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# Synthesis and electrical properties of lacunar lead apatites $Pb_8Na_{2-x}Li_x(VO_4)_6$

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## ABSTRACT

In order to obtain information about the electrical properties of $Pb_8Na_{2-x}Li_x(VO_4)_6$ $(0 \le x \le 2)$ apatites crystallizing in the anionic-deficient apatite structure, the compounds were synthesized and characterized by powder X-ray diffraction and infrared (IR) absorption spectroscopy. Electrical properties of the materials have been studied by the complex impedance spectroscopy. Correlations between electrical and structural properties are established.

KEYWORDS

Inorganic compounds;
Chemical synthesis;
Infrared spectroscopy;
Electrical properties.

## INTRODUCTION

Solid lithium ion conductors continue to attract great interest, especially for future application as solid electrolytes for all-solid lithium batteries[1] and may solve the safety problems of the rechargeable lithium ion battery using non-aqueous liquid electrolytes[2].

Recently, fast Li ion conductors with perovskite-like structure with high conductivity have been reported[3,4]. A wide variety of materials have been synthesized in the LISICON family[5].

Apatites have the general formula $Me_{10}(XO_4)_6A_2$, with Me divalent cation such as Ca, Sr, Ba, Pb; X: P, As, V and A: various anions, such as $OH^-$, $F^-$, $Cl^-$[6-12]. This formula may be written as $Me(II)_6Me(I)_4(XO_4)_6A_2$; where Me(I) and Me(II) metal ions occupy large sites (4f) and (6h) with nine and seven coordination, respectively. X is a four-coordinated tetrahedral site, and A is an anion site. The A sites lie in the center of channels which are parallel to the c-axis. These channels also contain the Me(II) sites, which form equilateral triangles that alternate in orientation and are stacked in the c-direction.

Although many chemical families including phosphates, silicates and vanadates are known to crystallize with an apatite structure, the type model is the natural mineral ''apatite'', which is basically a calcium fluorophosphates crystallizing in the hexagonal system (space group $P6_3/m$)[13]. The existence of enough large tunnels in the apatitic structure induces important mobility of ions. Because of the mobility of ions, the apatites could find interesting applications in the domain of catalysis, the detection of gas sensors, lasers, fluorescent lamps and cations removing[14-18].

As in many compounds, lead plays a peculiar role in the apatites. Indeed, it is of interest from two points of view. First, lead is known as a "bone seeker" in that it accumulates in bones and teeth, second, it may contribute to deviation from the general formula of apatites.

Several studies have been published on the orthophosphates and orthovanadates of alkaline and lead crystallizing without second anion $A^-$, especially the $Pb_8M_2(XO_4)_6$ apatites with M = Na[19-27], K[9,10,20,22,26], Ag[22,23,26,27]).

Structural studies on apatites with lack of $A^-$ anion, like $Pb_8M_2(XO_4)_6$ (X = P[25,26]; V[10,28]; M: monovalent cation) have shown that, the M alkaline ions are mainly localized in the column positions (4f) sites, while the triangular (6h) sites are totally occupied by the lead cations. It was noted that the $Pb^{2+}$ ions in the 6h positions contribute to the stabilization of the apatite structure when a deficit of $A^-$ anion occurs. The presence of the $6s^2$ electronic lone pairs (LPS) of $Pb^{2+}$ ions in the channels brings the local charge balance in the anionic vacancies.

Because of the mobility of Me and A ions in the apatites $Me_{10}(XO_4)_6A_2$, investigations on electrical measurements were performed. Several authors have established a correlation between structural properties and ionic conductivity[29-36]. In the case of apatites without anion A, investigations on the electrical properties have been carried out by several authors[32-36].

The present study reports the synthesis, the characterization and the ionic conductivity of $Pb_8Na_{2-x}Li_x(VO_4)_6$ $(0 \le x \le 2)$ apatites.

## EXPERIMENTAL

### Synthesis

The $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites have been prepared by solid state reaction using stoechiometric amounts of $PbCO_3$, $Na_2CO_3$, $Li_2CO_3$ and $V_2O_5$ according to the following reaction:

$$\mathbf{8\,PbCO_3 + (2-x)/2\,Na_2CO_3 + x/2\,Li_2CO_3 + 3\,V_2O_5 \longrightarrow Pb_8Na_{2-x}Li_x(VO_4)_6 + 9\,CO_2}$$

The mixtures were heated up to 673 K for one day and to 1023 K for ten days.

The progress of the reaction was controlled by X-ray diffraction.

### Characterization

The purity of the final products was checked by X-ray diffraction methode using a BRUKER D8-advance diffractometer with Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å). The lattice parameters were determined using the program FULLPROF[37].

