarry, Bellerberg volcano, Germany ($50^\circ 35' 14''\text{ N}$, $7^\circ 23' 54''\text{ E}$). Alfredcasparite is assumed to be isotypic with its Ba-analogue fresnoite, $\text{Ba}_2\text{TiO}(\text{Si}_2\text{O}_7)$ (Alfors et al. 1965; Höche et al. 2002), and also structurally closely related to the melilite-group minerals (Park and Navrotsky 2010; Krz̄ała et al. 2022).

In material sciences, alfredcasparite is known as the synthetic phase STS (Wong et al. 2012; Wisniewski et al. 2018; Gonon et al. 2021), which along with the other fresnoite-type compounds $\text{Ba}_2\text{TiSi}_2\text{O}_8$ (BTS), $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (BTG) and $\text{Ba}_2\text{VSi}_2\text{O}_8$ (BVS), is of interest due to their

piezoelectric and pyroelectric properties (Halliyal et al. 1985; Park and Navrotsky 2010; Sahu et al. 2018). Moreover, the $\text{Sr}_2\text{TiSi}_2\text{O}_8$ (STS) phase is considered a potential storage medium for the immobilisation of short-lived fission products, like radioactive Sr, from nuclear waste (Park and Navrotsky 2010; Bell et al. 2013; Sahu et al. 2018).

The new mineral (IMA2023-024), its proposed name and symbol (Afc) have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). The type material (polished fragment of alfredcasparite-bearing xenolith) was deposited in the Natural History Museum Mainz, State Collection for Natural History Rhineland-Palatinate, Reichklarstrasse 10, D-55116

Mainz, Germany, with catalogue number NHMMZ M 2023/1-LS. The name alfredcasparite is given in honour of Mr Alfred Caspar (1926–2022), who owned and operated the Caspar quarry in Bellerberg volcano for almost 50 years. He has shown a lot of understanding of mineral collectors and has always been open-minded towards a geological and mineralogical investigation of his deposit.

The following work presents a detailed description of alfredcasparite including chemical, structural and spectroscopic data. Moreover, the paper contains new chemical and Raman spectroscopic data for wesselsite, $\text{SrCuSi}_4\text{O}_{10}$, detected in the same xenolith and representing the second world occurrence.

2. Geological setting, occurrence and mineral association

The type locality of alfredcasparite – the Caspar quarry, a part of Bellerberg volcano, is an open quarry located within the Quaternary volcanic area in the Eastern Eifel, Rhineland-Palatinate, Germany (Hentschel 1987; Mihajlovic et al. 2004). The Bellerberg volcano itself is enclosed by two semi-circular shaped mountains that form the crater wall: Ettringer Bellerberg (to the west) and Kottenheimer Büden (to the east; Fig. 1a) (Hentschel 1987; Juroszek et al. 2018). It is characterised by the presence of various thermally transformed xenoliths within leucite-tephrite lava, which differ due to the high-temperature metamorphism conditions and variable protolith composition (Hentschel 1987; Juroszek et al. 2018, 2022). This leads to the formation of miscellaneous mineral assemblages, usually in the contact zones between xenolith and surrounding magma (Hentschel 1987; Juroszek and Ternes 2022; Juroszek et al. 2022). Therefore, the Bellerberg volcano area is an unusual geological locality with many new mineral findings (e.g. Abraham et al. 1983; Krause et al. 1999; Mihajlovic et al. 2004; Galuskin et al. 2016; Juroszek et al. 2018).

The xenolith specimen containing alfredcasparite (SK34.2 – authors sample symbol for the type material; Fig. 1b) was found and collected by Christof Schäfer on

25 July 1990 in the quarry, where at that time the quarrying activities were concentrated on the crater wall at Kottenheimer Büden Mt. The dimension of the xenolith was about $30 \times 20 \times 20 \text{ cm}^3$. The type material with alfredcasparite is highly divers, especially in the case of rock-forming and accessory minerals. The main components of the analysed xenolith include K-feldspar (sanidine), quartz, various pyroxenes like diopside-hedenbergite, aegirine, and less often clinoenstatite, wollastonite, titanite, gehlenite, fluorapatite, and cuspidine. Additionally, Fe-bearing wollastonite ($0.2 \text{ Fe}^{2+} \text{ pfu}$) and highly Fe-rich sanidine were also identified. Subordinately, wadalite, Sr-rich fluorapatite and minerals of the andradite-grossular and åkermanite-alumoåkermanite series were detected as well. The accessory minerals are represented by oxyspinel-group minerals (spinel, magnetite, magnesioferrite), perovskite, chalcopyrite, as well as Zr-bearing minerals such as zircon, baddeleyite, and phases stoichiometrically corresponding to calzirtite, $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, and baghdadite, $\text{Ca}_6\text{Zr}_2(\text{Si}_2\text{O}_7)_2\text{O}_4$. In addition to alfredcasparite, two other Sr-bearing accessory phases were identified: a potentially new mineral with a chemical composition close to $(\text{Sr}_2\text{Na})\text{Ti}(\text{Si}_2\text{Fe})\text{Si}_2\text{O}_{14}$, which could be a new member of the synthetic langasite compound family (Tyunina and Kuz'micheva 2007), and wesselsite, $\text{SrCuSi}_4\text{O}_{10}$, which represents the second world occurrence. Moreover, the cavities and cracks of the xenolith are filled by secondary, low-temperature minerals such as fluorapophyllite-(K), calcite, fluorite, gismondine-Ca, baryte and celestine.

3. Methods of investigation

Petrographic thin sections and polished fragments of studied samples from the alfredcasparite-bearing xenolith sample were examined using a Leica DM2700P optical microscope. In turn, chemical compositions of alfredcasparite and associated minerals, as well as the textural relationships, were carried out using a Phenom XL scanning electron microscope equipped with an EDS (energy-dispersive X-ray spectroscopy) detector (Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Sosnowiec, Poland).

Quantitative chemical analyses of mineral phases were performed using a CAMECA SX100 electron-microprobe operating in WDS (wavelength dispersive X-ray spectroscopy)



Fig. 1a – View of alfredcasparite type locality – the Caspar quarry, Bellerberg volcano (Author: R. Juroszek 2023). **b** – Polished fragment of type material specimen with alfredcasparite.

mode using a 15 kV acceleration voltage and 20 nA beam current (Faculty of Geology, University of Warsaw, Poland). The beam diameter was $\sim 1 \mu\text{m}$. The following lines and standards were used during the measurements: NaK α (albite); CaK α , SiK α and MgK α (diopside); KK α and AlK α (orthoclase); BaL α (baryte); SrL α (celestine); TiK α (rutile); MnK α (rhodonite); CuK α (cuprite); FeK α (Fe₂O₃).

