

# The crystal structure of the new mineral dynaesite-(La), $\text{Na}_8\text{Ce}^{\text{IV}}\text{REE}_2(\text{PO}_4)_6$

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## ABSTRACT

Dynaesite-(La),  $\text{Na}_{7.89}(\text{Ce}_{0.94}\text{Ca}_{0.06})_{\Sigma 1.00}(\text{La}_{1.14}\text{Ce}_{0.40}\text{Pr}_{0.10}\text{Nd}_{0.24}\text{Ca}_{0.12})_{\Sigma 2.00}(\text{PO}_4)_6$  is orthorhombic, *Pnma*,  $a = 18.4662(7)$ ,  $b = 16.0106(5)$ ,  $c = 7.0274(2)$  Å,  $V = 2077.7(1)$  Å<sup>3</sup>,  $Z = 4$ . The crystal structure is related to the group of  $\text{Na}_3\text{REE}(\text{XO}_4)_2$  compounds (with X = P, V, As), based on the aphthalite/glaserite structural type. Dynaesite is distinct in having ordered Na vacancies, and a rare-earth element (REE) site occupied preferentially by  $\text{Ce}^{4+}$ . This also distinguishes it from closely related vitusite-(Ce) [ $\text{Na}_3\text{REE}(\text{PO}_4)_2$ ]. The relation of their unit cells is:  $a_d = b_v$ ,  $b_d = 3a_v$ ,  $c_d = 1/2c_v$ . The distinct  $\text{Ce}^{4+}$  site in dynaesite-(La) has smaller coordination with shorter bond lengths than the other REE site in the same structure or the REE sites in vitusite-(Ce). It is adjacent to the predominately vacant Na site, which in its turn has the largest coordination of all Na sites in the structure. REE sites, or Na sites in a [010] row (similar to [100] in vitusite-(Ce)) assume two types of coordinations with and without mirror symmetry and two different configurations of surrounding  $\text{PO}_4$  tetrahedra. This summarizes the topological difference to vitusite-(Ce) where the corresponding coordinations are similar in the same row and intermediate in character to the two types in dynaesite-(La).

## Introduction

In the autumn of 2003 the author of this article was presented with several grains of a honey-coloured mineral with a greenish tint by Jørn Rønso for analysis by X-ray diffraction methods. The mineral was found as an accessory constituent of a lujavrite rock from the Ilimaussaq alkaline complex. By its appearance and results of the chemical analysis it closely resembled vitusite-(Ce) [ $\text{Na}_3(\text{Ce},\text{La},\text{Nd})(\text{PO}_4)_2$ ] with small but persistent differences in chemical composition and optical characteristics. An X-ray diffraction crystal-structure analysis showed this mineral to be a new species, structurally related closely to vitusite-(Ce) but with distinct features which characterize it as a new sodium-REE phosphate. The mineral and its name (dynaesite-(La)) were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA

2014-070). Its general chemical and physical properties are described in the article by Rønso *et al.* (2017). The details of its crystal structure are reported in the present work.

## Experimental data, crystal-structure solution and refinement

The investigated crystal grain was an irregular equant fragment with a honey-greenish colour and volume  $\approx 0.002$  mm<sup>3</sup>. The X-ray diffraction (XRD) measurements were undertaken on a Bruker-AXS diffractometer with the four-circle goniometer and a Smart1000 CCD area detector. The details of the data collection and crystal-structure refinement are presented in Table 1. The program used for the crystal inspection and measurement was *SMART*, *SAINT* was used for the calculation of reflection intensities and refinement of the unit-cell parameters, *XPREF* for the data correction. All are Bruker-AXS programs (Bruker AXS Inc., Madison, Wisconsin, USA) tailored for the instrument used.

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TABLE 1. Crystallographic data and structure refinement details.

Crystal size (mm)	0.144 × 0.126 × 0.108
Measurement temperature	298 K
Crystal formula	Na <sub>7.89</sub> Ca <sub>0.18</sub> Ce <sub>1.34</sub> La <sub>1.14</sub> Pr <sub>0.10</sub> Nd <sub>0.24</sub> P <sub>6</sub> O <sub>24</sub>
Formula weight	1151.6
Space group	<i>Pnma</i>
Unit-cell parameters (Å)	18.4662(7), 16.0106(5), 7.0274(2)
Unit-cell volume (Å <sup>3</sup> )	2077.7(1)
<i>Z</i>	4
<i>F</i> (000)	2153
Instrument	Bruker-AXS Smart1000CCD
Detector	CCD, 6.25 × 6.25 cm, 512 × 512 pixel
X-ray wavelength (Å)	0.71073
$\mu$ (mm <sup>-1</sup> )	6.744
$D_x$ (g cm <sup>-3</sup> )	3.6802
Range for data collection, $\theta$ (°)	2.21–36.28
Step rotation (°)	0.2
Limiting indices	$-28 \leq h \leq 28, -19 \leq k \leq 26, -11 \leq l \leq 9$
Reflections collected/unique/observed	23,594/4624/2477
$R_{int}$	0.0546
Data/restraints/parameters	4624/0/207
Goodness of fit	1.04
<i>R</i> indices (observed)*	$R_1 = 0.0372, wR_2 = 0.0604$
<i>R</i> indices (all data)	$R_1 = 0.0855, wR_2 = 0.0663$
Difference density (e/Å <sup>3</sup> )	-2.78, +3.98

\*Weighting scheme:  $1/(\sigma_1^2 + 0.0004I^2)$ .

