



Trade Science Inc.

ISSN : 0974 - 746X

Volume 6 Issue 1

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAJ, 6(1), 2011 [23-28]

Crystal structure of two phosphates belonging to the Sb_2O_5 - Cr_2O_3 - P_2O_5 system

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Received: 28th November, 2010 ; Accepted: 8th December, 2010

ABSTRACT

Structures of the two $\text{Sb}^{\text{V}}_{1.50}\text{Cr}^{\text{III}}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}^{\text{V}}_{0.50}\text{Cr}^{\text{III}}_{0.50})\text{P}_2\text{O}_7$ phases, obtained by solid state reaction in air atmosphere at 950°C, were determined at room temperature from X-ray powder diffraction using the Rietveld method. $\text{Sb}^{\text{V}}_{1.50}\text{Cr}^{\text{III}}_{0.50}(\text{PO}_4)_3$ belongs to the Nasicon-type structure ($R\bar{3}c$ space group, $Z = 6$, $a_{\text{hex.}} = 8.2770(1) \text{ \AA}$ and $c_{\text{hex.}} = 22.0605(2) \text{ \AA}$). Their structure is built up by corner-sharing $\text{Sb}(\text{Cr})\text{O}_6$ octahedra and PO_4 tetrahedra. XRD patterns of $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ is indexed on a cubic unit cell similar to that of ZrP_2O_7 ($\text{Pa}\bar{3}$ space group; $Z = 4$, $a = 7.818(2) \text{ \AA}$). Their structure is built up from corner-shared SbO_6 or CrO_6 octahedra and P_2O_7 groups. Within the structure, each P_2O_7 shares its six vertices with $\text{Sb}(\text{Cr})\text{O}_6$ octahedra and each $\text{Sb}(\text{Cr})\text{O}_6$ octahedra is connected to six P_2O_7 groups.

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KEYWORDS

X-ray powder diffraction;
Antimony and chromium
phosphate;
Nasicon;
Pyrophosphate;
Rietveld refinement.

INTRODUCTION

As part of a search for new materials likely to exhibit interesting physical properties, several $\text{M}^{\text{V}}_2\text{O}_5$ - $\text{M}'^{\text{III}}_2\text{O}_3$ - P_2O_5 systems ($\text{M} = \text{Ta, Nb, Sb; M}' = \text{Sb, Sc, In, Bi, Eu, Nd, Fe}$) have been partially or completely investigated and two principally $\text{M}^{\text{V}}_{1.5}\text{M}'^{\text{III}}_{0.50}(\text{PO}_4)_3$ and $(\text{M}^{\text{V}}_{0.50}\text{M}'^{\text{III}}_{0.50})\text{P}_2\text{O}_7$ families of compounds have been prepared^[1-9].

Depending on the nature of M and M' species, $\text{M}^{\text{V}}_{1.5}\text{M}'^{\text{III}}_{0.50}(\text{PO}_4)_3$ family of materials is shown to exhibit a variety of structure-types (e.g., Nasicon (N), $\text{Sc}_2(\text{WO}_4)_3$ (S) or $\text{Sb}^{\text{V}}_{1.50}\text{Bi}^{\text{III}}_{0.50}(\text{PO}_4)_3$ (B)) which are

