Synthesis of New Zirconium Based Ion Exchangers and Their Characterization

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(Received October 25, 2004)

Abstract

Inorganic ion-exchangers zirconium antimonophosphate (ZrSbP) and zirconium phosphotungstate (ZrPW) are synthesized and characterised as weakly acidic ion exchangers by potentiometric titrations against alkali metal hydroxides. Chemical composition, ion-exchange capacity for alkali and alkaline earth metal ions, distribution coefficients for a number of metal ions, effect of heat treatment on ion-exchange capacity are reported for the ion-exchangers. ZrSbP and ZrPW show excellent chemical stabilities towards most of the aqueous media except alkaline solutions. The exchanger ZrSbP loses only 30% of its ion-exchange capacity upto 200°C. An extensive study of distribution coefficients for various metal ions suggests that ZrSbP is selective for Fe²⁺, Pb²⁺ and Ba²⁺ ions while ZrPW is selective for Fe³⁺ ions. Structural studies of these materials are carried out using XRD, IR and chemical analysis.

Key words: Inorganic ion exchangers, structure, synthesis, characterisation, zirconium

1. Introduction

Hydrous oxides of group 4, 5, 6, 14 and 15 metals possess ion-exchange properties. They are characterised by having a bulk structure resembling to that of ceramic oxides like sodium aluminosilicate. Their surface is largely covered with hydroxyl groups and both coordinated and hydrogen bonded water molecules are present. The properties of these tunnel type structures of ZrO₂ and SnO₂ can be changed by the incorporation of framework hydrates, generally formed by metals in-group 5 and 15, in their higher oxidation states. In such resulting structures, hydronium ions are distributed among the crystallographic sites within the tunnels.

Ammonium phosphotungstate and ammonium molybdophosphate were probably the first materials which have been studied as ion-exchangers. Primarily, zirconium and tin (IV) based exchangers have been synthesized and most of the literature is available on the studies related to their synthesis and ion-exchange behaviour. Reviews of Clearfield4,5 and Sebesta6 deal with the subject matter in detail. Thind et al7 reported the synthesis of zirconium boratophosphate and applied it for the quantitative separation of lanthanides. Other zirconium based ion-exchangers reported are zirconium succinophosphate8, zirconium vanadophosphate9, zirconium arsenovanadate10, zirconium iodophosphate11 and zirconium phosphomolybdate12. Ion-exchangers based on metal ions other than tin (IV) and zirconium (IV) include synthetic studies on chromium (III) arsenosilicate13, iron (III) antimonosilicate14, antimony (III) molydbotungstate15 and antimony (III) tungstoselenite16. Antimony (V) arsenophosphate17 has been used to study the exchange kinetic behaviour of alkaline earth metal ions.

Insoluble salts of polyvalent metal ions such as phosphates, arsenates, vanadates, tungstates, antimonates and molybdates of tin, titanium and zirconium are generally obtained as amorphous or semicrystalline materials which undergo extensive hydrolysis in weakly alkaline or even in...
neutral solutions. By refluxing amorphous zirconium phosphate with phosphoric acid, Clearfield and Stynes obtained a crystalline zirconium phosphate with higher resistance to hydrolysis than the amorphous material.

Two new materials, namely zirconium antimonophosphate and zirconium phosphotungstate were prepared. The degree of crystallinity has been improved by adopting methodologies like refluxing in acidic medium and by use of hydrofluoric acid during synthesis.

2. Experimental

2.1 Reagents

Zirconium oxychloride octahydrate (Loba Chemie, India), potassium pyroantimonate (BDH, England), sodium tungstate (Loba Chemie, India), hydrofluoric acid, 40% v/v, (Ranbaxy, India) and phosphoric acid (BDH, England) were used for the synthesis of ion-exchangers. All other chemicals used were of AR grade.

Standard solutions for the analytical work were prepared by either direct weighing of AR grade reagents or by indirect standardisation. Demineralized water (DMW) was prepared by passing distilled water through a strongly acid-cation exchanger (Amberlite IR-120) packed in a column.

