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Parallel, Segregated Cs^+- and K^+-Filled One-Dimensional Tunnels in $Cs_2K_2Mo_8P_{12}O_{52}$

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The reaction of Cs_2MoO_4, K_2MoO_4, MoO_3, Mo, and P_2O_5 in a mole ratio of 1 : 1 : 4.33 : 1.33 : 6 in an evacuated silica tube for 48 hr at 900°C yields dichroic crystals (green when viewed parallel to the normal of the {010} sets and yellow when viewed parallel to the normal of the {001} sets) of $Cs_2K_2Mo_8P_{12}O_{52}$. The crystals are monoclinic, space group $P2_1/c$ (#14) with a = 6.388(2), b = 18.901(2), c = 18.805(2) Å, β = 92.07(2)°, and V = 2269.11(9) Å^3. The framework consists of (MoO_6) octahedra, (PO_4) phosphate, and (P_2O_7) pyrophosphate groups and contains two different types of parallel tunnel: a large tunnel in which an ordered array of Cs^+ and voids are found and a smaller one filled with K^+.

We and others have recently found that the molybdenum phosphate frameworks in the solid state system M–Mo–P–O (M = alkali metal) have great flexibility in terms of the Mo oxidation state, the Mo/P ratio, and the number and nature of the alkali metal cations. Some examples of these compounds include layered materials like $Cs_2Mo_4P_6O_{26}$ (*1*), tunnel structures in $Cs_4Mo_{10}P_{18}O_{66}$ (*2*), and metal–metal bonded $Mo_4O_4^{6+}$ cubes in $Cs_3Mo_5P_6O_{25}$ (*3*) and $Cs_3Mo_4P_3O_{16}$ (*4*). We report here an example of an unusual tunnel structure that contains two different alkali metal cations in parallel tunnels.

The reaction of Cs_2MoO_4, K_2MoO_4, MoO_3, Mo, and P_2O_5 in a mole ratio of 1 : 1 : 4.33 : 1.33 : 6 in an evacuated silica tube for 48 hr at 900°C yields $Cs_2K_2Mo_8P_{12}O_{52}$ (**1**). Crystals of (**1**) grow as needles with a square cross section, which have a Cs/K ratio near one from electron microprobe analysis, and display a pronounced dichroism when viewed perpendicular to the needle axis. The crystals are greenish when viewed parallel to the normal of the {010} sets and yellow when viewed parallel to the normal of the {001} sets. Both visual examination and the indexing of the powder pattern showed the material to be single phase.

After a preliminary examination of the single crystal X-ray diffraction data and determination of the unit cell constants, it was noted that the cell constants for compound (**1**) (monoclinic, $P2_1/c$ with a = 6.388(2), b = 18.901(2), c = 18.805(2) Å, β = 92.07(2)° were closely related to the cell constants of our previously determined structure (**1**) of $Cs_4Mo_8P_{12}O_{52}$ (**2**) (monoclinic, $P2_1$ with a = 6.398(1), b = 19.497(6), c = 9.835(2) Å, β = 107.06(3)°) with the difference that the c axis of (**1**) is approximately double that of (**2**).

Solution of the single crystal X-ray data

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(Table I) shows that (1) has the structure shown in Fig. 1. The fractional coordinates for (1) are given in Table II. The anionic molybdenum phosphate framework in (1) is very similar to that of (2), $Cs_4Mo_8P_{12}O_{52}$, as shown in Fig. 1, and both contain molybdenum in the Mo(V) oxidation state only. The framework is composed of molybdenyl (Mo=O), phosphate (PO_4), and pyrophosphate (P_2O_7) moieties. The most interesting structural feature of these materials is the presence of two different types of tunnel: a large tunnel in which an ordered array of Cs^+ and voids are found and a smaller one filled with K^+.

