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Preparation characterization and conductivity studies of Nasicon systems $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1)

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Abstract: *Materials belonging to NASICON family of compositions $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1) are prepared by sol-gel method. Ethylene glycol is used as a gelating agent. All the compositions are characterizedby powder X-ray diffraction and Fourier transform infrared spectroscopy All these phosphates are crystallized in rhombohedral lattice with space group ^{R3c} . These compounds exhibit characteristic PO_4 vibrational modes in their FT-IR spectra. The dc conductivity of $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1) was also investigated.*

Keywords*: Sol-gel method, Infrared Spectroscopy, Powder X-ray diffraction, Ionic conductivity.*

I. Introduction:

Skeletal materials based on Sodium Zirconium Silico Phosphate ($Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$, $0 < x < 3$), popularly known as NASICON and Sodium Zirconium Phosphate ($NaZr_2P_3O_{12}$) abbreviated as NZP, have attracted considerable attention during the last twenty five years and investigated by several groups. [1]

The reasons for such an explosive growth of investigations are not far to seek. The crystal chemistry of such materials is unique and possesses a framework structure with fast Na^+ transport comparable to that of β"-alumina.[1-2] The framework structure is a rigid, three-dimensional network of PO_4 (or SiO_4) tetrahedra sharing corners with ZrO_6octahedra encapsulating the mobile sodium ion in the interconnected interstitial space. Most of the materials belonging to NASICON or NZP type crystallize in the hexagonal lattice with space group R3C . It is abbreviated as AMM□P_3O_{12}, where site "A" can be occupied by alkali, alkaline earth ions, Cu^{2+}, Cu^+, Ag^+, H^+, H_3O^+, NH_4^+, while M and M□ can be filled with transition metal ions. Phosphorous can be partially substituted by silicon. Thus the structure is flexible for substitution at A, M, M□ and P sites, giving rise to large number of isostructural compounds. These materials possess fairly large ionic conductivity. For instance, the ionic conductivity of $Na_3Zr_2PSi_2O_{12}$ at 300^0C is about 0.2

$\Omega^{-1}cm^{-1}$ and can be potentially used in devices such as membranes, fuel cells and gas sensors.[3-5] As the structure is characterized by large tunnels, the surface area is fairly large and is hence used as catalyst supports.[6] These materials possess near zero thermal expansion.[7] The other potential applications of this class of compounds include host for radioactive waste,[8] ion exchange[9, 10] and insertion/extraction reactions.[11-16] The crystal structures of several materials of composition $AM^{III}M^V(PO_4)_3$ (A = Li or Na) have been reported.[17-21] However, the electrical properties have not been reported for many of these materials. Rrecently for $Ag_{3-2x}Al_{2-x}Ta_x(PO_4)_3$ system, the maximum conductivity of $8.4x10^{-6}$ S cm^{-1} at 298 K for x = 0.8 was obtained and it has been enhanced about three to five times by increasing the temperature upto 523K.[22-24] In this paper we report here the preparation, characterization and conductivity studies of NASICON-type solid solution of composition $Ag_{3-2x}In_{2-x}Ta_xP_3O_{12}$ (x = 0.6, 0.8 and 1.1)(here after abbreviated as AITP(1), AITP(2) and AITP(3)).

II. Experimental:

Solution A: preparation of $AITP_{(x)}$, Stoichiometric amounts of $AgNO_3$(SD-Fine chemicals-99.5%) was dissolved in 30 ml of de-ionized water. To this solution a 50 ml aqueous solution containing CA (the mole ratio of Ag: CA is 1:2) was added.

Solution B: stoichiometric amounts of Ta_2O_5(Aldrich-99.9%) was dissolved in HF (40%). Then ammoniasolution (25%) was added to this solution drop wise to obtain $Ta_2O_5.nH_2O$ precipitate. The resultant precipitate ($Ta_2O_5.nH_2O$) was filtered and washed with de-ionized water to remove remaining HF. The above precipitate was dissolved in 50 ml aqueous citric acid (CA) solution (the mole ratio of Ta : CA is 1:2) and warmed to 80 ºC to get a homogeneous solution.

Solution C: 0.5623 g (11.7439 mmols) of Indium metal, was dissolved in 10 ml of HNO_3solution. To thissolution, a 50 ml aqueous solution containing citric acid (CA) (4.9354 g, 23.48 mmols) (the mole ratio of In : CA is 1:2) was added.

Solution D: 4.0533 g (35.2368 mmols) of $NH_4H_2PO_4$ (SD-Fine chemicals-99.5%) was dissolved in 30 ml of de-ionized water.