2.2 Apparatus

An electric thermostated oven was used for drying the samples. An Equiptronics (India) pH meter was used for pH measurements. Spectrophotometric measurements were made by using a microprocessor based ECIL (India) spectrophotometer. X-ray diffractograms (powder patterns) were taken from Rigaku X-ray diffractometer using Cu-Kα radiations. Infrared studies were done with a Pye Unicam SP 300 Philips (ENGLAND) spectrophotometer. TGA and DTA studies were done on a Stanton-SP instrument Model STA–781 in air.

3. Synthesis of Ion-Exchangers

3.1 Synthesis of zirconium antimonophosphate (ZrSbP)

Five samples of zirconium antimonophosphate (ZrSbP) were prepared by adding zirconium oxychloride solution (0.1 M) (containing hydrofluoric acid 12 mL/L) to a continuously stirred mixture of phosphoric acid (0.1 M) and potassium pyroantimonate (0.1 M) (containing hydrofluoric acid 16 mL/L) solutions in a volume ratio of 2:1:1. Gelatinous white precipitates were obtained and the gel was refluxed in the mother liquor for two hours. The precipitates were filtered, washed until free from halides and then dried at 40°C in an air oven. The dried product broke down into small granules when immersed in water. The material was converted into the H+-form by keeping it in HCl (0.1 M) for 24 hours with intermittent changing the acid, washed with DMW to remove excess acid and finally dried at 40°C (Table 1).

3.2 Synthesis of zirconium phosphotungstate (ZrPW)

Five samples of zirconium phosphotungstate (ZrPW) were prepared by adding zirconium oxychloride solution (0.1 M) (containing hydrofluoric acid 12 mL/L) to a continuously stirred mixture of sodium tungstate (0.1 M) and phosphoric acid solutions (0.1 M) in a volume ratio of 2:1:1. The resulting gel was refluxed in the mother liquor for 16 hours. The gelatinous white precipitates so obtained were filtered, washed until free from halides and then dried at 40°C. The dried product broke down into small granules when immersed in water. The material was converted into the H+-form by keeping it in HCl (0.1 M) for 24 hours with intermittent changing the acid, washed with DMW to remove excess acid and finally dried at 40°C (Table 1).

4. Characterisation of Ion-Exchangers

4.1 Ion exchange capacity

Ion-exchange capacity of various samples was deter-

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Zirconium Antimonophosphate</th>
<th>Zirconium Phosphotungstate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conditions of Synthesis</td>
<td>Properties</td>
</tr>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>pH</td>
</tr>
<tr>
<td>1.</td>
<td>19</td>
<td>1.54</td>
</tr>
<tr>
<td>2.</td>
<td>19</td>
<td>1.38</td>
</tr>
<tr>
<td>3.</td>
<td>19</td>
<td>1.58</td>
</tr>
<tr>
<td>4.</td>
<td>17</td>
<td>1.42</td>
</tr>
<tr>
<td>5.</td>
<td>17</td>
<td>1.44</td>
</tr>
</tbody>
</table>
mined by column operation. About 400 mL of sodium nitrate (1.0 M) solution was passed through the ion-exchanger (1 g) column. Hydrogen ions eluted from the column were determined titrimetrically. Ion-exchange capacity was determined for some uni- and bivalent cations. Results are given in Table 2.

4.2 Regeneration of ion-exchangers

The exhausted exchanger was regenerated by keeping it overnight in hydrochloric acid (0.1 M). Even after five regenerations, the ion-exchangers lose only about 20–25% of their original capacities.

4.3 Chemical composition

The exchanger (0.5 g) was dissolved in concentrated HCl. Zirconium⁴⁺, phosphorus⁵⁺ and tungsten¹⁸⁺ and antimony¹⁹⁺ were determined spectrophotometrically.

