Supporting information

Ferroelectricity, ionic conductivity and structural paths for large cations migration in $Ca_{10.5-x}Pb_x(VO_4)_7$ single crystals, x = 1.9, 3.5, 4.9

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Table S1. Structural parameters for single crystals $Ca_{10-x}Pb_x(VO_4)_7$.

Crystal data			
Formula	$Ca_{8.6}Pb_{1.9}(VO_4)_7$	$Ca_7Pb_{3.5}(VO_4)_7$	$Ca_{5.6}Pb_{4.9}(VO_4)_7$
Formula weight (g)	1534.7	1813.1	2043.2
Temperature (K)	120	120	120
Cell setting		Trigonal	
Space group	*R*3*c*	*R*3*c*	*R*3*c*
Lattice Parameters			
a (Å)	10.9220(2)	10.9801(9)	11.0594(1)
c(Å)	38.3133 (9)	38.5568(1)	38.8813(1)
V (Å^3)	3958.1(1)	4025.7(3)	4118.5(4)
Z	6	6	6
Dx (g cm^{-3})	3.8632	4.4874	4.9429
Crystal size (mm)	0.24×0.22×0.15	0.21×0.23×0.26	0.35×0.30×0.28
Crystal form		Anhedral grain	
Crystal color	Light Yellow	Pink	Red
Data Collection			
Diffractometer		Bruker Smart Apex II	
Radiation; λ		MoK_α; 0.71069	
Absorption coefficient, μ (mm^{-1})	15.92	25.737	33.304
F (000)	4259	4877	5390
Data range θ(°);	4.06 – 56.22	2.39 – 30.69	2.37– 30.59
Limits *h*, *k*, *l*	–22<*h* <25, –25<*k*<24, –78<*l*<88	–15<*h*<15, –15<*k*<15, –54<*l*<54	–15<*h*<15, –15<*k*<15, –54<*l*<54
No. of measured reflections	69638	16900	17106
Total reflections/unique	5507 / 3621	1388 / 1294	1414 / 1208
Criterion for observed reflections		$I > 2\sigma(I)$	
Refinement			
Refinement on	Full-matrix least squares on *F*		
R_1, wR_2 (all reflection)	4.55 / 3.68	4.56 / 3.47	4.72 / 3.78

No. of refinement parameters	199	163	223
Weight scheme	$1/(\sigma^2\|F\|+ 0.0001F^2)$	$1/(\sigma^2\|F\|+ 0.001225F^2)$	$1/(\sigma^2\|F\|+ 0.0009F^2)$
Max./min. residual *e* density, (eÅ^{-3})	–2.34 / 1.91	–1.46 / 1.30	-1.62 / 2.89
GOF (Goodness of fit)	1.03	1.01	1.04

Note: $R_1 = \sum[|F_{obs}| - |F_{calc}|] / \sum|F_{obs}|$; $wR_2 = \{\sum[w(F_{obs}^2 - F_{calc}^2)^2] / \sum[w(F_{obs}^2)^2]\}^{1/2}$; GOF = $\{\sum[w(F_{obs}^2 - F_{calc}^2)] / (n - p)\}^{1/2}$ where n is a number of reflections and p is a number of refined parameters.

Table S2. Structural parameters for $Ca_{8.6}Pb_{1.9}(VO_4)_7$ (**1**), $Ca_7Pb_{3.5}(VO_4)_7$ (**2**) and $Ca_{5.6}Pb_{4.9}(VO_4)_7$ (**3**) single crystals.