TABLE I

EXPERIMENTAL X-RAY DATA

A. Crystal data	
Empirical formula:	$CsMo_4KP_6O_{26}$
Formula weight:	1157.59
Crystal color, habit:	Pale yellow-green, needle
Crystal dimensions (mm):	0.260 × 0.060 × 0.060
Crystal system:	Monoclinic
Lattice parameters:	a = 6.388 (2) Å
	b = 18.901 (2) Å
	c = 18.805 (2) Å
	β = 92.07 (2)°
	V = 2269.11 (9) Å^3
Space group:	$P2_1/c$ (#14)
Z value:	4
D_{calc}:	3.388 g/cm^3
μ(Mo$K\alpha$):	43.98 cm^{-1}
B. Intensity measurements	
Diffractometer:	Rigaku AFC6R
Radiation:	Mo$K\alpha$ (λ = 0.71069 Å)
Temperature:	23°C
Scan type:	ω-2θ
$2\theta_{max}$:	50.0°
No. of reflections measured:	Total: 4546
	Unique: 4151 (R_{int} = .040)
Corrections:	Lorentz-polarization
	Absorption
	(trans. factors: 0.75–0.79)
C. Structure solution and refinement	
Structure solution:	Direct methods
Refinement:	Full-matrix least-squares
Function minimized:	$\Sigma\, w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights:	$4F_o^2/\sigma^2(F_o^2)$
Anomalous dispersion:	All non-hydrogen atoms
No. observations ($I > 3.00\sigma(I)$):	2515
No. variables:	183
Reflection/parameter ratio:	13.74
Residuals: R; R_w:	0.052; 0.077
Goodness of fit indicator:	1.82
Max shift/error in final cycle:	0.01
Maximum peak in final diff. map:	2.29 e$^-$/Å^3
Minimum peak in final diff. map:	−3.40 e$^-$/Å^3

TABLE II

POSITIONAL PARAMETERS AND B(EQ) FOR $Cs_2K_2Mo_8P_{12}O_{52}$

Atom	x	y	z	B(eq)
Cs(1)	−0.3879(3)	−0.15476(9)	0.57411(8)	2.67(6)
Mo(1)	−0.3959(2)	−0.15809(8)	0.21768(7)	0.19(5)
Mo(2)	−0.8725(2)	−0.12295(8)	0.43789(7)	0.20(6)
Mo(3)	−0.8957(2)	−0.33354(8)	0.22131(7)	0.21(5)
Mo(4)	−1.3715(2)	−0.37087(8)	0.44492(7)	0.18(5)
K(1)	−0.8012(8)	−0.0008(2)	0.2217(3)	2.8(2)
P(1)	−0.1044(7)	0.0392(2)	0.4023(2)	0.26(7)
P(2)	−0.3713(7)	−0.0848(2)	0.3944(2)	0.29(7)
P(3)	−0.8690(7)	−0.4058(2)	0.4003(2)	0.29(7)
P(4)	−0.6068(7)	−0.5323(2)	0.4029(2)	0.25(7)
P(5)	−0.8911(7)	−0.1694(2)	0.2664(2)	0.22(7)
P(6)	−0.3903(7)	−0.3206(2)	0.2716(2)	0.24(7)
O(1)	−0.402(2)	−0.2076(7)	0.1456(7)	0.9(2)
O(2)	−0.844(2)	−0.2099(7)	0.4538(7)	1.1(2)
O(3)	−0.903(2)	−0.2879(7)	0.1457(7)	1.0(2)
O(4)	−0.346(2)	−0.2872(7)	0.4683(6)	1.0(2)
O(5)	−0.325(2)	−0.0017(6)	0.4039(6)	0.4(2)
O(6)	0.073(2)	−0.0102(6)	0.4215(6)	0.5(2)
O(7)	−0.085(2)	0.0682(6)	0.3272(6)	0.6(2)
O(8)	−0.131(2)	0.0994(6)	0.4550(6)	0.7(2)
O(9)	−0.565(2)	−0.0945(6)	0.4396(6)	0.6(2)
O(10)	−0.192(2)	−0.1237(6)	0.4335(6)	0.7(2)
O(11)	−0.400(2)	−0.0997(6)	0.3170(6)	0.7(2)
O(12)	−0.826(2)	−0.4892(6)	0.4047(6)	0.5(2)
O(13)	−0.691(2)	−0.3684(6)	0.4386(6)	0.8(2)
O(14)	−0.897(2)	−0.3902(6)	0.3224(6)	0.5(2)
O(15)	−0.070(2)	−0.3984(6)	0.4412(6)	0.8(2)
O(16)	−0.628(2)	−0.5931(6)	0.4540(6)	0.6(2)
O(17)	−0.594(2)	−0.5605(6)	0.3273(6)	0.6(2)
O(18)	−0.428(2)	−0.4820(6)	0.4195(6)	0.6(2)
O(19)	−0.709(2)	−0.1479(6)	0.2206(6)	0.6(2)
O(20)	−0.876(2)	−0.1233(6)	0.3329(6)	0.8(2)
O(21)	−0.085(2)	−0.1465(7)	0.2233(6)	0.8(2)
O(22)	−0.890(2)	−0.2478(6)	0.2863(6)	0.4(2)
O(23)	−0.389(2)	−0.2414(6)	0.2864(6)	0.7(2)
O(24)	−0.585(2)	−0.3441(6)	0.2269(6)	0.6(2)
O(25)	−0.207(2)	−0.3435(7)	0.2255(6)	0.9(2)
O(26)	−0.375(2)	−0.3632(7)	0.3390(7)	1.0(2)