The solutions A B and C were simultaneously mixed with solution D. The pH of this resultant solution was adjusted to 6-7 using dilute ammonia solution and kept on a hot plate under constant stirring. A few hours later ethylene glycol (gelating agent) was added such that the molar ratio of citric acid to ethylene glycol was 1:1.2. This mixture was heated at 100 ºC for 2-3 hours. When the solution started solidifying and forming a porous gel, the temperature was gradually increased to 160-180 ºC till a solid mass was obtained. This porous mass was ground in an agate mortar using spectral grade acetone. This ground solid was heated to about 300 ºC in small amounts in an electric burner. This resultant solid was named as

"precursor", which was heated at different temperatures in a muffle furnace. All these steps are shown in the form of flow chart in Figure 1. The products obtained by heating the precursor at 500 (5 h), 600 (5 h), 800 (5 h) and 950 ºC (5 h) in air are designated as AITP-500, AITP-600, AITP-800 and AITP-950 respectively. The probable reactions leading to the formation of AITP are given below

(i) $AgNO_3 + H_2O \rightarrow Ag(OH)(aq) + HNO_3$

(ii) $Ag(OH)(aq) + citricacid \rightarrow Ag(citrate)_x(aq)$

(iii) $0.5Ta_2O_5 + 5HF \rightarrow TaF_5(aq) + 2.5H_2O$

(iv) $TaF_5(aq) \xrightarrow{25\%NH_3} Ta(OH)_5\downarrow$

(v) $Ta(OH)_5\downarrow + citricacid \longrightarrow Ta(citrate)_x(aq)$

(vi) $In + HNO_3 \longrightarrow In(NO_3)$

(vii) $In(No_3) + citricacid \longrightarrow In(citrate)(aq)$

(viii) $Ag(citrate)_x(aq) + Ta(citrate)_x(aq) + In(citrate) + 3NH_4H_2PO_4(aq)$

Thus the phase formation range in the present AITP(x) series is 0.6 ≤ x ≤ 1.1 under the present experimental conditions.

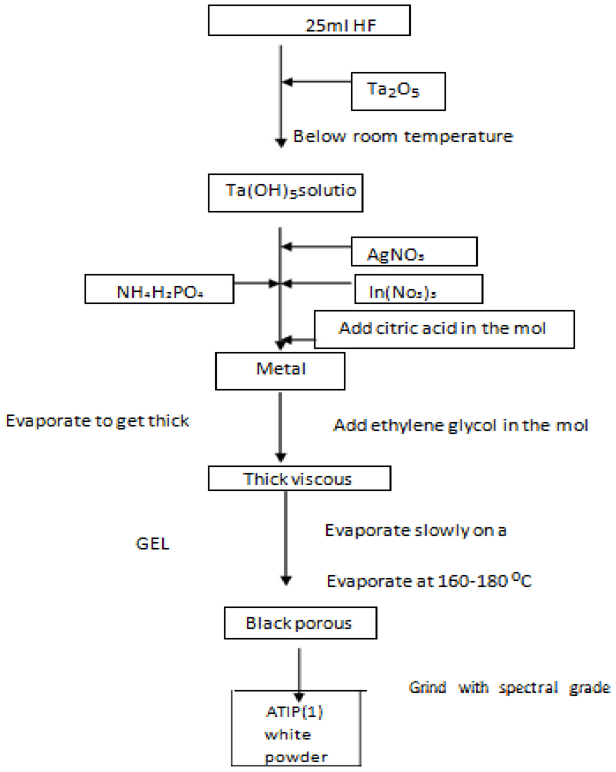

Fig.1 Flow chart of sol gel preparation procedure of ATP (1)

Powder X-ray diffractograms are recorded using Philips Expert Analytical X-ray diffractometer. Nickel filtered Cu-K□ radiation of wavelength 1.5406 A^0 is used. XRD patterns are indexed and lattice parameters are calculated. Experimental densities are measured by Archimedes' principle using xylene as an immersion liquid. Calculated densities are obtained from lattice parameters. Infrared spectra are recorded in the form of KBr pellets using JASCO FT/IR-5300 Spectrometer. The DC conductivities in the temperature range 300-573 K are measured using a two-probe method on the sintered pellets coated with silver paint. For this a conventional sample holder and Keithley Electrometer 6485C picoammeter are used.

III. Results and discussion

3.1 Powder XRD

The powder patterns of ATP (1), ATP (2) and ATP (3) are shown in Fig. 2. All the diffraction patterns are found to be free from impurities and can be compared with the diffraction patterns of NASICON type compounds reported earlier [21-24]. The d-lines of all the samples are similar to each other except the intensity. All these compositions crystallize in rhombohedral lattice with space group ^{R3c} .The unit cell parameters of all these compositions were obtained from XRD patterns using least square fit and are reported in Tabl 1. The values obtained in the present measurements are also compared with reported values $NaTi_2P_3O_{12}$ [PDF no 84-2008], $AgTi_2P_3O_{12}$ and $NaZr_2P_3O_{12}$ [PDF no 70-0233]. The observed and calculated densities of all these compositions are also presented in Table 1.