The infrared spectra were recorded on pellet using 1 mg of apatite powder in 300 mg of spectroscopic grade KBr, with a BRUKER spectrometer in the range of 4000-400 $cm^{-1}$.

The electrical conductivity was studied using impedance spectroscopy and the measurements were performed on an Hewlett-Packard 4192 A impedance analyzer, the signal frequency range is from 5 Hz to 13 MHz. The sample was pressed as a pellet and sintered at 873 K. Electrical measurements were done in the 540-873 K temperature range.

## RESULTS AND DISCUSSION

### X-ray powder diffraction

According to the X-ray diffraction patterns, the $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites crystallize in the hexagonal system with the space group $P6_3/m$ (no. 176). All the compositions have good crystallinity. TABLE 1 gives the lattice parameters of these apatites.

**TABLE 1 : Unit cell parameters of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites.**

| x [Li content] | a (Å) | c (Å) | V (Å$^3$) |
|---|---|---|---|
| 0[10] | 10.059 | 7.330 | 642.31 |
| 0.5 | 10.0471(4) | 7.3210(9) | 640.0(7) |
| 1 | 10.039(1) | 7.310(4) | 638.1(1) |
| 1.5 | 10.0251(8) | 7.2979(1) | 635.2(1) |
| 2 | 10.0148(1) | 7.2791(7) | 632.24(8) |

The variation of the unit cell parameters a, c and V as a function of the lithium content x is reported in Figure 1, where progressive substitution of the sodium by lithium induced a decrease of these parameters. This decrease is due to the substitution of sodium ($r(Na^+)$ = 1.02 Å) by smaller lithium ($r(Li^+)$ = 0.76 Å)[38]. Moreover, the linear variation of the parameters shows that the Na-Li substitution follows the Vegard law and indicates clearly that there is a complete solubility and so that these compounds form a solid solution from pure sodium to pure lithium apatites.

### Infrared absorption spectroscopy

The infrared spectra of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites are similar (Figure 2). In all cases, the two IR lines observed at 760 and 838 cm$^{-1}$, correspond to symmetric stretching $\nu_s(VO_4)$ and asymmetric stretching $\nu_{as}(VO_4)$ vibration modes of the $VO_4$ groups, respectively.

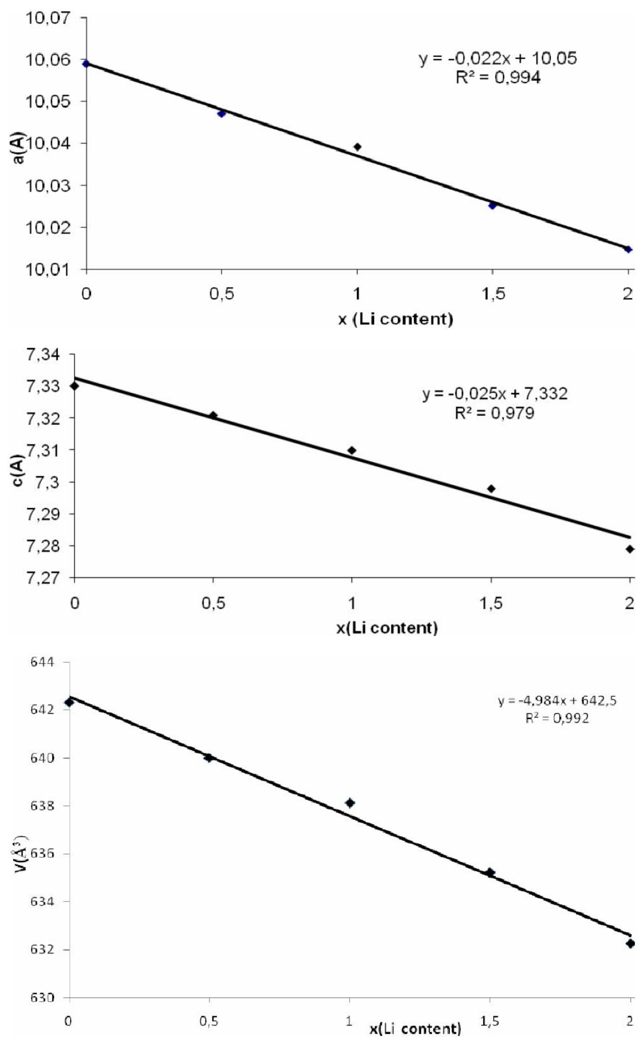

**Figure 1 : Unit cell parameters variations versus Li content (x) of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites**

