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Electronic Supplementary Information

Structural Diversities Induced by Cation Sizes in a Series of Fluorogermanophosphates: $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs)

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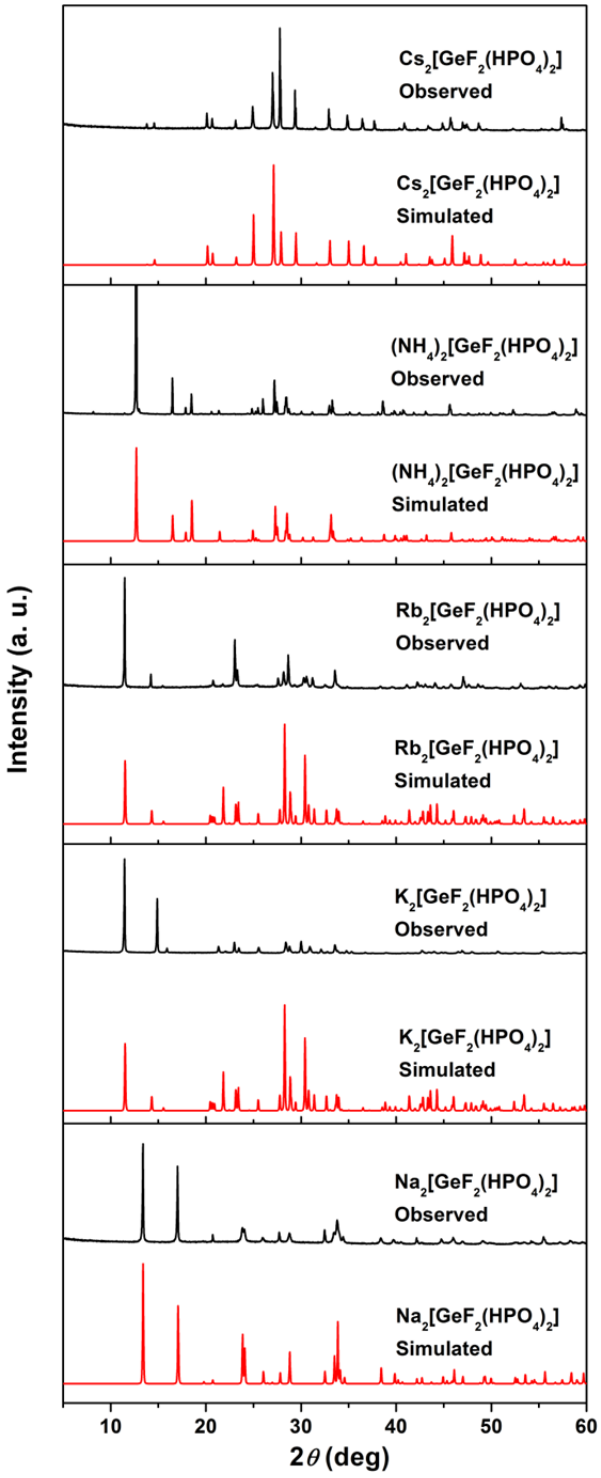

Figure S1. Powder X-ray diffraction patterns of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs), black patterns: observed data, red patterns: simulated data. Cu Kα radiation. Note that the intensity difference between the experimental and theoretical peaks for the K and Rb compounds could be caused by the preferential orientation of crystallites.

