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Silver-ion conduction pathways in $Ag_5IP_2O_7$

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Abstract

Pentasilver iododiphosphate, $Ag_5IP_2O_7$, is the compound with the lowest AgI content in the pseudo-binary system AgI–$Ag_4P_2O_7$. The X-ray single-crystal structure determination establishes that the coordination spheres of all the silver ions contain both oxide and iodide anions. Silver-ion conduction pathways in this solid electrolyte are modelled by the bond-valence technique.

Comment

In the course of our structural investigation of crystalline analogues of the ion-conducting silver iodide silver oxy-acid salt glasses (Adams, 1996, 1999; Adams & Maier, 1998), we synthesized the compound $Ag_5IP_2O_7$, which was first described by Takahashi *et al.* (1972). From the assumption that only silver ions coordinated by iodide should contribute to the silver-ion conductivity, these authors had postulated a segregation of AgI–$Ag_4P_2O_7$, yielding a network of AgI-like regions even for the glassy state. Our crystal structure determination rules out this hypothesis and reveals that all silver ions are coordinated by both diphosphate and iodide anions in crystalline $Ag_5IP_2O_7$. Furthermore, it is demonstrated that the diphosphate unit is completely ordered at room temperature (Fig. 1), whereas the diphosphate groups in the only other structurally characterized silver iododiphosphate, the AgI-rich superionic $Ag_{16}I_{12}P_2O_7$, are rotationally disordered among six positions according to the room-temperature structure analysis by Garrett *et al.* (1982).

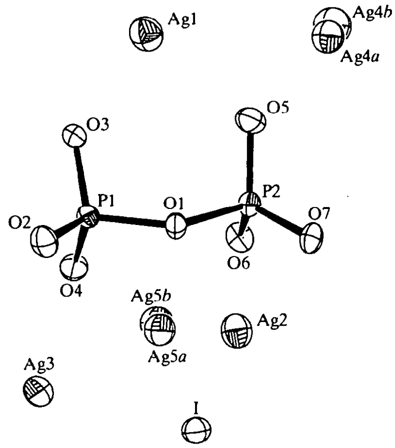

Fig. 1. An *ORTEP*III (Burnett & Johnson, 1996) plot of the asymmetric unit of the title compound with 50% probability displacement ellipsoids.

$Ag_5IP_2O_7$ is a moderate silver-ion conductor with an activation energy of 0.28 eV and a room temperature conductivity of about 3×10^{-6} *Omega*$^{-1}$ cm^{-1}. An analysis of the Ag bond-valence distribution throughout the unit cell of $Ag_5IP_2O_7$ suggests that long-range Ag migration pathways [modelled in Fig. 2(*a*) by the infinite bond-valence isosurface with the minimum Ag valence sum mismatch $\Delta V = 0.23$] involve all Ag sites. The Ag^+ conduction occurs preferably within layers extending perpendicular to the *c* axis. A detailed discussion on the modelling of ion-conduction pathways by bond-valence maps introduced by Garrett *et al.* (1982) will be published elsewhere (Adams, 1999). The basic features of the conduction-pathway model for $Ag_5IP_2O_7$ are thus in full accordance with our earlier findings for $Ag_8I_4V_2O_7$ (Adams *et al.*, 1996). The local hopping processes with the lowest activation energies should be jumps from the Ag4 or Ag2 sites to an interstitial site between these fully occupied sites (Fig. 2*b*).

