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Facile room temperature ion exchange synthesis of H⁺ doped KM_{0.33}Te_{1.67}O₆ (M = AI, Cr and Fe) and their photocatalytic and conductivity studies

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ABSTRACT

Materials belonging to defect pyrochlore structure have been the subject of considerable interest and expected to exhibit fast protonic conduction. The proton exchanged ternary metal oxides of composition $HM_{0.33}Te_{1.67}O_6$ (M = Al, Cr and Fe) are prepared for the first time by ion exchange method at room temperature. These materials are characterized by X-ray Diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), UV-vis diffuse reflectance spectroscopy (UV-vis DRS) and solid state NMR techniques. All the materials are crystallized in a cubic lattice with the $Fd\bar{3}m$ space group. Photocatalytic activity against methyl violet (MV) degradation under visible light irradiation is studied. The mechanistic degradation pathway of MV is studied by a fluorescence technique using terepthalic acid (TA) as a probe and Tertiary butanol (TB) as hydroxyl radical quencher. The dc conductivity of all three compositions is studied in the temperature range 300 – 673 K. The variation of dc conductivity with temperature is explained. Copyright © 2016 VBRI Press.

Keywords: Defect pyrochlore; ion exchange; sold state NMR; photodegradation; conductivity.

Introduction

In recent years, the search for multi-functional materials has been the subject of considerable interest in the energy and environmental fields. Material preparation and characterization are key stages in their development. It is well known that the particle size, morphology, surface area and phase purity of the materials influence their physical and chemical properties considerably. These properties of the materials can be tailored to suit the desired application. The catalytic and conducting properties of some of the binary and ternary metal oxides have been increased by cation / anion doping [1-5]. It is established that semiconductor mediated photocatalysis, one of the advanced oxidation process, has the potentiality to generate hydrogen through splitting of water [6-8]. Proton conducting ternary oxides have gained technological importance due to their prospective applications such as a sensor for hydrogen and humidity or as a solid electrolyte for hydrogen fuel cells and steam electrolysis. Ternary oxides belonging to pyrochlore family exhibit considerable ionic conductivity due to the presence of interconnecting channels present in the three dimensional skeletal structure [9 -11].

The general formula of pyrochlore is $A_2B_2O_6O'$ and its structure can be described as the interpenetrating networks of the B_2O_6 skeleton of BO_6 octahedra and A-O' chains of formula A_2O' [12]. The weak interactions between B_2O_6 network and A_2O' chains lead to vacancies in the latter. The vacancies at A and O' sites in the A_2O' chains has led to the formation of "defect pyrochlores" of composition, AB_2O_6 . The structure of AB_2O_6 , is built up of corner sharing BO₆ octahedra creating networks of hexagonal B₂O₆ tunnels. The "A" ions are present in these tunnels and can be easily exchanged. The mobility of A cations through the interconnecting channels in three dimensions is allowed. Thus, these oxides exhibit good ionic conductivity with negligible electronic contribution. Further, H⁺ doped defect pyrochlores show relatively high ionic / proton conductivity due to the high mobility of H⁺ ions through the whole structure because of its smaller ionic radius [13-14]. Of all the existing defect pyrochlores, $H_3OSbTeO_6$ shows proton conductivity of 10^{-1} S cm⁻¹ at 30 °C [15]. However, studies pertaining to the photocatalytic studies of protonated defect pyrochlore oxides are very scanty [8, 16]. In the present investigation, we report the preparation of H⁺ doped $KM_{0.33}Te_{1.67}O_6$, (M = Al, Cr and Fe) by employing a facile ion exchange method and their photocatalytic and conductivity studies, which to our knowledge is not reported so far.