Site	Mult.	Sample	*x*	*y*	*z*	U_{eq}, Å^2	Site occupancy
*M*1	18	1	0.7208(8)	-0.15557(8)	-0.0668(9)	0.0134(19)	Ca^{2+}
		2	0.0571(2)	0.5254(2)	-0.4024(2)	0.0116(7)	0.942(5) Ca^{2+} + 0.058(5) Pb^{2+}
		3	-0.2762(4)	-0.1424(3)	-0.0685(3)	0.0141(6)	0.750(6) Ca^{2+} + 0.250(6) Pb^{2+}
*M*2	18	1	0.8636(7)	-0.27597(8)	0.0688(9)	0.0127(18)	Ca^{2+}
		2	0.2801(2)	0.1264(2)	-0.4340(2)	0.0207(7)	0.900(2) Ca^{2+} + 0.100(1) Pb^{2+}
		3	-0.1293(3)	-0.2828(4)	0.0665(3)	0.0138(7)	0.785(5) Ca^{2+} + 0.215(5) Pb^{2+}
$M3_1$	18	1	0.5238(8)	0.0680(9)	0.0069(9)	0.0136(12)	0.549(7) Ca^{2+}
		2	0.7915(2)	0.1868(2)	-0.3422(2)	0.0267(2)	0.152(8) Ca^{2+} + 0.848(8) Pb^{2+}
		3	-0.5229(2)	-0.0637(4)	-0.0083(3)	0.0302(6)	0.921(7) Pb^{2+}
$M3_2$	18	1	0.5172(2)	0.0598(3)	0.0063(9)	0.0308(4)	0.451(3) Pb^{2+}
		3	0.5363(4)	0.0696(7)	0.0045(8)	0.053(15)	0.079(7) Pb^{2+}
$M4_1$	6	1	0.3333(2)	-0.3333(3)	-0.0198(9)	0.0444(19)	0.265(5) Pb^{2+}
		2	0.0571(2)	0.5254(2)	-0.4024(2)	0.0116(7)	0.058(1) Pb^{2+}
		3	-0.3333(3)	0.3333(5)	0.0150(3)	0.097(2)	0.500(2) Pb^{2+}
$M4_2$	6	1	0.3333(2)	-0.333333	-0.0103(9)	0.054(2)	0.127(5) Pb^{2+}
		2	0	0	-0.3351(13)	0.0220(2)	0.126(3) Pb^{2+}
$M4_3$	18	1	0.2571(3)	-0.3540(18)	-0.0234(10)	0.041(5)	0.035(7) Pb^{2+}
		2	-0.0777(2)	-0.1020(2)	-0.3114(13)	0.0080(3)	0.019(7) Pb^{2+}
*M*5	6	1	0	0	0	0.0185(2)	
		2	0	0	0	0.0126(8)	Ca^{2+}
		3	0	0	0	0.0130(10)	
V1	6	1	0.6667(2)	0.3333(2)	0.0665(9)	0.0114(17)	
		2	0.6667(1)	0.3333(4)	-0.4009(2))	0.0069(6)	V
		3	-0.6666(6)	-0.3333(3)	-0.0673(4)	0.0155(10)	
V2	18	1	0.8057(7)	0.1505(6)	-0.0330(9)	0.0111(16)	
		2	0.17424(2)	0.3167(2)	-0.3670(2)	0.0087(6)	V
		3	-0.1895(5)	0.1611(5)	-0.0331(3)	0.0120(9)	
V3	18	1	0.1930(8)	-0.15921(7)	0.0326(9)	0.0150(19)	
		2	0.4855(2)	0.0095(2)	-0.3002(2)	0.0062(5)	V
		3	-0.3445(7)	-0.1884(5)	0.0341(2)	0.0095(8)	
O11	6	1	0.6667(3)	0.3333(2)	0.0218(9)	0.0263(15)	
		2	0.6667(3)	0.3333(3)	-0.3559(12)	0.016(3)	O
		3	-0.6667(6)	-0.3333(3)	-0.0228(5)	0.009(3)	
O12	18	1	0.5207(3)	0.3416(4)	0.0794(9)	0.0258(11)	O

