

## Supplementary Information

### NASICON-type $\text{Na}_{3.6}\text{Y}_{1.8-x}\text{Sc}_x(\text{PO}_4)_3$ solid solutions: structure and luminescence

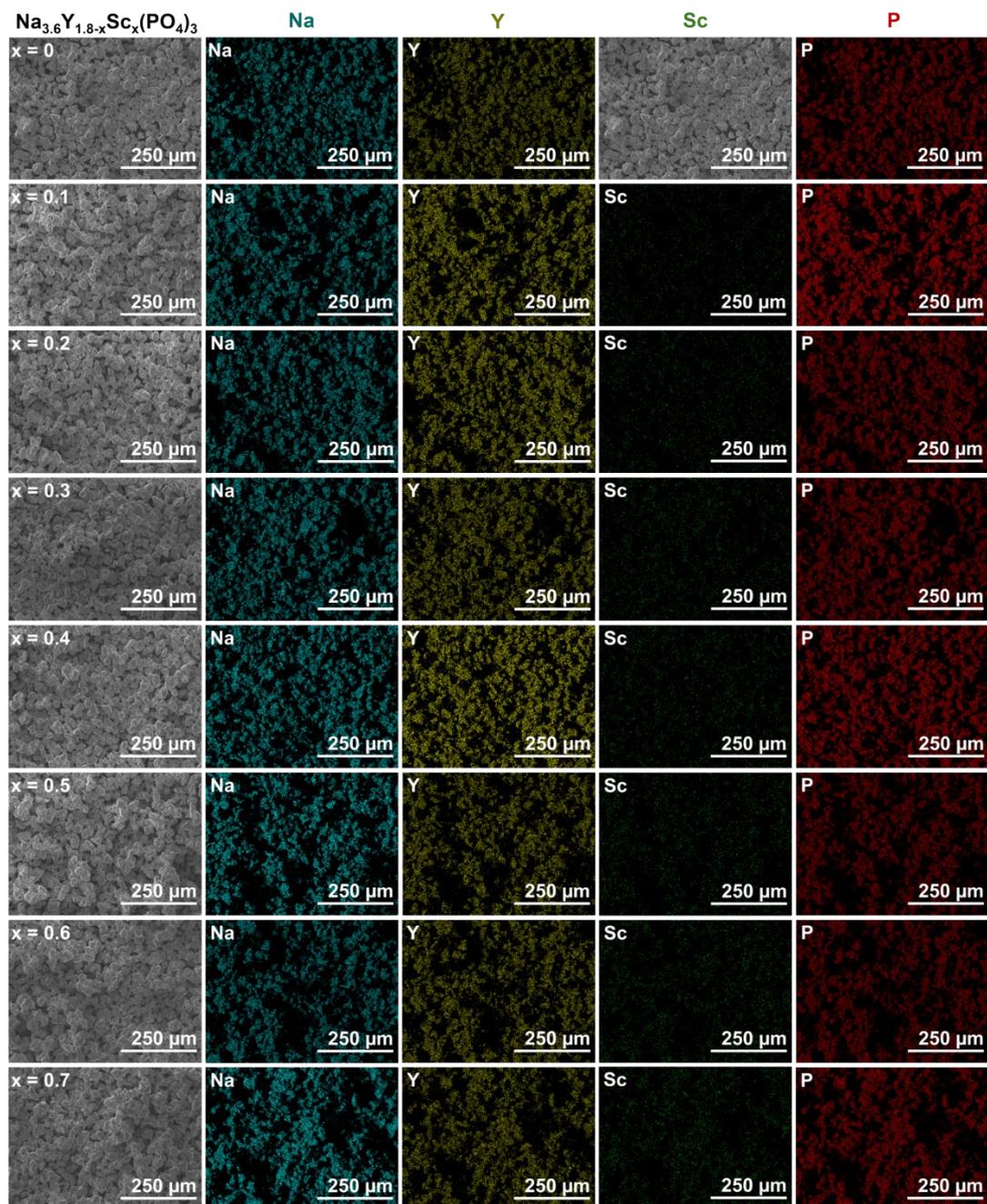
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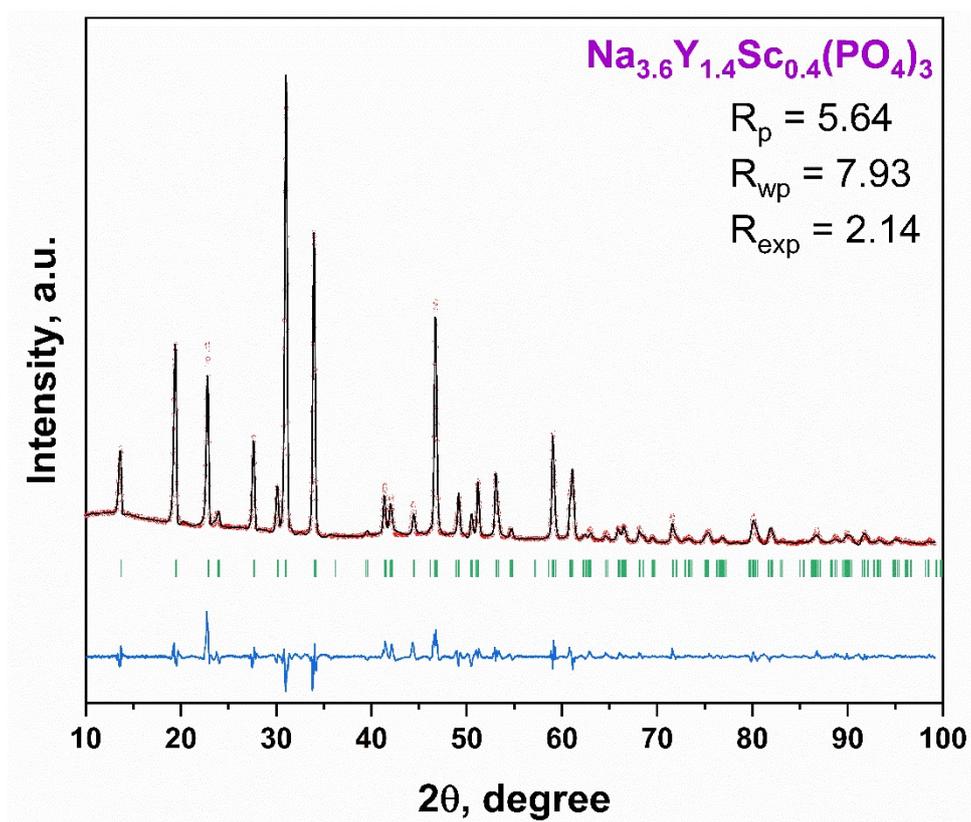
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**Fig. S1.** SEM images (left column) and elemental mapping of Na, Y, Sc and P for  $\text{Na}_{3.6}\text{Y}_{1.8-x}\text{Sc}_x(\text{PO}_4)_3$  ( $x = 0-0.7$ ) solid solutions.



