

# Synthesis And Characterization Of Two New Antimony Phosphates $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$ And $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$

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**Abstract:** Two new antimony phosphates  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  and  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  were synthesized for the first time by the solid-state reaction method. Their crystal structures have been refined at room temperature from X-ray powder diffraction data using Rietveld method.  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  crystallizes in the space group  $R\bar{3}c$  (N°167) ( $a_h = 8.23 \pm 0.01 \text{ \AA}$ ,  $c_h = 21.94 \pm 0.02 \text{ \AA}$ ).  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  crystallizes in the monoclinic space group  $P_{21/n}$  (N°14) ( $a_m = 11.54 \text{ \AA}$ ,  $b_m = 8.83 \pm 0.02 \text{ \AA}$ ,  $c_m = 8.39 \pm 0.01 \text{ \AA}$ ,  $\beta = 96.67^\circ \pm 0.09$ ). Raman and infrared spectra were recorded and assignments of the stretching and bending vibrations of the  $\text{PO}_4^{3-}$  tetrahedra were made. The number of the peaks observed is in good agreement with that predicted by the factor group analysis of the  $R\bar{3}c$  et  $P_{21/n}$  space group respectively. Vibrational spectral studies of two antimony phosphates were collected in-situ at room-pressure and at elevated temperatures, up to  $430^\circ\text{C}$ . At elevated temperatures in air,  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  seems to be stable, but  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  show a transition at  $380^\circ\text{C}$  and decomposes at  $930^\circ\text{C}$ . This result has been confirmed by differential scanning calorimetric study (DSC).

## I. Introduction

Most of the members of Nasicon type compounds of general formula  $\text{MA}_2(\text{PO}_4)_3$  known in literature are described in rhombohedral  $R\bar{3}c$ ,  $R\bar{3}$  or  $R32$  space groups with typical unit cell dimensions  $a \sim 8 \text{ \AA}$  and  $c \sim 22 \text{ \AA}$ , but cell distortions leading to a monoclinic symmetry  $C_{2/c}$ ,  $P_{21/n}$ ...etc, have been reported, for example the  $\text{Mn}_{0.5}\text{CrSb}(\text{PO}_4)_3$  [1].

The skeleton  $\text{A}_2(\text{PO}_4)_3$  [2] is build up by two chemical groups: the octahedral  $\text{AO}_6$  units and the tetrahedral  $\text{PO}_4$  units that share corners only through strong bonds like Ti-O-P. The  $\text{A}_2(\text{PO}_4)_3$  groups repeat along the threefold axis and the so-formed columns connect together in a hexagonal array. The distortion is due to rotation of  $\text{PO}_4$  to each other leading to loss of the threefold axis. Generally, The  $\text{PO}_4$  polyhedra rotate strictly around the two fold axis in the high temperature phase [3, 4]. To contribute to a better investigation and characterization of this type of compound, we have undertaken the synthesis and characterized by X-ray powder diffraction and vibrational spectroscopy of antimony-transition metal Nasicon phosphate  $\text{M}_{0.5}\text{M}'\text{Sb}(\text{PO}_4)_3$  ( $\text{M} = \text{Co}, \text{Mg}$  and  $\text{M}' = \text{Al}, \text{Fe}$ ) in the system  $\text{MO}-\text{M}'_2\text{O}_3-\text{Sb}_2\text{O}_3-\text{P}_2\text{O}_5$  for their great importance in technological applications such as solid electrolyte, electrode material [5], luminescence [6].

## II. Preparation

Powder samples of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  et  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  were prepared by solid-state reaction, by mixing  $\text{M}(\text{NO}_3)_2$  ( $\text{M} = \text{Mg}$  or  $\text{Co}$ ),  $\text{Sb}_2\text{O}_3$ ,

$(\text{NH}_4)_2\text{HPO}_4$  and oxide  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and heating the reaction mixtures in air up to  $600^\circ\text{C}$  (24 h). The resulting powder was progressively heated in air at  $250^\circ\text{C}$  (24 h),  $600^\circ\text{C}$  (24 h),  $800^\circ\text{C}$  (24 h) and  $900^\circ\text{C}$  (24 h) with intermitting regrinding.

