

# Synthesis and crystal structure of $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ phosphate

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A new Nasicon phosphates series  $[\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3 (0 \leq x \leq 1)]$  was synthesized by a coprecipitation method and structurally characterized by powder X-ray diffraction. The selected compound  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  ( $x=0.5$ ) crystallizes in the  $R\bar{3}c$  space group with the following hexagonal unit-cell dimensions:  $a_h=8.7285(3)$  Å,  $c_h=21.580(2)$  Å,  $V=1423.8(1)$  Å<sup>3</sup>, and  $Z=6$ . This three-dimensional framework is built of  $\text{PO}_4$  tetrahedra and Cr/CoO<sub>6</sub> octahedra sharing corners. Na atoms occupy totally M(1) sites and partially M(2) sites. © 2006 International Centre for Diffraction Data. [DOI: 10.1154/1.2190689]

Key words: Nasicon, crystal structure, powder diffraction, X-ray diffraction

## I. INTRODUCTION

Nasicon-type materials have been extensively studied after the discovery of sodium superionic conductors of  $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$  phosphates (Goodenough *et al.*, 1976). These materials were known to show relatively high chemical stability and have been proposed for use in various fields of solid state chemistry: solid electrolytes, electrode materials, low thermal expansion ceramics, etc. The three-dimensional (3D) framework of Nasicon family materials [with general formula  $\text{M}_n\text{AB}(\text{PO}_4)_3$ ] permit a large number of substitutions at M, A, and P sites giving rise to a range of composition (Alamo, 1993). The structure of these materials consists of a 3D network built up of  $\text{PO}_4$  tetrahedra sharing corners with  $\text{A}(\text{B})\text{O}_6$  octahedra. In this skeleton, there are two sites, usually labeled M(1) and M(2). The M(1) site is an antiprism formed by the triangular faces of two  $\text{A}(\text{B})\text{O}_6$  octahedra along  $c$  axis of the hexagonal cell. Thus, the network of the  $\text{M}_n\text{AB}(\text{PO}_4)_3$  can be considered as made up of infinite ribbons of composition  $[\text{O}_3\text{A}(\text{B})\text{O}_3\text{M}(1)\text{O}_3\text{A}(\text{B})\text{O}_3\text{O}_3\text{A}(\text{B})\text{O}_3\text{M}(1)\text{O}_3\text{A}(\text{B})\text{O}_3]_\infty$  connected by  $\text{PO}_4$  tetrahedra. The M(2) sites are located between these ribbons in large cavities with an eight-fold coordination. The M(1) and M(2) sites may be completely empty (Leclaire *et al.*, 1989), partially occupied (Chakir *et al.*, 2003; Krimi *et al.*, 2000), or full (Boilot *et al.*, 1983; Salmon *et al.*, 1979).

The previous study shows the existence of  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Mg}_x(\text{PO}_4)_3$  (Delmas *et al.*, 1986) and  $\text{Na}_4\text{CrNi}(\text{PO}_4)_3$  (Manoun *et al.*, 2004) materials which belong to the Nasicon family. To our knowledge, the compositions  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 1$ ) have not been reported. Their synthesis and X-ray diffraction (XRD) analysis are described here. Crystal structure of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  ( $x=0.5$ ) phosphate is also reported.

## II. EXPERIMENTAL

$\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 1$ ) compounds were prepared from  $\text{Na}_2\text{CO}_3$  dissolved in diluted nitric acid solution

(I) and aqueous solutions of  $\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  (II),  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  (III), and  $(\text{NH}_4)_2\text{HPO}_4$  (IV). After the addition of (IV) in a (I+II+III) mixture at room temperature and slow evaporation at about 60 °C, the resulting powder was heated progressively, with intermitting regrinding, at different temperatures (200–800 °C) in air.

X-ray powder diffraction spectra were recorded at room temperature on a Siemens D 5000 diffractometer ( $\text{Cu } K_\alpha$  radiation  $\lambda=1.5406$  Å). The data were collected in the 10–100°  $2\theta$  range by steps of 0.02° ( $2\theta$ ), with a constant counting time of 20 s per step.

