New ionic conducting ceramics of NASICON type: synthesis and characterizations

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In this work, we present a study of two NaSICON families of general formula Na2.800M1.775Si0.900P2.100O12 with M=Zr or Hf. The synthesis was carried out using sol-gel process and the synthesized precursors were characterized using coupled DTA-TG. The obtained oxides after pyrolysis of precursors were identified by X-ray diffraction. The electric properties of the sintered oxides were carried out by impedance spectroscopy (SIC). The obtained results at this conditions highlight a good improvement of electrical conductivity (σ_{tot} around 10^{-4} S.cm^{-1}). This value is comparable to total electrical conductivity at 300K given in the literature

Key words: NaSICON, Zirconium, Hafnium, sol-gel, electrical conductivity

INTRODUCTION

Generally, researches on the conducting solid electrolytes by alkaline ions were undertaken for the use of the ionic superconductors materials as constitutive elements of storage and energy production devices, sensors, electrochromic and super condensers mechanisms [1].

A series of Na^+-conductors $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \le x \le 3$) called NaSICON (Natrium Super Ionic CONductor) had been synthesized by HONG et al [2,3].

For a value of x =2 ($Na_3Zr_2Si_2PO_{12}$) and at temperature higher than 200°C, NaSICON can compete with β - alumina ($\sigma_{300°C}$(NaSICON)=0.27 S.cm^{-1} according to HONG).

According to the systematic study that we carried out on the series of NaSICON compound having general formula $Na_{2.8}Zr_{2-y}Si_{1.8-4y}P_{1.2+4y}O_{12}$ with $0 \le y \le 0.45$, we noted that composition y = 0.225 is better in term of conductivity [4]. But this conductivity remains worse than the classical composition $Na_3Zr_2Si_2PO_{12}$ [5-7]. Thereafter, we carried out a thermodilatometric study to optimise the sintering cycle in order to improve conductivity and thereafter to synthesis a new family of ionic conducting ceramics based on hafnium by complete substitution of Zr by Hf.

EXPERIMENTAL PART

Taking into account the difficulty in obtaining pure ceramics of NaSICON by solid state reaction, the precursors were prepared using a sol–gel method which implies the preliminary formation of an amorphous solid [8]. The used precursors were: $NaNO_3$, $(NH_4)_2HPO_4$ and $ZrO(NO_3)_2$. For hafnium precursor, we have used hafnium oxynitrate synthesized from hafnium tetrachloride $HfCl_4$ [9]. The synthesized precursors were characterized by coupled differential analysis and thermogravimetry (DTA-TG). After pyrolysis the obtained oxides were identified by X-ray diffraction (Siemens D5000, λ_{Cu}=1.5406 Å).

The ceramic electrical properties were determined by ac impedance spectroscopy measurements (impedancemeter Solatron 1260). The measurements were achieved between 100 Hz and 3.2 10^7 Hz in the temperature range 25 - 110°C under air. An applied voltage was fixed at 100mV. The sample was allowed to equilibrate for 1 h before measurements could be obtained of the reproducible impedance spectra.

RESULTS AND DISCUSSION

1- Coupled DTA-TG

Coupled DTA-TG has been carried out in order to study the thermal decomposition of precursors based on zirconium and hafnium. This enables us to optimise the calcination conditions of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ and $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$ studied compositions.

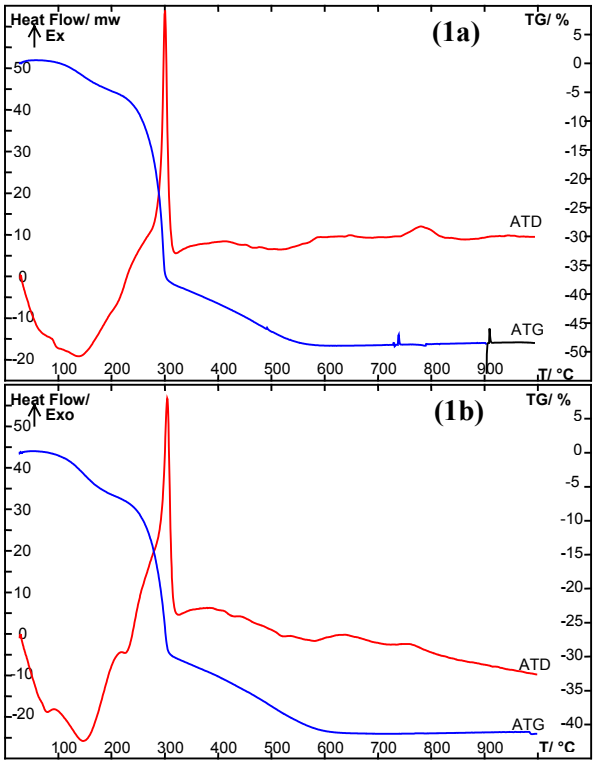

FIGURE 1: Obtained DTA-TG thermograms of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ (1a) and $Na_{2.800}Hf1_{1.775}Si_{0.900}P_{2.100}O_{12}$ (1b) compositions.