## III. Characterization Of Phosphates

### III-1. X-ray diffraction study

The X-ray diffraction analysis of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  (Fig. 1) show that this material is isostructural with  $\text{Mn}_{0.5}\text{AlSb}(\text{PO}_4)_3$  [1], which crystallize in the rhombohedral system, space group:  $R\bar{3}c$ . The lattice parameters  $a_h = 8.23 \pm 0.01 \text{ \AA}$ ,  $c_h = 21.94 \pm 0.02 \text{ \AA}$  are close to that of  $\text{Mn}_{0.5}\text{AlSb}(\text{PO}_4)_3$  [1].

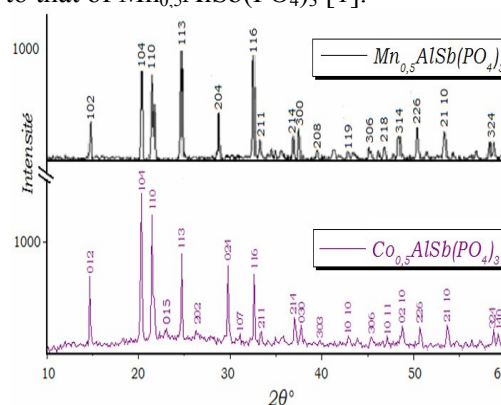
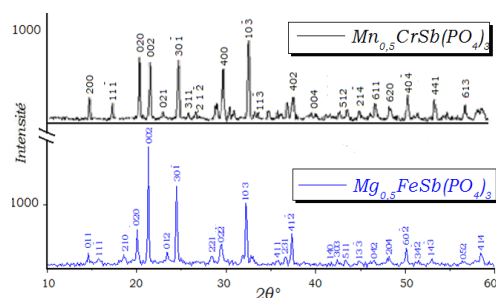


Figure 1: Indexation de  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$ .

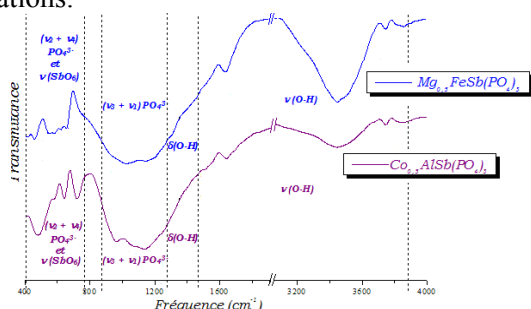
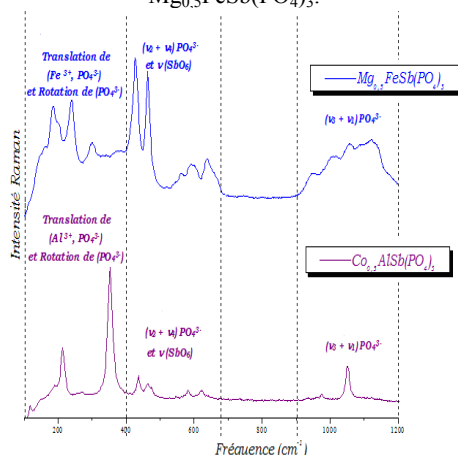
The observed lines of  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  were indexed by isotypy to  $\text{Mn}_{0.5}\text{CrSb}(\text{PO}_4)_3$  [1] (Fig.2), The diffraction lines were indexed in the monoclinic system ( $P_{21/n}$  space group), with lattice parameters  $a_m = 11.54 \pm 0.02 \text{ \AA}$ ,  $b_m = 8.83 \pm 0.01 \text{ \AA}$ ,  $c_m = 8.39 \pm 0.01 \text{ \AA}$ ,  $\beta = 96.67 \pm 0.09^\circ$ .

Figure 2 : Indexation de  $\text{Mg}_{0.5}\text{AlSb}(\text{PO}_4)_3$ 

### III-2. Infrared and Raman spectroscopy

Figures 3 and 4 show representative infrared and Raman spectra of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  and  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ . The broad bands observed in the Raman spectra of the two compounds were successfully deconvoluted with a Gaussian function.

With the crystallographic information, initial fitting is carried out with the number of bands indicated by the topology of the Raman spectra (maxima and inflections). The high frequency part 900–1200  $\text{cm}^{-1}$  of these spectra corresponds to the stretching vibrations of the  $\text{PO}_4$  tetrahedra. The peaks observed between 700 and 400  $\text{cm}^{-1}$  are assigned to the P–O bending vibrations.

Figure 3: Infrared spectra of phosphates  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  et  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ .Figure 4: Raman Spectra of phosphates  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  et  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ .

Tables 1 and 2 give the correlation scheme for the stretching modes of the  $\text{PO}_4$  groups through their site symmetry in the R-3 and  $\text{P2}_1/\text{c}$  crystalline cells and the number of predicted frequencies.