**Fig. S2.** Part of the observed, calculated and difference PXRD patterns for NYSP ( $x = 0.4$ ) sample. Tick marks denote the peak positions of possible Bragg reflections.

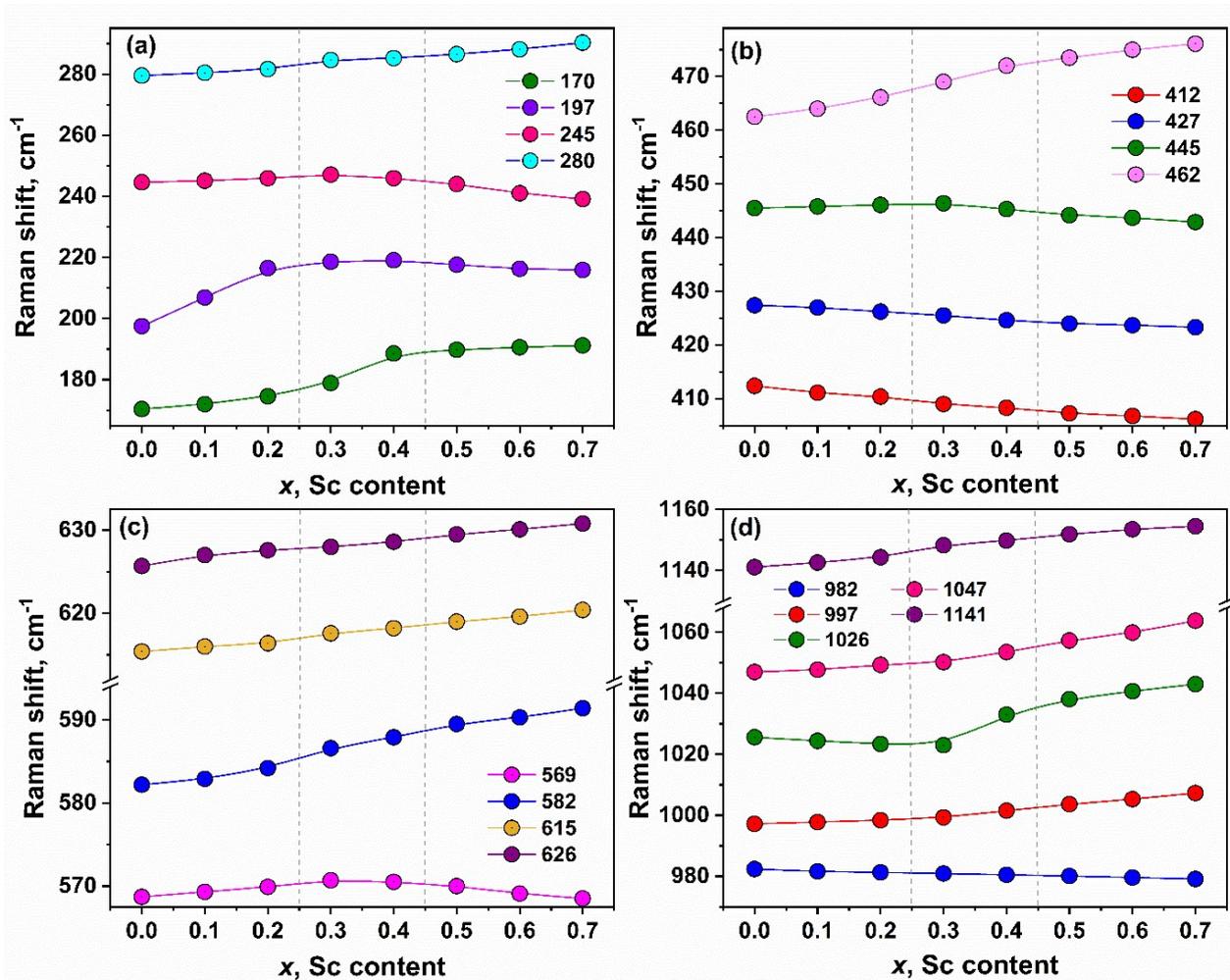


Fig. S3. Dependence of peak positions in the Raman spectra of NYSP samples on  $x$  value.

