SYNTHESIS AND CHARACTERIZATION OF MIXED METAL OXIDES FOR ENERGY AND ENVIRONMENT-RELATED REACTIONS

A.M. Banerjee, M. R. Pai and S. R. Bharadwaj

Chemistry Division

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ABSTRACT

A series of aliovalent and isovalent ions were substituted at A and B-site in Indium titanate, In$_{2+}$Ti$^{4+}$O$_5$ (A= Ni$^{2+}$ and Nd$^{3+}$, B =Fe$^{3+}$ and Cr$^{3+}$, x/y=0.0-0.2), with an objective to evaluate their photoactivity for water splitting reaction, as a function of substitution under actual sunlight and sunlight-like irradiation. Samples were prepared by means of a solid state reaction, the surface and bulk properties of the substituted samples were characterized by X-Ray Diffraction (XRD), Brunauer–Emmett–Teller (BET) N$_2$ sorption method, FTIR and DRUV techniques. The analytical results of DRUV show that Nd$^{3+}$ doping did not shift the main absorption band edge significantly, but some new absorption peaks attributable to 4f internal electron transition existed in the visible region. In case of Ni, Fe and Cr band edge was shifted in visible range.

Introduction

In view of global energy and environmental issues, significant efforts have been made, to develop suitable catalysts for the efficient splitting of water. Water splitting can be achieved through thermochemical, photocatalytic and other methods. With these aspects in view, we propose to develop Indium titanate based mixed oxides, for splitting of water stoichiometrically, under visible light irradiation.

Experimental

Catalyst Synthesis

Mixed oxides with nominal compositions In$_{(2-x)}$Nd$_x$TiO$_5$, In$_{(2-x)}$Ni$_x$TiO$_5$, In$_{(2-x)}$Fe$_x$O$_5$, In$_{(2-x)}$Cr$_x$O$_5$, were synthesized through ceramic route by using pre-dried In$_2$O$_3$, TiO$_2$, NiO, Nd$_2$O$_3$, Fe$_2$O$_3$ and Cr$_2$O$_3$ (99.99% purity), as starting materials, mixing them in appropriate stoichiometry as depicted by the following equations:

$$(1-x)\text{In}_2\text{O}_3 + \text{TiO}_2 + x\text{Nd}_2\text{O}_3 \rightarrow \text{In}_{2-(x)}\text{Nd}_x\text{TiO}_5 \quad (2x = 0.0, 0.1, 0.2, 0.3 and 0.4)$$

$$(1-x)\text{In}_2\text{O}_3 + \text{TiO}_2 + 2x\text{NiO} \rightarrow \text{In}_{2-(x)}\text{Ni}_x\text{TiO}_5 \quad (2x = 0.0, 0.1, 0.2, 0.3 and 0.4)$$

$$(1-x)\text{In}_2\text{O}_3 + (1-x)\text{TiO}_2 + x2\text{Fe}_2\text{O}_3 \rightarrow \text{In}_{2-(x)}\text{Ti}_x\text{Fe}_2\text{O}_5 \quad (x = 0.0, 0.05, 0.1, 0.15 and 0.2)$$

$$(1-x)\text{In}_2\text{O}_3 + (1-x)\text{TiO}_2 + x2\text{Cr}_2\text{O}_3 \rightarrow \text{In}_{2-(x)}\text{Ti}_x\text{Cr}_2\text{O}_5 \quad (x = 0.0, 0.1, and 0.2)$$

The pellets of homogeneous mixtures were calcined, first at 700°C for 65 h and then at 1000°C for 64 h and finally at 1250°C for 24 h, with intermittent
grindings, so as to ensure the uniformity and the completion of the reaction. All samples are abbreviated in text as M(x), where M is the dopant ion and x is the extent of substitution.

Catalyst Characterization

The Powder XRD patterns were recorded on a Philips diffractometer (model PW 1710), equipped with a graphite monochromator and Ni-filtered Cu-Kα radiation. The patterns were indexed using powder programme for determination of the unit cell parameters of the substituted samples. The crystallite size, \( D \), was calculated from XRD line width according to the Scherrer equation.

The SEM images were recorded on Model Tescan Vega MV 2300T/40, using an accelerating voltage of 25KV at the working distance — 10mm. EDS was recorded with Inca Crystal IC 250 at a working distance of 23 mm spectra.

Band Gap Measurements: Diffusion Reflectance Spectra (DRS)

Band gap measurements of all semiconductor oxide samples was estimated, by recording their Diffuse reflectance UV-Visible spectra using spectrophotometer of JASCO model V-530, Japan, scanned in the range of 200-1000 nm at the scanning speed of 200nm/min.