The two obtained thermograms (figure 1) are similar and present three weight losses associated with thermal phenomena (endothermic and exothermic). The total weight loss is 47% for the Zr composition and 42% for the hafnium composition.

The crystallization temperature of the two oxides was found to be close to 780°C.

2- X-Ray diffraction

We represent successively on figures 2 and 3 the obtained X-ray diffraction patterns of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ and $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$.

The diffractograms obtained at ambient temperature show that the synthesized compounds are single phase. The whole of the peaks correspond to the NaSICON phase (JCPDS N° 33-1313), without any detected trace of ZrO_2 which decreases conductivity. No other phase such as HfO_2, SiO_2, $ZrSiO_4$, Na_3PO_4, Na_2SiO_3 or Na_2ZrO_3 could be detected in these samples.

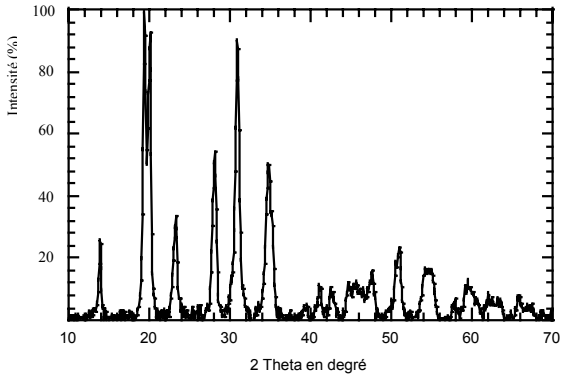

FIGURE 2: X-ray diffraction diagram of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition.

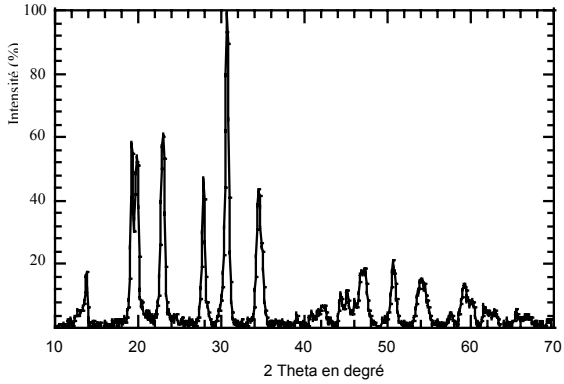

FIGURE 3: X-ray diffraction diagram of $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition.

3- Sintering

To still improve conductivity of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition, we carried out a thermodilatometric study on a calcined powder at 600°C in form of compacted pellet by uniaxial pressing (190 MPa).

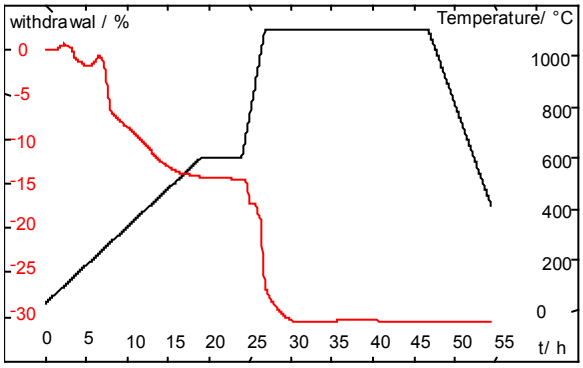

FIGURE 4: Thermodilatometric curve of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$composition

The thermal cycle is as follows:
Heating from 25 to 600°C with a speed of 0.5°C/min to avoid any crack and to make evacuate water delicately. At 600°C, we maintain the temperature constant during approximately 5 hours to ensure us of the calcinations of the residual organometallic products, oxidation and burning of the carbonaceous residues. After that, the sample was heated up to 1100°C with a rate of 3°C/min. The slow heat treatments lead to an organization of the cations (Na, Zr) causing the distortion of the SiO_4 and PO_4 tetrahedra [1]. The sintering stage is located at 1100°C during 20 hours. Finally the sample was cooled to room temperature at a mean rate (0.5°C/min) to avoid thermal shocks. Figure 4 shows the thermogram obtained by dilatometry for the composition y = 0.225. From ambient temperature up to 150°C, the compacted sample dilates slightly. This phenomenon is due to the boiling of water existing inside of sample and to the release of imprisoned air. The contraction of the sample observed from 900°C is indication of the beginning of the ceramics thickenings. At 1050°C, the sintering rate was maximum and after the isotherm of 5 hours at 1100°C, we don't observe any more withdrawal on the dilatometric curve. This fact translates the end of the sintering of the sample. The total withdrawal measured at the sintering time is very important (about 32%). Thus, we choose 1050°C (temperature corresponding to maximum sintering rate is maximum) for sintering in order to avoid the NaSICON decomposition [10]. Figure 5 shows the X-ray diffraction diagram of $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$ sintered at 1050°C during 5 hours.