**Table S1.** Raman spectroscopy data of  $\text{Na}_{3.6}\text{Y}_{1.8-x}\text{Sc}_x(\text{PO}_4)_3$  solid solutions.

LP	Wavenumbers [ $\text{cm}^{-1}$ ]								Characteristic	Affiliation	Ref.
	x=	0	0.1	0.2	0.3	0.4	0.5	0.6			
1	47.6	48	48.2	48.6	47.8	47.5	47	46.6	w, br	Complex lattice deformation (translation & libration) of (Na,Sc,Y) ion-oxygen polyhedra	[22,36,38-40,43-45]
2	170.4	172	174.6	178.9	188.6	189.8	190.6	191.2	mw, br		
3	197.5	206.9	216.5	218.6	219.1	217.6	216.3	215.9	mw, br		
4	244.6	245.1	245.9	247.1	245.9	244	241	239.1	mw, br, left shoulder		
5	279.5	280.4	281.6	284.6	285.2	286.5	288.1	290.3	mw, br		
6	n.d	n.d	n.d.	n.d.	n.d.	346.4	342.4	356	w, br, right shoulder		
7	412.4	411.1	410.4	409	408.3	407.3	406.8	406.2	mw, sh, left shoulder	In-plane ( $\nu_2$ ) deformations (scissoring, rocking) of $(\text{PO}_4)^{3-}$ groups	[22,33,35-45]
8	427.4	427	426.2	425.5	424.6	424	423.7	423.3	mw, sh		
9	445.5	445.8	446.1	446.4	445.3	444.2	443.7	442.9	m, sh		
10	462.5	464	466.1	469	472	473.5	475	476.1	mw, sh, right shoulder		
11	568.7	569.3	569.9	570.7	570.5	570	569.1	568.5	m, sh	Out-of-plane ( $\nu_4$ ) deformations (wagging, twisting) of orthophosphate groups $(\text{PO}_4)^{3-}$	[22,33,35-45]
12	582.2	582.9	584.2	586.6	587.9	589.5	590.3	591.4	mw, sh		
13	615.4	616	616.4	617.6	618.2	619	619.6	620.4	mw, sh	Transverse (mostly symmetric stretches) of bridging P-O-P vibrations	[22,31-33,35-45]
14	625.7	627	627.6	628	628.6	629.5	630.1	630.8	mw, sh		
15	956.7	959.7	962	964.1	963.9	963.7	963.4	962.9	mw, sh, left shoulder	Symmetric stretching POP & -O-( $\text{PO}_2$ )-O- vibrations of phosphate oxyanion groups. ( $\nu_1$ )	[22,31-42,44,45]
16	982.4	981.6	981.3	980.9	980.5	980.1	979.6	979.1	s, sh		
17	997.2	997.8	998.4	999.3	1001.5	1003.6	1005.3	1007.3	s, sh		
18	1025.6	1024.4	1023.4	1023	1033	1038.1	1040.7	1043	s, sh	Asymmetric -O-( $\text{PO}_2$ )-O- stretching of $(\text{PO}_4)^{3-}$ group vibrations. ( $\nu_3$ )	[22,31-45]
19	1047	1047.7	1049.3	1050.2	1053.5	1057.3	1059.9	1063.8	m, sh, right shoulder		
20	1067.8	1069.3	1071.9	1074	1077.9	1079.4	1078.9	1078.4	m, sh, right shoulder		
21	1126.5	1127.7	1128.2	1129.8	1130.5	1131.2	1132	1133	mw, br	Asymmetric stretching vibrations of terminal, depolarized $(\text{PO}_4)^{3-}$ groups	[22,31-37,39-42,44,45]
22	1141.1	1142.6	1144.3	1148.3	1149.8	1151.9	1153.5	1154.5	mw, br		

w – weak, mw - medium weak, m – medium, s – strong, br – broad, sh – sharp, n.d. – not distinguishable (not visible or too difficult to deconvolute)

