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Pb$_{2.63}$Cd$_2$V$_3$O$_{12}$, a cation-deficient garnet-type vanadate

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In the crystal structure of the cation-deficient garnet Pb$_{2.63}$Cd$_2$V$_3$O$_{12}$ (lead cadmium vanadium oxide), the Cd and V atoms fully occupy octahedral and tetrahedral sites, respectively, whereas the Pb atoms partially occupy a dodecahedral site. The total Pb and Cd content indicates that vanadium is slightly reduced from the +5 oxidation state.

Comment

Compounds with the garnet-type structure usually crystallize with cubic symmetry (space group $Ia\bar{3}d$, $a = 12.5$–13.5 Å). The structural formula $A_3B_2X_3O_{12}$ corresponds to three different cation positions; the A (24c) position is surrounded by eight O atoms forming a dodecahedron, the B (16a) position is octahedrally coordinated and the X (24d) position is tetrahedrally coordinated. O atoms occupy a single (96h) general position. In garnet-type vanadates, the V^{5+} cations occupy the X position. The interest in these compounds originates from the investigation of garnet-type ferrites, since the substitution of V^{5+} for Fe^{3+} strongly influences the magnetic properties of these materials (Geller et $al.$, 1964).

A great number of garnet-type vanadates have been reported, $viz.$ NaCa$_2M_2$V$_3$O$_{12}$ (Durif, 1960) and Ca$_3M$LiV$_3$O$_{12}$ (Bayer, 1965), where M = Mg, Co, Ni, Cu and Zn, Na$_3$Cr$_2$V$_3$O$_{12}$ (Schwarz & Schmidt, 1967), and Mn$_3$LiMV$_3$O$_{12}$ (M = Co and Cu; Hrichova, 1970). Ronniger and Mill prepared numerous AB_2M_2V$_3$O$_{12}$ compounds (A = Li, Na, K, Cu, Ag, Y, Bi and Pr–Lu; B = Na, Ca, Sr, Cd and Pb; M = Li, Mg, Sc, Mn, Co, Ni, Cu, Zn and Cd; Ronniger & Mill, 1971, 1973b; Mill & Ronniger, 1973). They also demonstrated that, in the case of vanadates, large cations can be accommodated in the garnet structure (Tl$^+$ and Pb^{2+} in the A position, and Cd^{2+} in the B position).

Although powder data for most of these compounds are available, the structural information is rather limited. The only reported vanadate with a fully ordered garnet structure is

Na$_3$Sc$_2$V$_3$O$_{12}$ (Belokoneva et $al.$, 1974; Lobanov et $al.$, 1990). Usually, the A and/or B positions are randomly occupied by different cations, for example, NaCa$_2$Cu$_2$V$_3$O$_{12}$ (Lipin & Nozik, 1971), NaCa$_2$Mg$_2$V$_3$O$_{12}$ (Nakatsuka et $al.$, 2003), NaCa$_2$Zn$_2$V$_3$O$_{12}$ (Nakatsuka et $al.$, 2004), AgCa$_2$Mn$_2$V$_3$O$_{12}$ (Rettich & Mullet-Buschbaum, 1998), Na$_{0.9}$Ca$_{2.38}$Mn$_{1.72}$V$_3$O$_{12}$ (Lobanov et $al.$, 1990) and Ca$_{2.3}$Na$_{0.7}$Mn$_2$As$_{0.24}$V$_{2.46}$Si$_{0.3}$O$_{12}$ (Basso, 1987), and Ca$_{2.3}$Na$_{0.7}$Mg$_{1.85}$Mn$_{0.15}$V$_{2.88}$P$_{0.12}$O$_{12}$ (Krause et $al.$, 1999).

Depending on the valence states of the metal atoms, a cation deficiency may appear in the A or B positions. For example, the structures of Na$_{0.9}$Ca$_{2.05}$Co$_2$V$_3$O$_{12}$ (Dukhovskaya & Mill, 1974) and Ca$_5$Mg$_3$ZnV$_6$O$_{24}$ (Muller-Buschbaum & von Postel, 1992) revealed a slight deficiency in the A position, while in Ca$_{10}$Mg$_5$Cu$_3$V$_{12}$O$_{48}$ (Vogt & Muller-Buschbaum, 1991) the deficiency was found in the B position. X-ray powder data for some cation-deficient garnets (Ca$_{2.5}M_2$V$_3$O$_{12}$, M = Mg and Ni; Pb$_{2.5}$Cd$_2$V$_3$O$_{12}$) were also reported (Ronniger & Mill, 1973a). However, no structure refinement was performed, and only a simple comparison of experimental and theoretical X-ray diffraction powder patterns was carried out to analyze the cation distributions.