Alfredcasparite crystals are too small for standard single-crystal X-ray diffraction, but the knowledge of its synthetic analogue with known crystal structure allows to use the EBSD method by fitting the patterns of the studied mineral to the synthetic one. The EBSD patterns were collected using a HKL EBSD system (HKL Technology Inc., Oxford Instruments Group) on a JEOL JSM-6480 scanning electron microscope (Institute of Materials Science, University of Silesia, Chorzów, Poland) with an accelerating voltage of 20 kV.

The Raman spectra of alfredcasparite and wesselsite were recorded on a WITec alpha 300R Confocal Raman Microscope (Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Sosnowiec, Poland) equipped with an air-cooled solid laser 488 nm and a CCD camera operating at -61°C . Laser radiation was coupled to a microscope through a single-mode optical fibre with a diameter of $3.5 \mu\text{m}$. An air Zeiss (LD EC Epiplan-Neofluar DIC-100/0.75NA) objective was used. Raman scattered light was focused by an effective pinhole size of $\sim 30 \mu\text{m}$ and a monochromator with a grating of 600 mm^{-1} . The power of the laser at the sample position was 40 mW, with 10 s integration time and an accumulation of 15 scans over 3 cm^{-1} resolution. The monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}). The spectra were processed using the GRAMS Spectralcalc software package, and the Raman bands were fitted using a Gauss-Lorentz cross-product function.

4. Results

4.1. Alfredcasparite

4.1.1. Physical properties and chemical composition

In the type material, alfredcasparite occurs in small cracks and spaces in the K-feldspar (sanidine)–quartz–pyroxene matrix of the xenolith (Fig. 2). Such mineral assemblage is most frequently observed in xenolith zones near the veins and fissures filled by low-temperature and secondary phases. In the analysed sample, alfredcasparite rarely forms flattened crystals up to $30 \mu\text{m}$ (Fig. 2b). Usually, irregular grains up to $15 \mu\text{m}$ in size are observed (Fig. 2d). The association of alfredcasparite with the

aforementioned potentially new langasite-type phase is a common feature of the studied xenolith (Fig. 2a–d).

Alfredcasparite is colourless, transparent, and has a vitreous lustre and white streak. It is brittle with an irregular fracture and exhibits good cleavage on (001) with no observed parting. The density of the new mineral could not be measured due to the thinness and rarity of alfredcasparite crystals. The calculated density $3.950 \text{ g}\cdot\text{cm}^{-3}$ was obtained on the basis of the empirical formula and unit-cell volume from the EBSD data. The Mohs hardness is $\sim 3\text{--}4$. Optically, alfredcasparite is uniaxial and non-pleochroic under transmitted light. Additional optical properties could not be determined because of the small crystal size.

The results of the electron probe micro-analyses of alfredcasparite are shown in Tab. 1. The empirical formula of alfredcasparite calculated on the basis of 8 O pfu is $(\text{Sr}_{1.54}\text{Ba}_{0.29}\text{Ca}_{0.10}\text{Na}_{0.03}\text{K}_{0.03})_{\Sigma 1.99}(\text{Ti}_{0.94}\text{Fe}_{0.04}\text{Mg}_{0.03})_{\Sigma 1.01}(\text{Si}_{2.04}\text{Al}_{0.01})_{\Sigma 2.05}\text{O}_8$, which leads to the simplified formula $(\text{Sr,Ba,Ca})_2(\text{Ti,Fe,Mg})\text{Si}_2\text{O}_8$. The ideal end-member formula $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$ corresponds to 50.88 wt. % of SrO, 19.61 wt. % of TiO₂ and 29.51 wt. % of SiO₂. The presented results show that alfredcasparite mainly exhibits a characteristic homovalent substitution $\text{Sr}^{2+} \rightarrow (\text{Ba}^{2+}/\text{Ca}^{2+})$ observed also in some synthetic counterparts (Wong et al. 2011; Kadyrova et al. 2012; Gonon et al. 2021).

Tab. 1 Chemical composition (wt. %) of alfredcasparite

Constituent	Sample SK 34.2		
	Mean n = 7	S.D.	Range
SiO ₂	29.61	0.33	29.33–30.27
TiO ₂	18.11	0.53	17.30–18.62
Al ₂ O ₃	0.17	0.17	0.01–0.42
MgO	0.26	0.13	0.05–0.38
CaO	1.33	0.75	0.62–2.60
FeO	0.61	0.26	0.18–0.80
SrO	38.49	1.11	36.54–39.46
BaO	10.72	1.61	7.92–11.71
Na ₂ O	0.25	0.10	0.14–0.44
K ₂ O	0.31	0.31	0.10–0.97
Total	98.86		
Calculated on the basis of 8 O			
Ba ²⁺	0.29		
Ca ²⁺	0.10		
Sr ²⁺	1.54		
K ⁺	0.03		
Na ⁺	0.03		
Sum X	1.99		
Ti ⁴⁺	0.94		
Fe ²⁺	0.04		
Mg ²⁺	0.03		
Sum T1	1.01		
Si ⁴⁺	2.04		
Al ³⁺	0.01		
Sum T2	2.05		

