Vanadate garnet, Ca$_2$NaMg$_2$V$_3$O$_{12}$

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The vanadate garnet Ca$_2$NaMg$_2$V$_3$O$_{12}$ (dicalcium sodium dimagnesium trivanadium dodecaoxide), synthesized by a floating zone method, has a notable structural feature in that the dodecahedral–dodecahedral shared edge length is longer than the unshared dodecahedral edge length. It is also noteworthy that the octahedral–dodecahedral shared edge length is as long as the unshared octahedral edge length. These unusual structural features are closely related to the weak repulsions between dodecahedral cations and between dodecahedral and octahedral cations.

Comment

Garnets, $^{VIII}[X_3]^{VI}\{Y_2\}^{IV}(Z_3)O_{12}$, have attracted much attention in the fields of materials and earth sciences because of their interesting magnetic and optical properties and their importance as constituents of the earth's crust and mantle. The crystal structure of garnets, first determined by Menzer (1926), has cations on the X site coordinated dodecahedrally, on the Y site coordinated octahedrally and on the Z site coordinated tetrahedrally by O^{2-} ions (Fig. 1). These three types of coordination polyhedra link in a complex manner: a tetrahedron shares edges with two dodecahedra, an octahedron with six dodecahedra, and a dodecahedron with two tetrahedra, four octahedra and four other dodecahedra, and the linkage between tetrahedra and octahedra is made by mutually sharing all corners. Garnets can accommodate various chemical species, and commonly have di- or trivalent cations on the X site, trivalent cations on the Y site and tetra- or trivalent cations on the Z site. The repulsions between these cations, with such a combination of valences, across the shared edges of the polyhedra contribute greatly to the structural stability of garnets (Nakatsuka *et al.*, 1995; Nakatsuka, Yoshiasa & Yamanaka, 1999; Nakatsuka, Yoshiasa, Yamanaka *et al.*, 1999).

Vanadate garnets $^{VIII}[Ca_2^{2+}Na^+]^{VI}\{M_2^{2+}\}^{IV}(V_3^{5+})O_{12}$ (M is Mg, Mn, Co, Ni, Cu or Zn; Bayer, 1965; Dukhovskaya & Mill, 1974; Kazeí *et al.*, 1982; Basso, 1987), represented by palenzonaite (idealized formula Ca$_2$NaMn$_2$V$_3$O$_{12}$), are characterized by mean formal valences of +1.67 on the X site, +2 on the Y site and +5 on the Z site. Hence, the effect of the cation–cation repulsions across the shared edges of the polyhedra on the crystal structure of vanadate garnets is expected to differ from that in garnets with common valence distributions. Investigating this difference is quite important for the general understanding of the structural stability of garnets. However, few detailed studies of the crystal chemistry of vanadate garnets have been published to date (*e.g.* Dukhovskaya & Mill, 1974; Basso, 1987). In the present study, the refined structure of the title compound, Ca$_2$NaMg$_2$V$_3$O$_{12}$, is reported for the first time.