4.4 Chemical stability

The exchanger (0.5 g) was kept separately in 20 mL of different solvents and then filtered. Zirconium⁴⁺, phosphorus⁵⁺ tungsten¹⁸⁺ and antimony¹⁹⁺ in the filtrate were determined spectrophotometrically. The results are reported in Table 3.

4.5 Thermal stability

Ion-exchanger samples were dried for 2 hours continuously at various temperatures ranging from 100°C to 900°C in a muffle furnace. Ion-exchange capacity and loss in weight were determined as a function of temperature. The results are shown in Fig. 1 and 2 respectively.

4.6 Density

The densities of all the ion-exchangers were determined using the specific gravity bottle. The ion-exchanger (2.0 g) was taken in a dried and weighed specific gravity bottle. It was then filled with n-nonane and weighed. The density of the ion-exchanger ρe was calculated using the equation²⁰:

$$\rho_e = \frac{Q}{V} \quad \text{and} \quad V = V_b - (Q_b - Q)/\rho$$

### Table 2 Ion Exchange Capacity of Zirconium Antimonophosphate and Zirconium Phosphotungstate for Some Uni- & Bivalent Cations

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Salt Solution Used (Molarity)</th>
<th>pH of Salt Soln.</th>
<th>ZrSbP</th>
<th>ZrPW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>Lithium Nitrate (1.0)</td>
<td>0.340</td>
<td>0.88</td>
<td>0.80</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium Nitrate (1.0)</td>
<td>0.276</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium Nitrate (1.0)</td>
<td>0.232</td>
<td>1.15</td>
<td>0.98</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Magnesium Nitrate (0.5)</td>
<td>0.70</td>
<td>0.36</td>
<td>1.35</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>Calcium Nitrate (0.5)</td>
<td>0.630</td>
<td>0.24</td>
<td>1.35</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>Strontium Nitrate (0.5)</td>
<td>—</td>
<td>0.20</td>
<td>1.25</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>Barium Nitrate (0.5)</td>
<td>0.590</td>
<td>0.16</td>
<td>1.10</td>
</tr>
</tbody>
</table>

### Table 3 Solubilities of Zirconium Antimonophosphate and Zirconium Phospho-tungstate Ion-exchangers in different Solvent Media

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Medium</th>
<th>Solubility (µg/200 mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrSbP</td>
<td>ZrPW</td>
</tr>
<tr>
<td>1.</td>
<td>DMW</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>2.</td>
<td>H₂SO₄ (0.1 M)</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>3.</td>
<td>HCl (0.1 M)</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>4.</td>
<td>HNO₃ (0.1 M)</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>5.</td>
<td>NaNO₃ (0.1 M)</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>6.</td>
<td>Acetic Acid (0.1 M)</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>7.</td>
<td>KOH (0.1 M)</td>
<td>8.0 1.8 2.6 16.0 2.3 6.0</td>
</tr>
<tr>
<td>8.</td>
<td>NaOH (0.1 M)</td>
<td>6.0 1.1 3.0 15 4.5 11.0</td>
</tr>
<tr>
<td>9.</td>
<td>Ethanol</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>10.</td>
<td>Dioxane</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>11.</td>
<td>DMF</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
</tbody>
</table>

Fig. 1 Weight loss (%) of ZrSbP and ZrPW as a function of temperature.

Fig. 2 Ion-exchange capacity of ZrSbP as a function of temperature.
Table 4  Distribution Coefficients ($K_d$) of Metal Ions on Zirconium Antimonophosphate, Tin (IV) Antimonophosphate and Zirconium Phosphotungstate

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>$K_d$ (mL/g)</th>
<th>Metal Ion</th>
<th>$K_d$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrSbP</td>
<td>ZrPW</td>
<td>ZrSbP</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>10</td>
<td>2</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>35</td>
<td>2</td>
<td>Cd$^{2+}$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>19</td>
<td>7</td>
<td>Pb$^{2+}$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>150</td>
<td>16</td>
<td>Zn$^{2+}$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>15</td>
<td>3</td>
<td>Al$^{3+}$</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>8</td>
<td>2</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>15</td>
<td>4</td>
<td>Dy$^{3+}$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>27</td>
<td>15</td>
<td>Pr$^{3+}$</td>
</tr>
</tbody>
</table>