Footnotes: S.D. = 1 σ standard deviation; n – number of analyses

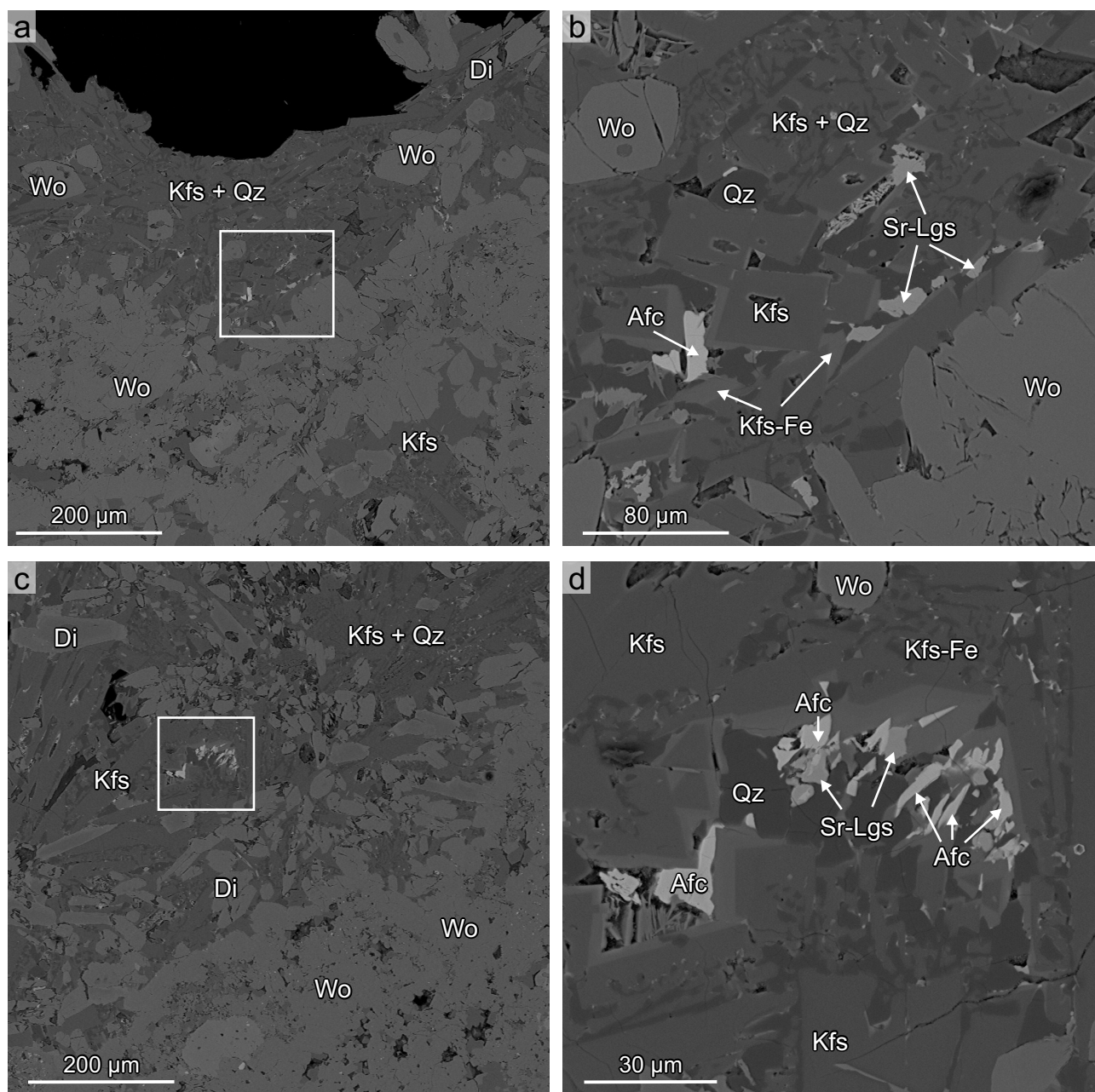


Fig. 2a–d – BSE (back-scattered electron) images of xenolith specimen with alfredcasparite and associated minerals. Framed sections in Figs. a and c are magnified in Figs. b and d. *Abbreviations:* Afc – alfredcasparite; Di – diopside; Kfs – K-feldspar; Kfs-Fe – Fe-rich K-feldspar (sanidine); Sr-Lgs – potentially new mineral of langasite compound family; Qz – quartz; Wo – wollastonite.

According to this substitution, alfredcasparite might be considered a complex solid solution which includes: 77 % of alfredcasparite, 15 % of fresnoite $\text{Ba}_2\text{TiO}(\text{Si}_2\text{O}_7)$ and 5 % of $\text{Ca}_2\text{TiO}(\text{Si}_2\text{O}_7)$ end-members. The content of other insignificant components is ~3 %.

4.1.2. Electron back-scattered diffraction

Structural data of alfredcasparite were obtained using the EBSD technique and fitted to the structural model of synthetic $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$ (Bell and Henderson 2013).

The EBSD pattern of alfredcasparite was acquired at 155 and 177 mm working distances. Fitting the EBSD pattern obtained at 177 mm (Fig. 3) for the used structural model (space group $P4bm$) gave the following unit-cell parameters: $a = 8.32 \text{ \AA}$, $c = 5.02 \text{ \AA}$, $V = 347.77 \text{ \AA}^3$, $Z = 2$, resulted in the mean angular deviation (MAD) parameter equal to 0.49° (good fit).

Because alfredcasparite occurs only in small concentrations, X-ray powder diffraction data were not collected. Consequently, a theoretical powder X-ray diffraction (XRD) pattern was calculated using the VESTA pro-

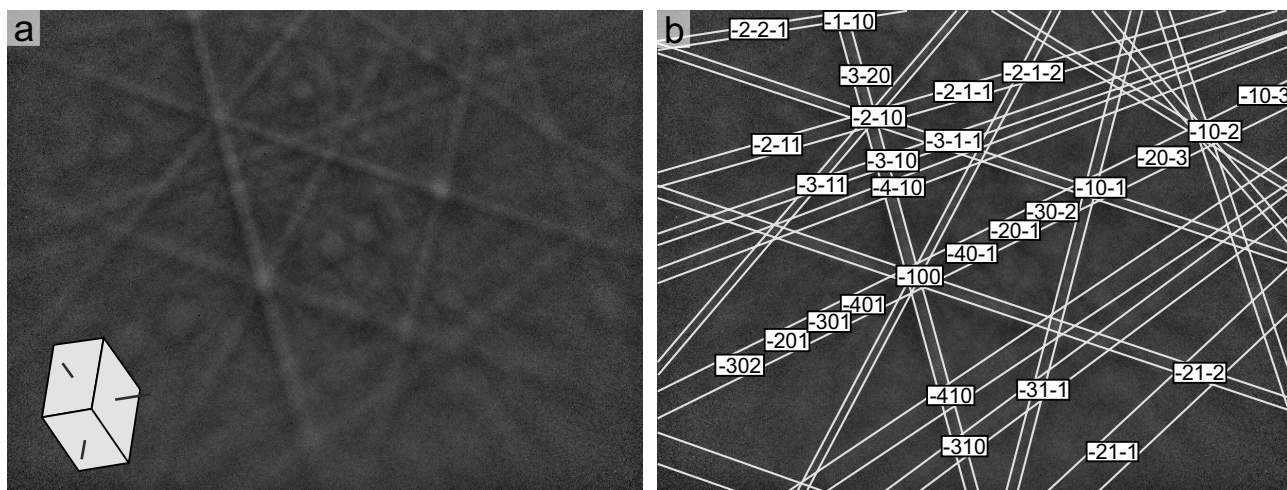


Fig. 3a – EBSD pattern of alfredcasparite collected at a detector distance of 177 mm and performed on a crystal presented in Fig. 2b (crystal orientation shown in the inset). **b** – Indexed EBSD pattern of alfredcasparite.

gram from the structural data of the synthetic analogue $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$ (Bell and Henderson 2013). The diffraction data are given in Electronic Supplementary Material ESM1.