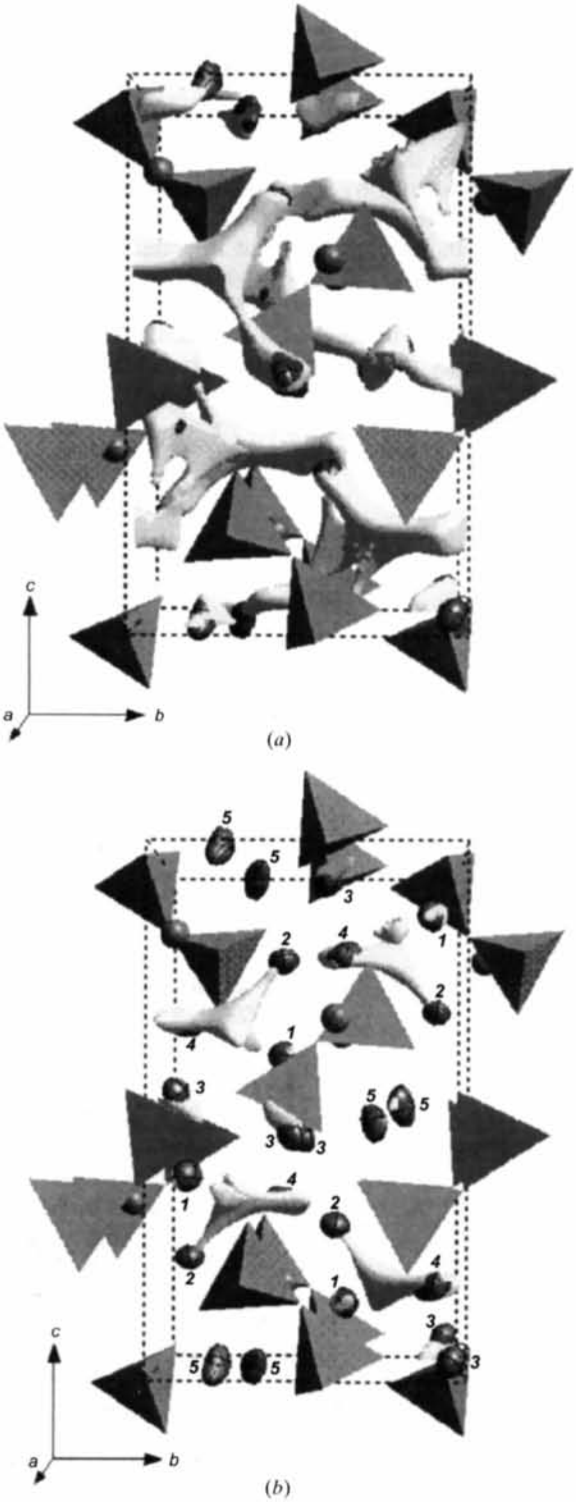

Fig. 2. Bond-valence model of silver-ion conduction pathways displaying (a) the infinite pathway of lowest valence mismatch $\Delta V = 0.23$ and (b) the localized low energy hopping processes between Ag2 and Ag4 for $\Delta V = 0.06$. Diphosphate units are shown as polyhedra, iodine as balls and silver as ellipsoids. The numbers refer to Ag site labels.

Experimental

$Ag_4P_2O_7$ and AgI were precipitated from aqueous solutions of $AgNO_3$ by $Na_2P_2O_7\cdot10H_2O$ and KI, respectively. The precipitates were washed several times with twice-distilled water and acetone. According to the phase diagram of the pseudo-binary system AgI–$Ag_4P_2O_7$ (Sayer *et al.*, 1982), $Ag_5IP_2O_7$ melts incongruently at T_m = 583 K. Therefore, 35 mol% $Ag_4P_2O_7$ and 65 mol% AgI were melted in an evacuated Pyrex tube and homogenized at 773 K for 2 h. Cooling the melt from 590 to 470 K at a rate of 0.5 K h^{-1} produced light-yellow crystals of the title compound. Subsequent natural cooling to room temperature prevented crystallization of the AgI-rich matrix.

Crystal data

$Ag_5IP_2O_7$
$M_r = 840.19$
Orthorhombic
$P2_12_12_1$
$a = 9.124\ (4)$ Å
$b = 7.7920\ (18)$ Å
$c = 13.059\ (4)$ Å
$V = 928.3\ (5)$ Å^3
$Z = 4$
$D_x = 6.011$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 118 reflections
$\theta = 13.08–17.97°$
$\mu = 14.037$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.23 × 0.20 × 0.19 mm
Light yellow

Data collection

Stoe AED diffractometer
ω–θ scans
Absorption correction: ψ scan (*EMPIR*; Stoe & Cie, 1989)
$T_{min} = 0.028$, $T_{max} = 0.067$
6643 measured reflections
1572 independent reflections (plus 1141 Friedel-related reflections)

2575 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 30.02°$
$h = -12 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$
3 standard reflections frequency: 120 min intensity decay: 3.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.063$
$S = 1.118$
2713 reflections
155 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2 + 2.7503P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.971$ e Å^{-3}
$\Delta\rho_{min} = -0.912$ e Å^{-3}

Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.00613 (18)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.02 (4)