The doubling of the c axis of (1) as compared with that of (2) is not due to the replacement of half the Cs^+ with K^+, but rather to the long range ordering of the Cs^+ in the large tunnel along the [001] direction. In (2), the molybdenum phosphate framework is essentially centric but the structure as a whole is acentric due to the ordering of the Cs^+ cations. In other words, the two Cs^+ in (2) that reside in the large tunnels are related only by the 2_1 axis that runs parallel to b, whereas the other Cs^+ in the smaller tunnel is crystallographically independent. In (**2**), each large tunnel is related to the next one by a simple translation along the [001] direction. However, in (**1**), the large tunnel is related to the next one encountered along the [001] direction by the *c* glide, thus doubling the *c* axis in (**1**) as compared to that in (**2**), where all the Cs^+ are crystallographically identical.

In summary, the parallel, segregated tunnels filled with Cs^+ and K^+ found in the structure of $Cs_2K_2Mo_8P_{12}O_{52}$ provides the first example of a solid molybdenum phosphate containing two different ordered alkali metal cations. According to the unit cell parameters found for crystals from a similar reaction to the one described here, but using mixtures of Rb and Cs instead of K and Cs, it is apparently also possible for mixtures of rubidium and cesium cations to order in the $Mo_8P_{12}O_{52}^{4-}$ framework in a similar manner.

a

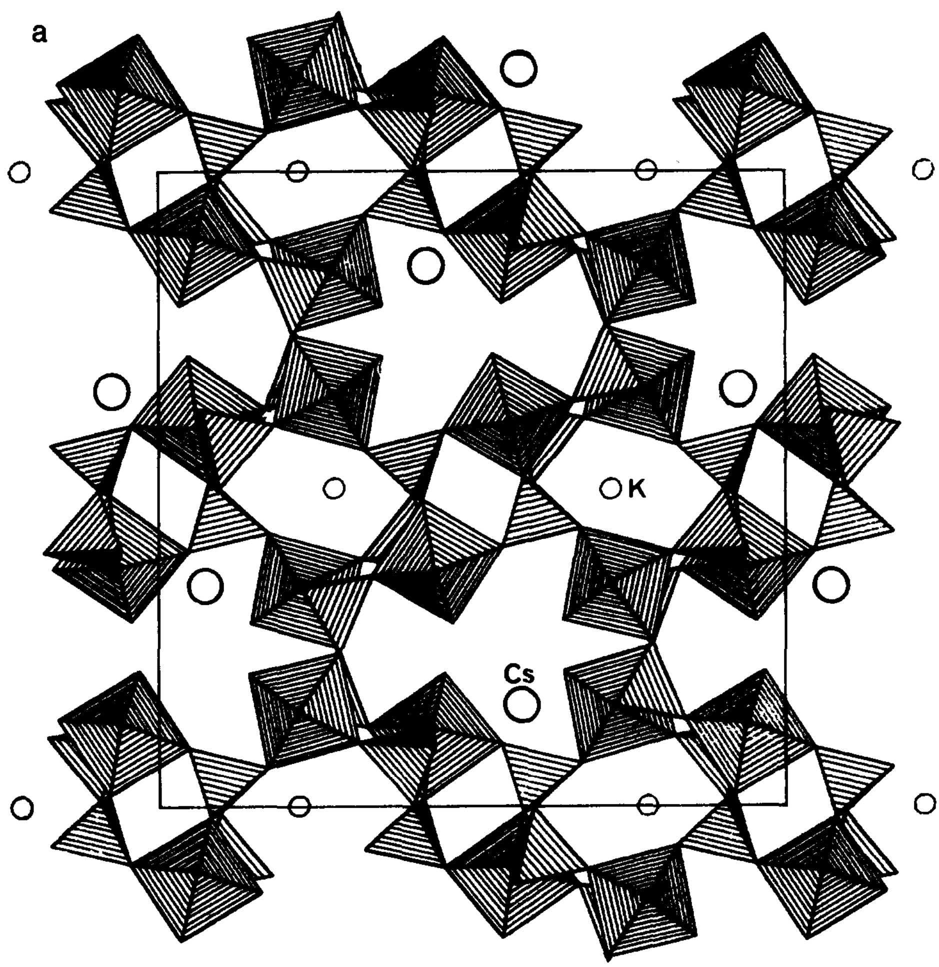

FIG. 1. Polyhedral (*5*) and ball-and-stick (*6*) representations of the structures of (**1**) (a and b) and (**2**) (c) all viewed parallel to the [100] direction with [001] horizonal. In (a) and (b), the larger circles are the Cs and the smaller circles the K.

