

## Synthesis and Characterization of Novel Highly Crystalline Layered Nanosized Zirconium-, Hafnium-, Titanium Tellurates from Their Parent Glassy Sodium Forms via HF Solution

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**Abstract:** Glassy zirconium-, hafnium-, titanium tellurates were prepared and characterized. Found to be amorphous with vitreous visual look. Their general formulae were  $MO(HTeO_4)_2.nH_2O$  ( where  $M=Zr, Hf, Ti$ ,  $n=3.35, 3.22, 3.99$ ), respectively. Novel crystalline layered nanosized  $ZrO(HTeO_4)_2.3.72H_2O$ ,  $HfO(HTeO_4)_2.2.98H_2O$  and  $Ti(TeO_4)(HTeO_4)_2.3.89H_2O$  of high degree of crystallinity, were prepared from crystallization of their parent glassy sodium forms with HF solution in Pyrex round bottom flask. They were characterized by chemical; X-ray diffraction (XRD), thermal gravimetric analysis (TGA) and Fourier transform spectroscopy (FT-IR). Their exchange capacities were determined. We think these materials crystallized during the conversion process in two steps: 1<sup>st</sup> their parent glassy sodium forms dissolved in HF solution forming a  $M^{IV}$  Fluoride complex, 2<sup>nd</sup> the crystalline products were gradually precipitated due to HF solution action on the Pyrex flask and to a certain extent evaporation of excess HF. This will explain the formation of high degree of crystallinity of the resulting layered materials. These materials can be considered new inorganic ion exchangers, proton conductance and as solid acid catalysts.

**Keywords:** glassy, crystalline zirconium-, hafnium-, titanium tellurates.

## 1 Introduction

Tetravalent metal hydrogen tellurates are insoluble compounds with good thermal stabilities, and possess good ion exchange capacities [1,2]. To date they have been known as amorphous. Amorphous zirconium tellurate and titanium tellurate were prepared from reactions of sodium hydrogen tellurate with  $ZrOCl_2.8H_2O$ , and  $TiCl_4$  solutions, respectively [3-5]. Their composition depends on the condition under which they are precipitated.

Amorphous zirconium-, titanium -, hafnium tellurates are considered one of the acid salts of tetravalent metal tellurates. Although preparations and characterization of crystalline layered tetravalent metal phosphates in  $\alpha$ ,  $\gamma$  and  $\theta$  forms of general formulae,  $\alpha$ - $M(IV)(HPO_4)_2.H_2O$ ,  $\theta$ - $M(IV)(HPO_4)_2.5H_2O$   $\gamma$ - $M(IV).PO_4.H_2PO_4.2H_2O$ , respectively, are well established [6-8], where  $M = Ti, Zr, Hf, Ge, Sn, Ce$  ...etc. However, research in tetravalent metal tellurates still in its infancy.

Previously we have found reactions of tetravalent metal salts,  $ZrOCl_2.8H_2O$  and  $HfCl_4$ , in 3M HF with telluric acid lead to formation of low yield and low degree of crystallinity of crystalline zirconium tellurate and hafnium

tellurate [9]. In contrast reactions of  $ZrOCl_2.8H_2O$  (or  $HfCl_4$ ) in 3M HF in Pyrex round bottle flask at 10°C with 4.6M  $H_3PO_4$  led to formation of highly crystalline (2-D) layered  $\theta$ -type zirconium-, hafnium phosphates[10].

Here we are reporting the preparation and characterization of novel glassy and novel crystalline-layered zirconium-, hafnium-, titanium tellurates of high degree of crystallinity.

## 2 Materials and Methods

### 2.1 Chemicals

$ZrOCl_2.8H_2O$ ,  $TiCl_4$  (from BDH),  $HfCl_4$  (98%) (From Aldrich), Telluric acid (from Fluka chemicals), HF 40% (from Reidel-DeHaen). Other chemicals used were of analytical grade.

### 2.2 Instruments used for characterization

X-Ray powder diffractometry Philips, using Ni-filtered  $CuK\alpha$  ( $\lambda = 1.54056\text{\AA}$ ), TG/DTA Analyzer model SIIExtra6000- 6300, Fourier Transform IR Spectrometer,

model IFS 25 FTIR Bruker, pH Meter GWG 52.