		2	0.6733(8)	0.4857(8)	-0.4133(2)	0.022(3)	
		3	-0.5211(1)	-0.3388(2)	-0.0795(5)	0.034(5)	
		1	0.8066(3)	0.1757(4)	0.0111(9)	0.0214(10)	
O21	18	2	0.1879(2)	0.2864(2)	-0.3233(2)	0.053(6)	O
		3	-0.2250(2)	0.1534(2)	0.0096(4)	0.063(9)	
		1	0.8862(5)	0.3117(4)	-0.0521(9)	0.0355(16)	
O22	18	2	0.0064(9)	0.2308(2)	-0.3810(2)	0.040(4)	O
		3	-0.1030(2)	0.3252(1)	-0.0476(4)	0.045(7)	
		1	0.6353(4)	0.0385(4)	-0.0449(9)	0.0269(13)	
O23	18	2	0.2880(8)	0.2774(7)	-0.3881(2)	0.014(3)	O
		3	-0.3434(1)	0.0474(1)	-0.0537(4)	0.018(4)	
		1	0.9029(3)	0.0725(3)	-0.0435(9)	0.0185(9)	
O24	18	2	0.2418(8)	0.4920(9)	-0.3742(2)	0.022(3)	O
		3	-0.0845(2)	0.0878(2)	-0.0399(5)	0.031(4)	
		1	0.3460(3)	-0.0432(3)	0.0551(9)	0.0173(9)	
O31	18	2	0.4053(7)	-0.1659(7)	-0.2898(2)	0.011(2)	O
		3	-0.4182(2)	-0.1031(2)	0.0529(4)	0.034(6)	
		1	0.2455(7)	-0.1418(5)	-0.0100(9)	0.050(2)	
O32	18	2	0.3764(9)	0.0695(8)	-0.2868(2)	0.018(3)	O
		3	-0.4032(1)	-0.3537(1)	0.0486(4)	0.027(4)	
		1	0.0821(3)	-0.0930(4)	0.0410(9)	0.0297(12)	
O33	18	2	0.6463(2)	0.0881(2)	-0.2802(2)	0.029(3)	O
		3	-0.1697(2)	-0.0937(9)	0.0441(5)	0.014(3)	
		1	0.1110(6)	-0.3307(4)	0.0459(9)	0.050(2)	
O34	18	2	0.5118(8)	0.0384(2)	-0.3436(2)	0.017(3)	O
		3	-0.3706(2)	-0.1936(2)	-0.0088(4)	0.034(6)	

Table S3. Anisotropic atomic displacement parameters (U_{ij}, Å^2) for $Ca_{8.6}Pb_{1.9}(VO_4)_7$ (**1**), $Ca_{7.0}Pb_{3.5}(VO_4)_7$ (**2**) and $Ca_{5.6}Pb_{4.9}(VO_4)_7$ (**3**) single crystals.