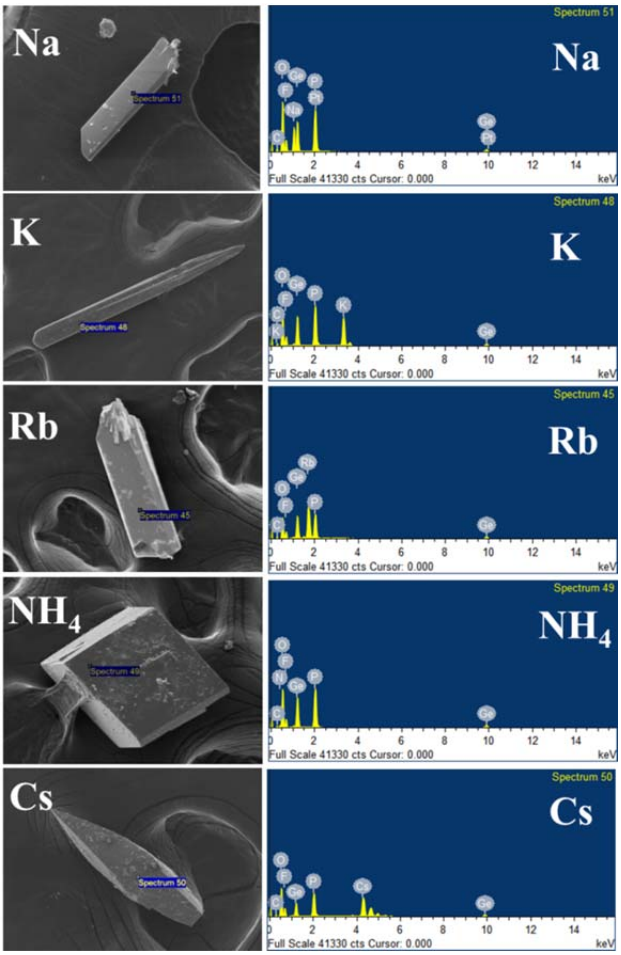

Figure S2. SEM and EDX results showing the crystal morphologies and chemical compositions of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs).

The morphologies and crystal sizes of the single crystals of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs) are shown in Figure S2. Energy dispersive X-ray spectra confirm the presence of N/K/Na/Rb/Cs, Ge, P, O and F elements in the title compounds.

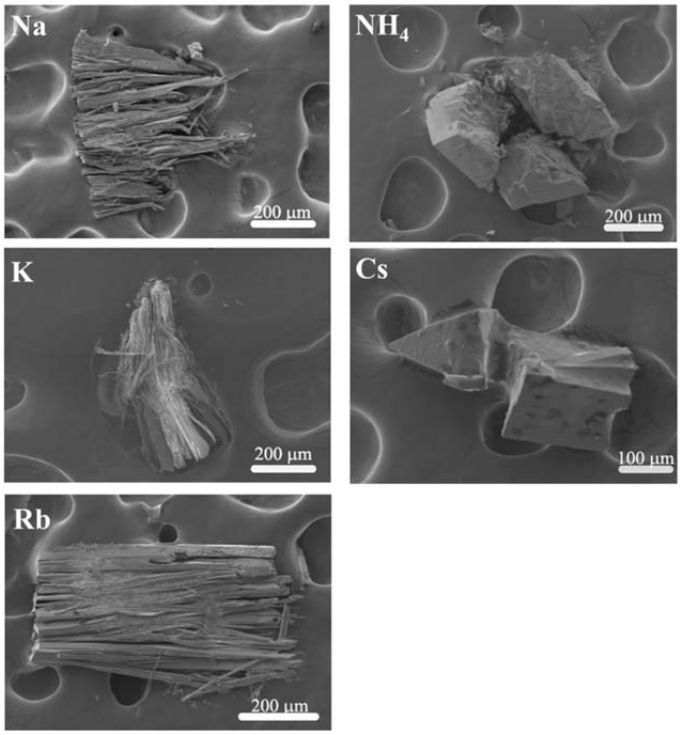

Figure S3. SEM images showing the cleavages of the single crystals of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs) after compression. $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb) have perfect cleavage behavior consistent with their chain-like structures, whereas $A_2[GeF_2(HPO_4)_2]$ (A = NH_4 and Cs) have only basal cleavages with their layered structures.