### 2.3 Preparation of glassy zirconium tellurate, $ZrO(HTeO_4)_2 \cdot 3.35H_2O$

11.2grams of telluric acid,  $H_2TeO_4 \cdot 2H_2O$ , was dissolved in 75 ml of distilled water, warmed up to 50°C. To that 80 ml of 0.5M  $ZrOCl_2 \cdot 8H_2O$  in 4M acetic acid was gradually added drop wise with constant stirring. Then the pH of the mixture was adjusted to pH 3 with 1.0M NaOH, the resultant gelatinous precipitate kept aged in mother liqueur for two hours, then diluted with distilled water up to 500 total volume with hot distilled water, then left to age at room temperature for 24h. The resultant precipitate was filtered, washed with distilled water, dried at 65°C. The resultant solid was cracked with distilled water, filtered and left to dry in air.

### 2.4 Preparation of glassy titanium tellurate, $TiO(HTeO_4)_2 \cdot 3.99H_2O$

6.3grams of telluric acid,  $H_2TeO_4 \cdot 2H_2O$ , was dissolved in 75 ml of distilled water, warmed up to 50°C. To that 80 ml of 0.5M  $TiCl_4$  in 4M acetic acid was gradually added drop wise with constant stirring. The pH of the mixture was adjusted to pH 3 with 1.0M NaOH, the resultant gelatinous precipitate kept aged in mother liqueur for two hours, then diluted with distilled water up to 500 total volume with hot distilled water, then left to age at room temperature for 24h. The resultant precipitate was filtered, washed with distilled water, dried at 65°C. The resultant solid was cracked with distilled water, filtered and left to dry in air.

### 2.5 Preparation of glassy hafnium tellurate, $HfO(HTeO_4)_2 \cdot 3.22H_2O$

6.0grams of telluric acid,  $H_2TeO_4 \cdot 2H_2O$ , was dissolved in 100 ml of distilled water, warmed up to 50°C. To that, 3.0g  $HfCl_4$  in 25ml 4M acetic acid was gradually added drop wise with constant stirring. The pH of the mixture was adjusted to pH 3 with 1.0M NaOH, the resultant gelatinous precipitate kept aged in mother liqueur for two hours, then diluted with distilled water up to 300ml total volume with hot distilled water, then left to age at room temperature for 24h. The resultant precipitate was filtered, washed with distilled water, dried at 65°C. The resultant solid was cracked with distilled water, filtered and left to dry in air.

### 2.6 Preparation of sodium forms of glassy zirconium-, titanium-, hafnium tellurates

Typically; 2.0grams of each of the resultant glassy tellurate were treated with 400 ml of 0.1M NaCl, stirred vigorously for one hour, then 0.1M NaOH solution was added to adjust the pH of the solution up to pH=8. The resultant product was filtered washed with distilled water to

pH =3.5, and left to dry in air.

### 2.7 Crystallization of glassy $M^{IV}$ tellurates sodium forms, $M=Zr, Hf, Ti$

#### 2.7.1 Crystallization of glassy zirconium tellurate sodium form

1.5grams of glassy zirconium tellurate sodium form was dissolved in 15 ml 7MHF aqueous solution in plastic bottle at room temperature ( $25^\circ C \pm 2^\circ C$ ), to obtain clear solution. The resultant clear solution was transferred in 100 ml Pyrex round bottom flask, kept at room temperature for 4 days, then heated at 60°C for 4hrs. The resultant precipitate was filtered, washed with distilled water and left to dry in air.

#### 2.7.2 Crystallization of glassy titanium tellurate sodium form

1.5grams of glassy titanium tellurate sodium form was dissolved in 15ml 6MHF aqueous solution in plastic bottle at room temperature ( $25^\circ C \pm 2^\circ C$ ), to obtain clear solution. The resultant solution was transferred in 100 ml Pyrex round bottom flask, kept at room temperature for 4 days, then heated at 60°C for 4hrs. The resultant precipitate was filtered, washed with distilled water and left to dry in air.

#### 2.7.3 Crystallization of glassy hafnium tellurate sodium form

1.5grams of glassy hafnium tellurate sodium form was dissolved in 15ml 7MHF aqueous solution in plastic bottle at room temperature ( $25^\circ C \pm 2^\circ C$ ), to obtain clear solution. The resultant solution was transferred in 100 ml Pyrex round bottom flask, kept at room temperature for 4 days, then heated at 60°C for 4hrs. The resultant precipitate was filtered, washed with distilled water and left to dry in air.

