



## Article

# Crystal structure and composition of hiärneite, $\text{Ca}_2\text{Zr}_4\text{Mn}^{3+}\text{SbTiO}_{16}$ , and constitution of the calzirtite group

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### Abstract

The crystal structure of hiärneite has been refined from single-crystal X-ray diffraction data ( $\lambda = 0.71073 \text{ \AA}$ ) on type material from Långban, Värmland, Sweden. The refinement converged to  $R_1 = 0.046$  based on 1073 reflections with  $F^2 > 4\sigma(F^2)$ . The tetragonal unit cell, space group  $I4_1/acd$ , has the parameters  $a = 15.2344(6) \text{ \AA}$  and  $c = 10.0891(6) \text{ \AA}$  with  $Z = 8$ . The mineral is isostructural with calzirtite, ideally  $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$ , with a structural topology derived from fluorite. In hiärneite,  $\text{Mn}^{3+}$  is ordered at a 4- to 8-fold coordinated site (with a distorted polyhedral coordination figure), without the atom splitting encountered at the corresponding Zr-dominated site of calzirtite. The end-member formula for hiärneite is established as  $\text{Ca}_2\text{Zr}_4\text{Mn}^{3+}\text{SbTiO}_{16}$ . The calzirtite group, with calzirtite, hiärneite and tazheranite (cubic  $\text{ZrO}_{2-x}$ ), has been approved by the IMA–CNMNC.

**Keywords:** hiärneite, crystal structure, calzirtite group, tazheranite, mineral nomenclature, Långban, Sweden

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### Introduction

Hiärneite,  $(\text{Ca}, \text{Na}, \text{Mn}^{2+})_2(\text{Zr}, \text{Mn}^{3+})_5(\text{Sb}, \text{Ti}, \text{Fe}^{3+})_2\text{O}_{16}$ , was described as a new mineral (Holtstam, 1997) from the famous Fe–Mn–(Ba–Pb–As–Sb–Be–B) deposit at Långban, in Värmland, Sweden (Holtstam and Langhof, 1999). It occurs in a phlogopite-rich skarn with magnetoplumbite, fluorapatite, oxyplumboroméite, pyrophanite and jacobsonite (Fig. 1), and was interpreted as a product of metasomatism and regional metamorphism. Hiärneite was the first mineral known to have an essential combination of Zr and Sb in its formula (the second one is usturite, a member of the garnet supergroup; Grew *et al.*, 2013).

Hiärneite, having a tetragonal unit cell with  $a = 15.264(1)$ ,  $c = 10.089(2) \text{ \AA}$ , space-group symmetry  $I4_1/acd$ , was inferred to be isostructural with calzirtite, ideally  $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$  (Holtstam, 1997). The crystal structure was, however, not studied in detail at the time of discovery. We have now collected single-crystal diffraction data and refined the crystal structure of type hiärneite (sample from the mineral collection of the Swedish Museum of Natural History, GEO-NRM #19920776).

### X-ray diffraction data and refinement

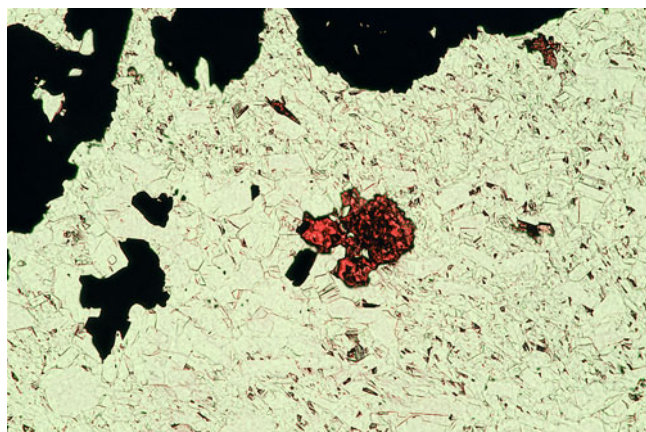
X-ray diffraction data of hiärneite were obtained with an Oxford Diffraction Xcalibur 3 diffractometer (MoK $\alpha$  radiation,  $\lambda =$