## III. RESULTS AND DISCUSSION

### A. Crystal structure of $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$

The structure of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  phosphate was refined with the Rietveld method using the FULLPROF program (Rodríguez-Carvajal, 2001). The atomic coordinates of  $\text{Na}_{4.5}\text{Yb}_{1.5}(\text{PO}_4)_3$  (Salmon *et al.*, 1979) were used as the starting structural parameters for Rietveld refinement. The experimental conditions and the results of the refinements, as well as different structural parameters, are given in Table I and II. Figure 1 shows good agreement between experimental and calculated X-ray spectra.

The structure of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  is based on a 3D

TABLE I. Results of the Rietveld refinement of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ .

$\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ $= [\square_{0.5}\text{Na}_{2.5}]_{\text{M2}}[\text{Na}]_{\text{M1}}[\text{Cr}_{1.5}\text{Co}_{0.5}]_{\text{A}}(\text{PO}_4)_3$
Space group, $R\bar{3}c$ ; $Z=6$ , $a_{\text{hex}}=8.7285(3)$ (Å); $c_{\text{hex}}=21.580(2)$ (Å); $V_{\text{hex}}=1423.8(1)$ (Å <sup>3</sup> )
Pseudo-Voigt function, $\text{PV}=\eta\text{L}+(1-\eta)\text{G}$ ; $\eta=0.596(3)$
Number of reflections; 339
Half-width parameters, $U=0.037(1)$ ; $V=0.023(1)$ ; and $W=0.012(2)$
Conventional Rietveld $R$ -factors, $R_F=5.2\%$ ; $R_B=7.0\%$ ; $R_p=9.3\%$ ; $R_{wp}=13.6\%$

TABLE II. Atomic coordinates and isotropic displacement parameters of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ .

Atom	Site	x	y	z	$B_{\text{iso}}$ ( $\text{\AA}^2$ )	Occ.	Valence sum (Exp.)	Valence sum (Th.)
Cr/Co	12c	0	0	0.147(1)	0.3(2)	1	2.77	2.75
Na(1)	6b	0	0	0	6.3(5)	1	0.90	1
Na(2)	18e	0.635(6)	0	0.250	2.4(1)	0.83	1.10	1
P	18e	0.291(1)	0	0.250	0.6(1)	1	514	5
O(1)	36f	0.181(1)	-0.032(1)	0.192(2)	1.1(1)	1	1.96	2
O(2)	36f	0.192(3)	0.167(8)	0.089(4)	1.9(1)	1	2.09	2

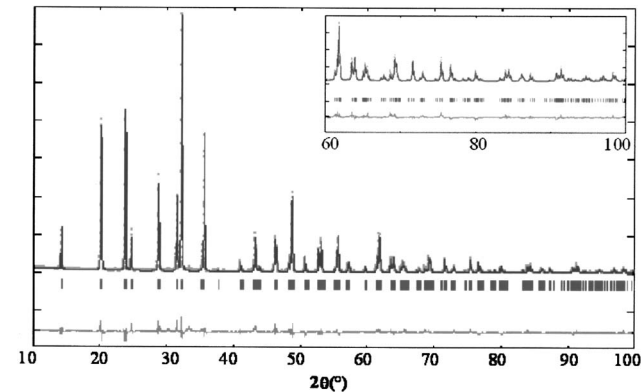


Figure 1. Experimental (···), calculated (—), and difference profile of the XRD pattern of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ .

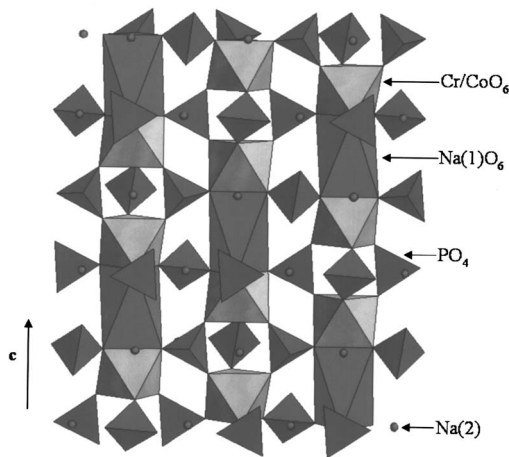


Figure 2. View of the  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  framework along  $c$  axis.