### 2.8 Exchange capacity determination

To 0.1g, of each of the resultant glassy and layered crystalline zirconium-, hafnium-, titanium tellurates, 20 ml of 0.1M NaCl were added, stirred vigorously for one hour, then titrated with 0.1M NaOH.

### 2.9 Thermal analysis

Thermal analyses for the resultant materials were carried out under atmospheric condition, at rate of 10°C/min.

## 3 Results and Discussion

Glassy zirconium-, hafnium-, titanium tellurates,  $ZrO(HTeO_4)_2 \cdot 3.35H_2O$ ,  $HfO(HTeO_4)_2 \cdot 3.22H_2O$  and  $TiO(HTeO_4)_2 \cdot 3.99H_2O$ , were prepared and characterized by chemical, X-ray diffraction (XRD), thermal gravimetric

analysis (TGA) and Fourier transform spectroscopy (FT-IR). Found to be amorphous with vitreous visual look.

### 3.1 XRD of resultant glassy tellurates

The resultant glassy tellurates found to be amorphous with vitreous look. Figure 1 shows typical XRD pattern of the glassy  $M^{IV}$  tellurates.

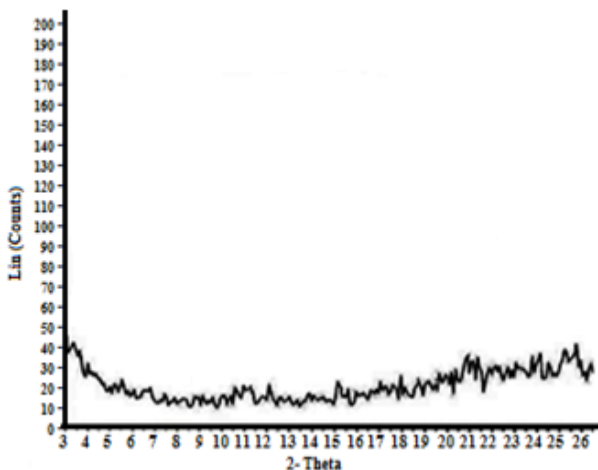


Fig 1: Typical XRD of glassy  $M^{IV}$  tellurates.

### 3.2 FT-IR spectrum of the resultant glassy tellurates

FT-IR spectra of the resultant glassy tellurates have been investigated, and found to follow the same trend. Figures 2 shows FT-IR spectrum of  $ZrO(HTeO_4)_2 \cdot 3.35H_2O$ , represents typical FT-IR spectra of amorphous  $M^{IV}$  tellurates. Broadband centered at  $3300\text{ cm}^{-1}$  which is due to OH-symmetric and asymmetric stretching of  $H_2O$ . Medium band at  $1625\text{ cm}^{-1}$  attributed to H-O-H bending, Band in the region  $1000\text{ cm}^{-1}$  correspond to different (in plane and out-of-plane deformation modes of Te-OH), strong bands at  $750\text{ cm}^{-1}$  and at  $500\text{ cm}^{-1}$ , attributed to  $HTeO_4$  and Te-O, respectively [4].

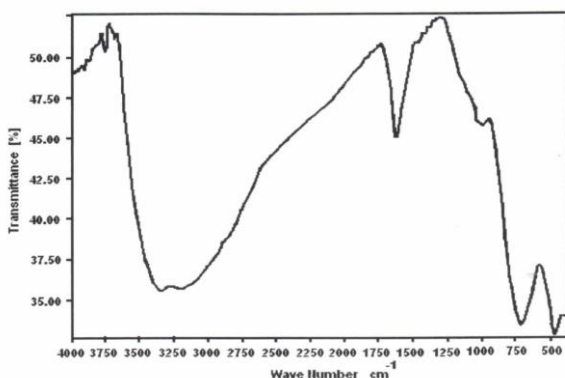


Fig 2: FT-IR spectrum of  $ZrO(HTeO_4)_2 \cdot 3.35H_2O$ .