The unit-cell parameters were determined from 5707 reflections with  $I > 10\sigma_I$ . The systematic extinctions and data statistics suggested space group *Pnma*. The basic details of the crystal structure were obtained by direct methods (program *SHELXS*, Sheldrick, 2008) that revealed the two *REE* sites and the four P sites. The positions of the Na and O atoms were revealed through subsequent refinements, difference-Fourier maps and inspection of interatomic distances. The program used for the crystal structure refinement was *JANA2006* (Petříček *et al.*, 2014).

The *REE* sites were initially refined as fully occupied by Ce. When their occupancy parameters were left unconstrained, the refinement resulted in an equal number of electrons per site (55.8), just slightly smaller than the atomic number of Ce. The atomic coordinations of the two sites were shown to be different, with Ce1 having, on average, smaller bond lengths than La2. As the valence balance of the formula obtained by electron microprobe analysis (EMPA) suggested the presence of Ce<sup>4+</sup>, Ce1 was considered to be occupied by this species with a small Ca substitution and La2 as housing the rest of the *REE* and Ca. The practically equal electron numbers found for both *REE* sites can be explained if equivalent amounts of Ca substitute at

both sites. The above assumptions were used as site contents in the last refinement.

After all of the fully occupied sites were defined, with refinement giving a residual factor  $R_1$  of 4.22% (with anisotropic atomic displacement factors), a small residual atomic site could still be seen in the difference electron density map. This site was found to correspond to the ‘missing’ Na of the vitusite structure (see Description of the crystal structure) and was subsequently refined as the Na site (Na6) with partial occupancy. The occupancies of Na1 to Na5 sites were also left unconstrained and attained close to full occupancy (0.94 to 0.99). The Na6 site was refined as mostly vacant (Table 2). The final crystallographic information file (cif), which includes a list of observed and calculated structure factors, has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from [http://www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

The final structural formula obtained with the above described refinement is Na<sub>7.89</sub>(Ce<sub>0.94</sub>Ca<sub>0.06</sub>)<sub>Σ1.00</sub>(La<sub>1.14</sub>Ce<sub>0.40</sub>Pr<sub>0.10</sub>Nd<sub>0.24</sub>Ca<sub>0.12</sub>)<sub>Σ2.00</sub>(PO<sub>4</sub>)<sub>6</sub>, to be compared with Na<sub>7.44</sub>Ca<sub>0.19</sub>Ce<sub>1.35</sub>La<sub>1.16</sub>Nd<sub>0.24</sub>Pr<sub>0.10</sub>Sm<sub>0.02</sub>Y<sub>0.01</sub>(P<sub>6.02</sub>Si<sub>0.03</sub>)O<sub>24</sub>, obtained by EMPA (Rønso *et al.*, 2017). Neglecting the

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TABLE 2. Final atomic parameters for dynaesite-(La).

Atom	$x/a$	$y/b$	$z/c$	$U_{eq}/\text{\AA}^2$	Multiplicity	Occupancy
Ce1	0.09591(2)	0.25	0.03835(4)	0.0126(1)	4	0.94
Ca1	0.09591(2)	0.25	0.03835(4)	0.0126(1)	4	0.06
La2	0.11977(1)	0.60603(1)	0.01020(3)	0.01417(7)	8	0.57
Ca2	0.11977(1)	0.60603(1)	0.01020(3)	0.01417(7)	8	0.06
Ce2	0.11977(1)	0.60603(1)	0.01020(3)	0.01417(7)	8	0.2
Pr2	0.11977(1)	0.60603(1)	0.01020(3)	0.01417(7)	8	0.05
Nd2	0.11977(1)	0.60603(1)	0.01020(3)	0.01417(7)	8	0.12
P1	0.79570(6)	0.58406(6)	0.2196(1)	0.0125(3)	8	1
P2	0.04062(9)	0.75	0.2362(2)	0.0122(4)	4	1
P3	0.03322(6)	0.07934(6)	0.1993(1)	0.0118(3)	8	1
P4	0.78307(9)	0.25	0.1940(2)	0.0139(5)	4	1
Na1	0.3649(1)	0.0717(1)	0.0102(2)	0.0177(6)	8	0.987(7)
Na2	0.3635(1)	0.75	0.0289(3)	0.030(1)	4	0.981(9)
Na3	0.7081(1)	0.75	0.1361(3)	0.023(1)	4	0.941(8)
Na4	0.4629(1)	0.5891(1)	0.1516(2)	0.0208(6)	8	0.965(6)
Na5	0.6976(1)	0.0804(1)	0.2294(2)	0.0242(7)	8	0.964(6)
O1	0.0246(2)	0.1013(2)	-0.0122(4)	0.024(1)	8	1
O2	0.0504(2)	0.75	0.0159(5)	0.019(1)	4	1
O3	0.8374(2)	0.5823(2)	0.4055(4)	0.037(1)	8	1
O4	0.0692(2)	0.1556(2)	0.2925(4)	0.022(1)	8	1
O5	0.7967(3)	0.25	-0.0203(5)	0.034(2)	4	1
O6	0.0770(2)	0.8285(2)	0.3127(3)	0.0180(9)	8	1
O7	-0.0426(2)	0.0633(2)	0.2777(4)	0.024(1)	8	1
O8	0.0816(2)	0.0037(2)	0.2313(4)	0.023(1)	8	1
O9	0.7140(2)	0.5929(2)	0.2490(4)	0.021(1)	8	1
O10	0.8178(2)	0.3292(2)	0.2735(5)	0.041(1)	8	1
O11	-0.0412(2)	0.75	0.2751(5)	0.015(1)	4	1
O12	0.7022(2)	0.25	0.2408(5)	0.022(1)	4	1
O13	0.8212(2)	0.6576(2)	0.0995(6)	0.057(2)	8	1
O14	0.8087(2)	0.5038(2)	0.1108(6)	0.060(2)	8	1
Na6	0.451(1)	0.25	0.154(2)	0.025	4	0.133(5)