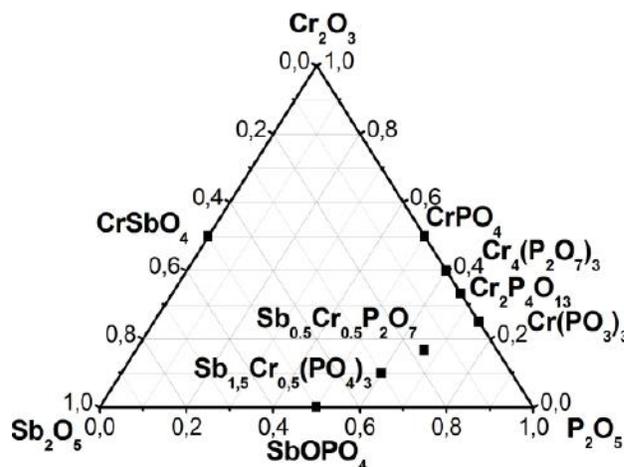


Figure 1 : Ternary diagram of Sb_2O_5 - Cr_2O_3 - P_2O_5

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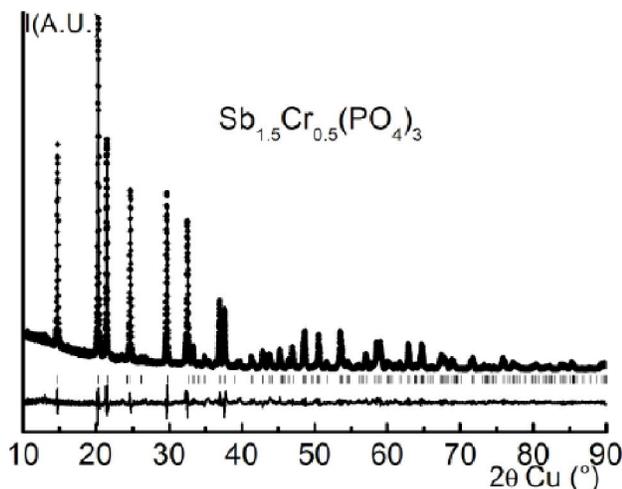


Figure 2 : Experimental (●●) calculated (—) and difference profile of the XRD pattern of $Sb_{1.5}Cr_{0.5}(PO_4)_3$

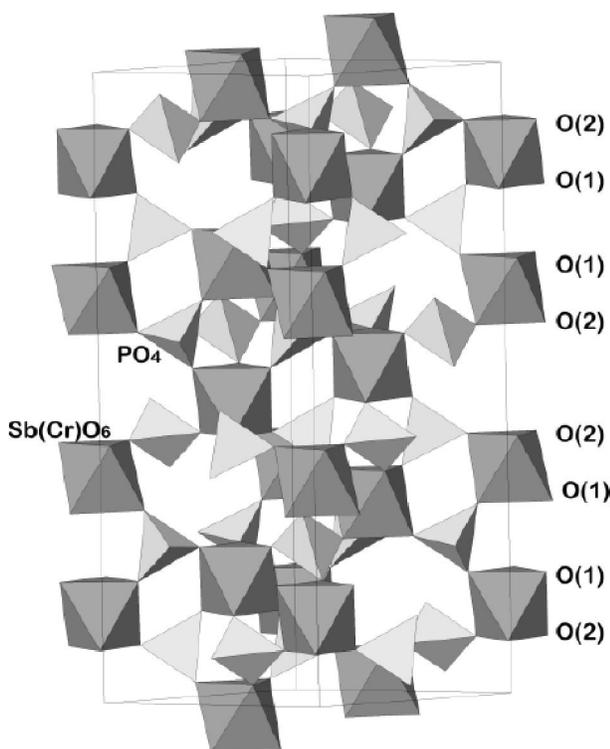


Figure 3 : View of the structure of $Sb_{1.5}Cr^{III}_{0.5}(PO_4)_3$

not simple distortions of each other. In the case of $Sb_{1.5}^{V}Sb_{0.5}^{III}(PO_4)_3$, two α - and β -forms for mixed-valence antimony are reported^[3-6]. The α -form is monoclinic ($P2_1/n$ space group) with an S-type structure whereas the β -form is trigonal ($R\bar{3}$ space group) and isotopic to the known B-type structure^[1]. XRD patterns of $M^{IV}X^V_2O_7$ compounds ($M=Si, Ge, Sn, Pb, Ti, Zr, Hf, Mo, W, Re, Ce, Th, U; X=P, V, As$) can be indexed, at least approximately, on a cubic