In this work, we present the first structural investigation of Pb$_{2.63}$Cd$_2$V$_3$O$_{12}$, a cation-deficient garnet containing lead and cadmium, which is uncommon for this structure type. The Pb atoms partially occupy the dodecahedral (A) sites, while the Cd and V atoms fully occupy the octahedral (B) and tetrahedral (X) sites, respectively. The CdO$_6$ octahedra share all six corners with VO$_4$ tetrahedra, thus forming a three-dimensional framework. The Pb atoms are situated in the interstices of this framework. The PbO$_8$ dodecahedron has two sets of Pb—O distances, $viz.$ 4 × 2.611 (5) Å and 4 × 2.722 (4) Å. The calculated bond valence sum (BVS) (Brown & Altermatt, 1985) for Pb is 1.82. The two significantly different Pb—O bond lengths may be caused by the presence of a lone electron pair. The BVS is slightly less than the expected value of 2.0 owing to the partial occupation of the Pb site.

The Cd and V atoms form almost regular polyhedra (octahedron and tetrahedron, respectively), which is typical for the
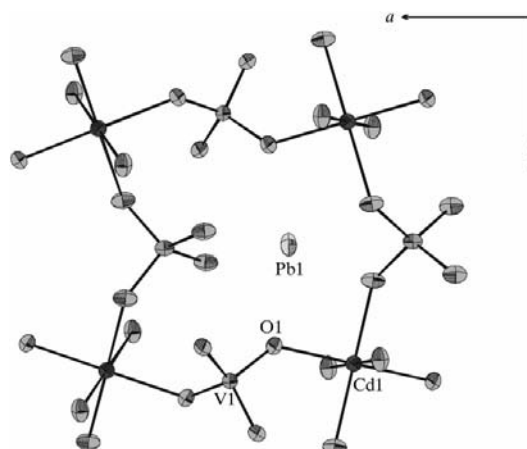

Figure 1
Fragment of the garnet structure viewed along the [001] direction. Displacement ellipsoids are drawn at the 80% probability level.

garnet structure. The Cd—O distance is 2.288 (4) Å and the associated BVS is 2.11. The V—O distance is 1.737 (5) Å and the corresponding BVS is 4.80, which indirectly confirms the partial reduction of the V atoms (see *Experimental*). Tetrahedral coordination is rather unusual for reduced V atoms; only two examples of tetrahedrally coordinated tetravalent vanadium are known, namely Ba_2VO_4 (Liu & Greedan, 1993) and β-Sr_2VO_4 (Gong *et al.*, 1991). In both structures, the $V^{4+}O_4$ tetrahedra are strongly distorted, and at least one V—O distance is longer than 1.8 Å. In $Pb_{2.63}Cd_2V_3O_{12}$, the oxidation state of vanadium (+4.93) is very close to +5 and the VO_4 tetrahedra are almost regular, with V—O distances of 1.72–1.74 Å, which are typical of pentavalent vanadium (Shannon & Calvo, 1973).

Oversluizen & Metselaar (1982) reported the formation of reduced vanadium in $NaCa_2Mg_2V_3O_{12}$, as characterized by optical spectroscopy and electron spin resonance spectroscopy. However, no structural investigation has been performed in this case. Our study of $Pb_{2.63}Cd_2V_3O_{12}$ demonstrates that the reduction of V atoms results in minor structural changes in comparison with other garnet-type vanadates. In particular, the dodecahedral–dodecahedral shared edge [3.162 (9) Å] is longer than the shortest dodecahedral unshared edge [3.033 (9) Å], contrary to one of the rules of Pauling (1929). One of the dodecahedral–octahedral shared edge [3.291 (8) Å] is also longer than the octahedral unshared edge [3.181 (7) Å]. On the other hand, Pauling's rule holds for the VO_4 tetrahedra; the shared and unshared edges are 2.734 (9) and 2.887 (8) Å, respectively. Long shared edges of metal polyhedra are typical for garnet-type vanadates (Dukhovskaya & Mill, 1974; Nakatsuka *et al.*, 2003, 2004), since the tetrahedral V cation has a high oxidation state (+5), whereas most of the other cations have a lower valence. Thus, the repulsion between the dodecahedral and octahedral cations (Pb and Cd in $Pb_{2.63}Cd_2V_3O_{12}$) is weak, and shared edges may become longer than unshared ones.

The present investigation clearly demonstrates that a slight change in the oxidation state of V atoms does not result in a noticeable structural transformation, such as that observed, for instance, in $Na_4VO(PO_4)_2$ (Shpanchenko *et al.*, 2006). This result is rather surprising, since tetrahedral coordination is not typical for reduced vanadium cations and usually such reduction immediately leads to structural changes.