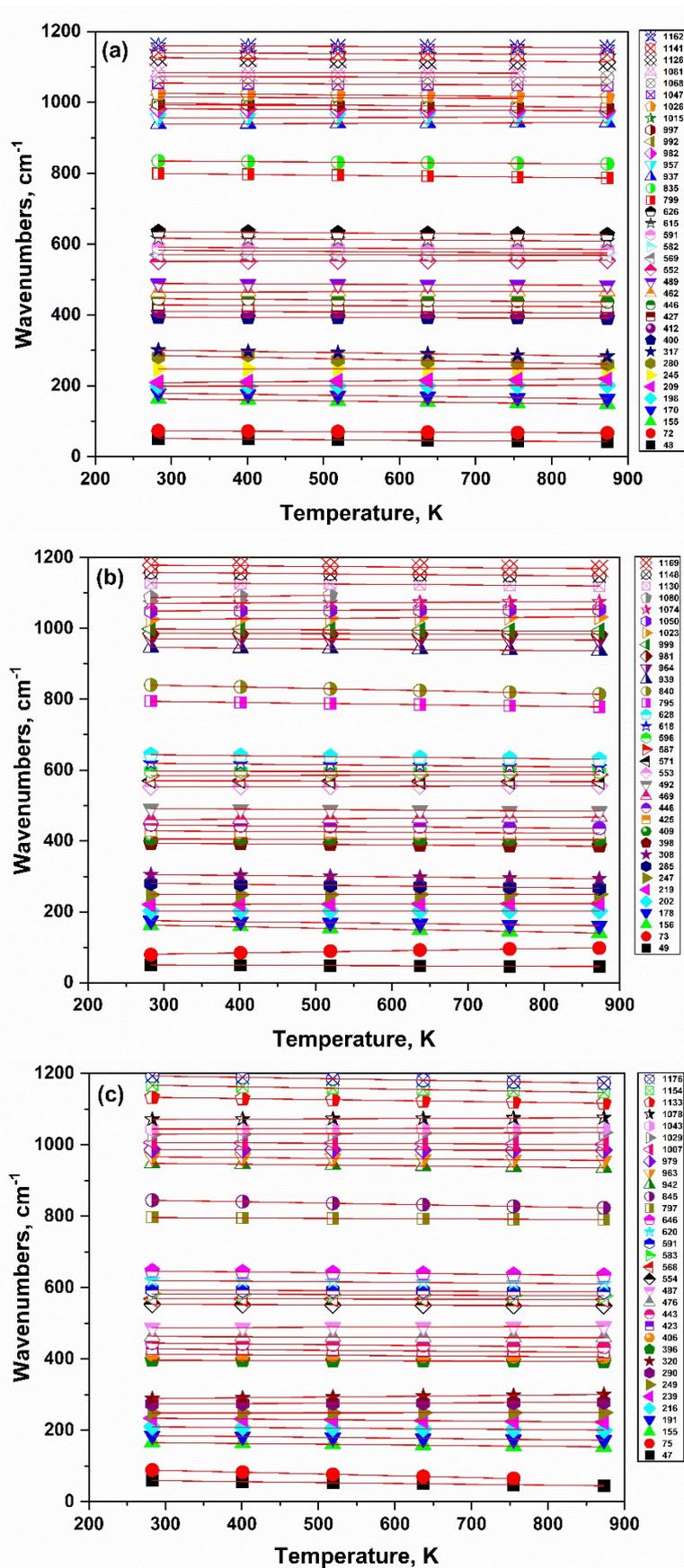


Fig. S4. Temperature dependence of peak positions in Raman spectrum of  $\text{Na}_{3.6}\text{Y}_{1.8-x}\text{Sc}_x(\text{PO}_4)_3$  at  $x = 0$  (a), 0.3 (b) and 0.7 (c).