The peaks situated below 400  $\text{cm}^{-1}$  are attributed to the external modes and consist of the translation modes of the  $\{\text{Al}^{3+}, \text{Fe}^{3+}, (\text{PO}_4)^{3-}\}$  [1]. The bands observed in the 640–622  $\text{cm}^{-1}$  region in the Raman and Infrared spectra can be attributed to the Sb–O vibrations in the  $\text{SbO}_6$  octahedra with Oh symmetry [7, 8].

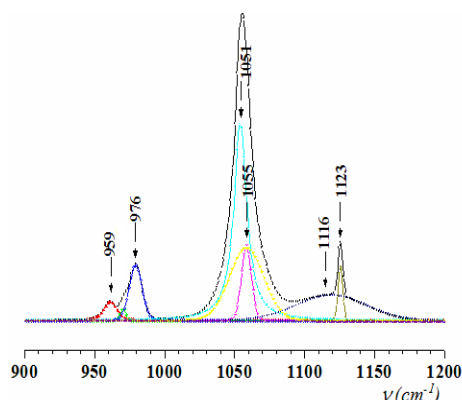
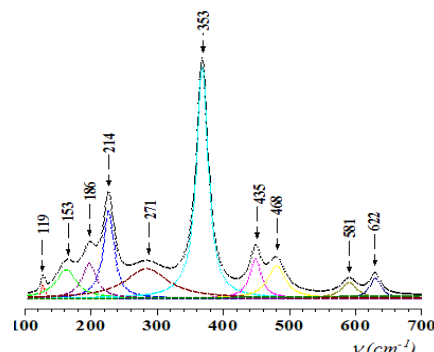
Figure 5 : Deconvolution results of the Raman spectrum of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  (range 900–1200  $\text{cm}^{-1}$ )Figure 6: Deconvolution results of the Raman spectrum of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  (range 100–700  $\text{cm}^{-1}$ )

Tableau 1: The stretching and bending vibrations of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  and empirical assignments in R-3c space group.

| Modes                                       | Raman Diffusion            |                            |
|---|----------------------------|----------------------------|
|   | stretching vibrations      | bending vibrations         |
| Empirical assignments                       | 6<br>( $2\nu_1 + 4\nu_3$ ) | 8<br>( $4\nu_2 + 4\nu_4$ ) |
| $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$ | 6                          | 3                          |

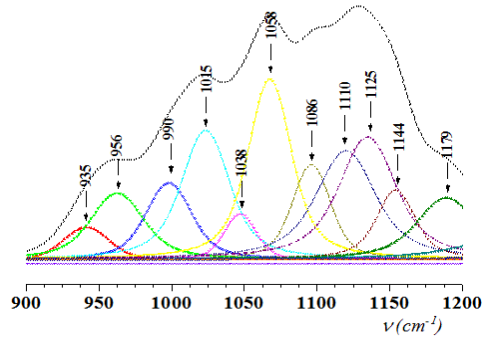


Figure 7: Deconvolution results of the Raman spectrum of  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  (range 900-1200  $\text{cm}^{-1}$ )

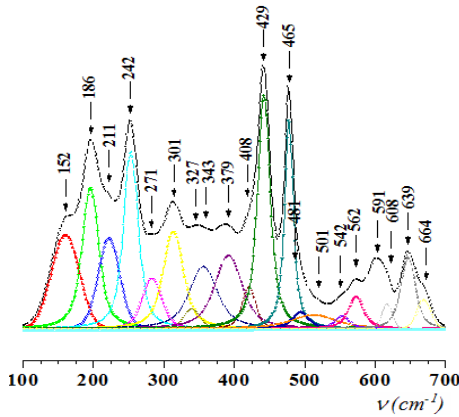


Figure 8: Deconvolution results of the Raman spectrum of  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  (range 100-700  $\text{cm}^{-1}$ )

Tableau 2: The stretching and bending vibrations of  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  and empirical assignments in  $\text{P2}_1/\text{n}$  space group

| Modes                                       | Raman Diffusion           |                           |
|---|---------------------------|---------------------------|
|   | stretching vibrations     | Bending vibrations        |
| Empirical assignments                       | 18<br>( $9\nu_1+9\nu_3$ ) | 18<br>( $9\nu_2+9\nu_4$ ) |
| $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ | 11                        | 10                        |

In order to facilitate the discussion we divided the spectra into two regions. Figs. 5 to 8 presents the bands appearing in the high-wavenumber region. From the deconvolution of the Raman spectra (Figs 5 to 8) we deduced that the spectrum of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  is unique and in good agreement with results of the factor group analysis of R-3c (Figure 4). Deng et al. [9] have proposed and tested for phosphate compounds the equation for the correlation between the Raman stretching vibration of P–O bond and bond length. We have applied this relation to  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  et  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  (Tableau 3). The results reported in Table 3 show that the values of P–O distances estimated from Raman data are in good agreement

with those obtained from X-ray diffraction and with those reported earlier in Nasicon compound [10, 11, 12, 13].

