The Crystal Structure of the Sodium Erbium Orthovanadate α-Na₃Er(VO₄)₂

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The structure of the low-temperature variety of $Na_3Er(VO_4)_2$ has been determined from Patterson and Fourier syntheses and refined by full-matrix least squares with single-crystal diffractometer data to $R=0.035$. The space group is $P2_1/n$ with $a=5.490$ (5), $b=9.739$ (8), $c=7.215$ (5) Å, $\beta=93.07$ (5)°, $Z=2$. The structure is a network of isolated tetrahedra in which the Na and Er atoms are arranged in an ordered way. The structure is described from a topological viewpoint.

Introduction

The X-ray diffraction study of the Na_3VO_4–$LnVO_4$ systems (Ln = Y, La, Pr, Dy, Ho, Er, Tm, Yb, Lu) has allowed the characterization of a series of compounds of general formula $Na_3Ln(VO_4)_2$ (Le Flem & Olazcuaga, 1968; Salmon, Parent, Daoudi & Le Flem, 1975).

$Na_3La(VO_4)_2$ and $Na_3Pr(VO_4)_2$ exist in only one allotropic variety. The determination of the crystal structure of $Na_3La(VO_4)_2$ has shown that it crystallizes with a β-K_2SO_4 type ordered structure (Vlasse, Salmon & Parent, 1976).

A high-temperature X-ray diffraction study shows that the $Na_3Ln(VO_4)_2$ compounds (Ln = Y, Dy, Ho, Er, Tm, Yb, Lu) have three allotropic forms: a low-temperature α monoclinic variety, a high-temperature β hexagonal variety and a γ variety, which is derived from the Na_2CrO_4 structure and is obtained by rapid quenching of the β variety (Salmon, Parent, Daoudi & Le Flem, 1975).

The structural similarities between $Na_3Y(VO_4)_2$, $Na_3Er(VO_4)_2$ and $Na_3Yb(VO_4)_2$ make possible the synthesis of mixed crystals of formula $Na_3(Y,Er,Yb)(VO_4)_2$ which can convert infrared to visible radiation.

To continue the crystal chemical study of these interesting materials and to understand the allotropic transformations of $Na_3Ln(VO_4)_2$ (Ln = Y, Dy, Ho, Er, Tm, Yb, Lu), a crystallographic study of the α-$Na_3Er(VO_4)_2$ phase has been undertaken.

Experimental

Specimen preparation

α-$Na_3Er(VO_4)_2$ was obtained in powder form from a stoichiometric mixture of Na_2CO_3, Er_2O_3 and V_2O_5 heated first to 600°C for 15 h and then at 700°C for 24 h.

Single crystals were prepared from a flux containing 5 mol of Na_3VO_4 and 2 mol of $Na_3Er(VO_4)_2$. The mixture was kept at 1050°C for 15 h in a Pt crucible, and then cooled to 700°C at a rate of 4° h⁻¹. Small needles were separated from the flux by repeated washing in hot water.

Single-crystal diffraction data

Inspection of the zero- and upper-layer Weissenberg and precession photographs indicates a monoclinic Laue symmetry $2/m$. The systematic extinctions, $h0l$: $h+l=2n+1$ and $0k0$: $k=2n+1$, are consistent with the space group $P2_1/n$ [4(*e*): $\pm(xyz; \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$]. The cell dimensions obtained and refined from single-crystal data are $a=5.490$ (5), $b=9.739$ (8), $c=7.215$ (5) Å, $\beta=93.07$ (5)°. The cell contains two formula units ($d_x=3.95$ (2), $d_c=3.99$ g cm⁻³).

A single crystal of α-$Na_3Er(VO_4)_2$ in the form of a rectangular prism $0.08 \times 0.06 \times 0.06$ mm was mounted about **b**. The intensities were collected on an Enraf–Nonius CD-3 three-circle automatic diffractometer with Mo $K\alpha$ radiation ($\lambda=0.70942$ Å), a pyrolytic graphite monochromator (002) and a 4° take-off angle. A scintillation counter and a θ–2θ multiple scanning technique with a scan rate of 10° (2θ) per min were used. The background was taken at each end of the scan range for a time equal to the actual scan time. Three control reflexions measured for every batch of 50 reflexions showed a random fluctuation of about 4%. 1985 independent reflexions were measured to a value of $2\theta_{max}=80°$. 1574 had $I>3\sigma(I)$, where $\sigma(I)=$ [total counts + backgrounds]¹ᐟ², and were considered to be observed. These intensities were corrected for Lorentz and polarization effects, but not for absorption ($\lambda_{Mo K\alpha}$, $\mu=160$ cm⁻¹).