TABLE 1 : Results of the rietveld refinement of $Sb_{1.5}Cr_{0.5}(PO_4)_3$

$Sb_{1.5}Cr_{0.5}(PO_4)_3$					
$R\bar{3}c$ Space Group ($Z = 6, a = 8.277(2) \text{ \AA}; c = 22.06(1) \text{ \AA}; V = 1309(1) \text{ \AA}^3$)					
Conventional Rietveld R-factors: $R_{WP} = 12.5\%; R_P = 8.8\%; R_B = 6.0\%; R_F = 5.7\%$					
Pseudo-Voigt Function: $PV = \eta L + (1-\eta)G$ ($\eta = 0.386(2)$)					
Half-Width Parameters: $U = 0.069(9), V = -0.019(7),$ and $W = 0.009(3)$					
atom	site	x	y	z	$B_{iso}(\text{\AA}^2)$
Sb(Cr)	12c	0	0	0.1440(2)	0.51(2)
P	18e	0.2901(4)	0	0.25	1.15(2)
O(1)	36f	0.1651(7)	0.9551(6)	0.1950(5)	1.42(2)
O(2)	36f	0.1900(8)	0.1570(6)	0.088(1)	1.42(2)

ZrP_2O_7 -structure type ($Z = 4, a \sim 8 \text{ \AA}, Pa\bar{3}$ space group). Preparation and thermal expansion of some $(M^{V}_{0.50}M^{III}_{0.50})P_2O_7$ ($MM' = TaBi, NbBi, TaSb, TaNd, TaAl, TaFe, TaGa, NbIn$ and NbY) pyrophosphate compounds produced by replacing M^{IV} , in $M^{IV}P_2O_7$, with mixed M^V/M^{III} cations were also reported^[4-7]. Their room-temperature XRD patterns were indexed on a cubic unit cell similar to that of ZrP_2O_7 but, up to now, no detailed structural determination for some of them was realized. More recently, our investigations on the $Sb_{1.5}^{V}M^{III}_{0.50}P_2O_7$ ($M = Fe, In$) systems were especially led to synthesis and structural determination of $Sb_{1.5}^{V}M^{III}_{0.50}(PO_4)_3$ and $(Sb_{0.50}^{V}M^{III}_{0.50})P_2O_7$ phases^[8,9]. $Sb_{1.5}^{V}Fe^{III}_{0.50}(PO_4)_3$ belongs to the N-type phase ($R32$ space group) whereas $Sb_{1.5}^{V}In^{III}_{0.50}(PO_4)_3$ is monoclinic ($P2_1/n$ space group) with an S-type structure. Both $(M^{V}_{0.50}M^{III}_{0.50})P_2O_7$ ($M' = Fe, In$) pyrophosphates phases are shown to be isotopic to the orthorhombic β - $Sb_{0.50}^{V}Sb_{0.50}^{III}P_2O_7$ -structure type^[2].

During the last years our interests were particularly focused on characterization of newly N-type phases (e.g.; $A_{0.50}Sb^VFe^{III}(PO_4)_3, A = Mn, Ca, Cd$)^[10,11]. In a continuation of our search the first objective of the present study is the synthesis and structural determination, using the Rietveld refinement of the XRD patterns of $Sb_{1.5}^{V}Cr^{III}_{0.50}(PO_4)_3$ and $(Sb_{0.50}^{V}Cr^{III}_{0.50})P_2O_7$.