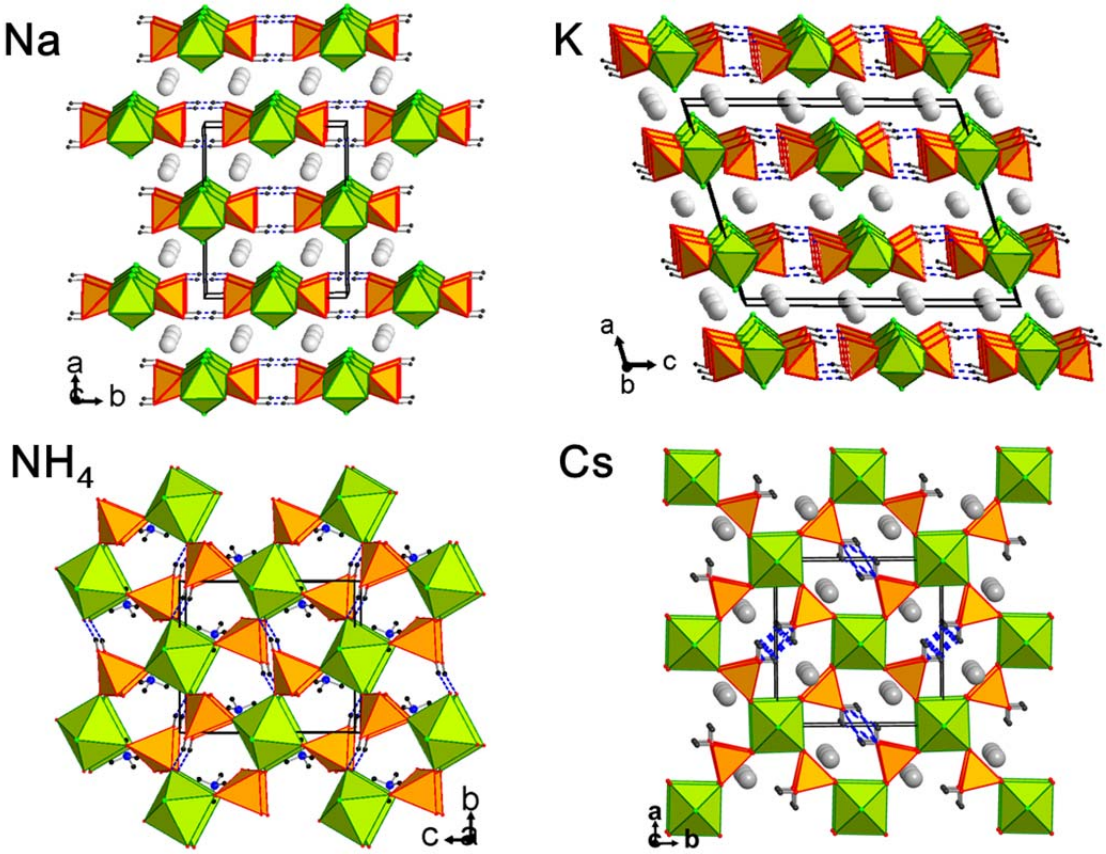

Figure S4. The hydrogen bonds between the neighboring chains or within the layers in the crystal structures of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, NH_4, and Cs).