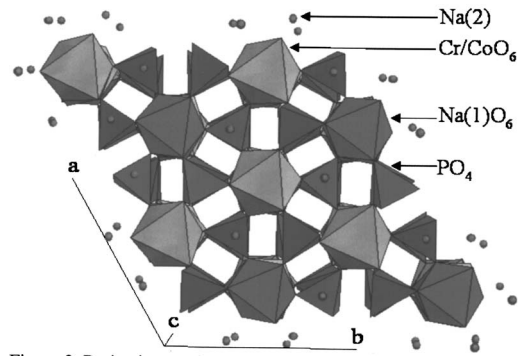


Figure 3. Projection of the  $ab$  plane of the  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  structure.

framework of  $\text{PO}_4$  tetrahedra and  $(\text{Cr}/\text{Co})\text{O}_6$  octahedra sharing corners (Figures 2 and 3).  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions occupy statistically the 12c sites.  $\text{Na}^+$  cations occupy totally the M(1) sites and partially the M(2) cavities with a statistical distribution. The cationic distribution is  $[\square_{0.5}\text{Na}_{2.5}]_{\text{M}2}[\text{Na}]_{\text{M}1}[\text{Cr}_{1.5}\text{Co}_{0.5}]_{\text{A}}(\text{PO}_4)_3$  ( $\square$ : vacancies sites).  $(\text{Cr}/\text{Co})$  atoms are slightly displaced from the center of the  $(\text{Cr}/\text{Co})\text{O}_6$  octahedron because of the smaller  $\text{Na}^+ - \text{Cr}^{3+}/\text{Co}^{2+}$  repulsions. The average  $(\text{Cr}/\text{Co}) - \text{O}$  distance (2.001  $\text{\AA}$ ) is slightly smaller than the value calculated from the ionic radii (2.050  $\text{\AA}$ ) (Shannon *et al.*, 1976). The  $\text{O} - (\text{Cr}/\text{Co}) - \text{O}$  angles vary between  $85.9^\circ$  and  $171.1^\circ$ . The  $(\text{Cr}/\text{Co}) - (\text{Cr}/\text{Co})$  distance along  $c$  axis (4.446  $\text{\AA}$ ) is inferior to the  $\text{Cr} - \text{Cr}$  distance in  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  (4.475  $\text{\AA}$ ) because of the cationic repulsions between ions in 12c sites. These repulsions are stronger in  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  (charge of  $\text{Cr}^{3+} = 3$ )

TABLE III. Bond distances and angles for  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$ .

Bond distances ( $\text{\AA}$ )		Angles ( $\text{\AA}$ )	
$(\text{Cr}/\text{Co}) - \text{O}(1) \times 3$	1.991(3)	$\text{O}(1) - (\text{Cr}/\text{Co}) - \text{O}(1)$	98.1(1)
$(\text{Cr}/\text{Co}) - \text{O}(2) \times 3$	2.011(1)	$\text{O}(1) - (\text{Cr}/\text{Co}) - \text{O}(2)$	86.9(1); 88.4(4); 17.1(1)
$\text{P} \times \text{O}(1) \times 2$	1.513(2)	$\text{O}(2) - (\text{Cr}/\text{Co}) - \text{O}(2)$	85.9(3)
$\text{P} - \text{O}(2) \times 2$	1.534(1)	$\text{O}(1) - \text{P} - \text{O}(1)$	114.3(3)
$\text{Na}(1) - \text{O}(2) \times 6$	2.497(3)	$\text{O}(1) - \text{P} - \text{O}(2)$	104.6(3); 11.7(3)
$\text{Na}(2) - \text{O}(1) \times 2$	2.575(4)	$\text{O}(2) - \text{P} - \text{O}(2)$	110.2(3)
$\text{Na}(2) - \text{O}(1) \times 2$	2.808(5)	$\text{O}(2) - \text{Na}(1) - \text{O}(2)$	66.6(2); 113.4(2); 180
$\text{Na}(2) - \text{O}(2) \times 2$	2.473(2)	$\text{O}(1) - \text{Na}(2) - \text{O}(1)$	82.5(4); 85.6(4) (1); 156.1(3)
$\text{Na}(2) - \text{O}(2) \times 2$	2.371(4)	$\text{O}(1) - \text{Na}(2) - \text{O}(2)$	54.7(2); 92.8(1); 150.4(3)
		$\text{O}(2) - \text{Na}(2) - \text{O}(2)$	61.2(2); 129.9(4); 160.3(1)