Determination and refinement of the structure

A Patterson synthesis was used to determine the positions of the heavy atoms. The two Na and four O atoms were located in a difference synthesis at an intermediate stage of the refinement. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with anisotropic temperature factors reduced $R=\sum||F_o|-$

Table 1. *Atomic coordinates and anisotropic temperature factors for* α-Na₃Er(VO₄)₂, *with standard deviations in parentheses*

The anisotropic temperature factor $T = \exp\left[-10^{-5}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Er	$\frac{1}{2}$	0	0	431 (7)	142 (2)	327 (4)	−5 (3)	−8 (3)	−7 (4)
V	0·0169 (2)	0·1825 (1)	0·2236 (1)	351 (17)	124 (6)	360 (11)	5 (4)	−7 (5)	−27 (7)
Na(1)	$\frac{1}{2}$	0	$\frac{1}{2}$	2114 (155)	884 (59)	1289 (93)	863 (104)	−1140 (99)	−761 (76)
Na(2)	0·5099 (6)	0·3567 (3)	0·2091 (5)	1034 (78)	384 (26)	927 (54)	114 (39)	154 (51)	−51 (33)
O(1)	0·0589 (8)	0·3577 (4)	0·2576 (6)	954 (111)	145 (30)	458 (61)	−57 (23)	89 (32)	−53 (34)
O(2)	0·1404 (9)	0·0997 (5)	0·4048 (7)	908 (116)	293 (39)	770 (78)	82 (54)	−101 (38)	170 (46)
O(3)	0·1684 (9)	0·1327 (5)	0·0328 (7)	852 (111)	324 (38)	590 (69)	155 (55)	150 (69)	−86 (43)
O(4)	0·7122 (8)	0·1361 (5)	0·2000 (7)	467 (94)	217 (33)	744 (72)	−88 (5)	−22 (32)	−111 (40)

$|F_c|/\sum|F_o|$ to 0·035, based on a data-to-parameter ratio of 24:1 with 67 independent parameters. A final $(F_o - F_c)$ synthesis confirmed the proposed solution.

$\sum\omega(|F_o| - |F_c|)^2$ was minimized with ω taken as unity for all reflexions. An overall scale factor was used with a final value of 3·68 $(F_o = kF_c)$. The form factors for Er³⁺, Na⁺, V⁵⁺ and O²⁻ were taken from McMaster, Kerr del Grande, Mallet & Hubbel (1969), with real and imaginary anomalous dispersion terms given by Cromer (1965).

The final atomic and thermal parameters are given in Table 1. Table 2 contains the interatomic distances and angles.

A table giving the calculated and observed structure amplitudes may be obtained on request from M.V.*

Results and discussion

A projection of the structure on (001) is given in Fig. 1. By comparison with the structure of Na₂CrO₄ shown in Fig. 2, which also seems to be the arrangement adopted by the metastable γ phase, the structure of α-Na₃Er(VO₄)₂ can be described as an ordered Na₂CrO₄ structure with Na and Er occupying, in an

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* α-Na₃Er(VO₄)₂ *with their standard deviations in parentheses*