4.1.3. Raman spectroscopy

The Raman spectrum of alfredcasparite (Fig. 4) is dominated by a strong band at 863 cm^{-1} with two shoulders characterised by relatively lower intensity, at 851 cm^{-1} and 874 cm^{-1} ; this indicates a complex character and is assigned to the ν_1 symmetric stretching SiO_3 vibration of the $(\text{Si}_2\text{O}_7)^{6-}$ group and ν_1 Ti–O vibrations of the $(\text{TiO}_5)^{6-}$ square pyramid. It was confirmed that in this case the Ti–O vibrations are related to the short bond between

the Ti set in the base and O2 placed at the apex of the tetragonal pyramid (Gabelica-Robert and Tarte 1981; Juroszek and Ternes 2022). A few bands in the $900\text{--}1010\text{ cm}^{-1}$ range in the alfredcasparite spectrum correspond to the symmetric and asymmetric vibrations of SiO_3 . The bridging symmetric stretching Si–O–Si vibrations of the disilicate group are assumed to cause the Raman band at 680 cm^{-1} with an additional band on the shoulder at a higher frequency of $\sim 712\text{ cm}^{-1}$. The spectral region between $\sim 540\text{ cm}^{-1}$ and 630 cm^{-1} corresponds to the bending SiO_3 vibrations. However, the intense band at 608 cm^{-1} may exhibit a mixed character and also be related to the TiO_4 vibrations from the $(\text{TiO}_5)^{6-}$ square pyramid (Juroszek and Ternes 2022). A series of Raman bands noted in the $\sim 250\text{--}510\text{ cm}^{-1}$ range, with characteristic ones at 256, 283, and 410 cm^{-1} , were attributed to the translational and symmetric bending vibrations of the $(\text{Si}_2\text{O}_7)^{6-}$ group and $(\text{TiO}_5)^{6-}$ square pyramid. Bands in the low-wavenumber region, below 250 cm^{-1} , are related to the stretching Sr–O, Ba–O and lattice vibrations.

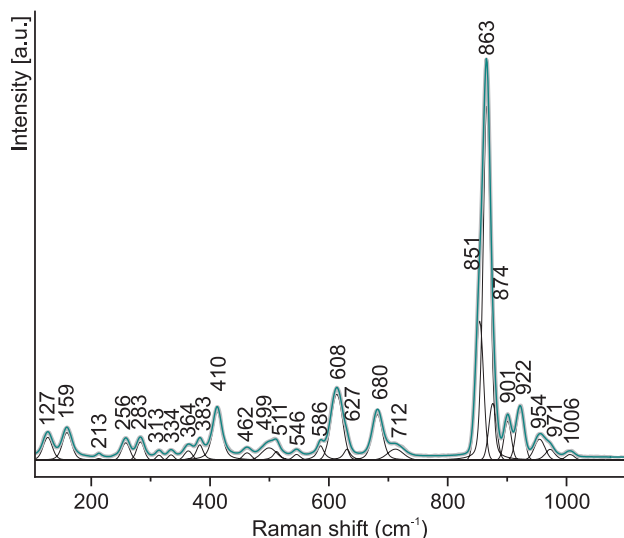


Fig. 4 Raman spectrum of alfredcasparite, grey line – experimental spectrum; green line – fitted spectrum; black lines – fitted peaks.

4.2. Wesselsite

4.2.1. Physical properties and chemical composition

Wesselsite, ideally $\text{SrCuSi}_4\text{O}_{10}$, is a very rare mineral described so far only from hydrothermally-altered sedimentary manganese deposits in the Wessels mine, Kalahari Manganese Field, Northern Cape Province, Republic of South Africa (Giester and Rieck 1996; Knight et al. 2010; Rumsey et al. 2013; Rieck et al. 2015). Wesselsite is a member of the gillespite group, which comprises gillespite, $\text{BaFe}^{2+}\text{Si}_4\text{O}_{10}$ (Schaller 1922), cuprovivaite, $\text{CaCuSi}_4\text{O}_{10}$ (Minguzzi 1938), and effenbergerite, $\text{BaCuSi}_4\text{O}_{10}$ (Giester and Rieck 1994).

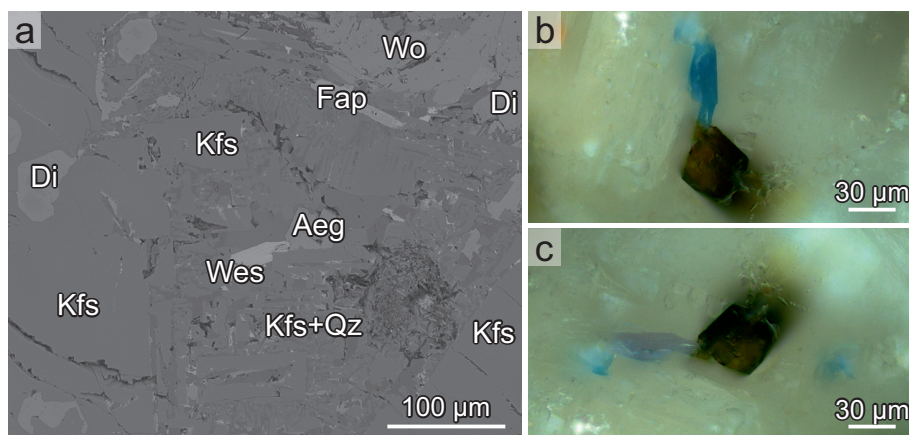


Fig. 5a – BSE image of wesselsite and associated minerals in xenolith sample from type locality. **b–c** – Optical images of wesselsite crystals performed at two different orientations with characteristic pleochroism. *Abbreviations:* Aeg – aegirine; Di – diopside; Fap – fluorapatite; Kfs – K-feldspar; Qz – quartz; Wes – wesselsite; Wo – wollastonite.