T.A.: Totally Adsorbed

where $V_s$ is the volume of specific gravity bottle, $Q$ is the weight of exchanger taken, $Q_b$ is the weight of n-nonane and the exchanger taken in the specific gravity bottle, $\rho$ is the density of n-nonane. The results are given in Table 1.

### 4.7 Potentiometric titrations

The pH titrations with LiOH, NaOH and KOH were performed by the added salt method\(^{21}\). The exchanger (0.5 g) was kept in contact with varying volumes of the base (0.1 M) and the salt solution (0.1 M) for 6 days with intermittent shaking of the bottles. pH of the supernatant liquid was measured and plotted against the volume of the base solution in each bottle.

### 4.8 Sorption studies

The distribution coefficients ($K_d$) for some of the metal ions were determined in DMW. The results are given in Table 4. The exchanger (0.2 g) was kept immersed in 20 mL of electrolyte solution containing 0.2 mM of the cation for 24 hours, with intermittent shaking. The exchanger was then filtered and cation concentration in the filtrate was determined by titrimetric method.

### 4.9 Structural studies

Structural studies like X-ray diffractograms (powder method), IR spectra and thermal analyses were carried out for the exchanger materials. X-ray diffractograms (powder method) of zirconium phosphotungstate and zirconium antimonophosphate were recorded and are shown in Figs. 3 and 4. To study structural changes accompanying the heating of the exchanger, IR spectra of zirconium antimonophosphate samples heated at various temperatures (100–700°C) were recorded and are reported in Table 5.

## 5. Results and Discussion

### 5.1 Synthesis

Zirconium oxychloride (0.1 M) in presence of hydroflu-
oric acid is known to exist as ZrF$_6^{2-}$. This solution is slowly added to a continuously stirred equimolar mixture of sodium tungstate/potassium pyroantimonate and phosphoric acid. The zirconium-fluoro complexes decompose slowly in the presence of phosphoric acid$^{22}$. In this manner, the rate of precipitation of the ion-exchangers is controlled and the materials with improved crystallinity are obtained. The gels so obtained are characterised as weakly acidic cation-exchangers by the potentiometric titrations. These titrations also indicate monofunctional behaviour of the ion-exchangers for alkali metal ions. Although, the purpose of using two heteropoly acids (phosphoric acid and tungstic acid/antimonic acid) was to introduce polyfunctionality in the ion-exchangers, yet the resulting ion-exchangers are showing monofunctionality. Similar results are reported by Nabi et al$^{23}$.

Conditions of synthesis and ion exchange characteristics like crystalline nature; ion-exchange capacity and density of the exchangers are reported in Tables 1 and 2. The materials have been checked for their reproducibility by synthesizing five different lots of each ion-exchanger, which show reproducible ion-exchange capacity within experimental errors (2–3%).

### 5.2 Ion-exchange capacity

Ion-exchange capacity of zirconium phosphotungstate for alkali metal ions increase with decrease in hydrated ionic radii indicating that the alkali metal ions move in the exchanger matrix as hydrated cations (Table 2). Clearfield$^{24}$ has also observed the dependence of the ion-exchange capacity on the size of the entering ion. Besides being a major contributing factor, size of the counter ion may not be the overall controlling factor for the magnitude of ion-exchange capacity. There may be some contribution due to the effective charge on the cation.