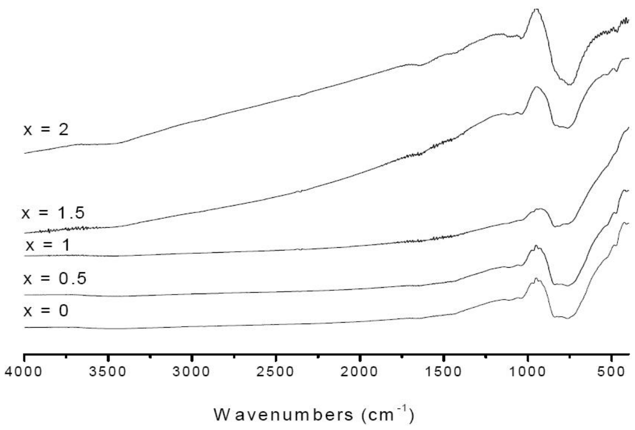

**Figure 2 : Infrared spectra of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites.**

No vibration characteristic of OH groups is observed in 3570 cm$^{-1}$ range. This confirms that the synthesized apatites do not contain hydroxyl ions.

There are no significant progressive shifts of the vibration modes of $VO_4$ groups when lithium content *x* increases. Theoretically these shifts could be explained either by the change in the molar mass or by the fact that $Na^+$ has a larger radius compared to that of $Li^+$ resulting in a weak decrease of the unit cell parameters.

## Electrical properties

The measurements were performed in the 540-873 K temperature range. Below 540 K, the conductivity appears too low to be measured.

For Li content x = 0.5-1, we assume the resolution of bulk and grain boundary semicircles at low temperatures (540 and 673 K). At middle temperatures (673 and 773 K), only a partial grain boundary contribution is observed and at high temperatures (873K) only the electrode response appears.

For Li content x = 1.5, the complex impedance diagram is given in Figure 3, at temperature 673 K only a bulk boundary contribution is observed, at middle temperatures (763 K), two semi-circles can be observed in the complex impedance diagrams, they are attributed to the grain boundary contribution at intermediate frequency and to the bulk conductivity, respectively. At high temperatures (823 K) only the partial grain boundary contribution is observed.

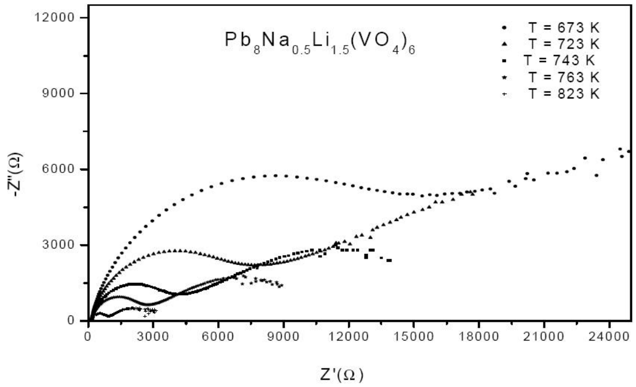

**Figure 3 : Typical complex impedance diagram of $Pb_8Na_{0.5}Li_{1.5}(VO_4)_6$.**

The temperature dependence of the conductivity is represented in Figure 4. A linear variation is observed in Arrhenius plots, following the relation: $\sigma T = \sigma_0 \exp(-E_a/KT)$, where $E_a$ is the activation energy, *K* the Boltzmann's constant, *T* the temperature and $\sigma_0$ the preexponential factor.

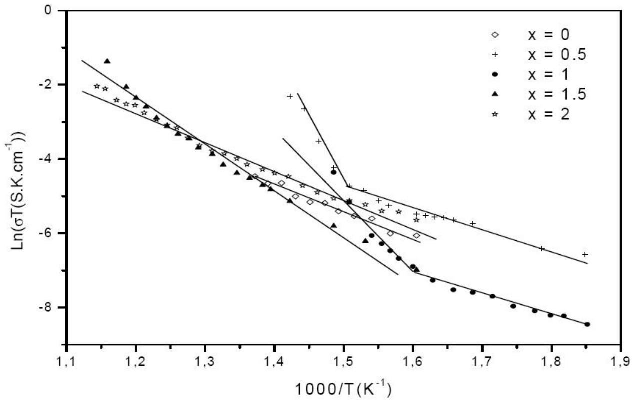

**Figure 4 : Arrhenius plots Ln(σT) = f(1000/T) of ionic conductivity for $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites.**

Activation energy has been calculated from the linear fitting of the conductivity data (TABLE 2).

For Li content x = 0.5-1, the evolution of the conductivity becomes non linear, this phenomenon can not be attributed to the decomposition phenomenon. It can be explained by the effect of the structurally disordered mobile ions on the electrical properties of these materials.