### 3.3 TGA of the resultant glassy $M^{IV}$ tellurates

Thermal gravimetric analysis, TGA, is a good tool for characterization of tetravalent metal phosphates and tetravalent metal tellurates [3-5], where at high temperature combustion the final product is  $M^{IV}$  pyrophosphate ( $M^{IV}P_2O_7$ ), in case of  $M^{IV}$  phosphates, while in case of  $M^{IV}$  tellurates the final products are ( $M^{IV}O_2$ ) and  $Te_2O_6$ .

Figures (3-5) show the thermograms, TG/DTA, of the resultant glassy zirconium-, titanium and hafnium tellurates.

TG/DTA of glassy zirconium tellurate is given in Figure 3, Its DTA indicates three endothermic process accompanied with weight loss. The thermal decomposition found to occur in two stages. The final products were  $ZrO_2 \cdot Te_2O_6$ . The total weight loss found to be 19.96%, accordingly it was formulated as  $ZrO(HTeO_4)_2 \cdot 3.35H_2O$ .

TG/DTA of glassy titanium tellurate is given in Figure 4 Its DTA indicates two endothermic peaks accompanied with weight loss. The thermal decomposition found to occur in two stages. The final products were  $TiO_2 \cdot Te_2O_6$ . The total weight loss found to be 20.99%, accordingly it was formulated as  $TiO(HTeO_4)_2 \cdot 3.99H_2O$ .

TG/DTA of glassy hafnium tellurate is given in Figure 5. Its DTA indicates two endothermic peaks accompanied with weight loss. The thermal decomposition found to occur in three stages. The final products were  $HfO_2 \cdot Te_2O_6$ . The total weight loss found to be 24 %, accordingly it was formulated as  $HfO(HTeO_4)_2 \cdot 3.22H_2O$ .

Schematic representation of thermal behavior of glassy  $M^{IV}$  tellurates (where  $M = Zr, Hf, Ti$ ) as follows:

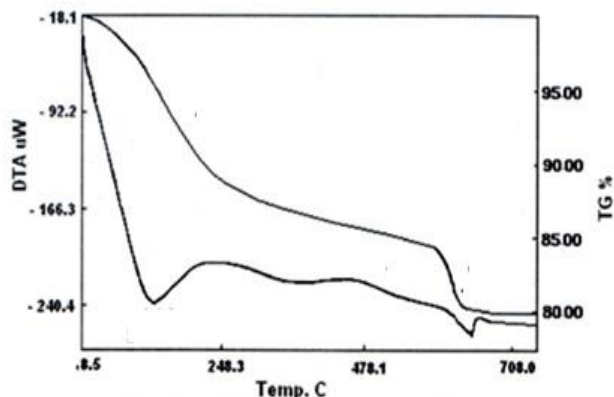
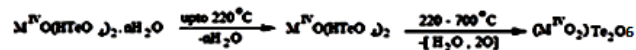


Fig 3: TG/DTA of glassy  $ZrO(HTeO_4)_2 \cdot 3.35H_2O$ .

Novel crystalline layered nanosized  $ZrO(HTeO_4)_2 \cdot 3.72H_2O$ ,  $HfO(HTeO_4)_2 \cdot 2.98H_2O$ , and  $Ti(TeO_4)(HTeO_4)_2 \cdot 3.89H_2O$  of high yield and high degree of crystallinity were prepared from conversion of their

parent glassy sodium forms with HF solution . They were characterized by chemical, X-ray diffraction(XRD), thermal gravimetric analysis (TGA) and Fourier transform spectroscopy ( FT-IR).

From thermal gravimetric analysis (TG/DTA), (using standard references: crystalline  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, and glassy ZrO(HTeO<sub>4</sub>)<sub>2</sub> .3.35 H<sub>2</sub>O as standard samples) . Their water content loss , occurs up to 220°C, found to be equal to(10.63, 9.7 and 10.1% in wt), respectively. The thermal behaviour found to follow the same thermal decomposition trend of M<sup>iv</sup> tellurates [4].