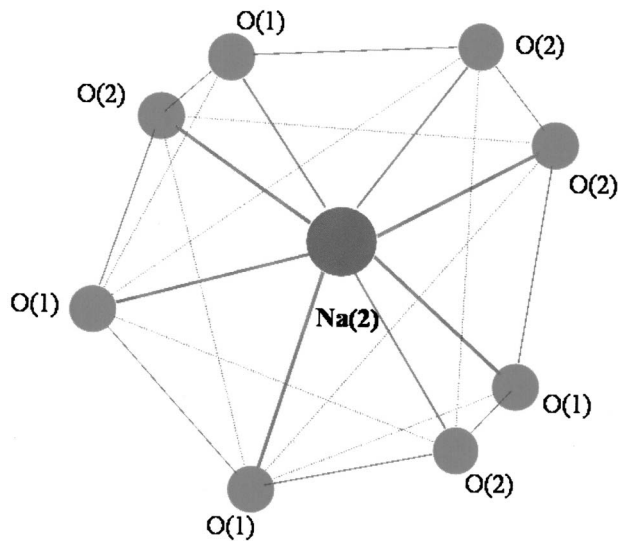


Figure 4. Illustration of Na(2)O<sub>8</sub> polyhedron in Na<sub>3.5</sub>Cr<sub>1.5</sub>Co<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub> phosphate.

than in Na<sub>3.5</sub>Cr<sub>1.5</sub>Co<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>. Therefore, we can explain why the  $c_h$  parameter of Na<sub>3+x</sub>Cr<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub> ( $0 < x$ ) are inferior to that of Na<sub>3</sub>Cr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>.

The P–O distances values (1.513 Å; 1.534 Å) are close to those typically found in Nasicon-type phosphates. O–P–O angles vary from 104.6° and 111.7°. The Na(1) atoms occupy the center of the M(1) site. Na(1)–O distance (Table III) (2.497 Å) is larger than that obtained from the ionic radii sum of Na<sup>+</sup> and O<sup>2-</sup> (2.42 Å) reflecting a higher degree of ionicity ( $B_{iso} \approx 6.3 \text{ Å}^2$ ). The Na(2) atoms, located in the M(2) site, are surrounded by eight oxygens (Figure 4), and the Na(2)–O distances [2.371 Å, 2.473 Å, 2.808 Å, 2.575 Å] are comparable to those generally found in Nasicon-type phosphates (Aatiq, 2004). Calculated valences ( $S_i = \sum \exp[(R_{ij} - d_{ij})/b]$  with  $b = 0.37 \text{ Å}$ ) based on bond strength analysis (Brese and O’Keeffe, 1991) are in good agreement with the expected formal oxidation states of P<sup>5+</sup>, Cr<sup>3+</sup>, Co<sup>2+</sup>, Na<sup>+</sup>, and O<sup>2-</sup> (Table II).