In the alfredcasparite-bearing xenolith from the Caspar quarry, a few blue platy crystals of wesselsite were identified. The crystals are tiny, usually around 15 µm in size, and the biggest one does not exceed 40 µm (Fig. 5). Wesselsite is brittle, with a perfect cleavage on (001), and exhibits a strong pleochroism from blue in ω to pale pink in ϵ (Fig. 5b–c). Similar optical properties were described for wesselsite from the type locality (Giester and Rieck 1996).

The electron probe micro-analyses of the German wesselsite indicate a enrichment of Ba at the Sr-

dominant site, with insignificant impurities of Ca, Na, and K (Tab. 2). In addition, the Cu site is substituted by Mg and Fe²⁺, so the final calculated empirical formula is presented as $(\text{Sr}_{0.67}\text{Ba}_{0.28}\text{Ca}_{0.04}\text{Na}_{0.01}\text{K}_{0.01})_{\Sigma 1.01}(\text{Cu}_{0.93}\text{Mg}_{0.04}\text{Fe}_{0.02})_{\Sigma 0.99}\text{Si}_{4.01}\text{O}_{10}$. Apart from the trace monovalent substituents, the studied wesselsite can be considered as a complex solid solution with the: 64 % of wesselsite, 26 % of effenbergerite, 4 % of both cuprorivaite and $\text{SrMgSi}_4\text{O}_{10}$, and 2 % of gillespite end-members. The previous reports suggest that wesselsite from the type locality is very close to the end-member formula

$\text{SrCuSi}_4\text{O}_{10}$, based on the chemical analyses obtained using SEM-EDX (Tab. 2) (Giester and Rieck 1996). However, the same authors, during a study of a wesselsite-effenbergerite association, confirmed the presence of a solid solution for both minerals with a characteristic Ba for Sr substitution (Rieck et al. 2015).

4.2.2. Raman spectroscopy

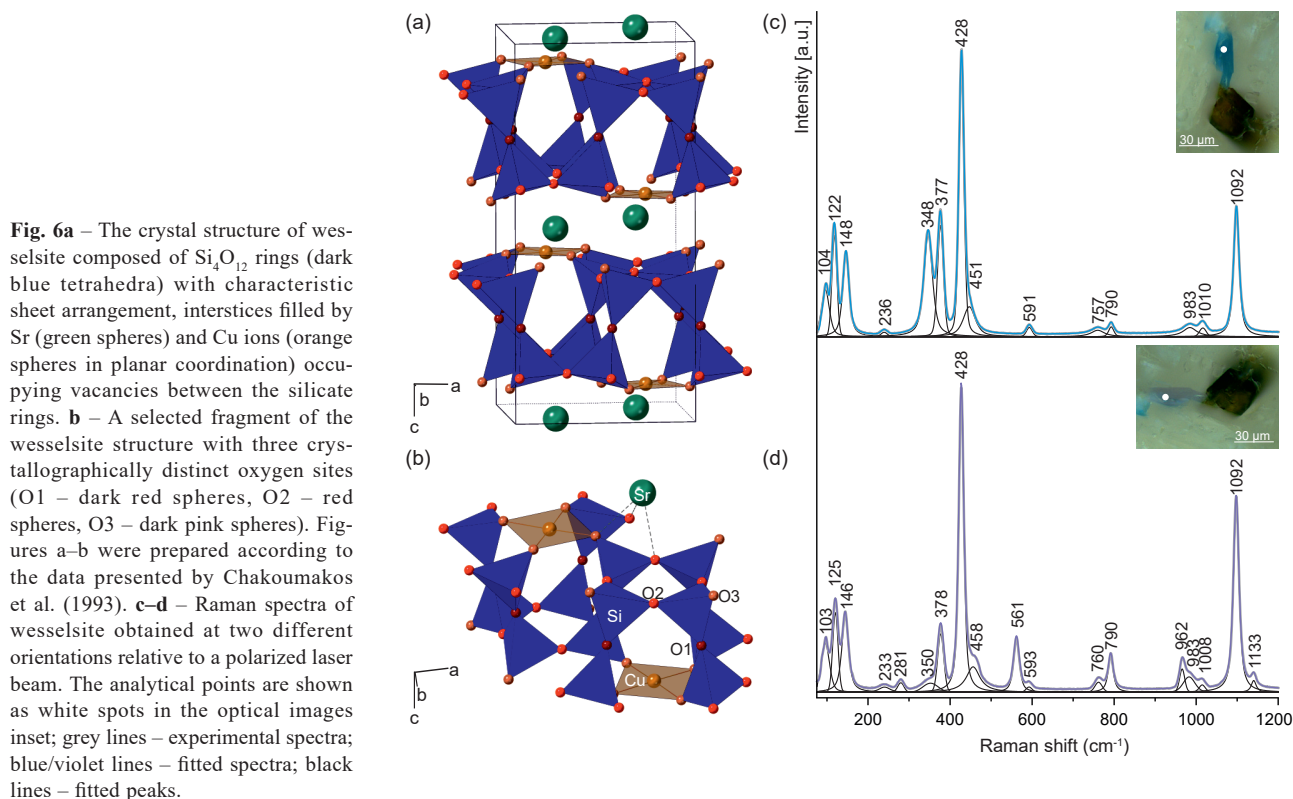
The Raman spectrum of wesselsite is similar to the spectra of other gillespite-group members for which the noticeable variations in band intensities are explained by the polarisation effect, which usually depends on the crystal orientation during the measurement (McKeown and Bell 1998; Pagès-Camagna et al. 1999; Kostomitsopoulou Marketou et al. 2020; Dariz and Schmid 2022). However,

Tab. 2 Chemical composition (wt. %) of wesselsite from the Caspar quarry, Bellerberg volcano, Germany and Wessels mine, Northern Cape Province, South Africa