The most notable structural feature of the title compound is that the dodecahedral–dodecahedral shared edge length [O^i···O^{ii} = 2.9740 (13) Å] is considerably longer than the shortest unshared dodecahedral edge [O^i···O^{iii} = 2.9173 (13) Å] of the three symmetrically non-equivalent ones (O^i···O^{iii}, O···O^{iii} and O^{iii}···O^{iv}) (Table 1), in contradiction of Pauling's third rule (Pauling, 1929). It is also noteworthy that the octahedral–dodecahedral shared edge length [O···O^i = 2.9509 (11) Å] is approximately equal to the unshared octahedral edge length [O···O^v = 2.9559 (11) Å]. In contrast, the tetrahedral–dodecahedral shared edge length [O···O^{vi} = 2.6832 (13) Å] is considerably shorter than the unshared tetrahedral edge length [O···O^{vii} = 2.8713 (11) Å] (Table 1), which is in accord with Pauling's rule. These features are also observed in Ca$_{2.05}$Na$_{0.9}$Co$_2$V$_3$O$_{12}$ [Dukhovskaya & Mill, 1974; O^i···O^{ii} = 2.97 (2), O^i···O^{iii} = 2.92 (2), O···O^i = 2.95 (2), O···O^v = 2.95 (2), O···O^{vi} = 2.68 (2) and O···O^{vii} = 2.87 (2) Å] and Ca$_{2+x}$Na$_{1-x}$Mn$_2$(V,As)$_{3-x}$Si$_x$O$_{12}$ with $x \simeq 0.3$ [Basso, 1987; O^i···O^{ii} = 2.921 (4), O^i···O^{iii} = 2.912 (5), O···O^i = 3.015 (4), O···O^v = 3.053 (4), O···O^{vi} = 2.677 (5) and O···O^{vii} = 2.879 (4) Å].

The cation–cation distances in the title compound (Table 1) rank among the longest observed in garnets, because of the large sizes of the Ca^{2+} and Na$^+$ cations. In addition, the dodecahedral and octahedral cations in the title compound have lower valences than those in common garnets, with di- or trivalent cations on the dodecahedral site, trivalent cations on the octahedral site and tetra- or trivalent cations on the tetrahedral site. Thus, the ^{VIII}(Ca^{2+},Na$^+$)–^{VIII}(Ca^{2+},Na$^+$) and ^{VIII}(Ca^{2+},Na$^+$)–^{VI}Mg^{2+} repulsions in the title compound are expected to be considerably weaker than X–X and X–Y repulsions in common garnets, respectively. Such fundamentally weak repulsions will not need to be largely shielded by the O^{2-} ions forming the shared edges. Hence it follows that the dodecahedral–dodecahedral and octahedral–dodecahedral shared edges are allowed to become unusually long under the geometric constraints (Novak & Gibbs, 1971; Meagher, 1975) brought about by the large sizes of the Ca^{2+} and Na$^+$ cations occupying the dodecahedral site.

On the other hand, thermal vibrations of the dodecahedral (Ca^{2+},Na$^+$) and tetrahedral (V^{5+}) cations (Fig. 2) are significantly smaller in the direction perpendicular to the tetrahedral–dodecahedral shared edge than in other directions,
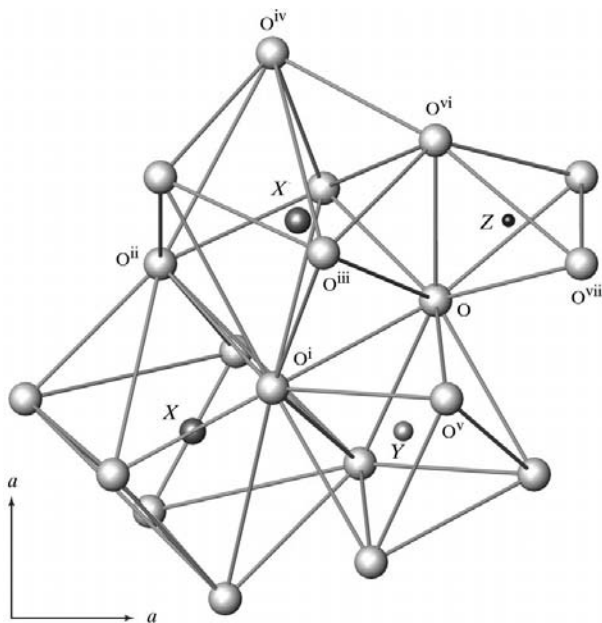
Figure 1
A schematic view of part of the garnet structure. Symmetry codes are as in Table 1.