EXPERIMENTAL

Syntheses of $Sb_{1.5}^{V}Cr^{III}_{0.50}(PO_4)_3$ and $(Sb_{0.50}^{V}Cr^{III}_{0.50})P_2O_7$ phosphates were carried out us-

TABLE 2 : Powder diffraction data of $\text{Sb}^{\text{V}}_{1.50}\text{Cr}^{\text{III}}_{0.50}(\text{PO}_4)_3$ ($\text{CuK}\alpha_1$; $\lambda = 1.54056 \text{ \AA}$)

$\text{Sb}^{\text{V}}_{1.50}\text{Cr}^{\text{III}}_{0.50}(\text{PO}_4)_3$			
hkl	$d_{\text{obs.}} (\text{\AA})$	100 I/I ₀ (obs)	100 I/I ₀ (cal)
012	6.0104	59	57
104	4.3711	100	100
110	4.1385	100	100
113	3.6065	50	50
024	3.0052	51	50
116	2.7486	41	40
211	3.6890	5	5
018	2.5737	3	3
214	2.4317	19	16
300	2.3894	17	17
208	2.1855	3	2
119	2.1090	5	5
220	2.0692	4	3
036	2.0035	5	3
312	1.9565	2	2
128	1.9326	5	5
0 2 10	1.8787	6	6
134	1.8703	9	9
226	1.8033	9	9
042	1.7688	1	1
2 1 10	1.7107	10	10
404	1.7043	1	1
137	1.6814	1	1
318	1.6126	3	2
324	1.5759	7	6
410	1.5642	7	7
0 1 14	1.5390	1	1
1 3 10	1.4768	6	5
2 0 14	1.4425	4	4
146	1.4393	6	6
4 0 10	1.3909	2	2
054	1.3875	3	3
330	1.3795	2	2
1 2 14	1.3621	3	3
3 2 10	1.3184	2	2
244	1.3155	3	2
514	1.2537	3	2
3 1 14	1.2349	2	2
600	1.1947	1	1
2 3 14	1.1377	2	2
526	1.0927	1	1

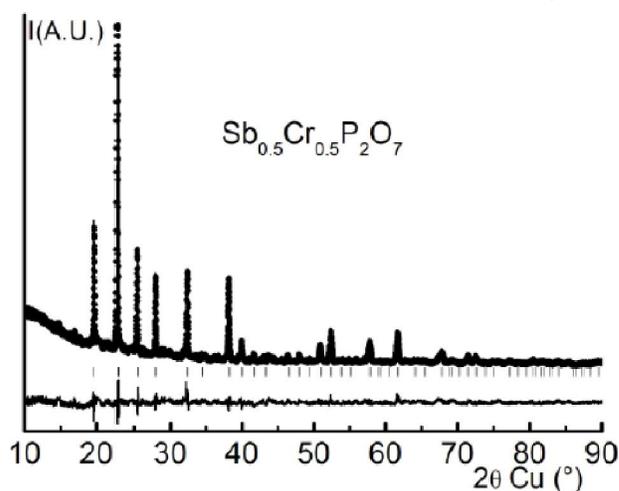


Figure 4 : Experimental (●●●) calculated (—) and difference profile of the XRD pattern of $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$

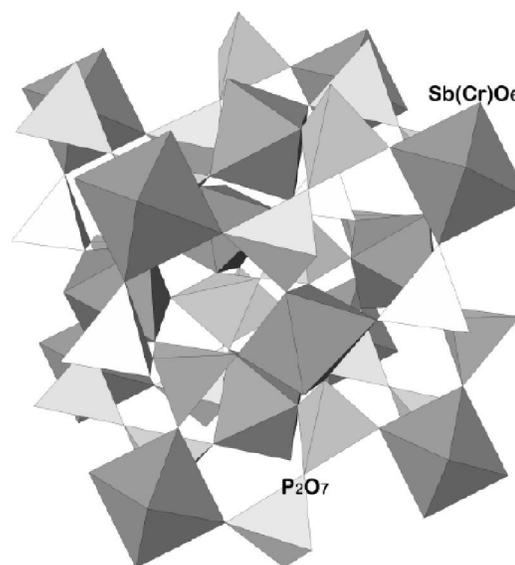


Figure 5 : View of the structure of the cubic $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ phase