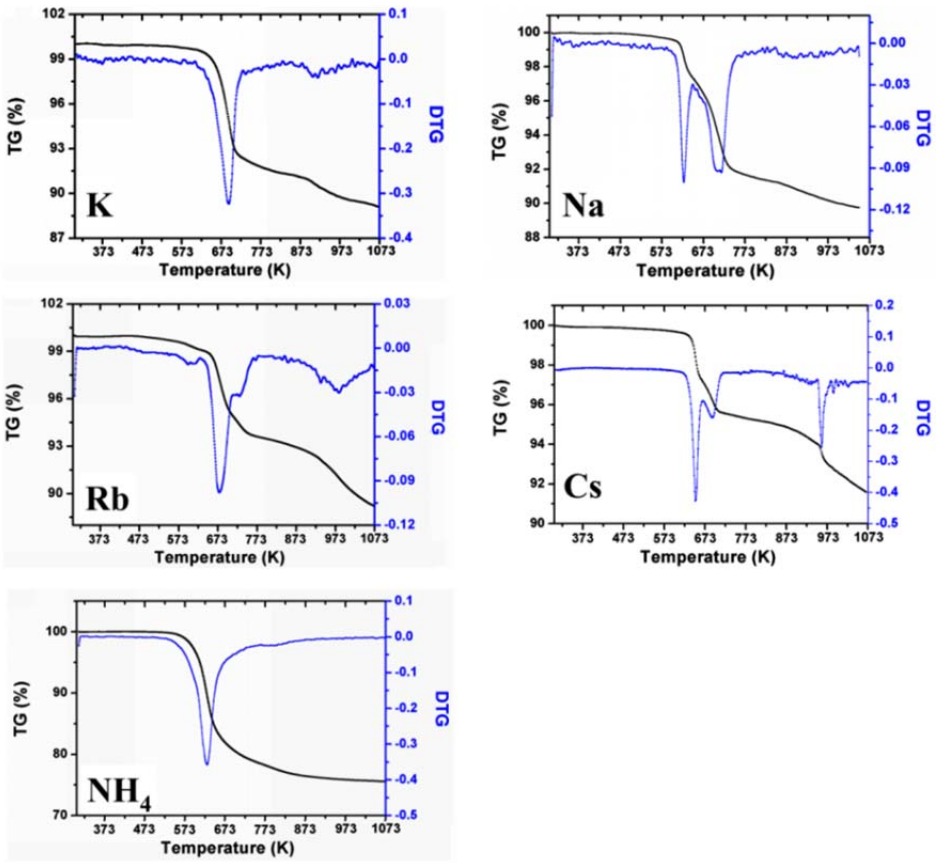

Figure S5. TG and DTG curves of $A_2[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, and Cs).

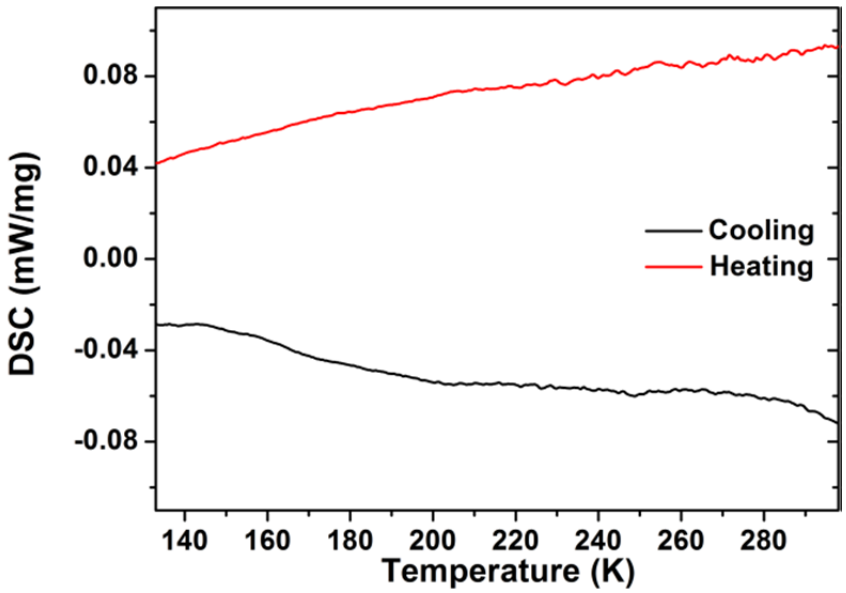

Figure S6. Differential scanning calorimetry (DSC) curves of $Cs_2[GeF_2(HPO_4)_2]$ in the temperature range from 133 K to 298 K. Black curve shows the cooling process, red curve showed the cooling process.