indicating the existence of strong $^{VIII}(Ca^{2+},Na^+)–^{IV}V^{5+}$ repulsion. The same situation is also observed in garnets with common valence distributions, such as $Mg_3(Mg_{0.05}Si_{0.05}Al_{1.90})Si_3O_{12}$ (Nakatsuka, Yoshiasa, Yamanaka *et al.*, 1999) and $Y_3Fe_5O_{12}$ (Nakatsuka *et al.*, 1995). Thus, the $^{VIII}(Ca^{2+},Na^+)–^{IV}V^{5+}$ repulsion in the title compound is as strong as $X–Z$ repulsions in common garnets, as is also expected from a comparison of the valence distributions in both structures. The
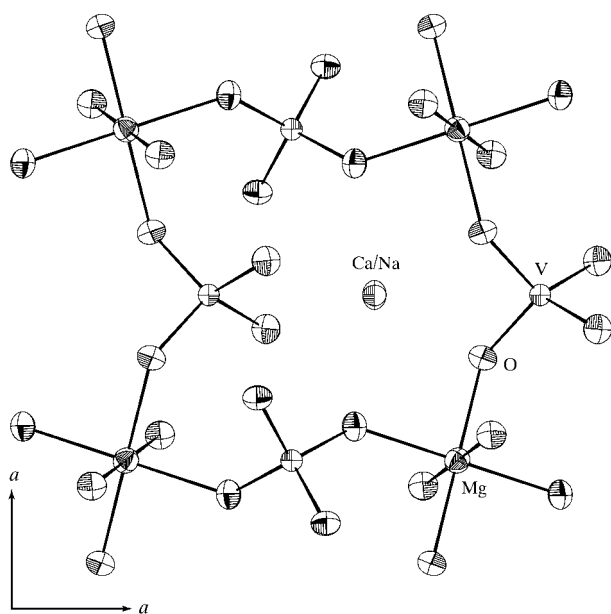
geometric constraints of the garnet structure force the tetrahedral–dodecahedral shared edge to become considerably shorter than the unshared tetrahedral edge (Meagher, 1975), and thereby the strong $^{VIII}(Ca^{2+},Na^+)–^{IV}V^{5+}$ repulsion is sufficiently shielded.

Experimental

Single crystals of the title compound was grown by a floating zone (FZ) method. The starting materials were powders of reagent grade Na_2CO_3, $CaCO_3$, MgO and V_2O_5. To eliminate weighing errors due to the presence of hydroxide in MgO and of VO_2 in V_2O_5, the MgO and V_2O_5 reagents were preheated for 10 h at 1293 K under a dry air flow and for 15 h at 773 K under an oxygen flow, respectively, and were then stored and weighed in a dry-box. Stoichiometric amounts of the starting materials (molar ratio Na_2CO_3:$CaCO_3$:MgO:V_2O_5 = 1:4:4:3) were mixed well together with acetone and nylon balls in a polyethylene bottle using a vibrating sample mill, and were then dried and calcined at 1123 K for 15 h. After mixing the calcined powder once again in a polyethylene bottle, it was placed in a sealed rubber tube to form a rod (8 mm in diameter and 60 mm in length) and hydrostatically pressed under a pressure of about 600 kg cm^{-2} (1 kg cm^{-2} = 98.1 kPa), after which the rod was sintered for 2 h at 1433 K in air. For crystal growth, the sintered rod was placed in a single ellipsoidal-type IR heating furnace with a 3.5 kW halogen lamp as a heat source (Nichiden Machinery Ltd, Model 50X). The experimental procedure and techniques for crystal growth are essentially the same as those described by Kimura & Shindo (1977). Crystal growth was carried out under a dry air flow at a flow rate of 200 ml min^{-1}. The upper and lower shafts were counter-rotated at a rate of 30 r min^{-1} and the growth rate was 0.5 mm h^{-1}. The chemical composition of the resulting single crystals was examined using an electron-probe microanalyzer (Shimazu EPMA-V6) operated with a 15 kV accelerating voltage, a 15 nA beam current and a 10 s measuring time.