small substitution by Ca, both results correspond to the idealized formula  $\text{Na}_8\text{Ce}^{4+}\text{REE}_2^{3+}(\text{PO}_4)_6$  of dynaesite-(La).

The amount of Na obtained by EMPA is slightly lower than required by valence balance, whereas the one obtained by XRD gives a good valence balance. There are no substitutions observed in Na sites. Five of them refine to almost full occupancy, whereas the sixth one has a very low occupancy. The sum of Na gives a content per formula unit that is smaller by 1/9 when compared to vitusite-(Ce), and justifies the 4+ valence state of Ce in dynaesite-(La), whereas vitusite-(Ce) contains  $\text{Ce}^{3+}$ .

### Description of the crystal structure

The crystal structure of dynaesite-(La) is related closely to that of vitusite (Mazzi and Ungaretti,

1994). A significant correspondence in unit-cell parameters can be discerned with  $a_d = b_v$ ,  $b_d = 3a_v$ ,  $c_d = 1/2c_v$ . The crystallographic and chemical differences, which make dynaesite-(La) a distinct mineral species, are summarized by Rønso *et al.* (2017). In shortened form they are: (1) the different sizes of unit cells; (2) different space-group symmetries; (3) different occupancies of Na sites, coupled to different oxidation states of REE; and (4) presence of satellite reflections in vitusite, which testify for supercells, not observed in dynaesite.

Mazzi and Ungaretti (1994) classified vitusite in the structural group of the high-temperature forms of  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , as suggested already by Rønso *et al.* (1979). However, as these structure prototypes are characterized by disorder in the orientation of  $\text{SO}_4$  tetrahedra (Miyake *et al.*, 1980; Eysel *et al.*, 1985), the nature of which is disputed (Arnold *et al.*, 1981), in the following the structures of vitusite and dynaesite