Results and Discussion

Crystal structure by XRD

The powder XRD patterns of all the doped and undoped samples are shown in Fig. 1. The \( \text{In}_2\text{TiO}_3 \) is isostructural with \( \text{In}_2\text{VO}_5 \). It crystallizes in the orthorhombic space group, with \( a = 0.7241 \text{ nm} \), \( b= 0.3427 \text{ nm} \), \( c= 1.4878 \text{ nm} \), cell volume = 0.3692 nm\(^3\) and \( Z = 4 \). The lines due to reactant oxides are missing in all substituted patterns thus confirming the completion of the solid-state reaction. Following are the XRD results as a function of individual dopants at A site by Nd and Ni, and at B-site by Fe and Cr.

A-site substitution, \( \text{In}_{2(1-x)}\text{Nd}_{2x}\text{TiO}_5 \):

The XRD patterns of all Nd\(^{3+} \) substituted \( \text{In}_2\text{TiO}_3 \) compositions, are presented in Fig. 1, as a function of x, where the XRD pattern of x = 0, 0.1 and 0.2 composition matches with that of orthorhombic \( \text{In}_2\text{TiO}_5 \) (JCPDS card No.30-0640) oxide. The XRD patterns as shown in Fig. 1 reveal that substitution by isovalent metal ion, Nd\(^{3+} \) at A-site in \( \text{In}_2\text{TiO}_5 \) has resulted in single-phase compositions isomorphic to \( \text{In}_2\text{TiO}_5 \) phase. Weak reflections present at 2\( \theta \) = 28.5°, 28.8°, 33.21°, attributable to new secondary phase were also visible in \( \text{In}_{1.7}\text{Nd}_{0.3}\text{TiO}_5 \). The lines corresponding to a new secondary phase were identified and attributed to the Nd\(^{3+} \cdot \text{TiO}_5 \) (JCPDS card No. 37-0944). The intensities of XRD lines due to this new phase, increased with increase in Nd content of \( \text{In}_{1.2}\text{Nd}_{0.3}\text{TiO}_5 \) and \( \text{In}_{1.8}\text{Nd}_{0.2}\text{TiO}_5 \) substituted samples.

The XRD results as a function of individual dopants at A-site by Nd and Ni, and at B-site by Fe and Cr. Fig. 1 also shows the powder XRD patterns of \( \text{In}_2\text{TiO}_5 \) and corresponding patterns observed due to aliovalent substitution of Ni\(^{2+} \) in place of In\(^{3+} \) at A-site. The XRD patterns of samples with \( \text{In}_{1.95}\text{Ni}_{0.05}\text{TiO}_5 \), \( \text{In}_{1.9}\text{Ni}_{0.1}\text{TiO}_5 \) and \( \text{In}_{1.8}\text{Ni}_{0.2}\text{TiO}_5 \) compositions, match with the XRD pattern of unsubstituted indium titanate sample, as shown in Fig. 1. Thus in these samples Ni substitution resulted in single phase due to formation of solid solution of Ni with the lattice of the parent compound, indium titanate. However, for samples, having Ni content higher than 10%, some low intensity lines in addition to parent phase were also observed.
Fig. 1: XRD patterns of In$_2$TiO$_5$, In$_{1.33}$Nd$_{0.67}$TiO$_5$, In$_{0.91}$Ni$_{0.09}$TiO$_5$ and In$_{0.8}$Ti$_{0.2}$Fe$_{0.0}$O$_{5-d}$, typical of secondary phase, were identified and attributed to be mixed phases. The lines corresponding to new phase (marked as *) are also visible which indicates the formation of secondary phase. Thus Cr substitution has resulted in mixed phases. The lines corresponding to new phase were identified and attributed to be Cr$_{0.26}$In$_{0.74}$O$_{5-\delta}$ (JCPDS card No. 30-416).

**B-site substitution In$_x$Ti$_{1-x}$Fe$_x$O$_{5-d}$**

The XRD pattern (Fig. 1), of x = 0, composition matches well with that of orthorhombic In$_2$TiO$_5$ (JCPDS card No. 30-0640) oxide. The XRD patterns of Fe substituted compositions, i.e. $0.05 \leq x \leq 0.2$ are presented in Fig. 1 (c & e). All these patterns reveal that Fe substitution has resulted in single-phase material comprised of In$_2$TiO$_5$ phase. Table 1 lists the change in lattice parameters and cell volume as a function of Fe content as generated by indexing the XRD patterns of substituted samples. This data reveals that as Fe content increases the cell volume decreases, which can be explained by inclusion of smaller cation, Fe (0.64 Å) in place of relatively larger size cation, Ti (0.68 Å).

**In$_x$Ti$_{1-x}$Cr$_x$O$_{5-d}$**

Fig. 1 presents the XRD patterns of B-site substituted In$_x$Ti$_{1-x}$Fe$_x$O$_{5-d}$ compositions. The XRD pattern of composition with In$_x$Ti$_{1-x}$Cr$_x$O$_{5-d}$ shows weak reflections attributable to new phase (marked as *) are also visible which indicates the formation of secondary phase. Thus Cr substitution has resulted in mixed phases. The lines corresponding to new secondary phase were identified and attributed to be Cr$_{0.26}$In$_{0.74}$O$_{5-\delta}$ (JCPDS card No. 30-416).