V–O(1)	1·737 (4)	O(1b)–Na(1)–O(2)	93·9 (3)
V–O(2)	1·650 (5)	O(1b)–Na(1)–O(2d)	86·1 (3)
V–O(3)	1·716 (5)	O(1b)–Na(1)–O(4)	106·6 (3)
V–O(4a)	1·732 (5)	O(1b)–Na(1)–O(4d)	73·4 (3)
⟨V–O⟩	1·708 (5)	O(2)—Na(1)–O(4)	87·4 (3)
		O(2)—Na(1)–O(4d)	92·6 (3)
Er–O(1f)	2·268 (4)		
Er–O(1c)	2·268 (4)	O(1)–V–O(2)	108·8 (3)
Er–O(3)	2·256 (5)	O(1)–V–O(3)	108·9 (3)
Er–O(3h)	2·256 (5)	O(1)–V–O(4)	112·9 (3)
Er–O(4)	2·240 (5)	O(2)–V–O(3)	107·5 (3)
Er–O(4h)	2·240 (5)	O(2)–V–O(4)	107·7 (3)
⟨Er–O⟩	2·255 (5)	O(3)–V–O(4)	110·7 (3)
		⟨O—V–O⟩	109·4 (3)
Na(1)–O(1b)	2·327 (4)		
Na(1)–O(1c)	2·327 (4)	O(1f)–Er–O(3)	83·1 (3)
Na(1)–O(2)	2·273 (5)	O(1f)–Er–O(3h)	96·9 (3)
Na(1)–O(2d)	2·273 (5)	O(1f)–Er–O(4)	92·5 (3)
Na(1)–O(4)	2·841 (5)	O(1c)–Er–O(4)	87·5 (3)
Na(1)–O(4d)	2·841 (5)	O(3)—Er–O(4)	89·3 (3)
⟨Na(1)–O⟩	2·480 (5)	O(3h)–Er–O(4)	90·7 (3)
O(1)–O(2)	2·755 (7)	O(1)—Na(2)–O(2e)	75·2 (3)
O(1)–O(3)	2·810 (7)	O(1)—Na(2)–O(2f)	118·3 (3)
O(1)–O(4a)	2·892 (6)	O(1)—Na(2)–O(3b)	99·7 (3)
O(2)–O(2i)	2·874 (7)	O(1)—Na(2)–O(4)	117·6 (3)
O(2)–O(3)	2·716 (7)	O(1)—Na(2)–O(1g)	165·4 (3)
O(2)–O(4a)	2·732 (7)	O(2e)–Na(2)–O(2f)	69·9 (3)
O(3)–O(4a)	2·838 (7)	O(2e)–Na(2)–O(3b)	110·5 (3)
⟨O–O⟩	2·802 (7)	O(2e)–Na(2)–O(4)	158·3 (3)
		O(2e)–Na(2)–O(1g)	109·2 (3)
Na(2)–O(1)	2·519 (5)	O(2f)–Na(2)–O(3b)	139·6 (3)
Na(2)–O(1g)	3·016 (5)	O(2f)–Na(2)–O(4)	88·4 (3)
Na(2)–O(2e)	2·623 (6)	O(2f)–Na(2)–O(1g)	76·0 (3)
Na(2)–O(2i)	2·384 (6)	O(3b)–Na(2)–O(4)	85·6 (3)
Na(2)–O(3b)	2·450 (6)	O(3b)–Na(2)–O(1g)	65·6 (3)
Na(2)–O(4)	2·421 (6)	O(4)—Na(2)–O(1g)	63·2 (3)
⟨Na(2)–O⟩	2·596 (5)		

Symmetry code
(a)	$x-1$,	y,	z	(f)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$z-\frac{1}{2}$
(b)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	(g)	$1+x$,	y,	z
(c)	$\frac{1}{2}-x$,	$y-\frac{1}{2}$,	$\frac{1}{2}-z$	(h)	$1-x$,	$\bar{y}$,	$1-z$
(d)	$\bar{x}$,	$\bar{y}$,	z	(i)	$\bar{x}$,	$\bar{y}$,	$1-z$
(e)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$				

Fig. 1. Projection of the α-Na₃Er(VO₄)₂ structure on the (001) plane.