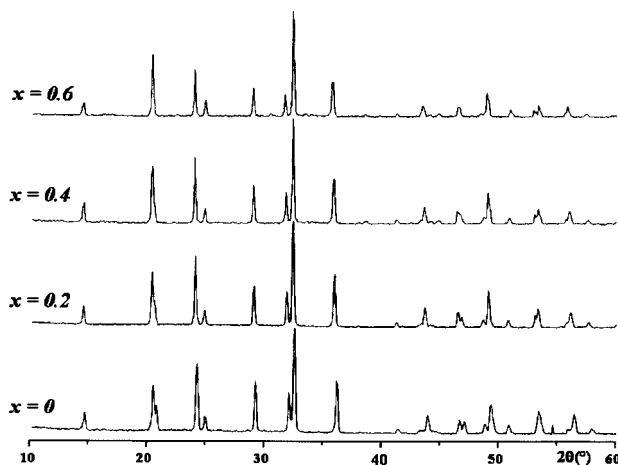


Figure 5. X-ray powder pattern of Na<sub>3+x</sub>Cr<sub>2-x</sub>Co<sub>x</sub>(PO<sub>4</sub>)<sub>3</sub> ( $0 \leq x \leq 0.6$ ).

TABLE IV. Powder diffraction data of Na<sub>3.5</sub>Cr<sub>1.5</sub>Co<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>.

$h$	$k$	$l$	$2\theta_{\text{obs}} (^{\circ})$	$d_{\text{obs.}} (\text{Å})$	$d_{\text{calc.}} (\text{Å})$	$100I/I_0$
0	1	2	14.29	6.194	1.191	16
1	0	4	20.20	4.393	4.391	51
1	1	0	20.32	4.366	4.364	19
1	1	3	23.82	3.733	3.731	57
0	0	6	24.72	3.598	3.597	14
0	2	4	28.80	3.097	3.096	36
2	1	1	31.54	2.834	2.832	32
1	1	6	32.21	2.777	2.776	100
2	1	4	35.51	2.526	2.525	4
3	0	0	35.58	2.521	2.520	27
2	0	8	41.05	2.197	2.196	4
1	1	9	42.97	2.103	2.102	2
2	1	7	43.10	2.097	2.096	3
2	2	3	43.28	2.089	2.088	15
1	3	1	43.30	2.088	2.087	4
1	2	8	46.23	1.962	1.961	15
1	3	4	46.41	1.955	1.954	8
3	1	5	48.19	1.887	1.886	4
0	2	10	48.51	1.875	1.874	6
2	2	6	48.73	1.867	1.866	34
0	4	2	48.87	1.862	1.861	4
0	0	12	50.70	1.799	1.798	6
1	3	7	52.75	1.734	1.734	11
3	2	1	52.91	1.729	1.729	2
2	1	10	53.11	1.723	1.722	15
3	1	8	55.44	1.656	1.655	5
3	2	4	55.59	1.652	1.651	5
4	1	0	55.56	1.650	1.650	7
2	3	5	57.17	1.610	1.609	3
1	4	3	57.21	1.609	1.608	2
0	4	8	59.68	1.548	1.548	3
3	2	7	61.26	1.512	1.511	2
0	1	14	61.30	1.511	1.510	2
1	3	10	61.62	1.504	1.504	9
4	1	6	61.80	1.500	1.499	9
3	0	12	63.49	1.464	1.464	5
0	5	4	63.88	1.456	1.456	3
3	3	0	63.93	1.455	1.455	6
3	1	11	65.03	1.433	1.432	3
2	0	14	65.29	1.428	1.427	5
4	0	10	65.60	1.422	1.422	3
2	4	4	67.75	1.382	1.381	2
1	1	15	68.60	1.367	1.366	4
1	2	14	69.17	1.357	1.357	5
4	2	5	69.17	1.357	1.356	3
5	1	1	69.23	1.356	1.355	5
3	2	10	69.47	1.352	1.352	3
5	1	4	71.59	1.317	1.317	8
1	5	5	72.94	1.296	1.295	3
6	0	0	75.37	1.260	1.260	5
5	1	7	76.59	1.243	1.243	4
3	1	14	76.66	1.242	1.242	3
0	0	18	79.95	1.199	1.199	3
1	2	17	83.13	1.161	1.160	2
2	3	14	83.84	1.153	1.152	4
5	2	6	84.29	1.148	1.147	4
3	4	8	86.04	1.129	1.129	3
1	5	11	87.20	1.117	1.116	3
4	3	10	91.32	1.077	1.077	6
0	1	20	92.20	1.069	1.068	2