ing conventional solid-state reaction techniques. Polycrystalline samples were prepared from mixtures of Cr_2O_3 (Prolabo, 99 %), Sb_2O_3 (Riedel-de Haën, 99.9 %), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Riedel-de Haën, 99 %) in stoichiometric proportions. The corresponding mixtures were heated progressively with intermittent grindings in air, between 200 and 950°C. The products of reaction were characterised by X-ray diffraction (XRD) at room temperature with a PANalytical X'Pert-PRO (θ -2 θ) diffractometer; using a diffracted-beam graphite and ($\text{CuK}\alpha$) radiation (45 kV, 40 mA). Experimental conditions included a divergence slit of 1° and antiscatter slit of 1°. XRD data were collected from 10 to 100°

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2θ , in steps of 0.0084° , with a counting time of 30 s per step. The Rietveld refinement of the structure was performed using the Fullprof program^[12].

RESULTS AND DISCUSSION

Preliminarily experimental investigation in the $Sb_2O_5-Cr_2O_3-P_2O_5$ ternary diagram foresees the possibility of two new $Sb^{V}_{1.50}Cr^{III}_{0.50}(PO_4)_3$ and $(Sb^{V}_{0.50}Cr^{III}_{0.50})P_2O_7$ phosphates within the pseudo-binary $SbOPO_4-Cr(PO_3)_3$ (Figure 1). Careful analysis of $Sb_{1.50}Cr_{0.50}(PO_4)_3$ XRD data (Figure 2) confirms the similarity of its structure to that of $MnTiCr(PO_4)_3$ Nasicon-type structure ($R\bar{3}c$ space group)^[13]. The general crystallographic formula for Nasicon phosphates can be written as $[M2]_3[M1]X_2(PO_4)_3$. Therefore, the two sites usually labelled M1 and M2 in Nasicon phases are normally empty in $Sb_{1.50}Cr_{0.50}(PO_4)_3$. Hexagonal cell parameters of $Sb_{1.50}Cr_{0.50}(PO_4)_3$ Nasicon-phase are $a_{hex.} = 8.2770(1) \text{ \AA}$ and $c_{hex.} = 22.0605(2) \text{ \AA}$. XRD spectrum of $(Sb^{V}_{0.50}Cr^{III}_{0.50})P_2O_7$ is completely indexed on the basis of an ideal cubic ZrP_2O_7 -type structure. Obtained value of cubic cell parameter is $a = 7.818(2) \text{ \AA}$. The following structural refinements were based upon the above mentioned assumptions.

Structure of $Sb^{V}_{1.50}Cr^{III}_{0.50}(PO_4)_3$

Initial starting parameters for the Rietveld refinement of $Sb^{V}_{1.50}Cr^{III}_{0.50}(PO_4)_3$ were based on those already reported for the $R\bar{3}c$ structure of $MnTiCr(PO_4)_3$ ^[12]. We have assumed that Sb and Cr atoms were randomly distributed within the Nasicon framework (i.e. $Sb(Cr)$ in the $Ti(Cr)$ (12c site)). P and O atoms were localised in the 18e and 36f positions respectively. This refinement leads to acceptable reliability factors (i.e., $R_B = 6.0\%$) (TABLE 1). A comparison of the experimental and calculated XRD profile of $Sb^{V}_{1.50}Cr^{III}_{0.50}(PO_4)_3$ is shown in figure 2. Rietveld refinement parameters and final atomic parameters are given in TABLE 1.