Table 1 Unit cell parameters and densities of $AHfMP_3O_{12}$(A = Na and Ag, M = Ti and Zr) and related systems

Compound	**a (Å)**	**c(Å)**	**d_{obs} (g cm^{-3})**	**d_{cal} (g cm^{-3})**	**Reference**
ATP (1)	8.61 (2)	22.18 (2)	3.38	3.47	present study
ATP (2)	8.68 (3)	22.40 (5)	3.42	3.63	present study
ATP (3)	8.62 (2)	22.28 (3)	3.69	3.98	present study

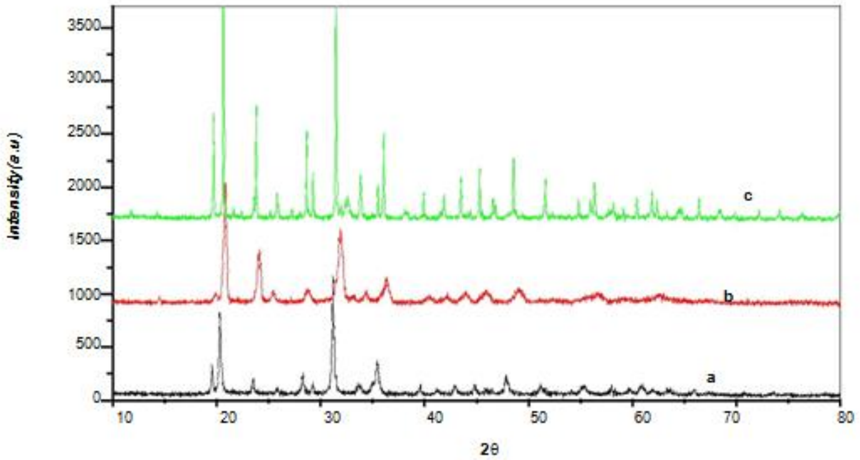

Fig.2. Powder X-ray diffractograms of $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1) (a) AITP(1) (b) AITP(2) (c) AITP(3)

3.2. IR spectroscopy:

The IR spectra of AITP(x) recorded in the range 2000-400 cm^{-1} is shown in Fig 3. All the compositions exhibit strong absorptions below 1500 cm^{-1}. Generally the vibrational modes of NASICON phases can be assigned to PO_4tetrahedra (internal and external modes) and to lattice modes of metal octahedra. Of these, the bands corresponding to PO_4 unit are intense than metal octahedral bands. The assignments for the observed bands have been made based on the predictions of factor group analysis. [25-27]

The PO_4 unit gives nine vibrational modes that are characterized by non degenerate symmetric $\nu_\sigma(PO)(\nu_1)$, antisymmetric triply degenerate $\nu_d(PO)$ (ν_3) of phosphorous non-bridging oxygen stretching and the symmetric doubly degenerate δ_δ(OPO) bending (ν_2) and antisymmetric triply degenerate δ_δ(OPO) bending (ν_4)[28,29]. These modes are observed in the frequency ranges 1270-1000 cm^{-1} (ν_3), 1000-900 cm^{-1}

(ν_1), 670-540 cm^{-1} (ν_4) and 450-440 cm^{-1} (ν_2) for all the compositions under investigation. The PO_4

external modes corresponding to vibrational and translational motions of these groups are generally observed below 300 cm^{-1}. Due to the instrumental constraints the spectra could not be recorded below 400 cm^{-1} and hence the corresponding assignments could not be made. The absence of any IR bands in the region 740-730 cm^{-1} proves the absence of pyro phosphate ($P_2O_7^{4-}$) impurity. Similar types of spectra are obtained for sodium and lithium analogues.[17]