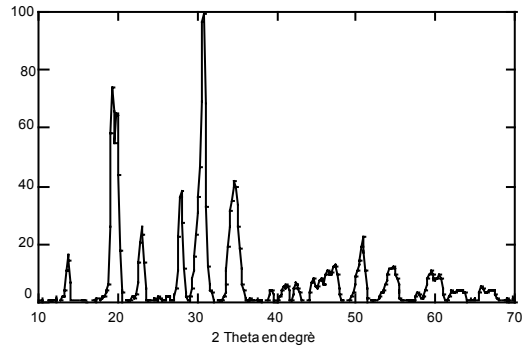

FIGURE 5: X-ray diffraction diagram of $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition after sintering.

4- Electrical measurements (impedance spectroscopy)

For all considered compositions (figures 6 and 7), the separation between the response of the grain boundaries and the electrode characteristic allows us to measure, without any ambiguity, the total resistance of a sample. On the other hand, these conditions are difficult, even impossible, to separate the contribution from grains and grain boundary. In table 1 we represent conductivity at 300K and activation energy values.

Table 1: Total conductivity at 300K and activation energy values.

Composition	Total Conductivity at 300K (Scm^{-1})	activation energy (eV)
$Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$	$8.25\ 10^{-5}$	0.18
$Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$	$1.12\ 10^{-4}$	0.28

According to the results of table I, we notice that we improved conductivity (of approximately 10 times more) for Zr by comparison with traditional thermal cycle used for sintering. This conductivity is comparable with total conductivity at 300K given in the literature [13,5]. This improvement is attributed to a synthesis method using soft chemistry leading to a NaSICON single phase with better homogeneity and also with the optimisation of the sintering conditions.

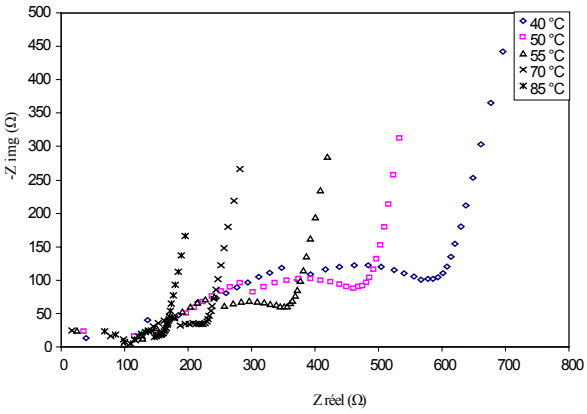

FIGURE 6: Nyquist diagram of $Na_{2.800}Hf_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition

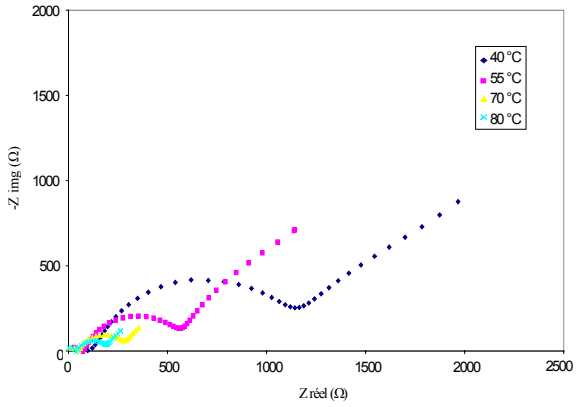

FIGURE 7: Nyquist diagram of $Na_{2.800}Zr_{1.775}Si_{0.900}P_{2.100}O_{12}$ composition

For the less conducting composition, the low value of conductivity can be explained by a blocking effect at the grain boundaries. Taking into account the influence of the microstructure on the amplitude of the blocking effect of the charge carriers [13,5], all comparison with other materials must be carried out with precaution.

CONCLUSION

In this paper, two families of conducting ceramics of general formula $Na_{1+x}M_{1.775}Si_{x-0.9}P_{3.9-x}O_{12}$ with x = 1.8 and M = Zr or Hf were studied. The powders were calcined and sintered under the same conditions. This study shows that under these conditions an improvement of electrical conductivity has been evidenced. This conductivity is comparable with total conductivity at 300K given in the literature.

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