A view of its crystal structure along c-axis is shown in figure 3. Structure is built up by a corner-sharing of $Sb(Cr)O_6$ octahedra and PO_4 tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedra. $Sb(Cr)-O$ distances values ($Sb(Cr)-O(1) = 1.944(3)$;

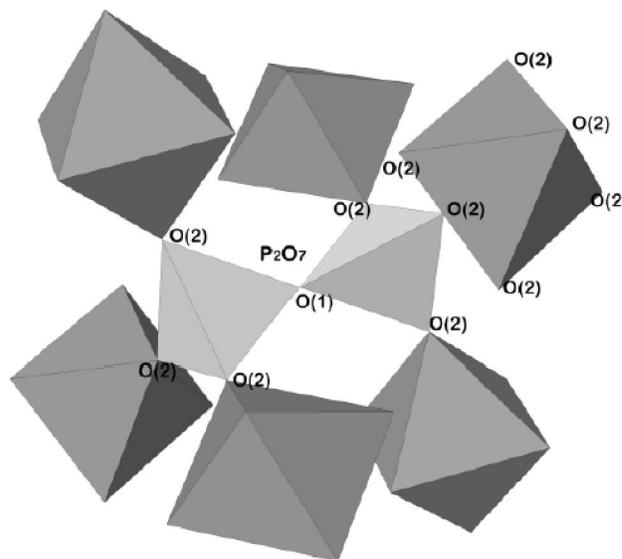


Figure 6 : Connectivity between $Sb(Cr)O_6$ octahedra and P_2O_7 group in $(Sb_{0.50}Cr_{0.50})P_2O_7$

$Sb(Cr)-O(2) = 1.909(3) \text{ \AA}$) are in agreement with the ionic radii values of Sb^{+5} and Cr^{3+} ions in six coordination^[14]. P-O distances values ($1.507(3) \text{ \AA}$; $1.515(3) \text{ \AA}$) are comparable to those generally found in Nasicon-like phosphate. X-ray powder data of $Sb_{1.5}Cr_{0.50}(PO_4)_3$ derived from the Rietveld refinement ($CuK\alpha 1 : 1.54056 \text{ \AA}$) are presented in TABLE 2.

Structure of $(Sb_{0.50}Cr_{0.50})P_2O_7$

The structural parameters of the cubic $(Ta_{0.50}Bi_{0.50})P_2O_7$ pyrophosphate^[4] were used as starting parameters for the Rietveld refinement of $(Sb_{0.50}Cr_{0.50})P_2O_7$. During the Rietveld refinement, Sb and Cr atoms in $(Sb_{0.50}Cr_{0.50})P_2O_7$ are supposed to reside in the $Ta(Bi)$ (000) 4a position. P, O(1) and O(2) atoms are located in the 8c, (1/21/21/2) 4b and 24d positions respectively. This refinement leads to acceptable reliability factors (i.e., $R_B = 7.2\%$) (TABLE 3). Observed, calculated, and difference XRD patterns of $(Sb_{0.50}Cr_{0.50})P_2O_7$ are given in figure 4. Final atomic coordinate and results of the Rietveld refinement are reported in TABLE 3. View of the structure of the cubic $(Sb_{0.50}Cr_{0.50})P_2O_7$ phase showing the linkage between $Sb(Cr)O_6$ octahedra and P_2O_7 groups are shown in figure 5. As shown in figure 6, the structure is built up from corner-shared $Sb(Cr)O_6$ octahedra and P_2O_7 groups. The P-O distance values ($P-O(1) = P-O(2) = 1.503(3) \text{ \AA}$) show that PO_4 tetrahedra are regular. There is one

TABLE 3 : Results of the rietveld refinement of $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$

$(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$					
Pa $\bar{3}$ Space Group (Z = 4, a = 7.818(2) Å; V = 478(1) Å ³)					
Conventional Rietveld R-factors:					
R _{WP} = 11.8%; R _P = 8.8%; R _B = 7.2%; R _F = 6.0%					
Pseudo-Voigt Function:					
PV = ηL + (1-η)G (η = 0.241(1))					
Half-Width Parameters:					
U = 0.538(2), V = -0.096(5), and W = 0.018(3)					
atom	site	x	y	z	B _{iso} (Å ²)
Sb(Cr)	4a	0	0	0	1.3(1)
P	8c	0.3890(3)	0.3890(3)	0.3890(3)	1.9(1)
O(1)	4b	0.50	0.50	0.50	2.3(1)
O(2)	24d	0.2010(4)	0.4071(6)	0.4250(5)	2.3(1)