### 5.3 Chemical composition

Results of chemical analysis of zirconium phosphotungstate and zirconium antimonophosphate indicate that Zr:P:W molar ratio is 3:1:2 and Zr:Sb:P molar ratio is 11:1:30. Therefore, following formulae can be tentatively suggested:

\[
\begin{align*}
\text{Zr}_3\text{P}_3\text{W}_2\cdot n\text{H}_2\text{O} \\
\text{Zr}_{11}\text{P}_{30}\text{Sb}_4\cdot n\text{H}_2\text{O}
\end{align*}
\]

The number of water molecules can be estimated from the percentage loss of weight of the exchanger upto 200°C, assuming that all the external water molecules are lost at this temperature. Zirconium phosphotungstate experiences a weight loss of 13% while zirconium antimonophosphate loses 4% weight up to a temperature of 200°C. The loss of weight beyond this temperature is not considered because that could be due to irreversible condensation of the acidic groups. With this much information, the number of external water molecules can be found out by using the Alberti formula$^{25}$. Using this formula, the number of water molecules comes to be 18 for ZrWP and 10 for ZrSbP. So a tentative molecular formula for the exchangers can be written as:

\[
\begin{align*}
\text{(ZrO}_2\text{)}_3\text{(H}_3\text{PO}_4\text{)}_1\text{(H}_2\text{WO}_4\text{)}_2\cdot 18\text{H}_2\text{O} \\
\text{(ZrO}_2\text{)}_{11}\text{(H}_3\text{PO}_4\text{)}_{30}\text{(H}_3\text{SbO}_4\text{)}_4\cdot 10\text{H}_2\text{O}
\end{align*}
\]

### 5.4 Chemical stability

The ion exchangers show excellent chemical stability towards strong acids, salt solutions and organic solvents (Table 3). They have a little solubility in alkali solutions like sodium hydroxides and potassium hydroxide. Hence these ion exchangers can be used in organic and most of the aqueous media without leaching problems. Similar observations are reported by Malik et al.$^{26}$ and Nabi et al$^{23}$.

### 5.5 Thermal stability

Zirconium antimonophosphate and zirconium phosphotungstate are quite thermally stable. Weight loss of the materials heated at different temperatures was recorded and is shown in Fig. 1. There is a sharp decline in weight of zirconium antimonophosphate and zirconium phosphotungstate upto 200°C probably due to the loss of coordinated water molecules, which is supported, by a sharp decline in its ion-exchange capacity (~30%) at 200°C. It further supports the hypothesis that most of the ion-exchange capacity is due to the coordinated water molecules. A gradual loss in weight is observed for both the exchangers on heating beyond 200°C, which may be due to the reason why hydroxyl groups combine to form water molecules. Similar observations were reported by other researchers$^{23,26,27}$.

Ion-exchange capacity was determined for zirconium antimonophosphate samples heated at various temperatures from 100°C to 900°C (Fig. 2). The ion-exchange capacity decreases with increasing temperature up to 200°C, probably due to the loss of coordinated water molecules. On further heating, the hydroxyl groups of antimonate and phosphate moieties coalesce to form metal-oxygen-metal bridges (like Sb─O─Sb, Sb─O─P). It is clear from Fig. 2 that the ion-exchange capacity decreases with successive heating and becomes almost zero at 900°C when the exchanger is reduced to the elemental oxides.

### 5.6 Distribution coefficient studies (Kd values)

The distribution coefficients on zirconium antimonophosphate

(80)
sphate and zirconium tungstophosphate are reported in Table 4. Zirconium antimonophosphate shows selectivity for Ba$^{2+}$, Fe$^{2+}$ and Pb$^{2+}$ while zirconium phosphotungstate shows extra affinity for Fe$^{3+}$ ions and possesses almost negligible selectivity for alkaline earth metal ions and some of the other transition metal ions. The observed higher values of $K_d$ on ZrSbP for the divalent metal ions as compared to that of ZrPW is due to the higher H$_3$PO$_4$ content in the former resulting in an increased charge density of the ion exchanger.