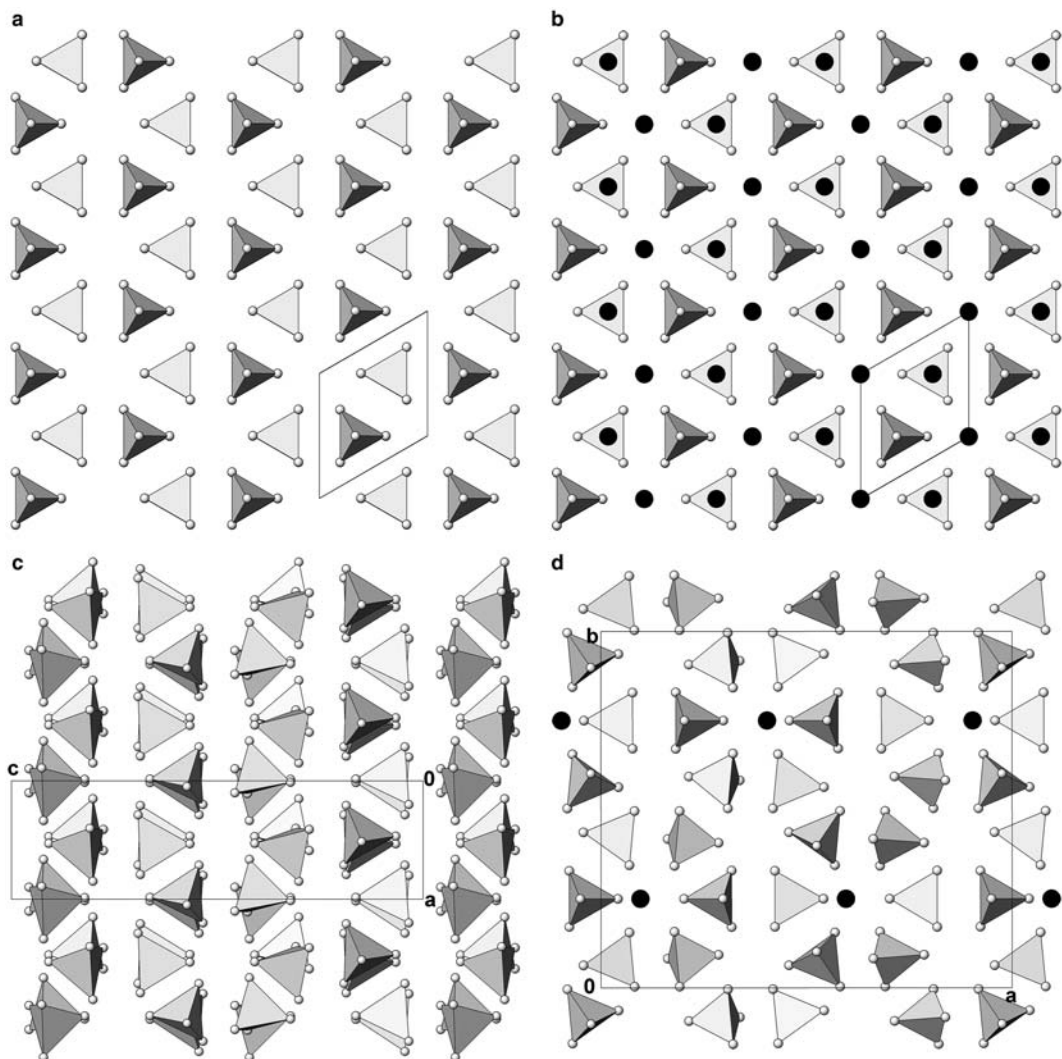


FIG. 1. The arrangement of anionic tetrahedra in the crystal structures of (a) aphthitalite; (b) aphthitalite with indicated large cation sites (black dots); (c) vitusite-(Ce) (sub-cell); and (d) dyrnaesite-(La) (black spots indicate Ce1 sites). Projections perpendicular to tetrahedral layers, unit cells indicated.

will be compared to the archetypal structure of aphthitalite/glaserite (Okada and Ossaka, 1980), which is the highest symmetry structure in the group with ordered orientation of anionic tetrahedra.

As noted by Vlasse *et al.* (1980), various  $\text{Na}_3\text{REE}(\text{XO}_4)_2$  crystal structures (where X represents a pentavalent element, P, V, or As) are topologically related to the archetypal structure of aphthitalite/glaserite ( $\text{KNaSO}_4$ ). Dyrnaesite is related topologically to the same family, but is unique in having ordered vacancies in Na sites,

coupled to the increased valence of 1/3 of REE, also ordered in a specific structural site.

Taking the tetrahedral units ( $\text{XO}_4$ ) alone, their 3D arrangement corresponds to hexagonal eutaxy (O'Keeffe, 1977). In aphthitalite, the tetrahedra in the same eutectic layer point in the same direction, and tetrahedra in successive layers point in the opposite directions (Fig. 1). The O atoms that form the bases of tetrahedra parallel to the layers make a kagome pattern (a pattern of triangles and hexagons). However, as the edges of tetrahedra are

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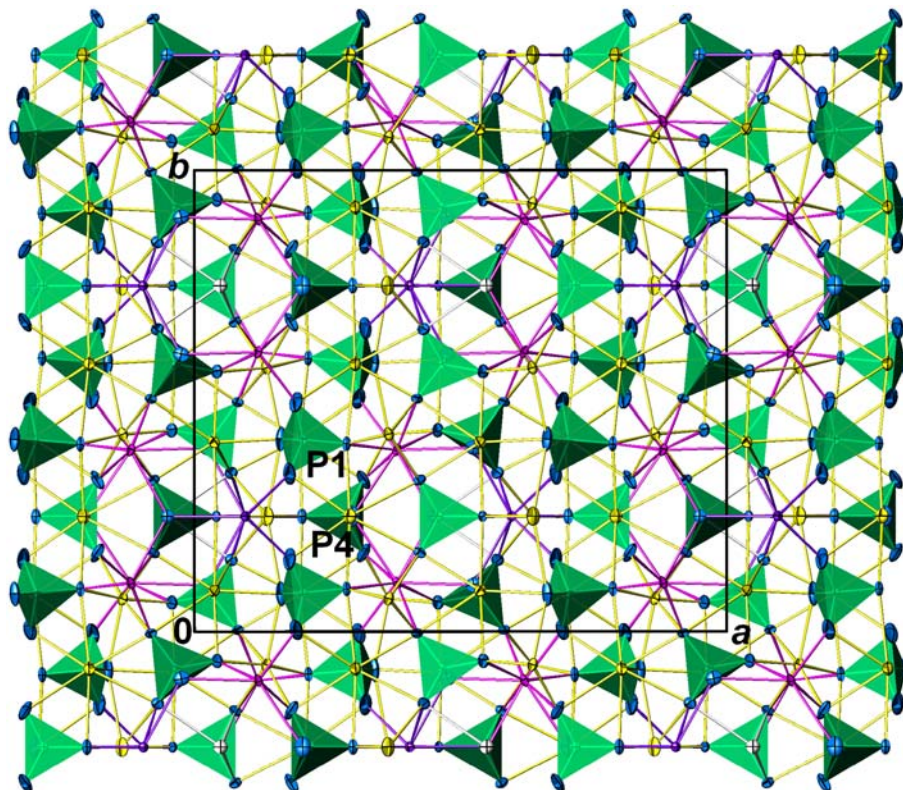