Figure 2
Thermal motion of the atoms in the $Ca_2NaMg_2V_3O_{12}$ garnet. Displacement ellipsoids are drawn at the 80% probability level.

Crystal data

$Ca_2NaMg_2V_3O_{12}$	Cell parameters from 25
$M_r = 496.57$	reflections
Cubic, $Ia\bar{3}d$	$\theta = 22.5–25.0°$
$a = 12.4386 (19)$ Å	$\mu = 4.16 \text{ mm}^{-1}$
$V = 1924.5 (5)$ Å^3	$T = 296$ K
$Z = 8$	Sphere, pale brown
$D_x = 3.429 \text{ Mg m}^{-3}$	0.10 mm (radius)
Mo $K\alpha$ radiation	

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.028$
$\omega/2\theta$ scans	$\theta_{max} = 50.0°$
Absorption correction: spherical	$h = 0 \rightarrow 26$
($RADY$; Sasaki, 1987)	$k = 0 \rightarrow 26$
$T_{min} = 0.556$, $T_{max} = 0.574$	$l = 0 \rightarrow 26$
4773 measured reflections	3 standard reflections
850 independent reflections	every 200 reflections
382 reflections with $F > 3\sigma(F)$	intensity decay: none

Refinement

Refinement on F	$\Delta\rho_{max} = 0.45 \text{ e Å}^{-3}$
$R = 0.011$	$\Delta\rho_{min} = -0.27 \text{ e Å}^{-3}$
$wR = 0.010$	Extinction correction: isotropic
$S = 1.58$	type I (Becker & Coppens,
382 reflections	1974*a,b*)
18 parameters	Extinction coefficient:
$w = 1/\sigma^2(F)$	$0.336 (5) \times 10^{-4}$
$(\Delta/\sigma)_{max} < 0.0001$	

Table 1
Selected interatomic distances (Å).

Ca/Na—O	2.4350 (7)	O—O^v	2.9559 (11)
Ca/Na—O^i	2.5441 (8)	O—O^{vi}	2.6832 (13)
Mg—O	2.0884 (7)	O—O^{vii}	2.8713 (11)
V—O	1.7208 (6)	Ca/Na—Ca/Na^{viii}	3.8085 (4)
O^i—O^{ii}	2.9740 (13)	Ca/Na—Mg	3.4767 (4)
O^i—O^{iii}	2.9173 (13)	Ca/Na—V	3.1097 (5)
O—O^{iii}	3.5928 (6)	Mg—Mg^{viii}	5.3861 (5)
O^{iii}—O^{iv}	4.2359 (14)	Mg—V	3.4767 (4)
O—O^i	2.9509 (11)	V—V^v	3.8085 (4)

Symmetry codes: (i) $\frac{1}{2}-z, 1-x, y-\frac{1}{2}$; (ii) $\frac{3}{4}-x, \frac{3}{4}-z, \frac{3}{4}-y$; (iii) $\frac{1}{4}+z, y-\frac{1}{4}, \frac{3}{4}-x$; (iv) $\frac{1}{2}-z, x, 1-y$; (v) $y, \frac{1}{2}-z, x-\frac{1}{2}$; (vi) $x, 1-y, \frac{1}{2}-z$; (vii) $\frac{5}{4}-x, \frac{1}{4}+z, \frac{3}{4}-y$; (viii) $y-\frac{1}{4}, \frac{1}{4}+x, \frac{1}{4}-z$.

Two cations, Ca^{2+} and Na^+, occupy the crystallographically equivalent dodecahedral site. The occupancy parameters of these cations were fixed at 0.6667 and 0.3333, respectively, on the basis of the chemical composition.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *RADY* (Sasaki, 1987); program(s) used to refine structure: *RADY*; molecular graphics: *ATOMS for Windows* (Dowty, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1417). Services for accessing these data are described at the back of the journal.

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