Site	Sample	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
*M*1	1	0.0139(2)	0.0130(2)	0.0116(2)	0.0053(2)	-0.0030(19)	-0.0006(19)
	2	0.0136(9)	0.0140(9)	0.0081(10)	0.0075(6)	-0.0001(5)	-0.0005(5)
	3	0.0157(8)	0.0154(8)	0.0138(8)	0.0097(6)	-0.0006(5)	0.0005(6)
*M*2	1	0.0112(2)	0.0140(2)	0.0117(2)	0.0055(19)	-0.0008(17)	-0.0004(18)
	2	0.0220(8)	0.0232(8)	0.0177(8)	0.0119(7)	-0.0048(6)	-0.0041(6)
	3	0.0141(8)	0.0158(9)	0.0138(9)	0.0092(7)	0.0017(9)	0.0032(6)
$M3_1$	1	0.0091(11)	0.029(2)	0.0064(11)	0.0122(13)	0.0079(7)	0.0091(8)
	2	0.0243(3)	0.0232(3)	0.0164(3)	-0.0002(2)	-0.0020(3)	-0.0090(3)
	3	0.0229(5)	0.0488(10)	0.0242(5)	0.0218(6)	0.0080(7)	0.0066(6)
$M3_2$	1	0.0288(5)	0.0462(6)	0.0250(4)	0.0246(5)	0.0103(3)	0.0085(4)
	3	0.036(9)	0.11(3)	0.035(8)	0.051(14)	0.024(6)	0.040(11)
$M4_1$	1	0.053(3)	0.053(3)	0.0271(14)	0.0265(14)	0	0
	2	0.0538(19)	0.0538(19)	0.034(3)	0.0269(9)	0	0
	3	0.082(2)	0.082(2)	0.126(5)	0.0412(11)	0	0
$M4_2$	1	0.051(10)	0.019(3)	0.036(5)	0.004(4)	0.013(6)	-0.004(2)
	2	0.014(2)	0.014(2)	0.038(5)	0.0068(10)	0	0
$M4_3$	1	0.0245(15)	0.0245(15)	0.114(7)	0.0122(8)	0	0
	2	0.023(2)	0.013(2)	0.026(5)	0.0071(10)	0	
*M*5	1	0.0235(3)	0.0235(3)	0.0085(4)	0.0118(16)	0	0
	2	0.0175(10)	0.0175(10)	0.0027(13)	0.0088(5)	0	0
	3	0.0167(12)	0.0167(12)	0.0058(16)	0.0083(6)	0	0
V1	1	0.0105(20)	0.0105(20)	0.0131(3)	0.0052(10)	0	0
	2	0.0068(7)	0.0068(7)	0.0071(13)	0.0034(4)	0	0
	3	0.0109(11)	0.0109(11)	0.025(2)	0.0054(5)	0	0
V2	1	0.0135(2)	0.0121(19)	0.0099(18)	0.0083(16)	-0.0006(15)	0.0008(15)
	2	0.0068(7)	0.0102(7)	0.0062(7)	0.0020(6)	-0.0013(6)	-0.0057(6)
	3	0.0155(12)	0.0115(11)	0.0081(10)	0.0060(10)	-0.0001(12)	0.0030(12)
V3	1	0.0208(3)	0.0114(2)	0.0129(2)	0.0080(2)	-0.0039(2)	0.0006(17)
	2	0.0085(7)	0.0042(7)	0.0036(7)	0.0013(6)	-0.0008(6)	-0.0002(5)
	3	0.0047(10)	0.0142(11)	0.0070(10)	0.0027(8)	0.0017(8)	0.0019(12)
O11	1	0.0313(19)	0.0313(19)	0.016(2)	0.0156(10)	0	0