Table 1. Details of the optimized reaction conditions for the five title compounds

	$Na_2[GeF_2(HPO_4)_2]$	$K_2[GeF_2(HPO_4)_2]$	$Rb_2[GeF_2(HPO_4)_2]$	$(NH_4)_2[GeF_2(HPO_4)_2]$	$Cs_2[GeF_2(HPO_4)_2]$
***A*Cl**	1 mmol (0.059 g)	1 mmol (0.074 g)	1 mmol (0.121 g)	1 mmol (0.053 g)	1 mmol (0.168 g)
GeO_2	1 mmol (0.104 g)	1 mmol (0.104g)	1 mmol (0.104 g)	1 mmol (0.104 g)	1 mmol (0.104 g)
H_3PO_4 (85 wt%)	3.7 mmol (0.25 mL)	3.7 mmol (0.25 mL)	3.7 mmol (0.25 mL)	3.7 mmol (0.25 mL)	3.7 mmol (0.25 mL)
HF (40 wt%)	1.12 mmol (0.05 mL)	1.12 mmol (0.05 mL)	1.12 mmol (0.05 mL)	1.12 mmol (0.05 mL)	1.12 mmol (0.05 mL)
TEA	2.00 mL	2.50 mL	2.50 mL	2.50 mL	2.50 mL
2-BuOH	4.00 mL	4.00 mL	4.00 mL	4.00 mL	4.0 mL
H_2O	0.25 mL	0.25 mL	0.25 mL	0.25 mL	0.25 mL

Table S2. Bond valence sums calculations of the atoms in $A[GeF_2(HPO_4)_2]$ (A = Na, K, Rb, NH_4, Cs)

$Na_2[GeF_2(HPO_4)_2]$				
***A*=Na**	**Ge1**	**P1**	**Na1**	**BVS**
F1	0.6850(×2)*	--	0.1277(×2)	**0.81**
O1	0.7356(×4)	1.2313(×2)	0.1793(×2)	**2.15**
O2	--	1.2057(×2)	0.2225(×2)	**1.43**
BVS	**4.31**	**4.87**	**1.06**	
$K_2[GeF_2(HPO_4)_2]$				
***A*=K**	**Ge1**	**P1**	**K1**	**BVS**
F1	0.7118(×2)	--	0.1708, +0.0594/(+0.0594)*, +0.0455/(+0.0455)	**0.99**
O1	0.7497(×2)	1.2129	0.1778	**2.14**
O2	0.7386(×2)	1.2014	0.1689, +0.0385/(+0.0385)	**2.15**
O3	--	1.3350	0.1417, +0.1300/(+0.1300)	**1.61**
O4	--	1.1407	0.1296, +0.0816/(+0.0816)	**1.35**
BVS	**4.40**	**4.89**	**1.14**	
$Rb_2[GeF_2(HPO_4)_2]$				
***A* = Rb**	**Ge1**	**P1**	**Rb1**	**BVS**
F1	0.7037(×2)	--	0.1939, +0.0782/(+0.0782), +0.0717/(+0.0717)	**1.05**
O1	0.7408(×2)	1.2247	0.1653	**2.13**
O2	0.7152(×2)	1.2280	0.1516, +0.0468/(+0.0468)	**2.14**
O3	--	1.3645	0.1653, +0.1361/(+0.1361)	**1.67**
O4	--	1.1416	0.1390, +0.0997/(+0.0997)	**1.38**
BVS	**4.32**	**4.96**	**1.25**	
$Cs_2[GeF_2(HPO_4)_2]$				
***A* = Cs**	**Ge1**	**P1**	**Cs1**	**BVS**
F1	0.7468(×2)	--	0.0520×4/(×4)	**0.95**
O1	0.7428(×4)	1.2447(×2)	0.0589×2/(×4)	**2.11**
O2	--	1.2447(×2)	0.1335(×2), +0.1030×2/(×4)	**1.58**
BVS	**4.46**	**4.98**	**1.12**	
$(NH_4)_2[GeF_2(HPO_4)_2]$				
***A* = NH_4**	**Ge1**	**P1**		**BVS**
F1	0.7331×2	--		**0.73**
O2	0.7501(×2)	1.2234		**1.97**
O3	0.7236(×2)	1.2138		**1.94**
O4	--	1.3917		**1.39**
O5	--	1.1136		**1.11**
BVS	**4.41**	**4.94**		

* (×*n*) or (+*n*) is for the BVS of column atoms, ×*n* or +*n* is for the BVS of line atoms.