Experimental

Material synthesis

The defect pyrochlores of composition $KM_{0.33}Te_{1.67}O_6$ (KMTO) (M = Al, Cr and Fe) are obtained by conventional solid state method as reported earlier [16]. The protonated defect pyrochlores, HMTO (M = Al, Cr and Fe) are

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obtained by ion exchange method. The preparation of $HAl_{0.33}Te_{1.67}O_6$ is as follows: 1 g of $KAl_{0.33}Te_{1.67}O_6$ (KATO) is added to 100 mL of 5M concentrated hydrochloric acid at room temperature and constantly stirred for 48 h. The resultant material is filtered off and dried. Here after, the material is designated as HATO. To confirm the exchange of potassium by H⁺, the supernatant liquid is evaporated and resultant powder (byproduct) is subjected to powder XRD. Similar procedure is followed to synthesize $HCr_{0.33}Te_{1.67}O_6$ (HCTO) and $HFe_{0.33}Te_{1.67}O_6$ (HFTO). All the protonated samples show color difference compared to their respective parent samples (**Fig. 1**).



Fig. 1. (a) powder XRD patterns of KMTO and HMTO (M=Al, Cr and Fe), (b) expanded XRD patterns, (c) Powder XRD pattern of KCl and (d) colors of KMTO and HMTO.

Characterization

The room temperature powder X-ray diffractograms are recorded using Rigaku miniplex powder X-ray diffractometer (Cu K α , $\lambda = 1.5406$ Å) in the 20 range 10 - 80° for phase confirmation. Infrared spectra are recorded in the form of KBr pellets in the wave number range 4000 – 400 cm⁻¹ using JASCO IR-5300 spectrometer. The room temperature ¹H solid-state MAS NMR spectra are recorded with a Bruker MSL-300 MHz solid-state high-resolution spectrometer operating at 121.49 MHz with a 10 kHz spinning speed. SEM images of all the materials are recorded on the HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM), JASCO V650. UV-vis spectrophotometer is used for UV-vis diffuse reflectance spectral (DRS) measurements in the range 200 – 800 nm. BaSO₄ is used as the reflectance standard.

Photocatalytic activity

The photocatalytic activity of HMTO is evaluated by photodegradation of methyl violet (MV) under visible light irradiation using HEBER visible annular type photo reactor equipped with a 300 watts W lamp (wavelength range: 380-840 nm). In a typical process, 50 mL of aqueous MV

solution with an initial concentration of 1×10^{-5} M and 50 mg of catalyst are taken in a cylindrical-shaped glass reactor at room temperature in air. The suspension is stirred in the dark for 60 min to establish adsorption - desorption equilibrium before irradiation. At regular time intervals of 30 min, about 2 - 3 mL of the solution is collected and centrifuged to remove the catalyst particles. The change in the concentration of MV is obtained by recording the absorbance at 580 nm using JASCO V650 UV-vis spectrophotometer. The amount of degradation is reported as C/C_{eq} where, C is the concentration of MV at each irradiated time and C_{eq} is the concentration of MV when adsorption-desorption equilibrium is achieved.

The formation of OH^{\bullet} radicals during photo-catalysis under visible light irradiation is followed by the measurement of fluorescence intensity. Typically, 50 mg of sample is suspended into 50 mL of a 0.02 mol L⁻¹ NaOH solution containing 3 mM terephthalic acid (TA). The suspension is stirred in the dark for 60 min before visible light (300 W tungsten lamp) illumination. Then, 2-3 mL of the suspension is taken out at 60 min intervals, filtered and recorded fluorescence spectra using Shimadzu RF-5301PC fluorescence spectrophotometer. The photo-generated OH[•] radicals react with TA to form 2-hydroxy terephthalic acid (TAOH), which shows a characteristic fluorescence band centered at 425 nm. The increase in the fluorescence intensity of TAOH is directly proportional to the concentration of photo-generated OH^{\bullet} radicals. The excitation wavelength is fixed at 320 nm.

DC conductivity

The DC conductivity measurements of HATO, HCTO and HFTO, are carried out in the temperature range 300–673 K by conventional two probe method on the sintered pellets (10 mm in diameter) coated with silver paint. A Keithley Electrometer 6485C is used to measure the current.