FIG. 2. The crystal structure of dyrnaesite-(La) as seen along [001]. P1 and P4 phosphate tetrahedra indicated. Blue = O, green = P, dark violet = Ce1, violet = La2, yellow = Na1–5, white = Na6. Displacement ellipsoids drawn at 50% probability level.

shorter than distances between them, the triangles in the pattern are of unequal sizes and the hexagons have two sets of sides of unequal lengths – i.e. the pattern is distorted trigonally. As the apices of tetrahedra in successive layers point in the opposite directions, the two different interlayers are formed: one between the apices and the other between the bases of tetrahedra. The eutactic arrangement means that the successive layers are displaced relatively to each other so that the tetrahedra of one layer are placed above the centres of hexagons of the successive layer. There are three large cation sites with three different types of coordinations in the structure. The first one is situated inside a layer of tetrahedra, in the centre of hexagons, capped from each side by a tetrahedron from a neighbouring layer. In the ideal structure its coordination number (CN) is 10. The other two lie in [001] channels with hexagonal cross-section, one between the apices, and the other between the

bases of tetrahedra. Their CN in the ideal structure are 6 + 6, and 6, respectively.

As noted by Mazzi and Ungaretti (1994), all structures of this type can be described as hexagonal close-packing of rods (O’Keeffe and Anderson, 1977). Considering the rod packings, the first coordination type lies in rod A where it interchanges with  $XO_4$  tetrahedra. The last two form rod B. In the  $Na_3REE(XO_4)_2$  structures, Na occupies the sites in the A rods, whereas REE and Na interchange in B rods (Vlasse *et al.*, 1980).

Various crystal structures in the group have generally the same disposition of large cations and tetrahedral groups, but differ in having differently rotated tetrahedra in relation to this general scheme (Vlasse *et al.*, 1980). The reason for the more complex sequence in the orientation of tetrahedral groups in the structures containing REE compared to the archetypal structure that contains only alkaline cations is in the crystal chemical

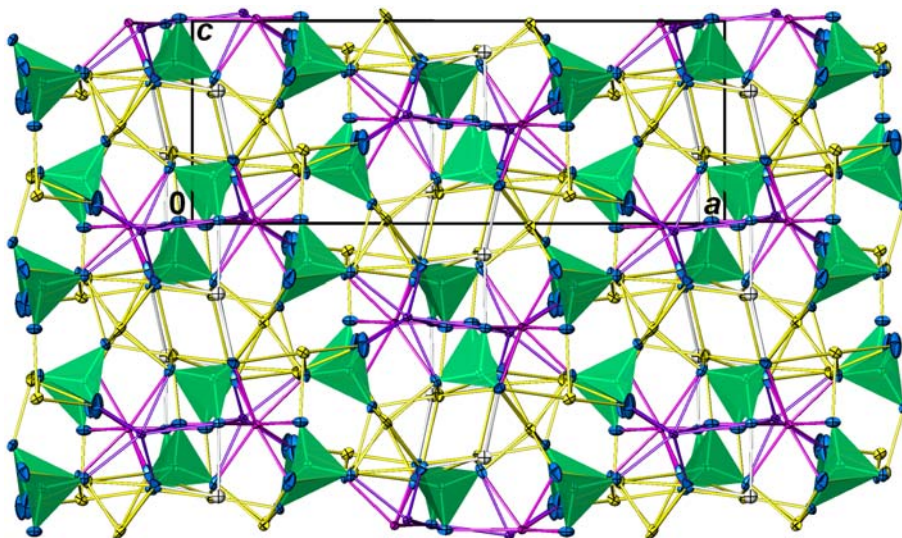


FIG. 3. The crystal structure of dymaesite-(La) as seen along [010]. The colouring is as in Fig. 2.

characteristics of *REE*. Their crystal chemical radii are shorter than that of  $K^+$  and approximately equal to that of  $Na^+$ . On the other hand, they typically form coordinations with higher coordination numbers than the latter, in this respect more resembling  $K^+$ . To achieve this, at least some of the tetrahedra surrounding *REE* atoms have to be rotated disturbing the ideal archetypal arrangement.

Dymaesite-(La) shows a relatively close relation to the structure of  $Na_3La(VO_4)_2$  (Vlasse *et al.*, 1976), which is almost identical to the structure of the sub-cell of vitusite-(Ce) (Mazzi and Ungaretti, 1994). Comparing the overall atomic arrangements in the crystal structures of dymaesite with those of  $Na_3La(VO_4)_2$  or the sub-structure of vitusite, one can notice a general similarity in topology (Figs 2, 3, 4 and 5). Considering the cations in B rods, in dymaesite every third *REE* site in a [010] row is Ce1 that houses  $Ce^{4+}$  and the (010) mirror planes are placed on its level, making the coordination mirror-symmetrical. This triples the period of the corresponding crystal axis in respect to the sub-cell of vitusite. In the sites located in A rods, every third Na site (Na6) in a [010] row is dominated by vacancies, which also lie on the level of (010) mirror planes. The main difference in the orientation of tetrahedral groups can be seen between P1 and P4 tetrahedra of dymaesite, which correspond to P3 and P4 in vitusite. Whereas in the sub-cell of vitusite all tetrahedra