$0.71073 \text{ \AA}$ ) fitted with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarisation corrections were done with the *CrysAlis RED* (Oxford Diffraction, 2006) software package. Crystal shape and dimension optimisation were performed with *X-shape* (Stoe and Cie, 1996), based on the *Habitus* program (Herrendorf, 1993). The set of reflections was corrected for absorption via a Gaussian analytical method and averaged according to the  $4/mmm$  point group. Following an absorption correction, the merging  $R$  for the data set decreased from 0.081 to 0.054. The analysis of the reflection conditions unequivocally led to the choice of the space group  $I4_1/acd$ . Given the close similarity in terms of unit-cell dimensions and crystal symmetry, the crystal structure was refined starting from the atomic coordinates of calzirtite, ideally  $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$  (Rossel 1982; Sinclair *et al.*, 1986; Rastsvetaeva *et al.*, 1995; Jafar *et al.*, 2016).

The site occupancy factor (s.o.f.) at the cation sites was allowed to vary (Mn vs. structural vacancy, Sb vs. structural vacancy, Ca vs. structural vacancy and Zr vs. structural vacancy for  $M1$ ,  $M2$ ,  $M3$  and  $M4$ , respectively) using scattering curves for neutral atoms taken from the *International Tables for Crystallography* (Ibers and Hamilton, 1974). The mean electron numbers obtained for each site were modelled considering the observed bond distances and the electron microprobe analysis (see below). These proportions were then fixed in subsequent refinement cycles (see Table 2 – constrained refinement). The full-matrix least-squares program *Shelxl-97* (Sheldrick, 2008) was used for the refinement of the structure. Convergence was easily achieved up to  $R_1 = 0.046$ . Atomic coordinates and bond distances are given in Tables 2 and 3, respectively. The crystallographic information file has been deposited with the Principal Editor of

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**Fig. 1.** Microphotograph in polarised light of a thin section with poikiloblastic hiärneite (orange) and magnetoplumbite/jacobsite (opaque) in a fine-grained phlogopite matrix. Field of view = 1 mm width. Specimen GEO-NRM #19920776.

**Table 1.** Crystal and diffraction experimental data.

Crystal data	
Ideal formula	Ca <sub>2</sub> Zr <sub>4</sub> Mn <sup>3+</sup> SbTiO <sub>16</sub>
Crystal dimensions (mm)	0.065 × 0.080 × 0.090
Crystal system, space group	Tetragonal, <i>I</i> <sub>4</sub> / <i>acd</i>
Temperature (K)	293(2)
<i>a</i> , <i>c</i> (Å)	15.2344(6), 10.0891(6)
<i>V</i> (Å <sup>3</sup> )	2341.6(2)
<i>Z</i>	8
Data collection	
Crystal description	Reddish block
Instrument	Oxford Xcalibur 3
Radiation type, wavelength (Å)	MoK $\alpha$ , 0.71073
$\theta$ range (°)	4.46 to 38.82
Absorption correction	Gaussian analytical
Number of measured, independent and observed reflections	4988, 1588, 1073
<i>R</i> <sub>int</sub>	0.054
Indices range of <i>h</i> , <i>k</i> , <i>l</i>	−8→26, −7→23, −17→12
Refinement	
Refinement	Full-matrix least squares on <i>F</i> <sup>2</sup>
Number of reflections, parameters, restraints	1588, 60, 0
<i>R</i> <sub>1</sub> [ <i>F</i> <sup>2</sup> > 4 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>R</i> <sub>2</sub> all	0.046, 0.081
GoF	1.04
<i>wR</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all)*	0.094, 0.113
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e <sup>−</sup> Å <sup>−3</sup> )	2.16, −2.20

\*Weighting scheme:  $w=1/[\sigma^2(F_o^2)+(0.0441P)^2+4.9070P]$  where  $P=(F_o^2+2F_c^2)$

Mineralogical Magazine and is available as Supplementary material.

### Crystal structure

The crystal structure (Fig. 2) is a derivative of the fluorite-type structure, with a tetragonal symmetry. Here we use the same site nomenclature previously used for calzirtite. The cations are arranged on planes parallel to (010) and constitute double heteropolyhedral layers (at  $y = 1/6, 1/3$ ) containing the M2, M3, and M4 sites (with 8-, 6- and 7-fold coordination, respectively), intercalated between M1 + M4 layers (at  $y = 0, 1/2$ ). A special feature of the calzirtite structure is the splitting of the Zr-dominated M1 site (Zr–Zr contact 0.54 Å) within a distorted cube of O atoms. In hiärneite, metal atoms occupying the 4- to 8-coordinated site

**Table 2.** Fractional atomic coordinates, site occupancies and equivalent isotropic displacement parameters (Å<sup>2</sup>) for hiärneite.