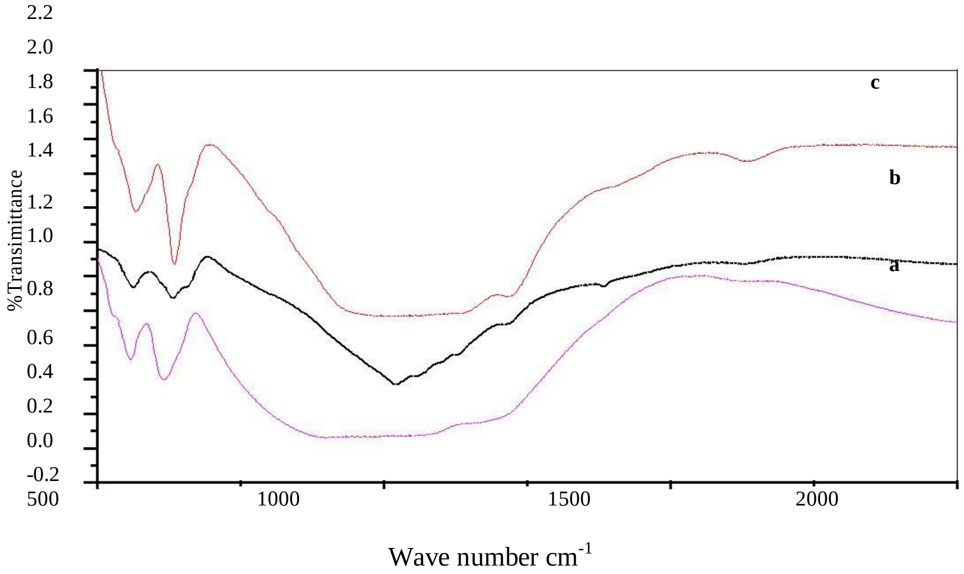

Fig.3. IR Patterns for $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1) (a) AITP(1) (b) AITP(2) (c) AITP(3)

3.3. DC conductivity:

The dc conductivity of AITP(x) compositions is obtained in the temperature range 300-623 K. The DC conductivity values are calculated from the bulk resistance and samples dimensions in the above temperature range. Fig 3 shows the variation of log(□ T) with 1000/T for all compositions and a linear relationship is obtained.. However, in the present investigation, the conductivity variation with temperature is similar for all the composition. It is observed from figure that the conductivity increases with increase in the temperature. The behavior of variation of conductivity with temperature is similar to that observed in other NASICON type of compounds. The data were fitted to Arrhenius equation

$$\sigma_{\delta\chi}T = \sigma_0 \varepsilon\xi\pi(-E_\sigma/\kappa T) \qquad .....(1)$$

ωηερεσ$_0$ ισ τηε πρε–εξπονεντιαλ φαχτορ, T ισ τηε αβσολυτε τεμπερατυρε, E$_\sigma$ ισ τηε αχτιϖατιον ενεργ ψ φορ

conduction and k is the Boltzmann's constant. From the slopes of these straight lines, the activation energies (E_a dc) for conduction are calculated and fall in the range 1.0 – 1.4 eV.

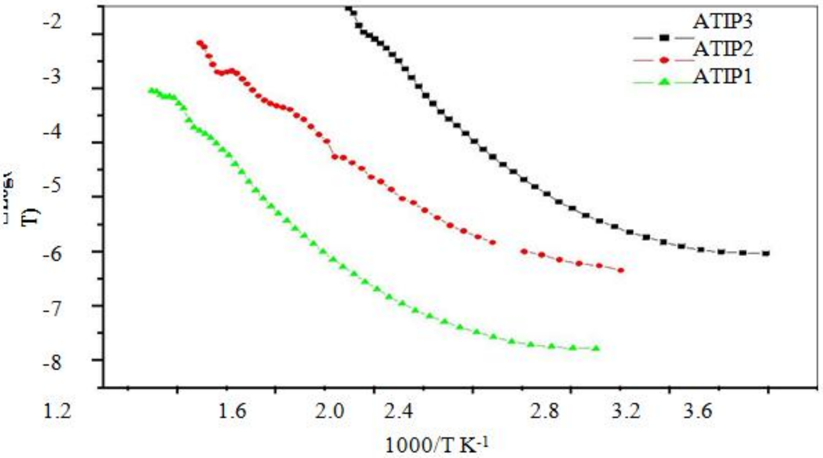

Fig.4. Arrhenius plots of $Ag_{3-2x}Ta_xIn_{2-x}(PO_4)_3$ (x = 0.6,0.8 and 1.1) (a).AITP(1) (b) AITP(2) (c) AITP(3)

IV. Conclusions:

New silver containing NASICON type compositions $Ag_{3-2x}In_{2-x}Ta_xP_3O_{12}$ (x=0.6 to 1.1) are prepared by low temperature sol –gel method. All the samples crystallize in rhombohedra lattice of framework. The unit cell parameters of ATP(1), ATP (2) and (3) are close to that of $NaZr_2(PO_4)_3$ The infrared spectra of these compositions show characteristic PO_4 vibrations. The ionic conductivities of ATP(1), ATP (2) and (3) are increses when incresing the Ta concentration in the phosphates. The ionic conductivties of ATP(1), ATP (2) and (3) are 7.6×10^{-5} 4.2×10^{-4} 6.4×10^{-3} S cm^{-1} respecively. The activation energies obtained from DC conductivities ATP(1), ATP (2) and (3) are 1.0, 1.2 and 1.4 eV respectively.

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