Results and discussion

XRD analysis

Parent $KM_{0.33}Te_{1.67}O_6$ and $HM_{0.33}Te_{1.67}O_6$, (M = Al, Cr and Fe) are prepared by solid state and ion exchange methods respectively. Fig. 1a shows room temperature XRD patterns of parent (KMTO) and proton substituted samples (HMTO). The d-lines of HATO, HCTO and HFTO are free from impurities, similar to each other and comparable with their parent oxides [16]. The powder patterns of HMTO show a systematic shift in the position of d-lines to lower angle compared to their parent oxides when plotted in an expanded scale (Fig. 1b). A shift in d-lines towards lower 2θ indicates expansion of unit cell volume. The similarity of KMTO and HMTO patterns shows that the lattice is undisturbed upon the substitution of K⁺ by H⁺. The unit cell parameters of HATO, HCTO and HFTO are refined by least square fitting the powder data using POWD software. It is observed that all the samples are crystallized in a cubic lattice with space group $Fd\bar{3}m$. The unit cell parameters and lattice volumes of all the samples are given in Table S1.

The unit cell parameters of HMTO increases slightly than that of KMTO. Since the ionic radius of H^+ is lower than

 K^+ , replacement of K^+ by H^+ is expected to shrink the unit cell. The observed expansion of lattice indicates that, in addition to H^+ , solvent water molecules might have entered into the pyrochlore lattice. The presence of water in HMTO samples is confirmed from FT-IR and NMR studies given in next sections. Further, the powder XRD result of the byproduct is consistent with the powder pattern of KCl (JCPDF: 893619) (**Fig. 1c**). Thus, the formation of KCl as byproduct and change in color of samples stands the



Fig. 2. FT-IR spectra of KMTO and HMTO (M = Al, Cr and Fe).

FT-IR analysis

The presence of water and OH groups in HMTO (M = AI), Cr and Fe) is verified from FT-IR spectra. Fig. 2 shows the infrared spectra of KMTO and HMTO (M = Al, Cr and Fe) in the 400 - 4000 cm⁻¹region. The FTIR spectrum of KMTO exhibits bands at around 500 cm⁻¹ and 800 cm⁻¹, region which can be attributed to the vibrational modes of $(M/Te)O_6$ octahedra in defect pyrochlore lattice [17]. The IR spectrum of HMTO differs from that of KMTO in two ways. First, the observed bands for HMTO are broad in nature and second, the new bands have appeared in the range 1000-4000 cm⁻¹. These two differences are endorsing the substitution of protonic species into the pyrochlore lattice. The new bands observed in HMTO around 1130, 1625 and 3500 cm⁻¹ region are due to the presence of protonic species in the form of H₂O and OH groups. The broad and sharp absorption bands around 3500 cm⁻¹ and 1625 cm⁻¹ are due to the stretching and bending modes of water, respectively. The absorption band around 1130 cm⁻¹ can be attributed to the M/Te-OH bending mode [17-19]. The observed spectra are similar to those reported for HNbWO₆ H₂O [17]. Thus, we conclude that HATO, HCTO and HFTO have both the hydroxyl (OH⁻) and hydrate (H₂O) protons. These results are further substantiated by ¹H MAS NMR results given below.

NMR analysis

Proton MAS-NMR is used to establish the presence of different protonic species such as OH^- , H_2O and H_3O^+ in defect pyrochlore structures of HATO, HCTO and HFTO. These species can be distinguished on the basis of their

characteristic chemical shift values. The ¹H MAS NMR spectra of HATO, HCTO and HFTO are shown in **Fig. 3**. Each spectrum is characterized by two peaks, in the 4 - 8.5 ppm range, indicating the presence of two types of protons in their lattice. It is reported that the chemical shifts for protons of H₂O and OH⁻ fall in the region of 5 - 8 ppm and that of H₃O⁺, in the 10.5 - 12 ppm range [**13, 20**]. Therefore, the two signals observed in the region 4 - 8.5 ppm can be assigned to the protons of H₂O and OH⁻. All the three compositions do not possess free H₃O⁺ species in their lattices as the NMR signal in the 10.5 - 12 ppm range is not observed.





Fig. 3. ¹H solid state NMR spectra of HATO, HCTO and HFTO.