in a [100] row (corresponding to [010] in dymaesite) have the same orientation, and both P3 and P4 coordinations show similar inclination to the [001] axis, in dymaesite the P1 and P4 coordination tetrahedra in the same [010] row are rotated by  $180^\circ$  relative to each other around the P–O bonds oriented approximately in the [100] direction, so that their apices point alternatively up and down when seen from the [001] direction (Figs 2, 3, 4 and 5). There are no significant differences in the disposition of other phosphate tetrahedra between the two structures.

The coordination tetrahedra of P in dymaesite-(La) are essentially regular, with just very small differences in bond distances for P1, P2 and P3, making them slightly eccentric in their surroundings (Table 3). The average P–O bonds in dymaesite-(La) and in the sub-cell of vitusite-(Ce) correspond very well (1.528, respectively 1.524 Å). The average bond distance in the 8x superstructure of vitusite is 1.54 Å (Mazzi and Ungaretti, 1994), which appears slightly too long.

The full coordination of Ce1 (Fig. 6a, deposited) has CN 9. The coordination form is a distorted tri-capped trigonal prism with O12 and two O1 as the capping atoms. It shares edges with three  $PO_4$  tetrahedra and vertices with additional three. The six closest O atoms (at distances up to 2.5 Å) make a distorted octahedral coordination. The Ce1 site is in a special position lying on a mirror plane. This

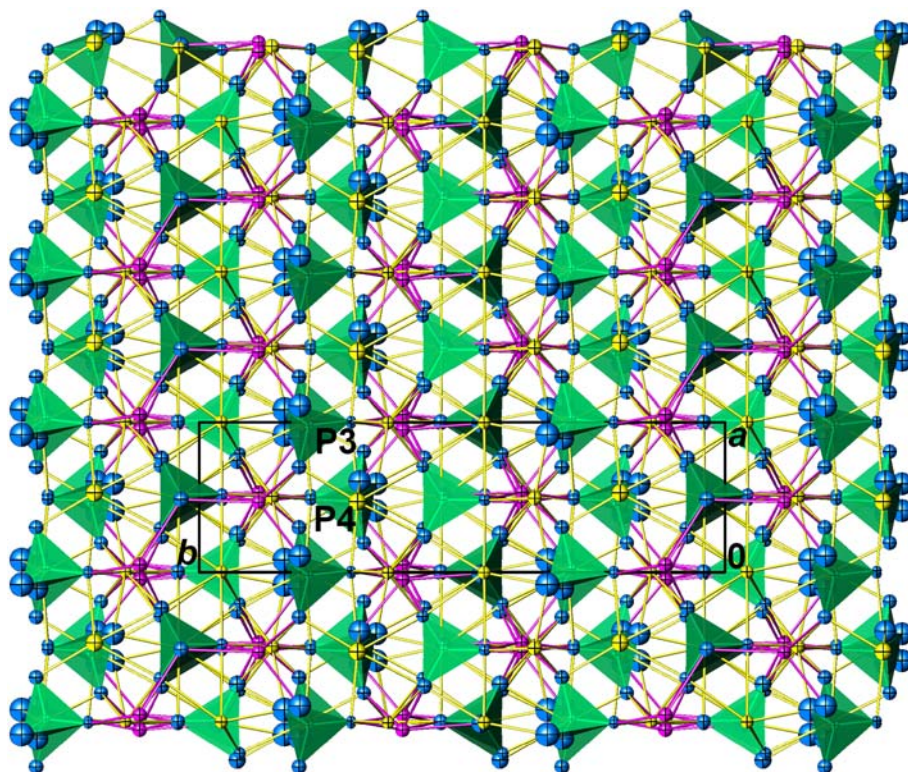


FIG. 4. The crystal structure of vitusite-(Ce) sub-cell (Mazzi and Ungaretti, 1994) as seen along [001]. P3 and P4 phosphate tetrahedra indicated. The colouring of atoms is as in Fig. 2, except for REE sites which both are violet, and Na sites which all are yellow. Note that, according to the authors, the structure was refined anisotropically but only the isotropic displacement factors were published.

coordination shows significantly shorter bonds to the closest six O atoms (2.40 Å on average) when compared to the other REE coordination in dynaesite-(La) (La2: 2.47 Å) or REE coordinations in vitusite-(Ce) (2.46 Å in the sub-cell, 2.44 to 2.52 Å in the 8x supercell). It is therefore considered predominantly occupied by Ce<sup>4+</sup>. Considering the disposition of the surrounding six PO<sub>4</sub> tetrahedra, this coordination is similar to that of Ce1 in vitusite-(Ce) (Figs 6a and 6c, deposited; note: Figs 6–9 have all been deposited with the Principal Editor of *Mineralogical Magazine* and are available from [http://www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html)).