Experimental

Single crystals of $Pb_{2.63}Cd_2V_3O_{12}$ were obtained by melting a mixture of $Pb_2V_2O_7$, CdO, V_2O_3 and V_2O_5 (in 3:2:4:1 ratio) at 1143 K in an evacuated (10^{-5} atm) silica tube, followed by slow cooling (5 K min^{-1}) to room temperature. The products contained roughly equal amounts of $Pb_{2.63}Cd_2V_3O_{12}$, CdV_2O_4 and (Cd,Pb)VO_3 (low-pressure modification) phases.

Crystal data

$Pb_{2.63}Cd_2V_3O_{12}$	$Z = 8$
$M_r = 1114.55$	Mo $K\alpha$ radiation
Cubic, $Ia\bar{3}d$	$\mu = 44.44$ mm^{-1}
$a = 13.1857$ (5) Å	$T = 173$ (2) K
$V = 2292.50$ (15) Å^3	$0.08 \times 0.05 \times 0.03$ mm

Data collection

Bruker SMART APEX CCD diffractometer	8263 measured reflections
Absorption correction: multi-scan (Bruker, 1997)	240 independent reflections
$T_{min} = 0.125$, $T_{max} = 0.349$ (expected range = 0.095–0.264)	193 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	18 parameters
$wR(F^2) = 0.058$	$\Delta\rho_{max} = 1.18$ e Å^{-3}
$S = 1.12$	$\Delta\rho_{min} = -0.55$ e Å^{-3}
240 reflections	

Table 1
Selected bond lengths (Å).

Pb1—O1	2.611 (5)	Cd1—O1	2.288 (4)
Pb1—O1^i	2.722 (4)	V1—O1	1.737 (5)

Symmetry code: (i) $x - \frac{1}{4}, -z + \frac{3}{4}, y + \frac{1}{4}$.

The set of reflection conditions hkl, $h + k + l = 2n$; $0kl$, $k, l = 2n$; hhl, $2h + l = 4n$; $h00$, $h = 4n$ led to an unambiguous assignment of the space group, namely $Ia\bar{3}d$. The atomic positions for the Pb, Cd, V and O atoms determined by direct methods revealed the garnet-type structure. The full occupancy of the 24c (A-type) special position by Pb atoms gave $R = 0.041$ and an isotropic displacement parameter for Pb twice as large as those for Cd and V (0.031 *versus* 0.013 and 0.014, respectively). The $Pb_3Cd_2V_3O_{12}$ composition corresponds to an average oxidation state of +4.67 for vanadium. According to the above discussion (see *Comment*), the tetrahedral coordination is not typical for reduced V atoms [see, for example, Zavalij & Whittingham (1999)]; therefore, the partial occupation of the 24c position by Pb atoms was proposed. The subsequent refinement of the displacement parameters and occupancy factor for the Pb atom (g_{Pb}) resulted in $R = 0.022$ and $g_{Pb} = 0.219$ (1). The calculated composition is $Pb_{2.63}Cd_2V_3O_{12}$ and the average oxidation state of V atoms is +4.91.

The possibility of fixing the oxidation state of vanadium as +5 was also checked. There are at least two ways to do so. The first is an increase of the deficiency in the lead position to $g_{Pb} = 0.20833$, which corresponds to the $Pb_{2.5}Cd_2V_3O_{12}$ composition. The second is to constrain the occupancies in the A- and B-type positions as $g_{Pb} + g_{Cd} = 0.375$, which corresponds to 4.5 divalent cations per formula unit, *viz.* $Pb_{2.5+x}Cd_{2-x}V_3O_{12}$. The first approach resulted in $R = 0.024$, while the second led to $R = 0.022$ and $x = 0.06$ (1). Thus, single-crystal structure refinement suggests three almost equivalent possibilities for the composition of lead–cadmium–vanadium garnet-type oxide, *viz.* $Pb_{2.63}Cd_2V_3O_{12}$, $Pb_{2.5}Cd_2V_3O_{12}$ and $Pb_{2.56}Cd_{1.94}V_3O_{12}$.