Fig. S1 shows the ²⁷Al MAS NMR spectra of KATO and HATO samples. Both samples gave a single peak at $\delta \approx -2.6$ ppm indicating only one type of chemical environment for trivalent aluminium in the lattice. McKenzie and Smith have reported that the chemical shift values for ²⁷Al are very sensitive to its coordination number [21]. The chemical shift values for ²⁷Al in octahedral (AlO₆) and tetrahedral (AlO₄) coordinations are found to be in the -5 to 15 and 60 to 90 ppm range, respectively [21]. In the present investigation, the NMR signal at $\delta \approx -2.6$ ppm can be attributed to AlO₆octahedra in KATO and HATO defect pyrochlore structures. The chemical shift values of the KATO and HATO are close to each other. Thus, the chemical environment of AlO₆ is not altered upon the substitution of K⁺ by H⁺.

SEM - EDS

Scanning electron microscopy (SEM) images are taken for morphological characterization of protonated samples, HATO, HCTO and HFTO and shown in **Fig. S2**. These samples are characterized by irregular octahedral shape with considerable aggregation. There is no considerable change in the morphology of HMTO compared to its parent KMTO (M = Al, Cr and Fe). The complete replacement of potassium by protons in KMTO lattice is substantiated by recording their energy dispersive spectra (EDS). **Fig. 4** shows the EDS of KMTO and HMTO samples. The absence of K peaks in EDS of HMTO (M=Al, Cr and Fe) indicate the complete exchange of K⁺ by H⁺ ions. Hence, the molecular formulas of HMTO (M=Al, Cr and Fe) can be written as $HAl_{0.33}Te_{1.67}O_{6.} xH_2O$, $HCr_{0.33}Te_{1.67}O_{6.} yH_2O$ and $HFe_{0.33}Te_{1.67}O_{6.} zH_2O$ respectively.



Fig. 4. EDS of KMTO and HMTO (M = Al, Cr and Fe).

UV-vis DRS analysis

The optical properties of HATO, HCTO and HFTO are studied by UV-visible diffuse reflectance spectroscopy to examine the effect of proton doping in the KATO, KCTO and KFTO lattices. **Fig. S3** shows the absorbance versus wavelength plots of HATO, HCTO and HFTO. It is observed that the absorption edges of protonated samples have been blue shifted by about 10-50 nm compared to their parent materials [16] and it is supported by change in color and optical properties. The bandgap energy (E_g) of HMTO samples is obtained from Kubelka-Munk (KM = (Khv)^{1/2}) vs hv plots (**Fig. S3, inset**) [16]. It is found to be 2.18, 1.32 and 2 eV for HATO, HCTO and HFTO, respectively. The introduction of proton into KMTO lattice increases the bandgap energy marginally.

Photocatalytic activity studies

The photocatalytic activity of HMTO (M = AI, Cr and Fe) is examined by the degradation of MV under the visible light irradiation. The temporal change in MV concentration with irradiation time in the absence and presence of HATO, HCTO and HFTO is shown in **Fig. 5a.** The decolorization of MV increases with an increase in the irradiation time. It is noticed that MV undergoes degradation to the extent of 10% in the absence of the catalyst which may be due to the photolysis. However, in the presence of catalyst, the degradation of MV is about 84 %, 80 % and 82 % for HATO, HCTO and HFTO respectively, after 180 min of visible light irradiation. A comparison of photocatalytic activity of HMTO with that of KMTO is worth mentioning.

The degradation of MV in the presence of KATO, KCTO and KFTO is 51 %, 43% and 45 % respectively under identical experimental conditions [16]. Thus, in the present investigation, HMTO shows higher photocatalytic activity against MV degradation compared to their parent materials.