	2	0.019(4)	0.019(4)	0.009(6)	0.009(2)	0	0
	3	0.025(4)	0.025(5)	0.019(4)	0.0188(10)	0	0
O12	1	0.0212(13)	0.0203(13)	0.0400(18)	0.0135(12)	0.0069(12)	-0.0054(12)
	2	0.020(4)	0.016(4)	0.035(5)	0.013(3)	0.013(3)	0.014(3)
	3	0.019(5)	0.034(6)	0.053(7)	0.015(5)	-0.006(5)	-0.017(6)
O21	1	0.0232(13)	0.0236(13)	0.0110(10)	0.0069(11)	-0.0011(9)	0.0004(9)
	2	0.026(5)	0.093(11)	0.012(4)	0.009(6)	-0.008(4)	-0.007(5)
	3	0.106(15)	0.049(9)	0.025(7)	0.031(10)	0.015(8)	0.000(6)
O22	1	0.050(2)	0.0256(17)	0.0291(16)	0.0180(17)	0.0015(16)	0.0132(13)
	2	0.009(4)	0.066(7)	0.017(4)	-0.001(4)	0.001(3)	-0.020(4)
	3	0.095(11)	0.024(6)	0.011(5)	0.026(7)	-0.018(6)	-0.004(4)
O23	1	0.0166(12)	0.041(2)	0.0212(13)	0.0133(13)	-0.0089(10)	-0.0105(13)
	2	0.026(4)	0.012(3)	0.012(3)	0.017(3)	0.001(3)	0.001(2)
	3	0.008(4)	0.036(6)	0.012(4)	0.011(4)	0.008(3)	0.014(4)
O24	1	0.0165(11)	0.0189(12)	0.0257(13)	0.0131(10)	-0.0015(9)	-0.0035(9)
	2	0.021(4)	0.018(4)	0.035(5)	0.015(3)	-0.012(3)	-0.010(4)
	3	0.004(4)	0.026(6)	0.053(8)	0.001(4)	-0.001(5)	0.014(5)
O31	1	0.0152(10)	0.0229(12)	0.0165(10)	0.0116(10)	-0.0045(8)	-0.0017(9)
	2	0.016(3)	0.002(3)	0.011(3)	0.001(2)	-0.004(2)	-0.003(2)
	3	0.038(7)	0.047(7)	0.036(7)	0.037(6)	0.002(6)	-0.003(6)
O32	1	0.091(4)	0.034(2)	0.0140(14)	0.022(3)	-0.0091(19)	-0.0021(13)
	2	0.027(4)	0.021(4)	0.016(4)	0.020(3)	0.001(3)	-0.002(3)
	3	0.034(6)	0.018(5)	0.013(5)	0.000(5)	-0.004(4)	0.000(4)
O33	1	0.0157(12)	0.0254(15)	0.048(2)	0.0101(12)	0.0001(12)	0.0181(14)
	2	0.019(4)	0.033(5)	0.023(4)	0.004(3)	-0.014(3)	-0.007(4)
	3	0.008(4)	0.013(4)	0.014(4)	0.000(3)	0.002(3)	0.002(4)
O34	1	0.082(4)	0.0149(14)	0.0321(19)	0.0089(18)	-0.019(2)	0.0072(13)
	2	0.024(4)	0.023(4)	0.006(3)	0.013(3)	0.005(3)	0.001(3)
	3	0.047(8)	0.038(7)	0.008(5)	0.015(6)	-0.010(5)	-0.005(5)

Table S4. The main interatomic distances, Å for (**1**), (**2**) and (**3**) crystals.

Bond		**1**		**2**		**3**	
		Ca	Pb	Ca	Pb	Ca	Pb
*M*1	O12	2.412(2)		2.508(7)		2.520(6)	
	O31	2.362(3)				2.310(2)	
	O34	2.390(4)		2.441(7)		2.491(5)	
	O32	2.440(4)		2.380(6)		2.378(2)	
	O33			2.281(5)			
	O24	2.502(1)		2.4846		2.525(1)	
	O24’	2.450(2)		2.6061		2.610(6)	
	O23	2.833(2)		2.564(7)		2.617(2)	
	O22	2.844(1)		3.107(0)		3.038(4)	
	<*M*1-O>	**2.530**		**2.547**		**2.561**	
*M*2	O21	2.380(4)		2.380(6)		2.410(2)	
	O23	2.410(4)		2.401(5)		2.418(2)	
	O22	2.321(4)		2.411(6)		2.439(2)	
	O12	2.506(2)		2.440(2)		2.455(5)	
	O31	2.524(1)		2.444(5)		2.816(3)	
	O31’			2.518(1)			
	O33	2.460(6)		2.821(1)		2.503(2)	
	O33’	2.587(1)				2.536(1)	
	O34	3.169(4)					
	O32			2.808(5)		2.811(1)	
	<*M*2-O>	**2.545**		**2.488**		**2.511**	
$M3_1$	O23	2.431(4)	2.420(4)	2.450(5)			2.475(4)
	O31	2.509(6)	2.481(1)				2.774(4)
	O11	2.576(2)	2.658(2)	2.637(1)			2.645(1)
	O34	2.633(2)	2.612(1)	2.662(2)			2.706(1)
	O34’			2.742(1)			2.734(2)
	O22	2.655(1)	2.636(1)	2.627(1)			2.650(1)
	O21	2.659(1)	2.672(1)	2.898(2)			3.032(1)
	O21’	2.705(1)	2.762(2)				
	O32	2.819(1)	2.741(2)	2.573(1)			2.645(1)
	O33			2.775(4)			