Site	Site occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
M1	Mn <sub>0.72</sub> Zr <sub>0.21</sub> Fe <sub>0.05</sub> Mg <sub>0.02</sub>	0	1/4	0.1250	0.0195(3)
M2	Sb <sub>0.685</sub> Ti <sub>0.295</sub> Fe <sub>0.020</sub>	0.16860(2)	0.41860(2)	0.1250	0.00732(12)
M3	Ca <sub>0.785</sub> Mn <sub>0.130</sub> Na <sub>0.085</sub>	0.33674(7)	0.41326(7)	0.3750	0.0120(3)
M4	Zr <sub>0.98</sub> Hf <sub>0.02</sub>	0.16019(3)	0.26721(3)	0.36310(5)	0.00848(12)
O1	O <sub>1.00</sub>	1/4	0.4716(4)	0.0000	0.0138(10)
O2	O <sub>1.00</sub>	1/4	0.3186(3)	1/2	0.0099(9)
O3	O <sub>1.00</sub>	0.0769(2)	0.4941(2)	0.0452(3)	0.0101(6)
O4	O <sub>1.00</sub>	0.3783(2)	0.3388(2)	0.0099(4)	0.0131(7)
O5	O <sub>1.00</sub>	−0.0609(2)	0.1772(2)	0.4948(3)	0.0106(6)

**Table 3.** Selected bond distances (Å) in hiärneite.

M1–O5	1.953(3)	×4	M4–O5	2.091(3)
M1–O4	2.669(4)	×4	M4–O2	2.0960(18)
<M1–O>	2.311		M4–O4	2.144(3)
			M4–O3	2.157(3)
M2–O1	1.945(2)	×2	M4–O5'	2.184(3)
M2–O4	1.959(3)	×2	M4–O4'	2.191(4)
M2–O3	1.980(3)	×2	M4–O3'	2.239(3)
<M2–O>	1.961		<M4–O>	2.157
M3–O2	2.327(3)	×2		
M3–O5	2.461(4)	×2		
M3–O1	2.532(4)	×2		
M3–O3	2.583(3)	×2		
<M3–O>	2.476			

M1 are fixed at (0, 1/4, 1/8) without any spreading of electron density. For the remaining parts, calzirtite has an identical structural topology as hiärneite. Bond distances are the same within 0.02 Å as obtained for previous studies of the calzirtite structure, except for average M1–O distances that are slightly longer in hiärneite (2.31 Å vs. 2.26 Å).

### Chemical composition

Calzirtite is normally chemically relatively pure, with minor Nb and Ta substituting for Ti, Hf for Zr and Fe for Ca (Bellatreccia *et al.*, 1999); it may also host rare earth elements and actinides at low concentrations (Pascal *et al.*, 2009). As the concentration of common Pb is usually negligible, calzirtite has proven to be useful for <sup>207</sup>Pb–<sup>206</sup>Pb age determination (Wu *et al.*, 2010). Hiärneite is more complex in composition (Table 4, data from Holtstam, 1997).

The distribution of the cations present at the structural sites of hiärneite is based primarily on ionic radii and electronic charge. Calcium, Na and a fraction of Mn<sup>2+</sup> are assigned to M3. The M2 site is a mixed Sb, Ti site with minor Fe<sup>3+</sup>. The M4 site, as for calzirtite, is dominated totally by Zr (+ Hf). The M1 site hosts mainly Mn and a small fraction of Zr. These cation assignments are supported by refined site-scattering values (Table 5) and bond-valence sums (Table 6). The deviation of 2% in the overall mean electron number is acceptable for an Sb-bearing compound. The corresponding empirical formula of hiärneite is  $M^3(Ca_{1.57}Na_{0.17}Mn_{0.26}^{2+}\Sigma_{2.00}M^4(Zr_{3.98}Hf_{0.02})\Sigma_{4.00}M^1(Mn_{0.36}^{3+}Mn_{0.35}^{2+}Zr_{0.21}Fe_{0.05}^{3+}Mg_{0.02})\Sigma_{1.00}M^2(Sb_{1.37}Ti_{0.59}Fe_{0.04})\Sigma_{2.00}O_{16}$ . The presence of Mn<sup>3+</sup> in hiärneite is confirmed by optical absorption spectroscopy (Holtstam, 1997). Ordering of Mn<sup>3+</sup> to a normally Zr-dominated site is a very rare phenomenon, but the similar ionic radii (0.65 and 0.72 Å, respectively) and electronic charges make it