Tableau 3: Comparison of P–O bond lengths  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  et  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  obtained from X-ray diffraction and Raman

| compound                                    | vibration                  | dP-O<br>(Å) |
|---|----------------------------|-------------|
|   | $\nu$ ( $\text{cm}^{-1}$ ) | Raman       |
| $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$ | $\nu_1$<br>( $A_1$ )=1123  | 1.50        |
|   | $\nu_1$<br>( $A_1$ )=1116  | 1.50        |
|   | $\nu_1$<br>( $A_1$ )=1053  | 1.52        |
|   | $\nu_3(T_1)$ =967          | 1.54        |
| $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ | $\nu_1$<br>( $A_1$ )=1149  | 1.50        |
|   | $\nu_1$<br>( $A_1$ )=1098  | 1.51        |
|   | $\nu_1$<br>( $A_1$ )=1037  | 1.52        |
|   | $\nu_3(T_1)$ =960          | 1.55        |

In this section we discuss the effect of high temperature on the Raman spectra of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  and  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$ . Figs. 9 and 10 present the temperature evolution of the Raman spectra up to 450 °C. The Raman spectra in this region show little changes, being observed only slight variations in the intensity of the bands. In fact, increasing temperature the two main effects on the  $\text{PO}_4$  and  $\text{SbO}_6$  stretching region are: a band at 1100  $\text{cm}^{-1}$ . This can be an indication that some change in the structure is taking place at that temperature, although other phenomena can explain changes in bands associated to internal mode vibrations. The broadening of the frequency Raman mode at different temperatures will be particularly analyzed.

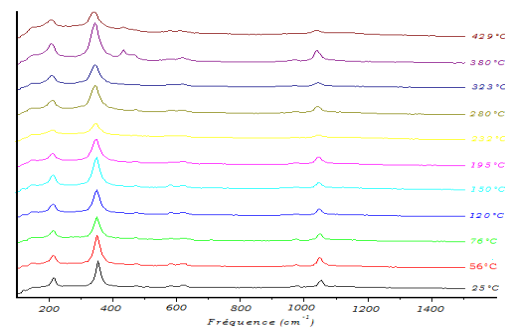


Figure 9 : Raman spectra of  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  at different temperature (25-429°C)

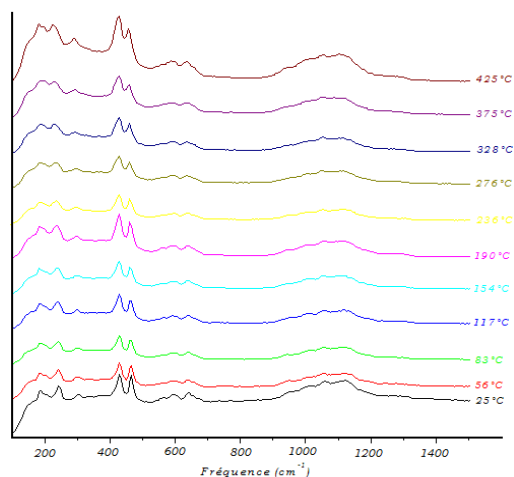


Figure 10 : Raman spectra of  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  at different temperature (25-425°C)

#### IV. Conclusion

A new phosphates  $\text{Co}_{0.5}\text{AlSb}(\text{PO}_4)_3$  and  $\text{Mg}_{0.5}\text{FeSb}(\text{PO}_4)_3$  have been obtained, respectively, by solid-state reaction method. The X-ray powder diffraction showed that two compound have Nasicon structure with R-3c et  $\text{P}_{21/n}$  space group respectively. The infrared and Raman vibrational study shows a good agreement between the factor group analysis results and the vibrational spectra assignment. Besides, the spectra confirm the existence of the vibration Sb-O in  $\text{SbO}_6$  octahedra .

#### V. References

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