The coordination of La2 (Fig. 6b, deposited) also shares edges with three PO<sub>4</sub> tetrahedra and vertices with the other three that surround it and the full first coordination sphere has CN 9. This full coordination has the form of a distorted capped square antiprism, with O1 as the capping atom. Taking into

consideration only the atoms closer than 2.7 Å (excluding O5) gives to the coordination the form of a distorted bi-capped trigonal prism with O1 and O14 as the capping atoms. In the disposition of the surrounding six phosphate tetrahedral, this coordination resembles Ce2 from vitusite-(Ce) (Figs 6b and 6d, deposited).

The coordination of Na1 (Fig. 7a, deposited) is a distorted octahedral one. It shares a vertex with each of the six surrounding PO<sub>4</sub> tetrahedra. It lies in the same rod B as La2. The disposition of the surrounding tetrahedra resembles that of Na1 and Na2 in vitusite-(Ce) (Figs 7a, 7c and 7d, deposited).

The Na2 site also lies in rod B and on the mirror plane in the same way as Ce1. It also has CN 6 and a distorted octahedral coordination, sharing a vertex with each of the six surrounding PO<sub>4</sub> tetrahedra (Fig. 7b, deposited). The two most distant oxygen atoms (O3) are at a rather long distance over 2.7 Å. The disposition of the surrounding PO<sub>4</sub> tetrahedra

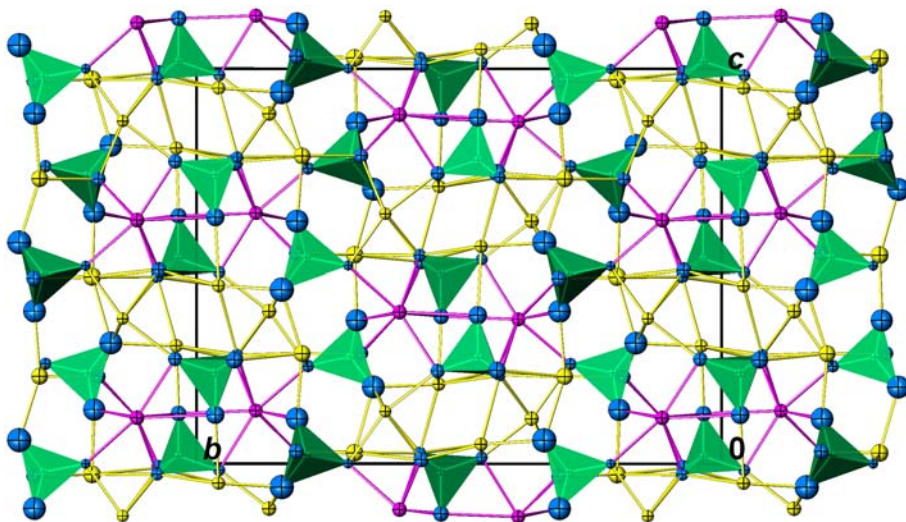


FIG. 5. The crystal structure of vitusite-(Ce) sub-cell as seen along [100]. The colouring of atoms is as in Fig. 4.

differs from Na1 in dynmaesite-(La) and Na1 and Na2 in vitusite-(Ce) in the 180° rotation of the P4 tetrahedron around the P4–O12 bond (Fig. 5).

The Na3 site also lies on the mirror plane but in rod A, surrounded by five PO<sub>4</sub> tetrahedra (Fig. 8a, deposited). It shares edges with tetrahedra from the

TABLE 3. Parameters of the cation coordinations calculated by the program *IVTON* (Balić-Žunić and Vicković, 1996). Distortion parameters are related to the centroid of coordination (Balić-Žunić and Makovicky, 1996). Volume-based values are used (Balić-Žunić, 2007).

	CN	Average bond length (Å)	Eccentricity	Asphericity	Volume distortion
P1	4	1.521(6)	0.02	–	0
P2	4	1.535(17)	0.05	–	0
P3	4	1.530(7)	0.02	–	0
P4	4	1.528(2)	0.01	–	0
Ce1	6	2.40(6)	0.04	0.07	0.14
	9	2.51(18)	0.22	0.16	0.05
La2	8	2.52(10)	0.17	0.04	0.08
	9	2.55(13)	0.20	0.09	0.06
Na1	6	2.41(11)	0.17	0.08	0.08
Na2	4	2.40(19)	0.51	–	0.33
	6	2.52(24)	0.16	0.27	0.25
Na3	7	2.62(12)	0.28	0.03	0.50
	9	2.68(15)	0.26	0.03	0.09
Na4	5	2.47(11)	0.13	0.10	0.34
	7	2.56(18)	0.30	0.13	0.18
Na5	7	2.61(15)	0.29	0.10	0.44
	9	2.68(19)	0.29	0.09	0.11
Na6	7	2.72(10)	0.11	0.06	0.15

CN – coordination number.



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TABLE 4. Interatomic distances (in Å) inside the first coordination sphere for large cations.