Constituent	Caspar quarry			Wessels mine
	Mean ¹ n = 7	S.D.	Range	Mean ² n = 3
SiO ₂	55.67	1.07	54.79–57.71	56.90
MgO	0.34	0.67	0.02–1.70	n.d.
CaO	0.47	0.06	0.42–0.58	n.d.
FeO	0.25	0.09	0.16–0.40	n.d.
CuO	17.00	0.62	15.75–17.32	18.80
SrO	16.13	1.18	15.13–17.97	24.00
BaO	9.89	1.65	7.60–11.91	n.d.
Na ₂ O	0.07	0.05	0.03–0.17	n.d.
K ₂ O	0.11	0.13	0.04–0.37	n.d.
Total	99.93			99.70
Calculated on the basis of 10 O				
Ba ²⁺	0.28			–
Ca ²⁺	0.04			–
Sr ²⁺	0.67			0.98
K ⁺	0.01			–
Na ⁺	0.01			–
Sum M	1.01			0.98
Mg ²⁺	0.04			–
Fe ²⁺	0.02			–
Cu ²⁺	0.93			1.00
Sum B	0.99			1.00
Si⁴⁺/Sum T	4.01			4.01

Footnotes: S.D. = 1 σ standard deviation; n – number of analyses; n.d. – not detected; ¹ – this work;

² – type locality;



without knowledge of the crystal structure of wesselsite, the interpretation of the Raman spectrum might be constricted. Wesselsite has a phyllosilicate-type structure composed of Si_4O_{12} rings that are linked together by bridging oxygens and alternately arranged within the sheets (Fig. 6a). The vacancies between silicate rings in the layers are occupied by Cu^{2+} in square-planar. The interstitial Sr^{2+} cations connect the silicate sheets (Fig. 6a). In this structure type the $(\text{SiO}_4)^4$ tetrahedra contain three crystallographically distinct oxygen sites: the O1 (bridging oxygen), which links two tetrahedra from different silicate rings within the layers of each silicate sheet and forms a $(\text{Si}_2\text{O}_7)^{6-}$ double tetrahedron (Fig. 6a–b), the O2 (ring oxygen) within the Si_4O_{12} rings (Fig. 6b), and the O3 (terminal/non-bridging oxygen), which coordinates Cu^{2+} and Sr^{2+} (Fig. 6b) (Chakoumakos et al. 1993; McKeown and Bell 1998; Knight et al. 2010).

For the present study, two Raman spectra of wesselsite were obtained with a special regard to the crystal orientation and laser beam polarisation direction (Fig. 6c–d). Due to the slight differences in both spectra, the assignment of single Raman bands is discussed based on the spectrum given in Fig. 6d. In general, according to the previous works of gillespite-group members, the wesselsite spectrum can be roughly divided into internal Si–O stretching vibrations of the four-membered silicate rings at ≥ 800 cm^{-1} , bending/deformation vibrations in an intermediate spectral range of 150–800 cm^{-1} , and crystal lattice modes

at ≤ 150 cm^{-1} (McKeown and Bell 1998; Dariz and Schmid 2022). The low-wavenumber region is characterised by three Raman bands at 103, 125, and 146 cm^{-1} , which are attributed mainly to the lattice modes, where Si_4O_{10} sheet deformation vibrations (rotation+translation) can occur with Sr and Cu displacements. The intermediate spectral region in both spectra is dominated by an intense peak at 428 cm^{-1} with some shoulder around 450–460 cm^{-1} (Fig. 6c–d). These Raman bands are assigned to the combination of deformation and breathing modes of bridging oxygen (O2) within the four-membered rings, whereas the band doublet at ~ 350 and ~ 378 cm^{-1} is related to the Si–O3 rocking vibrations. Low-intensity Raman bands at around 230 cm^{-1} and 280 cm^{-1} are ascribed to the Si–O2 translation and O2 z-translation + O3 xy-translation modes, respectively. The O3–Si–O1 symmetric bending modes are related to the Raman band located at ~ 560 cm^{-1} , in turn the band at ~ 590 cm^{-1} can be associated with Si translation along Si–O1. The spectral range 760–790 cm^{-1} with a characteristic peak doublet is assigned to the ring Si_4O_{12} deformation vibrations. The high-wavenumber region in the wesselsite spectra contains a Raman band at 1092 cm^{-1} attributed to the symmetric Si–O1–Si stretching vibrations of the $(\text{Si}_2\text{O}_7)^{6-}$ groups. In turn, peaks between 960 cm^{-1} and 1010 cm^{-1} are related to the Si–O3 and Si–O2 stretching modes. A Raman band near 1133 cm^{-1} might be treated as a shoulder of the intense peak at 1092 cm^{-1} and has a similar assignment.

5. Discussion

5.1. Crystal structure variability

The lack of high-quality and relatively large alfredcasparite crystals did not allow to conduct the appropriate single-crystal XRD investigation despite several attempts. Alfredcasparite is a Sr-analogue of fresnoite, which suggest a structural similarity of these two phases. Fresnoite and alfredcasparite crystallise in $P4bm$ space group and their crystal structure consists of layers extended parallel to the ab plane, which are composed of corner-sharing TiO_5 square-base pyramids and SiO_4 tetrahedra combined into Si_2O_7 disilicate units (Fig. 7a). Tenfold-coordinated Ba^{2+} cations in fresnoite, and Sr^{2+} cations in alfredcasparite are located between the successive titanosilicate layers (Fig. 7a). In a projection along $[001]$ the TiO_5 pyramids and Si_2O_7 disilicate groups are linked into the five-membered heterocyclic rings indicating the structural resemblance to the melilite-group minerals (Fig. 7b) (Moore and Louisnathan 1969; Bindi et al. 2006; Krz̧ała et al. 2022).

At present, there are several structural models of natural fresnoite (Alfors et al. 1965; Bindi et al. 2006; Krz̧ała et al. 2022; Chukanov et al. 2023) and structurally related synthetic counterparts known as BTS (Masse et al. 1967; Moore and Louisnathan 1969; Markgraf et al. 1985, 1990; Withers et al. 2002). In both cases, the structural models were obtained based on powder or single-crystal XRD data confirming the tetragonal crystal system with the $P4bm$ space group. Natural fresnoite crystals from different localities exhibit similar unit-cell parameters, e.g. $a = 8.52 \text{ \AA}$, $c = 5.21 \text{ \AA}$ for fresnoite from Eastern Fresno County in California, USA (Alfors et al. 1965), $a = 8.5262 \text{ \AA}$, $c = 5.2199 \text{ \AA}$ for fresnoite from the Hatrurim Complex in Israel (Krz̧ała et al. 2022), and $a = 8.5104 \text{ \AA}$, $c = 5.1975 \text{ \AA}$ for fresnoite from the Löhley quarry in Germany (Chukanov et al. 2023), and

are characterised by an average crystal structure. Similar relations of the unit-cell parameters were observed for synthetic BTS compounds (Masse et al. 1967; Moore and Louisnathan 1969), even for the phase with unit-cell parameters calculated at various temperature steps (Markgraf et al. 1985).