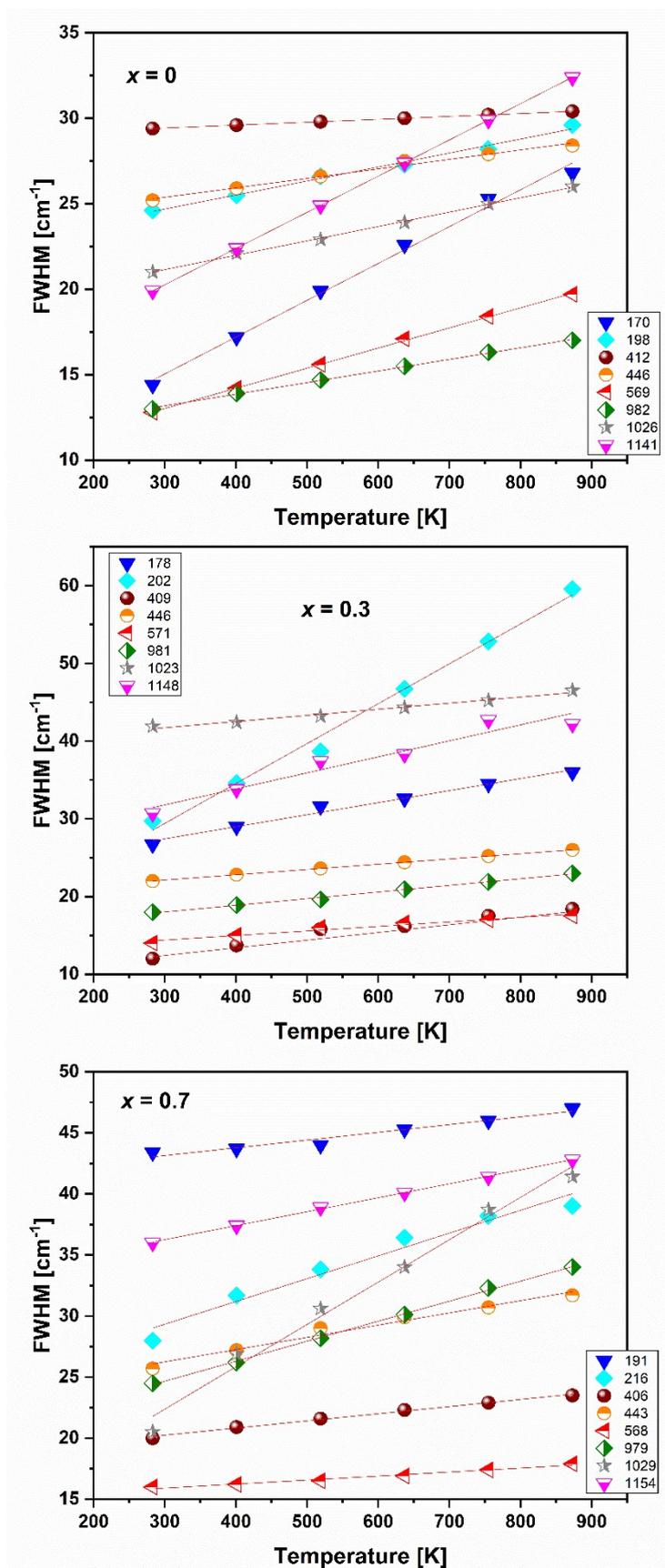


Fig. S5. Temperature dependence of FWHM in Raman spectrum of  $\text{Na}_{3.6}\text{Y}_{1.8-x}\text{Sc}_x(\text{PO}_4)_3$  at  $x = 0, 0.3$  and  $0.7$ .

**Table S2.** Raman Modes at 293 K ( $\omega_{RT}$ ), and their temperature coefficients ( $d\omega_{LT}/dT$ ) for selected NYSP solid solutions.