Ce1	–O13 (2x)	2.338(4)	Na3	–O5	2.415(4)
	–O4 (2x)	2.392(3)		–O13 (2x)	2.575(4)
	–O11	2.424(4)		–O9 (2x)	2.640(3)
	–O12	2.502(4)		–O6 (2x)	2.752(4)
	–O2	2.730(4)		–O10 (2x)	2.886(4)
	–O1 (2x)	2.743(3)		Na4	–O3
La2	–O14	2.357(4)	–O1		2.382(3)
	–O9	2.437(3)	–O7		2.493(3)
	–O8	2.449(3)	–O6		2.499(4)
	–O6	2.498(3)	–O11		2.628(2)
	–O10	2.526(4)	–O8		2.773(4)
	–O7	2.567(3)	–O4	2.801(3)	
	–O2	2.636(2)	Na5	–O3	2.366(3)
	–O1	2.667(3)		–O8	2.485(4)
	–O5	2.775(3)		–O14	2.592(4)
	Na1	–O7		2.269(4)	–O4
–O9		2.359(3)		–O10	2.667(4)
–O10		2.363(4)		–O12	2.718(2)
–O6		2.373(3)	–O9	2.793(3)	
–O8		2.504(3)	–O13	2.900(4)	
Na2	–O3	2.586(4)	–O14	2.948(4)	
	–O11	2.233(4)	Na6	–O2	2.54(1)
	–O12	2.249(4)		–O4 (2x)	2.68(2)
	–O4 (2x)	2.566(3)		–O6 (2x)	2.76(1)
	–O3 (2x)	2.767(3)		–O10 (2x)	2.81(2)

same layer and one topping tetrahedron, whereas with the last one it shares only one vertex and has thus CN 9. This full coordination is in a rather peculiar form, which can be described as a combination of a hexagonal pyramid and a trigonal prism, or better as a hexagonal bi-pyramid with one ‘split’ apical vertex. If the two O atoms representing the split vertex, which are at rather long distances of 2.89 Å (O10) are excluded, only the hexagonal pyramid remains. The Na3 site is placed below its base in the direction of these two most distant O atoms. The phosphate surrounding shares general features with Na5 and Na6 in vitusite-(Ce) (Fig. 8, deposited).

The Na4 site is also situated in rod A, but is not lying on the symmetry plane. Taking into account only O atoms closer than 3 Å, the first coordination sphere polyhedron has the form of a distorted pentagonal bipyramid (CN 7). It shares edges with only two of the equatorial tetrahedra, due to the inverted orientation of the third one with which it shares only one vertex as well as with the two topping ones (Fig. 9a, deposited). If only O atoms closer than 2.7 Å are considered, the coordination reduces to a distorted square pyramid (CN 5). This

coordination shows apparent similarities with coordinations of Na3 and Na4 in vitusite-(Ce), to which it also corresponds in the general structural disposition (Figs 9c and 9d, deposited).

The last practically fully occupied Na site, Na5, is in the same [010] row as Na3 and therefore corresponds to Na5 and Na6 in vitusite-(Ce) (Fig. 8b). The coordination shape can be described as a split hexagonal bipyramid (CN 9) as in the case of Na3. As the two most distant O atoms (O13 and O14) form the ‘split’ vertex of the bi-pyramid, if they are excluded from the coordination it also reduces to a hexagonal pyramid. Apart from the difference in symmetry (Na3 lies on the mirror plane) the orientations of the surrounding PO<sub>4</sub> tetrahedra are also essentially different, due to the opposite rotations of P1 and P4 tetrahedra in the two coordinations (Figs 8a and 8b, deposited). For the surroundings of Na5 and Na6 in vitusite-(Ce), it can be said that they assume an intermediate situation between the two types of surroundings in dynaesite-(La) (Fig. 8, deposited).

The mostly vacant Na6 site is in rod A, lies on the mirror plane, and is in the same [010] row as Na4. It

is characterized by relatively long Na–O distances, longer than those characteristic for Na (Table 4), and by a relatively regular coordination, which is in the form of a moderately distorted mono-capped trigonal prism with CN 7 (Fig. 9b). Similarly to Na4, its surroundings resemble those of Na3 and Na4 in vitusite-(Ce). The rotation of P1 and P4 tetrahedra is in the opposite sense compared to Na4 coordination. Thus, like in the case of Na3 and Na5, the tetrahedral disposition around the corresponding sites in vitusite-(Ce) is intermediate to the two Na coordinations in dyrnesite-(La) (Fig. 9, deposited).

Summarizing the similarities and differences in large cation coordinations in dyrnesite-(La) and vitusite-(Ce), one can conclude that there is a general similarity between the two structures in the coordinations of equivalent sites. The main differences are in the fact that in dyrnesite-(La) the coordinations lying in the same [010] row tend to form two distinct types (pairs Ce1–La2, Na1–Na2, Na3–Na5 and Na4–Na6), whereas the corresponding pairs in the crystal structure of vitusite-(Ce) tend to resemble each other and assume the type of coordinations that are intermediate between the two types in dyrnesite-(La). This is connected to the disposition of P1–P4 pairs of PO<sub>4</sub> tetrahedra in dyrnesite-(La), which assume opposite orientations, whereas the corresponding P3–P4 PO<sub>4</sub> tetrahedra in vitusite-(Ce) assume an intermediate orientation when compared to them.

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