However, a few works, mostly devoted to the crystal structure of synthetic fresnoite (BTS) indicated the presence of variable closely related types of incommensurate modulations (Markgraf et al. 1990; Höche et al. 1999; Withers et al. 2002; Wong et al. 2011). Markgraf et al. (1990), using electron diffraction of a BTS crystal, reported the existence of a satellite reflection set along the a^* and b^* direction, originating from incommensurate modulations. These reflections are accompanied by the presence of a superstructure along $[001]$, which leads to the doubling of the unit-cell c parameter. These authors suggest that the modulation is associated with the large Ba^{2+} cations, which causes distortions in the basal Si_2O_7 and TiO_5 linkage and postulated that the phase transition between the modulated and non-modulated structure should be correlated with the property anomalies observed at 160°C (Markgraf et al. 1990). Similar observations related to the modulation in BTS were confirmed using transmission electron microscopy (TEM) by Höche et al. (1999). In turn, Withers et al. (2002) showed that the presence of satellite reflections in BTS diffraction patterns and the mechanism responsible for the incommensurate modulation can arise from the rigid unit modes (RUM), which are assigned to the rotation of SiO_4 tetrahedra and TiO_5 square pyramids perpendicular to the c -axes. It was assumed that rotation of polyhedral units around $[001]$ is energetically more preferable compared to their deformation, and leads to relieving the tensions within the sheets in crystal structure. However, the displacement of a rigid framework can generate phase transition and polymorphism (Withers et al. 2002).

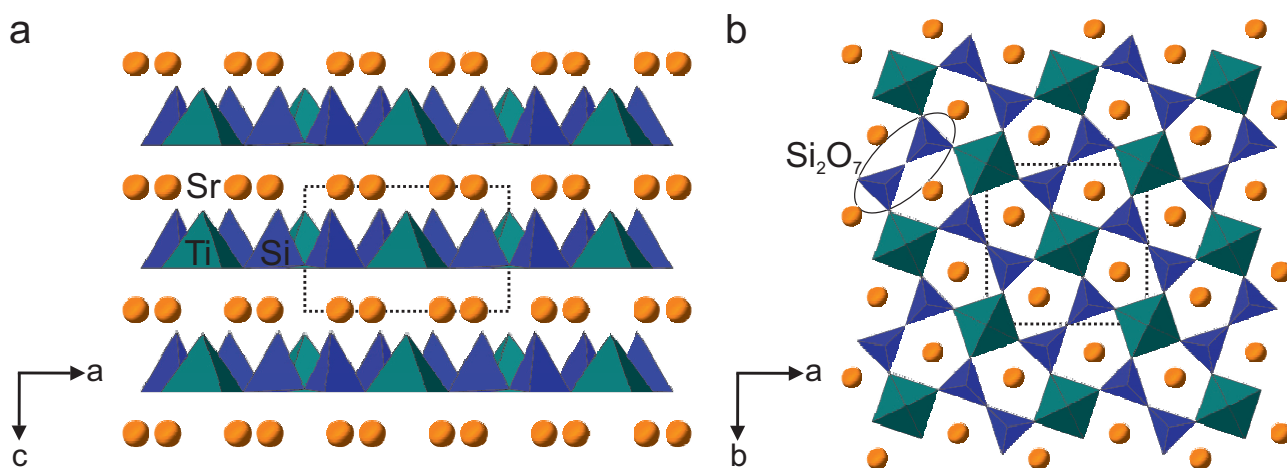


Fig. 7 General views of the crystal structure of alfredcasparite: projections along $[010]$ (a) and $[001]$ (b). The unit-cell is shown as a dotted line. The figure was prepared based on Bell and Henderson (2013).

Hitherto, among all average structures of natural fresnoite, there is only one research work, in which a structure modulation was observed and discussed. The measurement and structure refinement were performed on a natural fresnoite crystal from Fresno County, California, by Bindi et al. (2006). These authors observed an incommensurate structure in the five-dimensional superspace group $P4bm(\alpha, \alpha, \frac{1}{2})(-\alpha, \alpha, \frac{1}{2})0gg$, with the unit-cell parameters $a = 8.5353(6)$, $c = 10.4128(7)$ Å, and modulation vectors $q_1 = 0.3020(3)$ ($\mathbf{a}^* + \mathbf{b}^*$), $q_2 = 0.3020(3)$ ($-\mathbf{a}^* + \mathbf{b}^*$). Their structure refinement indicated the modulation of atomic positions, which caused strong anisotropy of displacement parameters, mostly for Ba, O1, and O3 atoms. Their positional modulation leads to the deformation of pentagonal rings, noticed in the projection along [001], caused by the partial change of Ba coordination from ten-fold to eight- and nine-fold throughout the structure (Bindi et al. 2006).

In the case of synthetic alfredcasparite (STS phase) a few different crystallographic models were developed (Höche et al. 1999, 2002; Bell and Henderson 2013; Bell et al. 2013). Based on high-resolution synchrotron X-ray powder diffraction data of STS performed at 293 K, the structure was refined as tetragonal, space group $P4bm$, with the unit-cell parameters $a = 8.3200(3)$ and $c = 5.0239(2)$ Å (Bell and Henderson 2013). The same authors also carried out measurements at 87–1223 K and confirmed that the $P4bm$ 293 K structure is preserved over this temperature range (Bell et al. 2013). Höche et al. (1999) analysed STS together with BTS, and noticed that the electron diffraction patterns of STS are more complex, as each normal reflection is surrounded by twelve satellites, instead of eight noted for BTS. The satellite spots occur at $0.4a^*$, $0.4b^*$, $0.6a^*$ and $0.6b^*$, and additionally at $0.43a^*$, $0.43b^*$, $0.57a^*$ and $0.57b^*$. Both structures exhibited incommensurate modulation, however, the greater number of satellite reflections was not correlated with the increase of the c parameter along the [001] direction in the STS example (Höche et al. 1999). The same researchers investigated STS crystals prepared by three techniques including Czochralski pulling, flux growth, and electrochemically induced nucleation (Höche et al. 2002). The results revealed an incommensurately modulated crystal structure with the 5D superspace group $P4bm(-\alpha, \alpha, \frac{1}{2})(\alpha, \alpha, \frac{1}{2})0gg$ with $\alpha = 0.3$, and unit-cell parameters $a = 8.312(2)$, and $c = 10.07(1)$ Å. The later report confirmed the doubling of the c unit-cell parameter and the authors suggested that the subtle changes within the modulated structure are caused by the various crystal-growth methods (Höche et al. 2002). Such conclusion was also presented by Wong et al. (2011), who based on selected area electron diffraction (SAED) patterns and via high-resolution transmission electron microscopy (TEM) of $(\text{Ba}, \text{Sr})_2\text{TiSi}_2\text{O}_8$