$x = 0.0$		$x = 0.3$		$x = 0.7$	
$\omega_{RT}$ [cm <sup>-1</sup> ]	$d\omega_{HT}/dT \times 10^3$ [cm <sup>-1</sup> /K]	$\omega_{RT}$ [cm <sup>-1</sup> ]	$d\omega_{HT}/dT \times 10^3$ [cm <sup>-1</sup> /K]	$\omega_{RT}$ [cm <sup>-1</sup> ]	$d\omega_{HT}/dT \times 10^3$ [cm <sup>-1</sup> /K]
48	-15.06 ± 0.81	49	-7.51 ± 0.76	47	-24.46 ± 0.26
72	-10.58 ± 0.26	73	30.80 ± 2.27	75	-50.00 ± 0.51
155	-25.06 ± 0.34	156	-37.17 ± 0.80	155	-19.73 ± 0.32
170	-26.39 ± 0.52	178	-24.14 ± 0.55	191	-21.96 ± 0.42
198	4.99 ± 0.18	202	0.85 ± 0.01	216	-15.86 ± 0.42
209	17.82 ± 0.88	219	4.84 ± 0.16	239	-18.64 ± 0.23
245	2.13 ± 0.09	247	2.08 ± 0.06	249	2.01 ± 0.07
280	-41.67 ± 7.89	285	-22.37 ± 0.27	290	7.87 ± 0.28
317	-29.44 ± 0.68	308	-19.81 ± 0.35	320	19.49 ± 0.44
400	-4.19 ± 0.18	398	-14.04 ± 0.19	396	-6.13 ± 0.29
412	-8.45 ± 0.39	409	-4.43 ± 0.18	406	-12.59 ± 0.34
427	-8.30 ± 0.15	425	-11.62 ± 0.30	423	-15.18 ± 0.42
446	-15.57 ± 0.70	446	-16.46 ± 0.66	443	-19.88 ± 0.32
462	3.61 ± 0.13	469	12.64 ± 0.65	476	-5.38 ± 0.32
489	-8.57 ± 0.31	492	-13.15 ± 0.50	487	7.14 ± 0.13
552	5.35 ± 0.20	553	4.79 ± 0.20	554	-7.07 ± 0.38
569	-3.08 ± 0.21	571	-4.89 ± 0.16	568	-3.15 ± 0.25
582	-9.78 ± 0.31	587	5.45 ± 0.15	583	-9.81 ± 0.07
591	-12.40 ± 0.21	596	-2.74 ± 0.16	591	-9.83 ± 0.22
615	-13.70 ± 0.24	618	-18.40 ± 0.20	620	-16.03 ± 0.26
626	-14.67 ± 0.31	628	-22.62 ± 0.31	646	-20.39 ± 0.27
799	-21.38 ± 0.36	795	-27.26 ± 0.62	797	-9.84 ± 0.89
835	-13.70 ± 0.56	840	-43.68 ± 0.43	845	-36.68 ± 0.38
937	8.26 ± 0.21	939	-16.08 ± 0.37	942	-20.90 ± 0.34
957	4.67 ± 0.26	964	-6.37 ± 0.26	963	-16.54 ± 0.46
982	-9.73 ± 0.77	981	-4.09 ± 0.17	979	-2.81 ± 0.11
992	-4.24 ± 0.49	999	-10.34 ± 0.38	1007	-8.79 ± 0.21
997	-19.76 ± 0.59	1023	11.02 ± 0.76	1029	8.64 ± 0.39
1015	-8.14 ± 0.17	1050	8.50 ± 0.17	1043	5.81 ± 0.43
1026	-18.67 ± 0.53	1074	7.12 ± 0.16	1078	8.38 ± 0.37
1047	-11.19 ± 0.52	1080	27.97 ± 1.96	1133	-27.48 ± 0.28
1068	-4.55 ± 0.18	1130	-14.94 ± 0.27	1154	-33.80 ± 0.28
1081	-3.98 ± 0.32	1148	-17.70 ± 0.13	1178	-33.70 ± 0.29
1126	-21.55 ± 0.82	1169	-16.39 ± 0.27		
1141	-9.44 ± 0.34				
1162	-9.37 ± 0.81				

Blueshifting modes – marked as blue; red – additional modes to those mentioned in Table S1.