	O12			3.117(3)
	<*M*3-O>	**2.623**	**2.670**	**2.753**
$M3_2$	O23	2.420(4)		2.330(4)
	O31	2.481(1)		2.898(3)
	O11	2.658(2)		
	O34	2.612(1)		3.573(7)
	O34’			3.421(7)
	O22	2.636(1)		2.470(5)
	O21	2.672(1)		2.331(6)
	O21’	2.762(2)		3.010(7)
	O32	2.741(2)		2.469(6)
	O33			
	O12			3.517(5)
	<$M3_2$-O>	**2.623**		**2.961**
*M*5	O33 × 3	2.290(3)	2.320(5)	2.337(2)
	O24 × 3	2.311(3)	2.290(5)	2.292(2)
	<*M*5-O>	**2.301**	**2.305**	**2.314**
$M4_1$	O32× 3	2.728(4)		
	O12× 3	3.062(1)	3.136(2)	
	O21× 3		2.781(5)	
	<$M4_1$–O>	**2.900**	**2.959**	
$M4_2$	O32 × 3	2.703(1)		
	O34 × 3	3.256(3)		
	O21× 3		2.8044	2.7971
	O22× 3		3.0629	
	O12× 3			3.2505
	<$M4_2$–O>	**2.980**	**2.934**	**3.024**
$M4_3$	O32	2.438(1)	2.954(4)	2.468(5)
	O32’	2.505(1)		
	O12	2.754(1)	2.787(2)	
	O12’	2.915(4)	2.977(1)	
	O23	3.106(4)		2.694(1)
	O34	3.172(2)		3.421(1)
	O21		2.356(1)	2.331(2)

	O21’		2.582(2)	3.010(4)
	O22		3.094(2)	2.470(1)
	O31			2.898(2)
	<$M4_3$–O>	**2.815**	**2.792**	**2.756**
V1	O11	1.710(5)	1.740(7)	1.730(3)
	O12 × 3	1.714(2)	1.710(2)	1.708(2)
	<V1–O>	**1.713**	**1.725**	**1.714**
V2	O24	1.708(2)	1.704(2)	1.737(2)
	O21	1.710(5)	1.740(7)	1.701(2)
	O23	1.701(2)	1.721(3)	1.727(2)
	O22	1.690(2)	1.680(2)	1.671(2)
	<V2–O>	**1.702**	**1.711**	**1.709**
V3	O33	1.723(2)	1.710(3)	1.721(2)
	O31	1.740(2)	1.718(2)	1.691(2)
	O34	1.701(2)	1.701(7)	1.702(2)
	O32	1.710(5)	1.710(2)	1.691(2)
	<V3–O>	**1.718**	**1.710**	**1.701**