Table 1. *Selected bond lengths (Å)*

Ag1—O7^{i}	2.274 (5)	Ag4*b*—O3^{ix}	2.552 (9)
Ag1—O3	2.515 (4)	Ag4*b*—O6^{i}	2.553 (8)
Ag1—O2^{ii}	2.538 (5)	Ag4*b*—O5	2.665 (9)
Ag1—I	2.7653 (11)	Ag4*b*—I	2.797 (6)
Ag1—O5	2.830 (6)	Ag5*a*—O3^{vi}	2.304 (10)
Ag2—O4^{iii}	2.334 (5)	Ag5*a*—O4	2.376 (10)
Ag2—O5^{i}	2.439 (5)	Ag5*a*—O6	2.406 (8)
Ag2—O7	2.662 (5)	Ag5*a*—O5^{vi}	2.649 (9)
Ag2—O1	2.665 (4)	Ag5*a*—I^{iv}	3.025 (8)

Ag2—I^{iv}	2.7885 (10)	Ag5*b*—O4	2.320 (10)
Ag2—I^{i}	3.1692 (10)	Ag5*b*—O3^{vi}	2.329 (10)
Ag3—O2^{v}	2.388 (5)	Ag5*b*—O6	2.373 (7)
Ag3—O4	2.401 (5)	Ag5*b*—O5^{vi}	2.575 (8)
Ag3—O6^{vi}	2.454 (5)	Ag5*b*—I^{iv}	3.171 (9)
Ag3—O7^{vii}	2.460 (5)	P1—O3	1.509 (4)
Ag3—I^{iv}	3.0217 (11)	P1—O4	1.511 (5)
Ag4*a*—O2^{viii}	2.327 (7)	P1—O2	1.519 (5)
Ag4*a*—O6^{i}	2.429 (7)	P1—O1	1.614 (4)
Ag4*a*—O5	2.535 (9)	P2—O7	1.512 (5)
Ag4*a*—O3^{ix}	2.692 (9)	P2—O5	1.521 (5)
Ag4*a*—I	2.890 (6)	P2—O6	1.522 (5)
Ag4*b*—O2^{viii}	2.361 (8)	P2—O1	1.633 (5)
P1—O1—P2	133.2 (3)		

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

The data collection included all Friedel pairs in the specified *hkl* range in order to confirm the correctness of the absolute structure. The description of the silver density distribution in a silver-ion conductor by displacement ellipsoids yields only approximate values. Since the quality of the crystals and the data-to-parameter ratio did not allow for a full anharmonic treatment, only the most prominent anharmonicities have been accounted for by the introduction of split positions for Ag4 and Ag5. The occupancies of these split positions were not refined.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *CERIUS*^{2} (Molecular Simulations, 1995).

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Cadmium sodium trivanadate

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Abstract

The crystal structure of $Cd_{3.23}Na_{1.41}V_{0.36}(VO_4)_3$ has been resolved. This structure is built up of MO_6 (M = Cd, Na and V) octahedral chains linked by VO_4 tetrahedra, and is characterized by cationic disorder and tunnels running along the *c* axis.

Comment

The orthovanadate formed with cadmium and sodium, $Cd_4Na(VO_4)_3$, was synthesized by Olazcuaga *et al.* (1977) and the crystal structure was later reported in the non-centrosymmetric space group $Pn2_1a$ (Ben Amara, Vlasse *et al.*, 1979). Later still, a new refinement of the same structure was carried out in the centrosymmetric space group *Pnma* (Abrahams & Marsh, 1983) when non-linear and piezoelectric tests evidenced no asymmetric character of the lattice. In the present work, we report the crystal structure of a new monoclinic cadmium sodium vanadate.

The network is composed of VO_4 tetrahedra [V—O 1.702 (3)–1.734 (3) Å] and MO_6 octahedra (M = Cd, Na and V). Cadmium is encountered in four different sites, three octahedral and one square planar, while sodium is located with cadmium in two mixed sites; however, one of these is almost entirely occupied by sodium, the amount of cadmium being very small but not negligible. The three MO_6 octahedra show various degrees of deformation from idealized geometry. $Cd4O_6$ is regular, $Cd3/V3O_6$ is slightly deformed and $Cd1/Na1O_6$ is quite irregular, with Cd1/Na1—O distances in the range 2.342 (3)–2.709 (3) Å. VO_4 tetrahedra are linked to MO_6 octahedra by the sharing of a corner. $Cd1/Na1O_6$