ordered way, one of the Na sites of the Na_2CrO_4 lattice. This relationship between α-$Na_3Er(VO_4)_2$ and Na_2CrO_4 ($a=5\cdot861$, $b=9\cdot259$, $c=7\cdot138$ Å) can be easily established, but a more generalized approach can be more valuable in the description of an
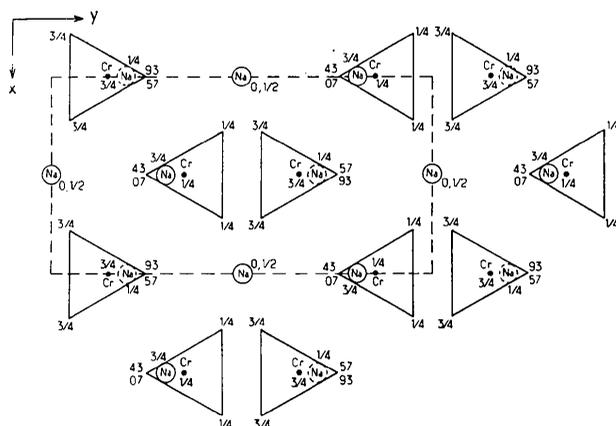
Fig. 2. Projection of the orthorhombic Na_2CrO_4 structure on the (001) plane.
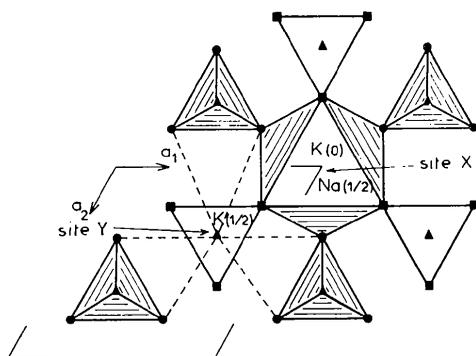
Fig. 3. The glaserite structure shown as a polyhedral diagram. Oxygen atoms having the same symbol are on the same level.
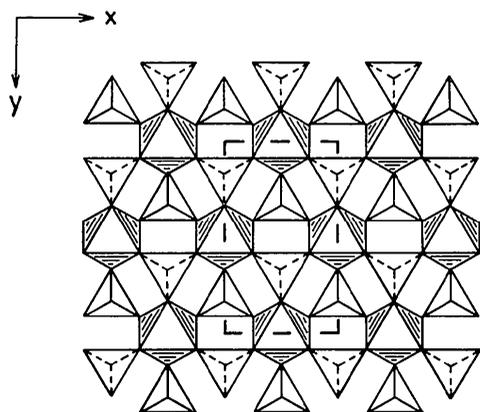
Fig. 4. Condensation of pinwheels corresponding to an idealized sheet of the α-$Na_3Er(VO_4)_2$ structure. The actual cell is outlined.

$A_xB_y(TO_4)_{(x+y)/2}$ structure. The fact that most of the sulphate, orthosilicate and orthovanadate compounds have structures made up of isolated tetrahedra linked only by cations, as well as pseudo-hexagonal symmetry suggests a more topological approach (Moore & Araki, 1972; Moore, 1973).

Glaserite $K_3Na(SO_4)_2$ and the structurally similar aphtitalite $K_2Na_2(SO_4)_2$ have a simple atomic arrangement whose hexagonal geometry defines the substructure observed in other compounds of this type such as $Ca_3Mg(SiO_4)_2$, α-Ca_2SiO_4, β-Ca_2SiO_4 and β-K_2SO_4. This structure can thus be used as an ideal model in the establishment of structural interrelationships among these phases.

The structure of glaserite is shown in Fig. 3. Two large cationic sites appear in this structure. In a large ideally twelve-coordinated polyhedron (X site) six O atoms make up a trigonal antiprism; six additional meridional anions constitute a hexagonal ring around this antiprism with $\overline{3}m$ symmetry. The trigonal antiprism found inside the twelve-coordinated polyhedron is in itself an octahedral site. The arrangement of the tetrahedra around this octahedron defines a 'pinwheel' where the apical O atoms point either up or down. A second large cation polyhedron (Y site) is ideally ten-coordinated with $3m$ symmetry; again, six anions are found on the vertices of a meridional hexagon, three above share the tetrahedral base and one below a tetrahedral apex.