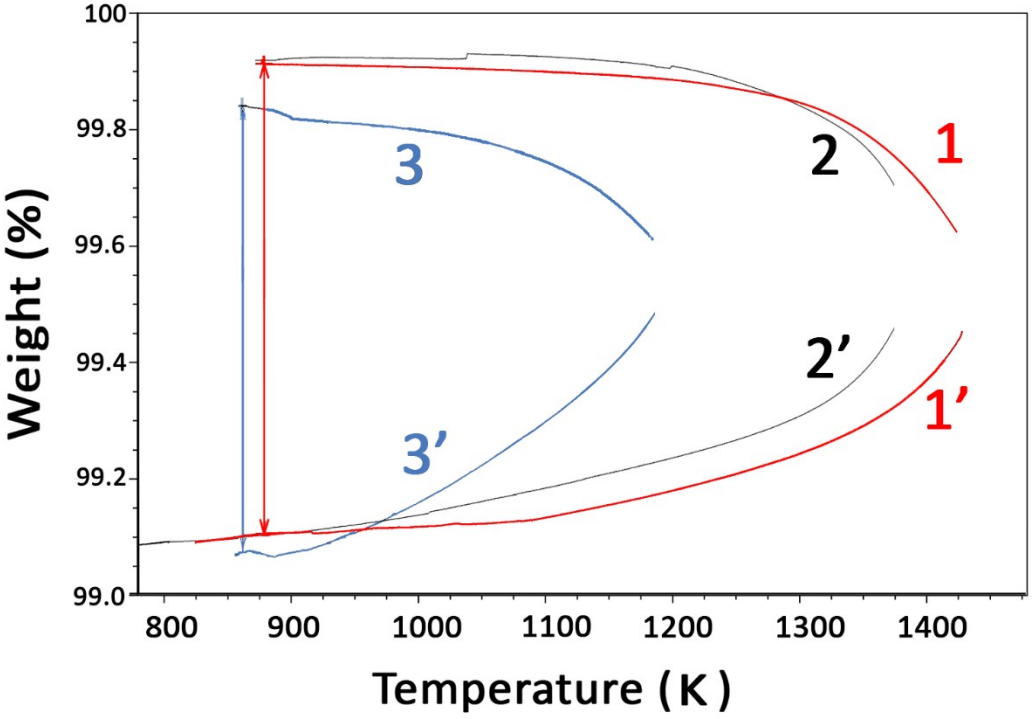

Fig. S1. Thermogravimetric curves for crystals (**1**), (**2**), and (**3**) in the heating (1, 2, 3)-cooling (1', 2', 3') circles.

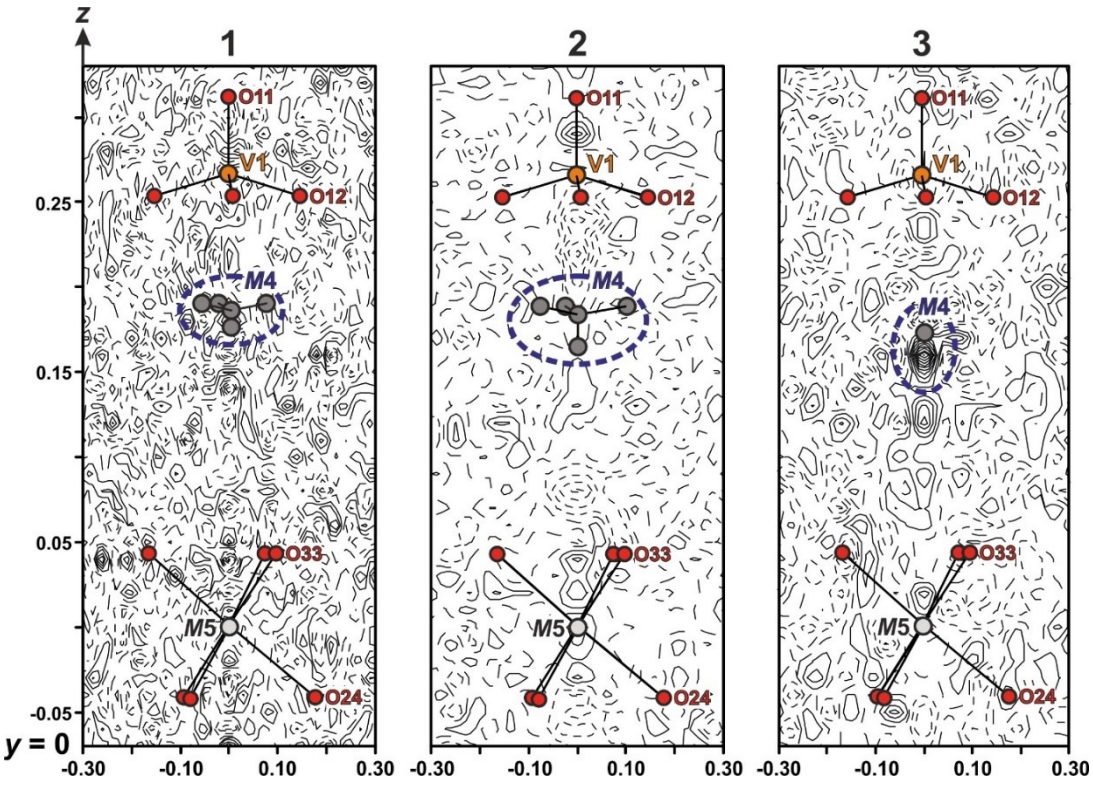

Fig. S2. The difference of electron density map around the *M*4-site in the structure of crystals (**1**), (**2**), and (**3**). The positive electron density is indicated by solid lines and the negative electron density is designated by dashed lines. Contour intervals are 0.1 eÅ^{-3}.