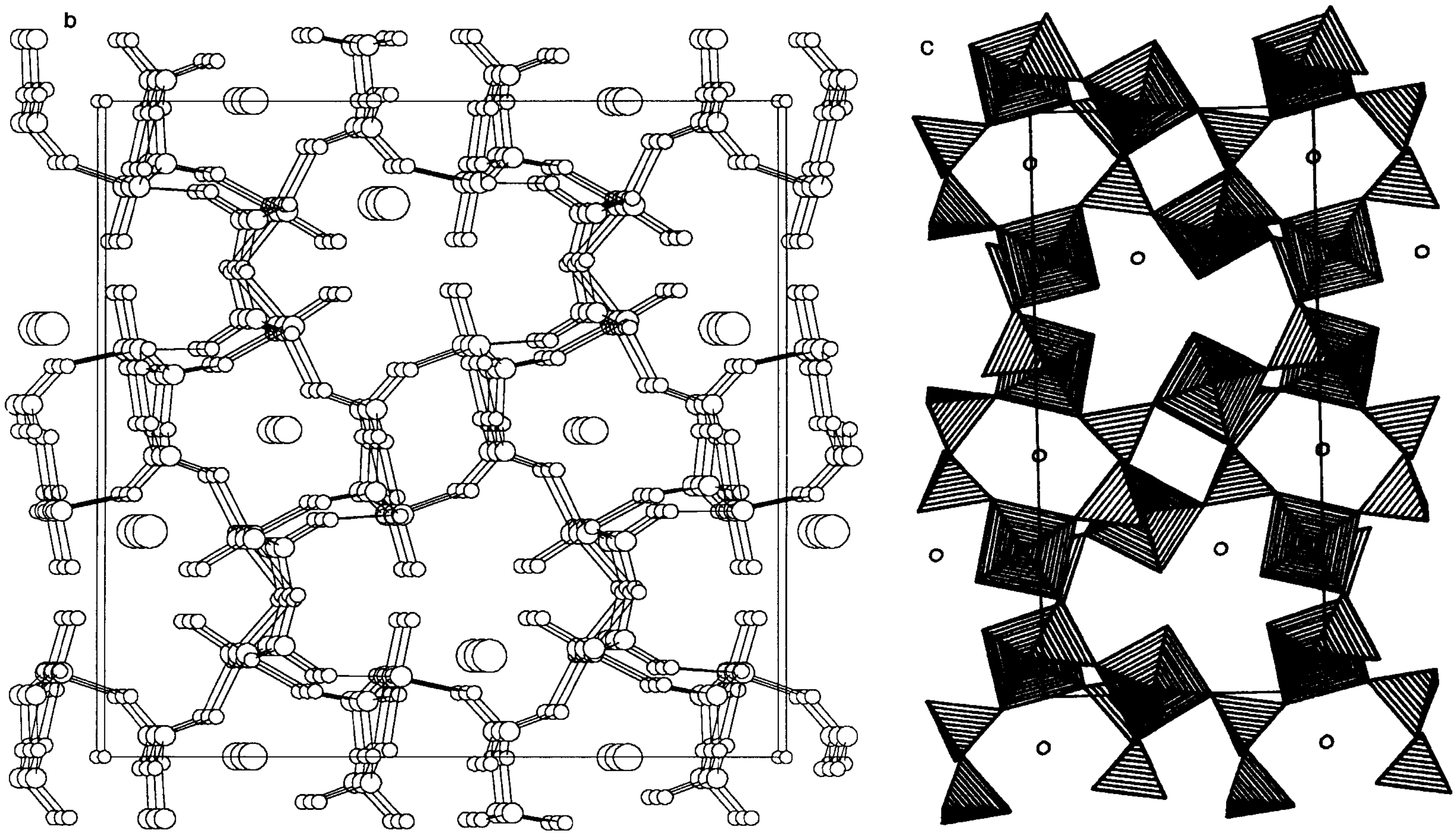

FIG. 1—*Continued*

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