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Crystal structure of sodium caesium zinc phosphate, $\text{NaCsZnP}_2\text{O}_7$

Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	$0.25 \times 0.15 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å)
μ :	8.723 mm^{-1}
Diffractometer, scan mode:	Multiwire proportional, Φ and ω -scans
θ_{max} , completeness:	26.4° , 100%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5402, 1505, 0.0334
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1398
$N(\text{param})_{\text{refined}}$:	110
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], OLEX2 [4]

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Abstract

$\text{NaCsZnP}_2\text{O}_7$, monoclinic, $P2_1/n$ (no. 14), $a = 7.3873(3)$ Å, $b = 7.6637(2)$ Å, $c = 12.9658(4)$ Å, $\beta = 91.249(3)^\circ$, $V = 733.87(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0221$, $wR_{\text{ref}}(F^2) = 0.0569$, $T = 293(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents employed were commercially available and used as received without further purification.

Experimental details

The raw materials Na_2CO_3 (1 mmol, 0.107 g), NaF (1 mmol, 0.042 g), ZnO (2 mmol, 0.163 g), $\text{NH}_4\text{H}_2\text{PO}_4$ (8 mmol, 0.92 g),

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.09609(3)	0.78029(3)	0.89360(2)	0.02010(14)
Zn1	−0.15993(6)	1.01716(5)	0.62474(3)	0.01113(15)
P1	0.03416(13)	0.72499(11)	1.20409(8)	0.0095(2)
P2	0.18158(13)	0.78392(11)	0.58893(8)	0.0099(2)
Na1	−0.1172(2)	0.5184(2)	0.61397(12)	0.0157(3)
O1	0.3186(3)	0.7985(3)	0.6872(2)	0.0134(6)
O2	0.0490(4)	0.7733(3)	1.3182(2)	0.0159(6)
O3	−0.0013(4)	0.8177(3)	0.6378(2)	0.0159(6)
O4	0.1139(4)	0.5421(3)	1.1921(2)	0.0165(6)
O5	0.1871(4)	0.6034(3)	0.5457(2)	0.0187(6)
O6	0.2376(4)	0.9286(3)	0.5156(2)	0.0177(6)
O7	0.1031(3)	0.8584(3)	1.1313(2)	0.0172(6)

and Cs_2CO_3 (3 mmol, 0.978 g), were ground in an agate mortar, pressed into a pellet, placed in a Pt crucible and preheated in a muffle furnace at 723 K for 12 h to eliminate the water and gas. And then, it was reground thoroughly, placed in a Pt crucible and heated at 1073 K for 38 h to homogenize the solution, then cooled to 1023 K at a rate of $30 \text{ K} \cdot \text{h}^{-1}$, and slowly cooled to 773 K at a rate of $2 \text{ K} \cdot \text{h}^{-1}$ before the furnace was turned off. Colorless and block crystals were obtained.

Discussion

Phosphate crystals have garnered the wide attention attributed to some important applications like laser hosts, phosphors, electrode materials, birefringent optics and

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nonlinear optical materials [5–8]. Distinct from structural diversity of borates [9–13], phosphates only possessing the PO₄ strict tetrahedron are more likely to produce orderly arrangements such as infinite chain, ring, and isolated clusters [14]. However, combination of the PO₄ and ZnO₄ tetrahedra has been investigated relatively less. Thus, synthesis of new zinc phosphate compounds are instructive to crystal chemistry and materials science.

The new compound NaCsZnP₂O₇ crystallizes in a monoclinic crystal system with the space group *P*₂₁/*c*. Its asymmetric unit is composed of one crystallographically independent Cs atom, one Na atom, one Zn atom, two P atoms, and seven O atoms. Each P or Zn atom is linked to four O atoms to form PO₄ or ZnO₄ tetrahedra with P–O or Zn–O bond lengths varying from 1.4894(26) to 1.5232(26) Å or 1.9309(26) to 1.9423(26) Å. The bond lengths are close to those reported in the literature [14–16]. Viewing down the *a* axis, the three-dimensional structure is built up of [Zn₄P₆O₃₀]^{22–} ten-membered rings obtained from the alternate linkages of P₂O₇, ZnO₄, and PO₄ groups. And the large rings via O-sharing stack along the *a*-axis direction to produce the large channels. The Cs and Na cations reside in the channels and maintain the charge balance.

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