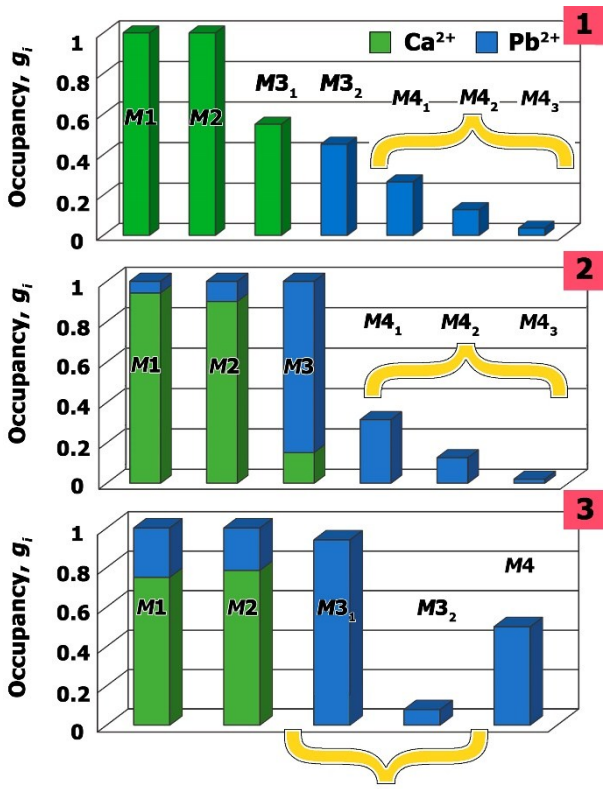

Fig. S3. Occupancy of the *M*(1–4) site by Ca^{2+} and Pb^{2+} in the crystal structures of (**1**), (**2**) and (**3**) crystals.

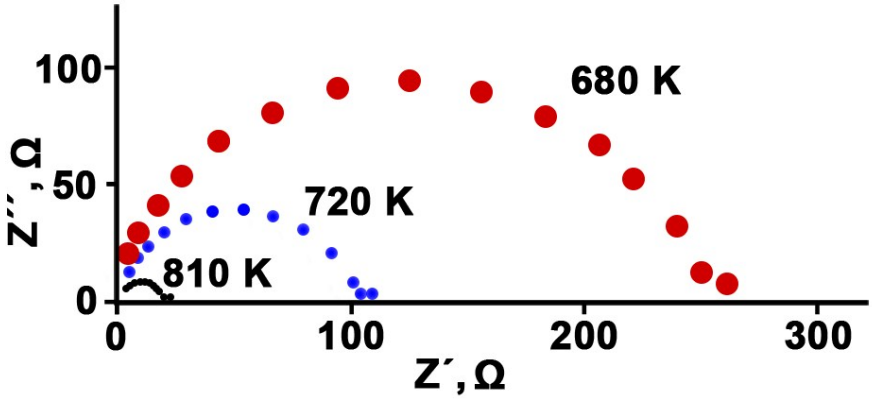

Fig. S4. Complex impedance plot of $Ca_{5.6}Pb_{4.9}(VO_4)_7$ at selected temperatures, demonstrating absence of noticeable electronic contribution. The total electric conductivity values for the sample at 680, 720 and 810 K corresponds to (0. 23; 0.6; 2.4) 10^{-3} $\Omega^{-1}cm^{-1}$, respectively.