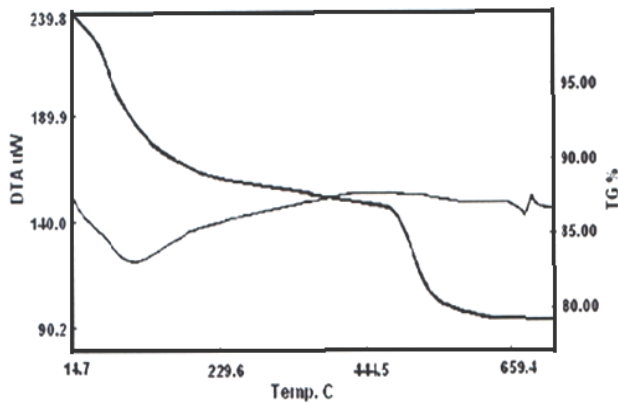


Fig 4: TG/DTA of glassy TiO(HTeO<sub>4</sub>)<sub>2</sub> . 3.99H<sub>2</sub>O.

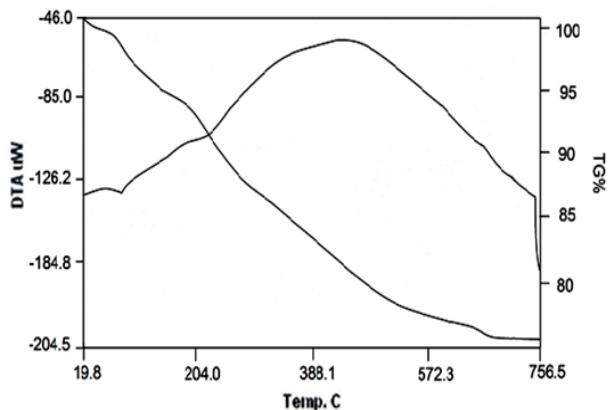


Fig 5 : TG/DTA of glassy HfO(HTeO<sub>4</sub>)<sub>2</sub> .3.22H<sub>2</sub>O.

### 3.4 XRD of the resultant nanosized crystalline layered M<sup>iv</sup>tellurates

Figures (6-8) show X-ray diffractogram patterns of the resultant novel crystalline layered M<sup>iv</sup>O(HPO<sub>4</sub>)<sub>2</sub>.nH<sub>2</sub>O (where M= Zr, Hf) and  $\gamma$ -Ti(TeO<sub>4</sub>)(HTeO<sub>4</sub>)<sub>2</sub> .3.2H<sub>2</sub>O, that were obtained from conversion of their parent glassy sodium forms via HF solution. Evaluation of the X-ray peaks of crystalline layered ZrO(HTeO<sub>4</sub>)<sub>2</sub> .3.72H<sub>2</sub>O and HfO(HTeO<sub>4</sub>)<sub>2</sub> .2.98H<sub>2</sub>O based on the position of the first peaks (Figures 6, 7) showed that they are similar to two dimensional crystalline  $\alpha$ - layered type structure of tetravalent metal phosphates, i.e follow the same trend of layered  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O structure . The materials show

high degree of crystallinity, as is represented by the intensity of the peaks. Both show almost the same degree of crystallinity. Their interlayer space found to be 7.91 Å and 8.01 Å, respectively. From their X-ray diffractogram patterns we can conclude that these two materials are isostructural.

The average diameter of crystalline  $\alpha$ - layered type structure ZrO(HTeO<sub>4</sub>)<sub>2</sub>.3.72H<sub>2</sub>O and HfO(HTeO<sub>4</sub>)<sub>2</sub>.2.98H<sub>2</sub>O found to be 23.92 nm , and 40.60 nm, respectively, which was calculated from the full width at half maximum of the peak using Scherer's equation:

$$D = \frac{0.9\lambda}{\beta \cos 2\theta_{\text{maxima}}}$$

Where **D** is the average crystal size in nm,  $\lambda$  is the characteristic wave length of x-ray used ( $\lambda=1.54056 \text{ \AA}$ ),  $\theta$  is the diffraction angle , and the  $\beta 2\theta$  is the angular width in the radius at intensity equal to half of the maximum peak intensity [11].