We have prepared three powder samples of the corresponding compositions using solid-state reactions (in air and in an evacuated silica tube in the case of reduced vanadium) at 1033 K for 30 h followed by additional annealing at 1073 K for 30 h, and the cell parameters of the garnet-type phases were compared. An increase of the number and/or size of the divalent cations in the unit cell results in a corresponding increase of the cell parameter [$Pb_{2.5}Cd_2V_3O_{12}$, $a = 13.1741$ (3) Å; $Pb_{2.56}Cd_{1.94}V_3O_{12}$, $a = 13.1792$ (2) Å; and $Pb_{2.63}Cd_2V_3O_{12}$, $a = 13.2233$ (2) Å]. The cell parameter determined at 173 K for the single crystal [$a = 13.1857$ (5) Å] is also in good agreement with a decrease of average oxidation state for V atoms. Thus, the garnet-type phases containing pentavalent vanadium only have a smaller lattice parameter than the single crystal (even when measured at 173 K). Note that the powder pattern of $Pb_{2.63}Cd_2V_3O_{12}$ taken at room temperature revealed a larger lattice parameter owing

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to thermal expansion. One may consider the cell parameter *versus* composition trend as an indirect proof of the correctness of the $Pb_{2.63}Cd_2V_3O_{12}$ composition determined from single-crystal refinement. The formation of reduced V atoms in the crystal can be easily explained by the synthetic procedure using an evacuated silica tube. A dark-grey color of the crystals additionally supports the conclusion about the presence of the reduced V atoms in the structure, since all compounds synthesized in air were yellow in color.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3044). Services for accessing these data are described at the back of the journal.

References

Basso, R. (1987). *Neues Jahrb. Miner. Monatsh*. pp. 136–144.

Bayer, G. (1965). *J. Am. Ceram. Soc.* **48**, 600.

Belokoneva, E. L., Mill, B. V., Simonov, M. A. & Belov, N. V. (1974). *Kristallografiya*, **19**, 374–375. (In Russian.)

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dukhovskaya, E. L. & Mill, B. V. (1974). *Kristallografiya*, **19**, 84–88. (In Russian.)

Durif, A. (1960). *Solid State Physics in Electronics and Telecommunications; Proceedings of an International Conference*, Brussels, June 2–7, 1958, edited by M. Deésirant & J. L. Michiels, pp. 500–502. London/New York: Academic Press.

Geller, S., Espinosa, G. P., Williams, H. J., Sherwood, R. C. & Nesbitt, E. A. (1964). *J. Appl. Phys.* **35**, 570–572.

Gong, W., Greedan, J. E., Liu, G. & Bjorgvinsson, M. (1991). *J. Solid State Chem.* **94**, 213–219.

Hrichova, R. (1970). *J. Am. Ceram. Soc.* **53**, 112.

Krause, W., Blass, G. & Effenberger, H. (1999). *Neues Jahrb. Miner. Monatsh.* pp. 123–124.

Lipin, Yu. V. & Nozik, Yu. Z. (1971). *Vestis Lat. PSR Zinat. Akad.* pp. 123–124.

Liu, G. & Greedan, J. E. (1993). *J. Solid State Chem.* **103**, 228–239.

Lobanov, N. N., Butman, L. A. & Tsirelson, V. G. (1990). *Zh. Strukt. Khim.* **30**, 113–122. (In Russain.)

Mill, B. & Ronniger, G. (1973). *Vanadates with Garnet Structure*, in *Physics and Chemistry of Ferrites*, pp. 98–115. Moscow: MSU Publishing House. (In Russian.)

Muller-Buschbaum, Hk. & von Postel, M. (1992). *Z. Anorg. Allg. Chem.* **615**, 101–103.

Nakatsuka, A., Ikuta, Y., Yoshiasa, A. & Iishi, K. (2003). *Acta Cryst.* C**59**, i133–i135.

Nakatsuka, A., Ikuta, Y., Yoshiasa, A. & Iishi, K. (2004). *Mater. Res. Bull.* **39**, 949–956.

Oversluizen, G. & Metselaar, R. (1982). *J. Phys. C Solid State Phys.* **15**, 4869–4880.

Pauling, L. (1929). *J. Am. Chem. Soc.* **51**, 1010–1026.

Rettich, R. & Mullet-Buschbaum, Hk. (1998). *Z. Naturforsch. Teil B*, **53**, 291–295.

Ronniger, G. & Mill, B. (1971). *Kristallografiya*, **16**, 1035–1036. (In Russian.)

Ronniger, G. & Mill, B. (1973*a*). *Kristallografiya*, **18**, 303–307. (In Russian.)

Ronniger, G. & Mill, B. (1973*b*). *Kristallografiya*, **18**, 539–543. (In Russian.)

Schwarz, H. & Schmidt, L. (1967). *Inorg. Nucl. Chem. Lett.* **3**, 199–203.

Shannon, R. D. & Calvo, C. (1973). *J. Solid State Chem.* **6**, 538–549.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Shpanchenko, R. V., Dikarev, E. V., Mironov, A. V., Mudretsova, S. N. & Antipov, E. V. (2006). *J. Solid State Chem.* **179**, 2681–2689.

Vogt, R. & Muller-Buschbaum, Hk. (1991). *J. Less Common. Met.* **171**, 345–351.

Zavalij, P. Y. & Whittingham, M. S. (1999). *Acta Cryst.* B**55**, 627–663.