**Table S3.** The temperature coefficients of the Raman linewidths ( $d\Gamma/dT$ ) for selected NYSP.

$x = 0.0$		$x = 0.3$		$x = 0.7$	
Peak label initial position $\omega_0$ [ $\text{cm}^{-1}$ ]	FWHM Temp. coefficient $\times 10^3$ ( $d\Gamma/dT$ ) [ $\text{cm}^{-1}/\text{K}$ ]	Peak label initial position $\omega_0$ [ $\text{cm}^{-1}$ ]	FWHM Temp. coefficient $\times 10^3$ ( $d\Gamma/dT$ ) [ $\text{cm}^{-1}/\text{K}$ ]	Peak label initial position $\omega_0$ [ $\text{cm}^{-1}$ ]	FWHM Temp. coefficient $\times 10^3$ ( $d\Gamma/dT$ ) [ $\text{cm}^{-1}/\text{K}$ ]
48	$15.4 \pm 1.2$	49	$17.4 \pm 0.6$	47	$8.2 \pm 0.2$
72	$9.6 \pm 0.4$	73	$66.7 \pm 3.9$	75	$21.4 \pm 0.9$
155	$13.4 \pm 0.7$	156	$44.5 \pm 2.9$	155	$29.5 \pm 3.8$
170	$21.5 \pm 0.9$	178	$15.5 \pm 1.0$	191	$6.3 \pm 0.7$
198	$8.2 \pm 0.4$	202	$51.4 \pm 2.4$	216	$18.7 \pm 1.8$
209	$7.5 \pm 0.2$	219	$41.0 \pm 1.6$	239	$17.1 \pm 0.3$
245	$1.9 \pm 0.2$	247	$8.5 \pm 0.8$	249	$1.8 \pm 0.1$
280	$13.8 \pm 0.1$	285	$19.6 \pm 2.2$	290	$18.8 \pm 1.9$
317	$23.5 \pm 0.4$	308	$30.6 \pm 0.3$	320	$6.8 \pm 0.2$
400	$18.3 \pm 0.3$	398	$6.0 \pm 0.9$	396	$1.9 \pm 0.2$
412	$1.7 \pm 0.6$	409	$10.6 \pm 1.0$	406	$5.9 \pm 0.2$
427	$8.6 \pm 0.4$	425	$13.0 \pm 1.0$	423	$29.1 \pm 1.5$
446	$5.5 \pm 0.3$	446	$6.8 \pm 0.1$	443	$10.0 \pm 0.8$
462	$13.4 \pm 0.7$	469	$11.3 \pm 0.9$	476	$7.9 \pm 0.6$
489	$7.1 \pm 0.1$	492	$20.4 \pm 0.7$	487	$10.2 \pm 0.5$
552	$1.7 \pm 0.1$	553	$9.8 \pm 0.5$	554	$2.0 \pm 0.1$
569	$11.8 \pm 0.1$	571	$5.9 \pm 0.5$	568	$3.2 \pm 0.2$
582	$10.2 \pm 0.1$	587	$3.4 \pm 0.2$	583	$13.1 \pm 1.0$
591	$12.0 \pm 0.4$	596	$19.7 \pm 0.6$	591	$10.4 \pm 0.2$
615	$22.3 \pm 0.2$	618	$21.0 \pm 1.0$	620	$16.1 \pm 0.9$
626	$7.2 \pm 0.2$	628	$8.7 \pm 0.6$	646	$9.6 \pm 0.3$
799	$2.4 \pm 0.1$	795	$4.1 \pm 0.2$	797	$10.3 \pm 0.8$
835	$9.5 \pm 0.1$	840	$3.2 \pm 0.2$	845	$11.6 \pm 0.2$
937	$17.0 \pm 0.2$	939	$20.4 \pm 1.7$	942	$23.3 \pm 0.1$
957	$10.7 \pm 0.5$	964	$18.7 \pm 1.7$	963	$10.2 \pm 0.1$
982	$6.8 \pm 0.1$	981	$8.5 \pm 0.3$	979	$16.4 \pm 0.3$
992	$8.1 \pm 0.1$				
997	$3.7 \pm 0.1$	999	$10.2 \pm 0.3$	1007	$3.3 \pm 0.2$
1015	$2.4 \pm 0.3$				
1026	$8.4 \pm 0.2$	1023	$7.9 \pm 0.5$	1029	$34.7 \pm 2.1$
1047	$10.9 \pm 0.1$	1050	$20.9 \pm 0.2$	1043	$10.5 \pm 0.7$
1068	$8.1 \pm 0.1$	1074	$10.3 \pm 0.6$		
1081	$39.3 \pm 0.1$	1080	$19.8 \pm 0.8$	1078	$7.6 \pm 0.2$
1126	$47.8 \pm 0.1$	1130	$55.2 \pm 3.4$	1133	$36.2 \pm 2.1$
1141	$21.2 \pm 0.1$	1148	$20.6 \pm 2.5$	1154	$11.4 \pm 0.2$
1162	$21.1 \pm 0.1$	1169	$14.9 \pm 1.5$	1176	$20.0 \pm 1.4$