In the 623-873 K temperature range, the activation energy is higher in the case of Li apatite than of Na apatite, this phenomenon can be connected to the great power polarising of Li[39]. Similar results were obtained in $Ca_{10-x}Na_x(PO_4)_{6-x}(SO_4)_xF_2$[30] and $Ca_{10-x}Li_x(PO_4)_{6-x}(SO_4)_xF_2$[31].

**TABLE 2 : Activation energy of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites.**

| Activation energy (eV) | x [Li content] | | | | |
|---|---|---|---|---|---|
| | 0 | 0.5 | 1 | 1.5 | 2 |
| $E_{a1}$ | - | 0.41<br>[540-623 K] | 0.44<br>[540-623 K] | - | - |
| $E_{a2}$ | 0.59<br>[623-729 K] | 2.01<br>[639-703 K] | 2.44<br>[633-688 K] | 1.03<br>[623-873 K] | 0.69<br>[623-873 K] |

Furthermore, the general cationic diffusion in $Pb_8Na_{2-x}Li_x(VO_4)_6$ could be similar to that $Ca^{2+}$ demonstrated by Den Hartog in fluorapatite, the conductivity is dominated by cationic mobility and presents anisotropy[29]. But, due to the high polarizing character $Ca^{2+}$ compared to $Na^+$ and $Li^+$, the $Ca^{2+}$ diffusion is rather limited and can be only observed at high temperature ($T$>1473K). The mobility mechanism of these cations has been explained by the formation of thermally activated defects such as Frenkel defects with high activation energies because the apatite materials are stoichiometric. This conductivity mechanism can be also assigned to the tri-dimensional character of the diffusion process[30,31].

In the $Pb_8K_{2-x}Na_x(PO_4)_6$ system, Laghzizil et al.[32] showed that the disorder defect increases the conductivity and that only monovalent cations contribute to the conductivity phenomenon which is related to the variation of the apatite tunnels size.

The conductivity variation of the materials versus lithium content x is shown in Figure 5. The conductivity increases with the substitution of sodium by lithium in $Pb_8Na_{2-x}Li_x(VO_4)_6$ up to x = 0.5 which has the best ionic conductivity. But, for larger lithium content the conductivity decreases and the fully substituted lithium apatite $Pb_8Li_2(VO_4)_6$ has a similar conductivity to that of the $Pb_8Na_2(VO_4)_6$ compound.

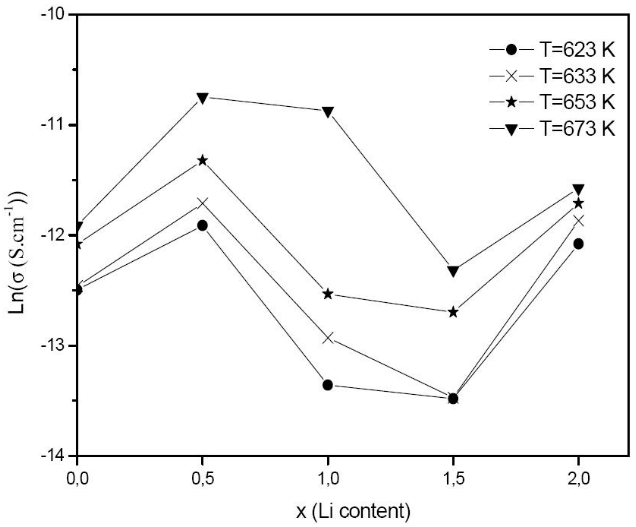

**Figure 5 : Conductivity isotherms as a function of Li content (x) for $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites.**

So, the reduction of $\sigma$ and the increase of Ea when substituting a large amount of Na by Li ($x$>1) can be explained by considering a geometrical difference of apatite tunnels, the ionic radius of $Li^+$ is much smaller than of $Na^+$. It was expected for the Li compound to show a relatively high ionic conductivity. This may be associated to a change in diffusion mechanism, which is still to be explained. The same conduction phenomenon has been observed with mixed anionic mobility in system $Ca_{10-x}Ln_x(PO_4)_6(OH)_{2-x}O_x$ (Ln=La, Y)[14,15].

## CONCLUSION

This paper presents a study of synthesis, characterization and ionic conductivity of $Pb_8Na_{2-x}Li_x(VO_4)_6$ apatites. X-ray diffraction study shows that these apatites crystallize in the hexagonal system with the space group $P6_3/m$. Infrared spectra of all the compositions are similar. The conductivity study shows that, at low temperatures (540-673 K), the best conductivity and the lowest activation energy are observed for the x = 0.5 composition.

At high temperatures (623-873 K), the best conductivity and the lowest activation energy are observed for the pure sodium apatite.

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