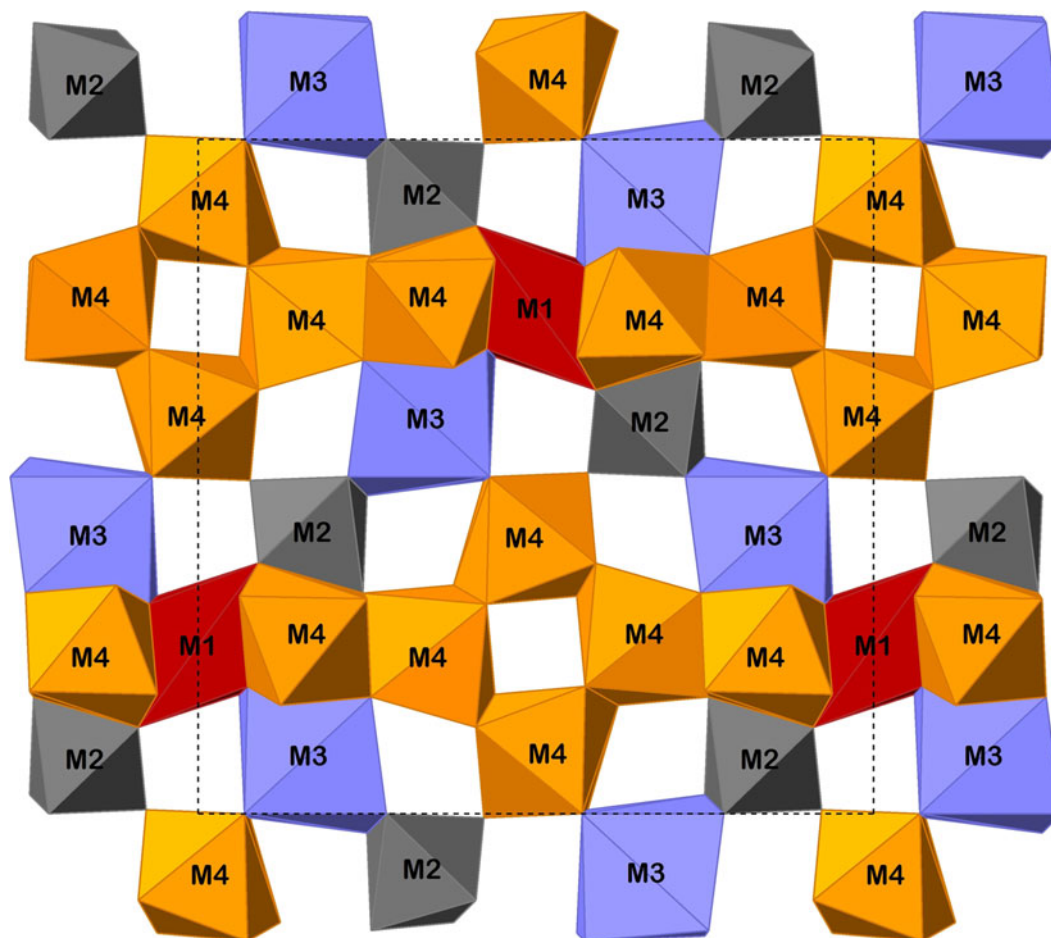


Fig. 2. The crystal structure of hiärneite seen along [001].

Table 4. Compositional data for hiärneite based on electron-microprobe point measurements\*.