Condensation of the 'pinwheels' can lead to a hexagonal close-packed sheet shown in Fig. 4. The comparison of this geometrically idealized structure with the actual structure shown in Fig. 1 reveals their close relationship and corroborates the pseudo-hexagonal character of α-$Na_3Er(VO_4)_2$. Furthermore, the hexagonal parameters of the high-temperature β phase of $Na_3Er(VO_4)_2$ are $a=5\cdot64$, $c=7\cdot46$ Å, while for glaserite they are $a=5\cdot65$, $c=7\cdot29$ Å. This leads to the conclusion that β-$Na_3Er(VO_4)_2$ has indeed a glaserite-type structure, while α-$Na_3Er(VO_4)_2$ is a distorted variation of this glaserite structure and can be derived from a corresponding condensation of idealized 'pinwheels'.

Ideally in this structure four different types of polyhedra can be expected: a tetrahedron TO_4; a twelve-coordinated polyhedron $X^{(12-p)}$ with $p=0$ and an octahedron $M^{[6]}[X^{(12-p)}$ with $p=6]$, both having a common centre (Figs. 3 and 4), and finally a ten-coordinated polyhedron $Y^{[10]}$ with its centre above or below the tetrahedra (Figs. 3 and 4). Actual structural distortion, due to the need for these sites to accommodate cations of different size and charge, leads to lower coordination numbers as is observed in most of these compounds.

In α-$Na_3Er(VO_4)_2$ three of the above sites are occupied, but with lower coordination for Y. We thus have a network of isolated vanadate tetrahedra forming the skeleton of this structure. Er and Na(1) occupy the central M octahedra with coordination six while Na(2) are in the Y sites also with six-coordination. The

actual formula can be written as $Y_2^{[6]}M_2^{[6]}[TO_4]_2$ as compared to the geometrical ideal of $X^{[12]}Y_2^{[10]}M^{[6]}[TO_4]_2$.

The occupation of the different sites by the various atoms is in accordance with the observations of Moore (1973) for a number of similar compounds. When two cations of different charges are present, the lower charged ion will preferentially occupy the Y polyhedron (Er^{3+} in $M^{[6]}$, Na^+ in Y). A similar observation was made for $Na_3La(VO_4)_2$ (Vlasse, Salmon & Parent, 1976).

The average V–O distance in the tetrahedron, 1·708 Å, is within the range reported by Robertson & Kostiner (1972) (1·660 to 1·806 Å) and by Gopal & Calvo (1973) ($\langle V-O \rangle = 1$·691 to 1·701 Å) as well as those found in $Na_3La(VO_4)_2$ ($\langle V-O \rangle = 1$·673 to 1·726 Å). The average Na–O distances fall into two classes: a short distance for Na(1), 2·480, and a long distance for Na(2), 2·569 Å. This difference can be explained by the presence of Na in two different sites. Na(1) is found in the M site with very little cation–cation repulsion, while Na(2) occupies the Y site where there exists severe cation–cation repulsion between this polyhedron and the highly charged tetrahedron with which it shares a face. In this latter site we can expect longer bonds.

The Er–O average distance of 2·255 is comparable to that found by Baglio & Sovers (1971) 2·270 Å for $ErVO_4$.

All O–O distances are normal with an average of 2·802 Å. The average O–V–O angle of 109·4° is also normal. For $Na_3La(VO_4)_2$ $\langle O-O \rangle = 2$·800 Å and $\langle O-V-O \rangle = 109$·4°.

In conclusion, in structures which are made up of isolated TX_4 tetrahedra we observe that these tetrahedra can arrange themselves in a variety of ways by simply rotating around their centres and condensing themselves in 'pinwheels' in such a way that they can accommodate in their network a number of different cations with different coordinations. This explains the fact that $Na_3Er(VO_4)_2$ can exist in several allotropic modifications, all closely related to the glaserite structure. The α form corresponds to a distortion of the glaserite structure and to an ordered distribution of the Na and Er atoms in the X sites.

The transformation $\alpha \rightarrow \beta$ is characterized by a reorientation of the tetrahedra as well as a disordering of the Na and Er atoms. A rapid quenching of the β phase gives rise to the γ variety where Na and Er are also disordered. The fact that the metastable γ phase cannot be obtained directly from the low-temperature α phase can also be explained by the large X site in which Na and Er can be found, with very little cation–cation repulsion, and where an ordered arrangement is energetically much more favourable.

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