synthetic fresnoites revealed that the commensurate-incommensurate regions within the structure are related to the chemical inhomogeneities, better described as nanometric domain intergrowths. The presence of these domains and perturbation of the average fresnoite structure can be correlated with the starting material obtained during the synthesis process and the observed phase transition in micro- and nano-metric scales might depend on temperature and annealing time (Wong et al. 2011). Their work indicated that the presence of satellite reflection causing the incommensurate modulation occurs in the domain intergrowths characterised by chemical inhomogeneity, while for the less chemically disordered domains, the modulation is not observed (Wong et al. 2011).

The above assumptions presented for the natural and synthetic fresnoite-type phases ambiguously point out that the possible incommensurate modulation and distribution of satellite reflections do not specify completely the modification of average structures, as the modulated and non-modulated domains can be found within one crystal. It causes difficulties in reconstructing the real crystal structure as presented in previous publications. In the case of alfredcasparite, the quality and size of crystals did not allow to perform a high-resolution structural investigation. Thus, alfredcasparite may have either an average structure or it may show modulations caused by tiny inhomogeneous intergrowths even within the optically homogenous single crystal.

5.2. Origin of alfredcasparite

In general, the thermally metamorphosed xenoliths from the Bellerberg volcano carry a wide variety of mineral species due to the high-temperature transformations related, among others, to the different protolith compositions (Hentschel 1987; Juroszek et al. 2018, 2022). The parameters allow the formation of miscellaneous mineral assemblages, usually in the contact zones of xenolith and surrounding magma (Juroszek and Ternes 2022; Juroszek et al. 2022). It was proposed that the formation of some rare Ba-minerals found in the intergranular spaces between rock-forming minerals from the Bellerberg volcano occurs as an effect of crystallisation of residual melt enriched in incompatible elements like Ba, Sr, Ti, or P at a temperature of $\sim 1000^\circ\text{C}$ (Juroszek and Ternes 2022). In the case of alfredcasparite and the $(\text{Sr}_2\text{Na})\text{Ti}(\text{Si}_2\text{Fe})\text{Si}_2\text{O}_{14}$ phase, as well as considering associated minerals, its genesis can be similar. Its high-temperature origin can be proven by its relation with the synthetic counterparts. A high-temperature XRD study confirmed that the stability of the synthetic STS phase in glass ceramics is maintained up to 1000°C (Gonon et al. 2021). In turn, for some precursor powders with (Ba, Sr) fresnoite com-

position, the crystallisation required a temperature above 900 °C (Wong et al. 2012).

In contrast, the wesselsite from the type locality, the Wessels mine, Kalahari Manganese Field, Northern Cape Province, South Africa, occurs in a hydrothermally-altered sedimentary Mn-deposits in association with the hennomartinite, sugilite, pectolite, xonolite and quartz (Giester and Rieck 1996). Besides effenbergerite, some later works confirmed also the presence of other and new barium, strontium and copper-bearing minerals like scottyite, $\text{BaCu}_2\text{Si}_2\text{O}_7$ (Yang et al. 2013), diegogattaite, $\text{Na}_2\text{CaCu}_2\text{Si}_8\text{O}_{20}\cdot\text{H}_2\text{O}$ (Rumsey et al. 2013), lavinskyite, $\text{K}(\text{LiCu})\text{Cu}_6(\text{Si}_4\text{O}_{11})_2(\text{OH})_4$ (Yang et al. 2014), and colinowensite, $\text{BaCuSi}_2\text{O}_6$ (Rieck et al. 2015) in association with wesselsite. It was assumed that the hydrothermally altered Mn-ore body at this locality has might formed in the temperature range around 300–400 °C (Gutzmer and Beukes 1996; Rumsey et al. 2013).

The formation conditions suggested for alfredcasparite can be related also to the wesselsite from the Caspar quarry. It is hard to speculate which of these minerals crystallised first, however, the morphology and the size of wesselsite in comparison to alfredcasparite suggests that wesselsite crystallised first. In this case, the Cu may have been removed from the altered sulphides, mostly chalcopyrite, and it migrated with the residual melts between the rock-forming minerals. Subsequently, as a result of melt enrichment, the wesselsite could start to crystallise. The proposed high-temperature origin of wesselsite might be supported by the work devoted to the synthetic wesselsite-effenbergerite solid solution, which was obtained at temperatures around 900–1000 °C (Knight et al. 2010).

6. Conclusions

The present work describes the new mineral alfredcasparite, $\text{Sr}_2\text{TiO}(\text{Si}_2\text{O}_7)$, a Sr-analogue of fresnoite, from the Caspar quarry, Bellerberg volcano in Germany, as well as provides new chemical and spectroscopic data for wesselsite, $\text{SrCuSi}_4\text{O}_{10}$. It is worth to mention that in association with alfredcasparite and wesselsite, another potentially new Sr-bearing mineral was identified. Chemically it could be related to the langasite compound family and is characterised by the end-member formula $(\text{Sr}_2\text{Na})\text{Ti}(\text{Si}_2\text{Fe})\text{Si}_2\text{O}_{14}$. Moreover, alfredcasparite, among a limited number of naturally identified mineral species, is another titanosilicate featuring a five-fold coordinated Ti^{4+} site. However, the crystal quality made it impossible to perform the structural measurements, only EBSD data being available, which prevented us from characterising the details of the crystal structure and the presence of possible modulations observed in synthetic counterparts.

For the first time, the Raman spectrum of natural wesselsite was obtained and described in detail with respect to its crystal structure. Furthermore, for wesselsite, the Caspar quarry is the second world occurrence.

Acknowledgements: The authors are also thankful to Jan Cempírek and Uwe Kolitsch for their helpful and constructive comments, which improved the manuscript.

Electronic supplementary material. The calculated powder patterns for alfredcasparite are available online at the Journal web site (<http://dx.doi.org/10.3190/jgeosci.394>).

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