	1	2	3	4	5	6	7	8	mean	2σ
Na <sub>2</sub> O	0.59	0.46	0.72	0.62	0.50	0.42	0.45	0.59	0.54	0.21
MgO	0.09	0.10	0.13	0.11	0.07	0.03	0.08	0.10	0.09	0.06
CaO	9.15	9.08	8.87	8.83	9.36	9.41	9.02	9.14	9.11	0.41
MnO**	4.01	5.24	3.74	4.78	4.07	3.83	5.81	4.58	4.51	1.47
Mn <sub>2</sub> O <sub>3</sub> **	3.71	0.98	3.90	2.98	3.13	4.39	1.65	3.03	2.97	2.29
TiO <sub>2</sub>	4.66	5.26	4.30	4.25	5.28	6.09	4.57	4.60	4.88	1.25
ZrO <sub>2</sub>	53.94	54.63	52.90	52.28	54.11	53.40	53.23	53.31	53.48	1.47
Sb <sub>2</sub> O <sub>5</sub>	22.87	21.97	23.45	24.31	21.93	21.01	24.07	23.91	22.94	2.40
Fe <sub>2</sub> O <sub>3</sub>	0.81	1.12	0.71	0.67	0.88	0.52	0.57	0.70	0.75	0.38
HfO <sub>2</sub>	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	-
Total	100.33	99.34	99.22	99.33	99.83	99.60	99.95	100.46	99.76	

\*Analytical conditions: wavelength-dispersive spectroscopy, 20 kV accelerating voltage and 12 nA beam current. HfO<sub>2</sub> concentration is estimated from energy-dispersive X-ray spectrometry. Data from Holtstam (1997), reproduced with permission.

\*\*Calculated from stoichiometry (9 cations, 16 oxygen atoms).

feasible. The assignment of Mn<sup>3+</sup> to the M1 site, and the presence of both Sb<sup>5+</sup> and Ti<sup>4+</sup> at the M2 site, form the basis for a definition of the ideal formula of hiärneite: Ca<sub>2</sub>Zr<sub>4</sub>Mn<sup>3+</sup>SbTiO<sub>16</sub>. The formula is expressed in this way to conform with the listed International Mineralogical Association (IMA) formula of calzirtite (from which its name is directly derived, and where Zr<sub>5</sub> represents the combined contents of M1+M4). The point-analysis closest to the hiärneite end-member represented here (no. 6 in Table 4)

has the composition  $M^3(\text{Ca}_{1.61}\text{Na}_{0.13}\text{Mn}_{0.26}^{2+})_{\Sigma 2.00}M^4(\text{Zr}_{3.98}\text{Hf}_{0.02})_{\Sigma 4.00}M^1(\text{Mn}_{0.53}^{3+}\text{Mn}_{0.26}^{2+}\text{Zr}_{0.17}\text{Fe}_{0.03}\text{Mg}_{0.01})_{\Sigma 1.00}M^2(\text{Sb}_{1.24}\text{Ti}_{0.73}\text{Fe}_{0.03})_{\Sigma 2.00}\text{O}_{16}$ .

In hiärneite, the average sum of trivalent ions at M1 (Mn<sup>3+</sup> + Fe<sup>3+</sup>) is 0.41 atoms per formula unit (apfu), a marginally higher value than (Mn<sup>2+</sup> + Mg) with 0.37 apfu. Minor changes in the chemical compositions could make the sum of divalent cations dominant instead, and thus the hypothetical end-member formula Ca<sub>2</sub>Zr<sub>4</sub>Mn<sup>2+</sup>Sb<sub>2</sub>O<sub>16</sub> becomes valid according to the

**Table 5.** Site-scattering (s.s.) values (epfu) for hiärneite.

Site	W.*	Refined s.s.	Site population (apfu)	Calculated s.s.
M1	8b	25.2	Mn <sub>0.72</sub> Zr <sub>0.21</sub> Fe <sub>0.05</sub> Mg <sub>0.02</sub>	27.7
M2	16f	81.2	Sb <sub>1.37</sub> Ti <sub>0.59</sub> Fe <sub>0.04</sub>	83.9
M3	16f	38.6	Ca <sub>1.57</sub> Na <sub>0.17</sub> Mn <sub>0.26</sub>	39.8
M4	32g	160.0	Zr <sub>3.98</sub> Hf <sub>0.02</sub>	160.6
Sum		305.0		312.0

\* Wyckoff position

**Table 6.** Weighted bond-valence sums (in valence units) for hiärneite according to the parameters of Brese and O'Keeffe (1991) for all the elements (site occupancies in Table 2) apart from Sb<sup>5+</sup>, which was calculated according to Mills *et al.* (2009a).