The photocatalytic degradation of organic dyes in the presence of semiconducting materials is initiated by the photogenerated electrons and holes which subsequently generate free radicals such as OH^{\bullet} and $O_2^{\bullet-}$. The degradation rate is directly proportional to the probability of the formation of these radicals on the catalyst surface and their reaction with the dye molecules [22]. The generation of hydroxyl radicals during the MV degradation process in the presence of HATO has been determined experimentally using tertiary butanol (TB) as hydroxyl radical quencher [23-24]. The photodegradation of MV is carried out by adding 2 ml of TB in the presence of HATO under identical conditions. The photocatalytic performance of HATO is inhibited for the first 30 min of irradiation by addition of TB, but subsequently degraded the dye about 36 % in 180 min of irradiation (Fig. 5b). Therefore, in addition to OH^{\bullet} , other radical species are also participating in the dye degradation. The possible MV degradation process using HATO, HCTO and HFTO photocatalysts is shown below:

$$HATO / HCTO / HFTO + hv \rightarrow e_{CB}^{-} + h_{VB}^{+}$$

$$H_2O + h_{VB}^{+} \rightarrow OH^{\bullet} + H^{+}$$

$$O_2 + e_{CB}^{-} \rightarrow O_2^{\bullet-}$$

$$O_2^{\bullet-} + H^{+} \rightarrow HO_2^{\bullet}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \rightarrow 2OH^{\bullet}$$

$$HO_2^{\bullet} \text{ or } O_2^{\bullet-} \text{ or } OH^{\bullet} + MV \rightarrow Byproducts$$

The participation of OH^{\bullet} in the photodegradation process of MV is further substantiated by a fluorescence

technique using TA as a probe. The OH^{\bullet} species react with TA to give 2-hydroxyterephthalic acid (TAOH) which exhibits characteristic fluorescence signal at 426 nm. **Fig. 5c** shows the fluorescence intensity at 426 nm of TA solution in the presence of HATO at regular time intervals of visible light irradiation. The escalation in fluorescence intensity with the rise in visible light irradiation time is observed. Higher emission intensity signals at 426 nm for

HATO catalyst indicates higher concentration of OH^{\bullet} (or formation of TAOH) compared to KATO [25]. The photocatalytic efficiency of the catalyst to degrade the organic dyes is proportional to the extent of formation of

active OH^{\bullet} radicals during the irradiation process [22]. Thus, the higher photoactivity of HATO than KATO can be attributed to this fact. Estimating the durability and reusability of a catalyst is essential for evaluating its practical and commercial applications. Therefore, the photodecomposition of MV is carried out using the same

catalyst three times. After the first cycle, the catalyst is separated and the same is used for the fresh batch of MV solution and irradiated for 180 min of visible light. The same procedure is adopted for the third cycle. These cyclic experiments are repeated for all the three catalysts. The results are shown in **Fig. 5d**. It is observed that all the catalysts retain their activity up to at least three cycles and are not photocorroded. Thus, HMTO may be considered as a potential photocatalyst for industrial waste/pollutant purification.



Fig. 5. (a) Photocatalytic degradation of MV in presence of HATO, HCTO and HFTO, (b) Photocatalytic degradation of MV in the presence of HATO with TB and without TB, (c) Fluorescence spectra of visible-light irradiated HATO suspensions in 3 mM TA ($\lambda_{excitation} = 320$ nm) at different time intervals and (d) Cyclic runs in photocatalytic degradation of MV in the presence of HATO, HCTO and HFTO.

Conductivity study

The DC conductivity of HATO, HCTO and HFTO is studied in the temperature region 300 – 673 K. The variation of conductivity with temperature is shown in **Fig. 6**. At low temperature the conductivity of HMTO initially decreases up to 373 K thereafter the conductivity increases with temperature (**Fig. 6**, **inset**). The decrease in conductivity at low temperature region corresponds to dehydration of the adsorbed water which results no free movement of ions occurs in the lattice. The variation in conductivity of HMTO in the temperature range 373-673 K follows Arrhenius equation given by

$$\sigma_{dc}T = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right)$$

The activation energy (E_a) for conduction and preexponential factor (σ_0) are regarded as approximately temperature independent. The experimental data are fitted to the above equation. The activation energies for HMTO are calculated from the slope of the linear fits in the Arrhenius plots and listed in **Table 1** along with their dc conductivity value at 673 K. A comparison of the conductivity of KMTO and HMTO shows the following features: (a) at any given temperature, the conductivity of these samples follows the order HATO>KATO >HCTO> KCTO >HFTO>KFTO, (b) the conductivity of HMTO is higher compared to that of KMTO and (c) HATO, HCTO and HFTO exhibits 2-fold, 2-fold and 10-fold increase in conductivity compared to their respective parent samples.