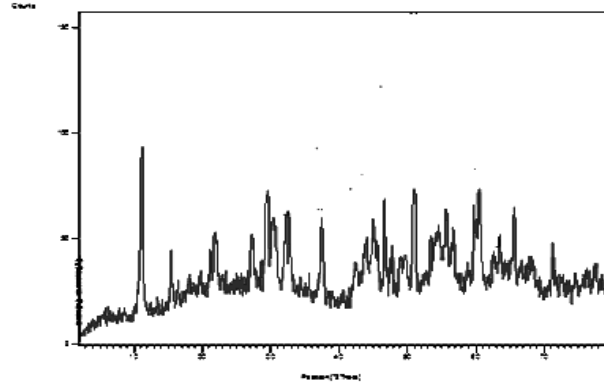


Fig 6: XRD of crystalline zirconium tellurate.

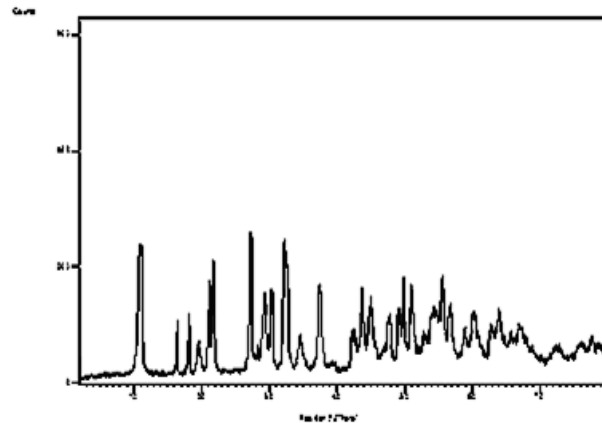


Fig 7: XRD of crystalline hafnium tellurate.

Figure 8 shows X-ray diffractogram pattern of the resultant novel crystalline layered titanium tellurate. Its interlayer space found to be 11.82 Å. Accordingly its structure was proposed as  $\gamma$ -Ti(TeO<sub>4</sub>)(HTeO<sub>4</sub>)<sub>2</sub> .3.89H<sub>2</sub>O.

The average diameter of proposed crystalline  $\gamma$ -Ti(TeO<sub>4</sub>)(HTeO<sub>4</sub>)<sub>2</sub> · 3.89H<sub>2</sub>O. was found to be equal to 33.75 nm, which was calculated from the full width at half maximum of the peak using Scherer's equation[11].

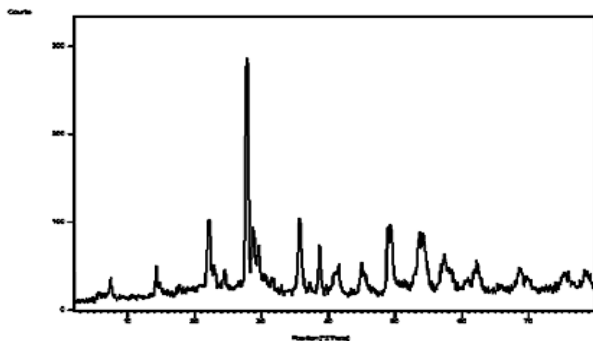


Fig 8: XRD of crystalline titanium tellurate.

### 3.5 FT-IR spectrum of the resultant crystalline layered M<sup>IV</sup>tellurates

FT-IR spectra of the resultant crystalline layered zirconium-, hafnium tellurates (Figures 9,10). Exhibit broadband centered at 3270 cm<sup>-1</sup> that is due to OH-symmetric and asymmetric stretching of H<sub>2</sub>O. Medium band at 1623 cm<sup>-1</sup> was assigned to H-O-H bending. Band at 1180 cm<sup>-1</sup> correspond to different (in plane and out-of-plane deformation modes of (Te-OH)). Bands at the regions 750 -500 cm<sup>-1</sup> were attributed to, HTeO<sub>4</sub> and Te-O , respectively[4].

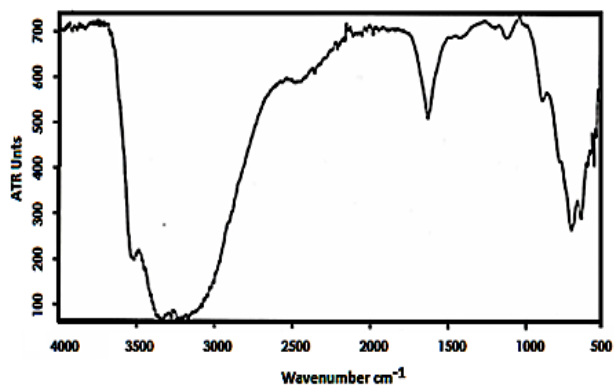


Fig 9: FT-IR spectrum of crystalline zirconium tellurate.