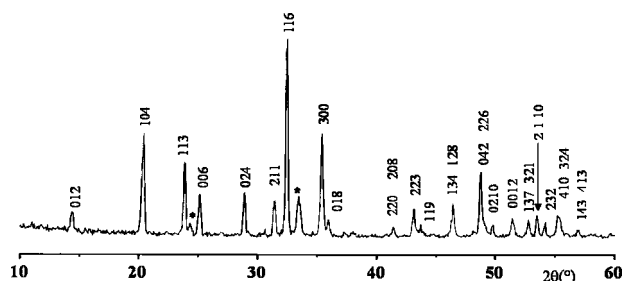


Figure 6. X-ray powder pattern of  $\text{Na}_4\text{CrCo}(\text{PO}_4)_3 [\cdot \text{Cr}_2\text{O}_3]$ .

## B. X-ray characterization of $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$ ( $0 \leq x \leq 1$ ) phosphates

Figure 5 shows XRD patterns of  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 0.6$ ). The samples with  $0 < x \leq 0.6$  compositions crystallize in rhombohedral structure ( $R\bar{3}c$  space group), while the  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  ( $x=0$ ) compound crystallizes in monoclinic structure (Delmas *et al.*, 1986). X-ray powder diffraction data of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  ( $x=0.5$ ) are given in Table IV. XRD patterns obtained for  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0.6 < x \leq 1$ ) indicate essentially the presence of  $\text{Na}_4\text{CrCo}(\text{PO}_4)_3$  and  $\text{Cr}_2\text{O}_3$  (Figure 6).

The hexagonal cell parameters variations of  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 0.6$ ) as a function of  $x$  are given in Figure 7. The progressive substitution of chromium atoms by sodium and cobalt provokes an increase of the  $a_h$  parameter and a decrease of the  $c_h$  parameter. This decrease can be explained by the electrostatic repulsions between  $[\text{Cr}/\text{Co}]^{n+}$  ( $n=3-x/2$ ) cations, smaller than the Cr–Cr one ( $n=3$ ). The  $a_h$ -parameter increase is related to the occupation of M(2) sites by Na atoms.

## IV. CONCLUSION

Polycrystalline sample of  $\text{Na}_{3.5}\text{Cr}_{1.5}\text{Co}_{0.5}(\text{PO}_4)_3$  phosphate has been prepared and characterized by XRD analysis. Its structure (Nasicon type) has been refined in  $R\bar{3}c$  space group. X-ray powder diffraction study shows the existence of  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  solid solution in the  $0 \leq x \leq 0.6$  range. The  $c_h$ -parameter variations results mainly from the electrostatic repulsions between ions occupy the A site. The  $a_h$ -parameter evolution is a result of the  $\text{Na}^+$  amount present in the M(2) sites.

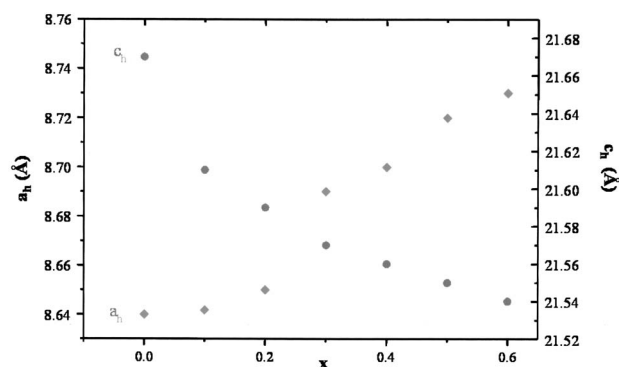


Figure 7. Cell parameters evolution versus composition of  $\text{Na}_{3+x}\text{Cr}_{2-x}\text{Co}_x(\text{PO}_4)_3$  ( $0 \leq x \leq 0.6$ ).

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