	M1	M2	M3	M4	ΣO
O1		0.840 <sup>x21→</sup>	0.206 <sup>x21→</sup>		2.092
O2			0.357 <sup>x21→</sup>	0.633 <sup>x2→</sup>	1.980
O3		0.774 <sup>x21</sup>	0.179 <sup>x21</sup>	0.537	1.923
				0.433	
O4	0.104 <sup>x41</sup>	0.816 <sup>x21</sup>		0.489	1.967
				0.558	
O5	0.717 <sup>x41</sup>		0.247 <sup>x21</sup>	0.644	2.107
				0.499	
ΣM	3.281	4.860	1.978	3.793	
Ideal	3.000	4.500	2.000	4.000	

**Table 7.** Minerals of the calzirtite group.

	Calzirtite <sup>1</sup>	Hiärneite <sup>2</sup>	Tazheranite <sup>3</sup>
Formula	M <sup>3</sup> Ca <sub>2</sub> M <sup>4</sup> Zr <sub>4</sub> M <sup>1</sup> Zr M <sup>2</sup> Ti <sub>2</sub> O <sub>16</sub>	M <sup>3</sup> Ca <sub>2</sub> M <sup>4</sup> Zr <sub>4</sub> M <sup>1</sup> Mn M <sup>2</sup> (SbTi) <sub>2</sub> O <sub>16</sub>	ZrO <sub>2-x</sub> , x ≈ 0.25
Space group	I <sub>41</sub> /acd	I <sub>41</sub> /acd	Fm $\bar{3}$ m
Z	8	8	4
a (Å)	15.094(2)	15.2344(6)	5.111(1)
c (Å)	10.043(3)	10.0891(6)	

<sup>1</sup>Sinclair *et al.* (1986); <sup>2</sup>this work; <sup>3</sup>Rastsvetaeva *et al.* (1998).

dominant-constituent rule. The application of the site-total-charge (STC) approach (Bosi *et al.*, 2019), however, gives a STC value of +2.81 for M1 and +9.33 for M2, close to +3 and +9, respectively. The dominant atomic arrangement is then Mn<sup>3+</sup> at M1 and (SbTi)<sup>9+</sup> at M2, giving the end-member formula presented here.

## Classification

As calzirtite and hiärneite are nearly isostructural, and consist of similar chemical components, they constitute a mineral group (Mills *et al.*, 2009b). The calzirtite group was introduced informally by Strunz and Nickel (2001), and includes calzirtite, an orthorhombic modification, calzirtite-1O (described by Callegari *et al.*, 1997), hiärneite and the structurally closely related cubic mineral tazheranite (Zr,Ti,Ca)(O, $\square$ )<sub>2</sub> (where  $\square$  = vacancy). Tazheranite is considered as a natural form of ZrO<sub>2</sub>, 'cubic zirconia', stabilised by impurity elements and oxygen vacancies (Rastsvetaeva *et al.*, 1998; Konzett *et al.*, 2013). Its structure is characterised by Zr and Ca, Ti etc. distributed randomly over the regular 8-coordinated sites in a fluorite-type Fm $\bar{3}$ m unit cell, whereas the anion sites are only partially occupied for charge compensation (also shown for synthetic analogues; Howard *et al.*, 1988). In calzirtite and hiärneite, the ordering of the cations over

specific sites leads to a lower symmetry and a tripled *a* parameter and doubled *c* parameter (Table 7). More pure variants of cubic ZrO<sub>2</sub> have also been reported to form from shock-metamorphism of zircon (e.g. Kenny and Pasek, 2021). All of the group members belong to the Nickel-Strunz subdivision 4.DL (Strunz and Nickel, 2001). The calzirtite group, with calzirtite, hiärneite and tazheranite, has been accepted by the Commission on New Minerals, Nomenclature and Classification of the IMA, along with the new formula of hiärneite presented here (proposal 21-G, Miyawaki *et al.*, 2022).

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2022.19>

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