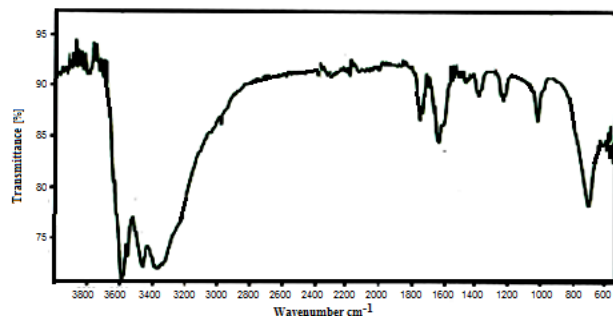


Fig 10: FT-IR spectrum of crystalline hafnium tellurate.

FT-IR spectrum of the resultant crystalline-layered titanium tellurate (Figure 11) exhibit broadband centered at 3350 cm<sup>-1</sup> which is due to OH-symmetric and asymmetric stretching of H<sub>2</sub>O. Medium band at 1610 cm<sup>-1</sup> was related to H-O-H bending. Bands at 1070 cm<sup>-1</sup>, 1000 cm<sup>-1</sup> correspond to different (in plane and out-of-plane deformation modes of (Te-OH)). Bands in the region 800-590 cm<sup>-1</sup> can be attributed to HTeO<sub>4</sub> and Te-O, respectively [4].

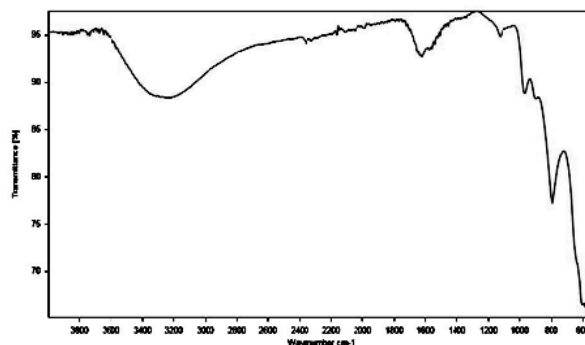


Fig 11: FT-IR spectrum of crystalline titanium tellurate.

### 3.6 Exchange capacities

Exchange capacities of resultant glassy tellurates found to be equal to 3.62, 3.22, 3.84. Meq/g, respectively. For crystalline layered tellurates found to be equal to 3.57, 3.24, 3.0 Meq/g, respectively. The data of the exchange capacities were obtained from sodium ion titration curves of the resultant M<sup>IV</sup> tellurate, that were obtained from addition of 0.1M NaCl solution to the materials , followed by titration with 0.1 MNaOH up to pH=10.5.

## 4 Conclusion

This is first report about novel crystalline-layered tetravalent metal tellurates. These materials were synthesized from their novel parent glassy sodium forms. It is proposed that the chemical structure of crystalline-layered zirconium-, hafnium tellurates is similar to two-dimensional structure of crystalline  $\alpha$ - layered tetravalent metal phosphates, while the resultant crystalline titanium tellurate was proposed of  $\gamma$ -type structure . We think these materials crystallized during the conversion process in two steps: 1<sup>st</sup> their parent glassy sodium forms dissolved in HF solution forming HF complex, 2<sup>nd</sup> the crystalline products were gradually precipitated due to HF solution action on the Pyrex flask and to a certain extent evaporation of excess HF.

This will explain the formation of high degree of crystallinity of the resulting layered materials. The average diameter of two dimensional crystalline ZrO(HTeO<sub>4</sub>)<sub>2</sub> · 3.72H<sub>2</sub>O and HfO(HTeO<sub>4</sub>)<sub>2</sub> · 2.98H<sub>2</sub>O , and  $\gamma$ -Ti(TeO<sub>4</sub>)(HTeO<sub>4</sub>)<sub>2</sub> · 3.89H<sub>2</sub>O , found to be 23.92 nm , 40.60 nm and 33.75 nm, respectively, that was calculated from the full width at half maximum of the peak using Scherer's

equation. These materials can be considered new inorganic ion exchangers, proton conductance and as solid acid catalysts.

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