TABLE 4 : Powder diffraction data of $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ (CuKα₁; λ = 1.54056 Å)

$(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$			
hkl	d _{obs.} (Å)	100 I/I ₀ (obs)	100 I/I ₀ (cal)
111	4.5137	36	36
200	3.9090	100	100
210	3.4963	29	28
211	3.1917	25	25
220	2.7640	26	24
311	2.3572	24	24
222	2.2568	6	6
230	2.1683	2	2
400	1.9545	1	1
410	1.8961	1	1
331	1.7935	4	4
240	1.4781	7	6
422	1.5958	5	5
511	1.5045	9	8
440	1.3820	3	2
351	1.3214	2	2
442	1.3029	2	2
260	1.2361	1	1
533	1.1922	1	1

P_2O_7 group-type. The two PO_4 tetrahedra within a P_2O_7 group are connected via the O(1) oxygen (Figure 6). Every P_2O_7 group is connected to six Sb(Cr)O₆ octahedra. Note that Sb(Cr) atoms are coordinated by six O(2) atoms (Figure 6). The Sb(Cr)-O(2) distance within a Sb(Cr)O₆ octahedra has a value of 1.828(3) Å. X-ray powder data of $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ derived from the Rietveld refinement (CuKα₁ : 1.54056 Å) are presented in TABLE 4.

CONCLUSION

Structures of the two new $\text{Sb}_{1.50}\text{Cr}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ phosphates using Rietveld technique on the polycrystalline compounds, have been carried out. $\text{Sb}_{1.50}\text{Cr}_{0.50}(\text{PO}_4)_3$ crystallizes in the rhombohedral (R $\bar{3}c$ space group) Nasicon structure whereas $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ is shown to be isotypic with the cubic pyrophosphate ZrP_2O_7 (Pa $\bar{3}$ space group). A statistical cationic distribution of Sb⁵⁺ and Cr³⁺, within both $\text{Sb}_{1.50}\text{Cr}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ frameworks, has obtained. It is of interest to note that in the case of an ordered cationic distribution, the expected space group should be R $\bar{3}$ or R32 for Nasicon phase and Pna2₁ for the pyrophosphate compound. Generally, ordering of two cations, within a framework, is dependent on the size difference and/or charge imbalance between them. In our recently reported study, on the $\text{Sb}^{\text{V}}_2\text{O}_5\text{-Fe}^{\text{III}}_2\text{O}_3\text{-P}_2\text{O}_5$ system, we have shown the presence of a high tendency of an ordered cationic distribution between Sb⁵⁺ and Fe³⁺ cations within the two $\text{Sb}_{1.50}\text{Fe}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}_{0.50}\text{Fe}_{0.50})\text{P}_2\text{O}_7$ frameworks. The cation ordering, within the octahedral framework of both $\text{Sb}_{1.50}\text{Fe}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}_{0.50}\text{Fe}_{0.50})\text{P}_2\text{O}_7$ compounds, was shown to be dependant of the difference between oxidation states of Sb⁵⁺ and Fe³⁺ cations. In fact, since the ionic radii values of Sb⁵⁺ and Cr³⁺ cations are relatively comparable, the force driving behind the absence of a cation ordering, within the octahedral framework of both $\text{Sb}_{1.50}\text{Cr}_{0.50}(\text{PO}_4)_3$ and $(\text{Sb}_{0.50}\text{Cr}_{0.50})\text{P}_2\text{O}_7$ compounds, is not completely understood.

ACKNOWLEDGEMENTS

The authors acknowledge Prof. H. Hannache and Dr. Y. Abboud (Centre d'analyse et de recherche du compus Ben M'Sik (CARB) for technical assistance.

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