Some of the possible combinations for separation of metal ions on zirconium antimonophosphate and zirconium phosphotungstate ion-exchangers are given below:

ZrSbP
i) Mg$^{2+}$-Ba$^{2+}$, Mn$^{2+}$-Ba$^{2+}$, Sr$^{2+}$-Ba$^{2+}$
ii) Zn$^{2+}$-Pb$^{2+}$, Cd$^{2+}$-Pb$^{2+}$, Fe$^{3+}$-Pb$^{2+}$
iii) Fe$^{3+}$-Fe$^{2+}$, Ni$^{2+}$-Fe$^{2+}$, Co$^{2+}$-Fe$^{2+}$, Cd$^{2+}$-Fe$^{2+}$, Zn$^{2+}$-Fe$^{2+}$, Al$^{3+}$-Fe$^{2+}$

ZrPW
Mg$^{2+}$-Fe$^{3+}$, Ca$^{2+}$-Fe$^{3+}$, Sr$^{2+}$-Fe$^{3+}$, Mn$^{2+}$-Fe$^{3+}$, Co$^{2+}$-Fe$^{3+}$, Ni$^{2+}$-Fe$^{3+}$, Cu$^{2+}$-Fe$^{3+}$, Cd$^{2+}$-Fe$^{3+}$, Pb$^{2+}$-Fe$^{3+}$, Zn$^{2+}$-Fe$^{3+}$, Al$^{3+}$-Fe$^{3+}$, Fe$^{2+}$-Fe$^{3+}$, Dy$^{3+}$-Fe$^{3+}$, Pr$^{3+}$-Fe$^{3+}$

5.7 Structural analysis
Zirconium Antimonophosphate and Zirconium Phosphotungstate: Sharp peaks in the X-ray diffractograms of zirconium antimonophosphate (Fig. 4) indicate the crystalline nature of the ion-exchanger while the diffused patterns for zirconium phosphotungstate (Fig. 3) reveal an amorphous character of the material. Preliminary analysis suggests layered type structure for ZrSbP with interlayer spacing in the range of 0.25-0.46 nm. Weak Vander waals forces hold these layers together. It also indicates a well-ordered arrangement of the polymeric functional groups connected through metal-oxygen bonds.

The assignment of absorption bands in the infrared spectrum of zirconium phosphotungstate indicates the presence of Zr–O–Zr stretching bands of medium intensity at 495 cm$^{-1}$. Sharp and strong bands at 818 cm$^{-1}$ and 1062 cm$^{-1}$ indicate the presence of WO$_4^{2-}$ and PO$_4^{3-}$ groups, respectively. The spectrum shows that water molecules, both coordinated and hydrogen bonded are present as indicated by a sharp and strong band at 1620 cm$^{-1}$ assigned as bending mode of O–H of water molecules while a broad and strong absorption band at 3365 cm$^{-1}$ corresponds to O–H stretch of coordinated water molecules.

An extensive IR analysis was done for the zirconium antimonophosphate samples heated at various temperatures from 100°C–700°C. Assignment of absorption bands for all the samples is given in Table 5. Following observations can be made from the results of IR analysis:

i) With increase in temperature from 40°C, the weak absorption band at 650 cm$^{-1}$ due to symmetric P–O stretch of PO$_4^{3-}$ is reduced to a weak shoulder band at 300°C. With further increase in temperature, this PO$_4^{3-}$ absorption band becomes prominent and regains the shape of a sharp but weak absorption band at 700°C. This indicates the reorganization of phosphate functional groups with change in temperature.

ii) A sharp and strong absorption band at 1620 cm$^{-1}$ is assigned to the bending mode of O–H of water of crystallization and is indicative of the ion-exchange capacity. The intensity of this band decreases with increase in temperature from 40°C to 700°C. Ion-exchange capacity for the heated samples strongly supports the hypothesis that coordinated water is also responsible for the ion-exchange capacity which decreases with increase in temperature.

iii) Absence of the absorption band in the range 850–950 cm$^{-1}$ corresponding to P–O–P stretch indicates that the phosphate groups are probably not present on adjacent positions and might be arranged alternately with antimonate groups.

References