Table 1. DC conductivities (at 663 K) and activation energies of HATO, HCTO and HFTO.

Sample	KATO	HATO	КСТО	НСТО	KFTO	HFTO
DC conductivity at 673 K (S cm ⁻¹)	3.32x10 ⁻⁴	6.352x10 ⁻⁴	4.69x10 ⁻⁵	9.81x10 ⁻⁵	1.12x10 ⁻⁵	1.82x10 ⁻⁴
E _a (eV)	0.82	0.77	0.67	0.78	0.45	0.67

The role of H_3O^+ ions and water of crystallization in conduction mechanism of hydrogenated oxides has not been fully explained [10, 14]. Further, the influence of the metal ion M in octahedral coordination may be important in determining the electrical behavior of the pyrochlores [15]. S.V. Bhat et al have tried to explain the mechanism of protonic conductivity in hydrogenated oxides of the defect pyrochlore and layered type oxides [13].



Fig. 6. Arrhenius plots of the proton conductivity for the HMTO (M=Al, Cr and Fe). Inset shows the Arrhenius plot of HATO in the temperature range 300-673 K.

It is concluded that in the defect pyrochlore compounds the conduction occurs via the exchange of protons of H₂O molecules and OH⁻ groups. In the layered compounds, in contrast, the H_3O^+ ions undergo translational diffusion. Therefore, the higher conductivity of HMTO compared to KMTO can be attributed to the exchange of protons of H₂O molecules and OH⁻ groups through interconnecting channels of their lattice. The presence of crystallized water and hydroxyl protons in HMTO are already confirmed by NMR and FT-IR results. It is well documented that the highly polarizable B-O-B linkages favour fast A⁺ ion mobility in the defect pyrochlore lattice [16, 26]. The differences in proton conductivity of HMTO samples can also be explained based on polarizability of B-O-B linkages. Due to smaller ionic size of Al³⁺ compared to Cr³⁺ and Fe³⁺, Al/Te units are tightly bound to the oxygen in the lattice, compared to that of Cr/Te and Fe/Te units, leading to higher polarizability in (Al/Te)-O-(Al/Te) linkages. Therefore, HATO has higher conductivity than HCTO and HFTO.

Conclusion

The protonated defect pyrochlores, HMTO (M = AI, Cr and Fe) are obtained by facile ion exchange method using 5M concentrated HCl at room temperature. All the materials are

crystallized in cubic lattice with Fd3m space group. The proton exchange of all the materials is confirmed by (i) shift in d-lines (ii) color of the samples (iii) FT-IR analysis (iv) EDS profiles and (v) the formation of KCl as byproduct. The bandgap energy of HATO, HCTO and HFTO is found to be 2.18, 1.32 and 2 eV respectively. The photocatalytic activity of HATO, HCTO and HFTO against methyl violet degradation under visible light irradiation followed the order, HATO > HCTO > HFTO. Protonated KMTO shows higher photocatalytic activity against MV degradation compared to parent material, KMTO. The existence of hydroxyl radicals during the photocatalytic degradation of methyl violet (MV) is confirmed using tertiary butanol (TB) as hydroxyl radical quencher and a fluorescence technique using Terepthalic acid as a probe. All the catalysts retain their activity up to at least three cycles and are not photocorroded. HMTO may be considered as a potential photocatalyst for industrial waste/pollutant purification. HATO, HCTO and HFTO exhibit 2-fold, 2-fold and 10-fold increase, respectively, in conductivity compared to their respective parent samples. At any given temperature, the conductivity of these samples follows the order HATO > KATO > HCTO > KCTO > HFTO > KFTO.

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Supporting information

Table S1. The unit cell parameters of HMTO (M = Al, Cr and Fe).



Fig. S1. ²⁷Al NMR Spectra of HATO and KATO.



Fig. S2. SEM images of HATO, HCTO and HFTO.



Fig. S3. Absorption spectra of HATO, HCTO and HFTO, inset shows the KM plot of HATO, HCTO and HFTO.