Thus, cationic substitution of Fe$^{3+}$ at B-site has resulted in single-phase material, isomorphic to In$_2$TiO$_5$ phase, whereas Ni$^{2+}$, Nd$^{3+}$ and Cr$^{3+}$ resulted in mixed phases due to limited solubility of these ions in In$_2$TiO$_5$ lattice. Fe$^{3+}$ and Cr$^{3+}$ are transition elements of same valence and ionic radii when substituted at B-site in In$_2$TiO$_5$ under identical conditions; their implications in the lattice were varied and cannot be generalized. Thus, the nature of cation, its transport properties and diffusion characteristics play an important role in solid-state reaction.

**Table 1 : Lattice parameters of In$_x$TiO$_{5-x}$Fe$_x$O$_{5-d}$ samples**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample</th>
<th>Lattice parameters (Å)</th>
<th>Cell Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>1</td>
<td>In$<em>{0.0}$Ti$</em>{0.9}$O$_{5-d}$</td>
<td>7.241 (2) 3.427 (2) 14.878 (6)</td>
<td>369.24</td>
</tr>
<tr>
<td>2</td>
<td>In$<em>{0.1}$Ti$</em>{0.9}$O$_{5-d}$</td>
<td>7.227 (8) 3.425 (8) 17.873 (6)</td>
<td>368.26</td>
</tr>
<tr>
<td>3</td>
<td>In$<em>{0.2}$Ti$</em>{0.9}$O$_{5-d}$</td>
<td>7.225 (6) 3.408 (5) 14.853 (1)</td>
<td>365.82</td>
</tr>
</tbody>
</table>
Though Fe substituted samples are single-phase compositions, there is a slight distortion of lattice as may be caused either by the generated substitution-induced non-stoichiometry or due to decrease in crystallinity of these samples. This data indicates that even on substitution of up to 20% Fe in place of Ti the structure remains intact despite of the incorporated distortion. This may be attributed to the almost identical ionic radii of Ti$^{4+}$ and Fe$^{3+}$.

**Diffuse Reflectance Spectroscopy (DRS)**

The metal ion substitution affects the electronic structure of the semiconducting photocatalysts which is manifested in their DRUV-Vis spectra. Fig. 2a. illustrates the light absorption properties for the In$_2$TiO$_5$ and metal ion substituted at A and B-site. The band gap of these compounds can be estimated from plots of the Kubelka-Munk functions $F(R)$ versus photon energy. One of the most characteristic features is that, the $E_g$ value ($E_g$ is band gap) is narrowed with Fe or Cr doping. The band gap is changed from 3.2 eV (In$_2$TiO$_5$) to 2.1 eV (In$_2$Ti$_{1.8}$Fe$_{0.2}$O$_{5-\delta}$) and 1.9 in case of Cr doping (In$_2$Ti$_{0.8}$Cr$_{0.2}$O$_{5-\delta}$). This is considered largely to be a consequence of the Fe 3d or Cr 3d level. Ni has also resulted in lowering of band gap from 3.02 to 2.0 eV. The band gap change in Ni-doped compounds can be attributed to internal transitions in a partially filled d shell. The wavelength at the absorption edge, $\lambda$ was determined as the intercept on the wavelength axis for a tangent line.

Fig. 2b shows the UV–VIS diffuse reflectance spectrum of In$_2(1-x)$Nd$_{2x}$TiO$_{5-\delta}$ as a function of x. The spectrum indicates that In$_2$TiO$_5$ has an optical gap of 3.02 eV. The presence of several peaks at 529.5, 588.5, 741, 802, 866 and 879 nm in the spectra of Nd substituted samples, reveals that the Nd$^{3+}$ substitution has enabled the sample to absorb in visible region considerably. These peaks are attributed to possible charge transfer transitions between Nd 4f and other bands. The intensity of peaks was found to increase with increase in Nd content. The band gap is likely to occur between the top of the oxygen 2p band and the bottom of the oxygen 2p band.
Ti 5d \((t_{2g})\) band. In particular, a much broader absorption in the range 300–400 nm suggests, possible charge-transfer transitions between Nd 4f and other bands. \(\text{In}_2\text{Ti}_{1-x}\text{Fe}_x\text{O}_5\) samples show that the visible absorption spectra of these compounds, are characteristic of photocatalysts which are able to respond to visible light.

**SEM**

Fig. 3 shows the SEM micrograph of a typical sample of \(\text{In}_2\text{TiO}_3\), where we can see that the particles have clear facet grain boundaries, whereas on the substituted samples, the facets disappear. Also the particle size is in micron range, due to high temperature sintering.

![SEM image of a) In\(_2\)TiO\(_3\) b) enlarged portion showing the facets in surface of In\(_2\)TiO\(_3\) c) Nd (0.2) substituted sample](image)

**About the Authors**

Mr. Atindra Mohan Banerjee completed his Master of Science in Chemistry from Calcutta University in 2004. He undergone a one year Orientation Course in Nuclear Science and Engineering from BARC Training School (OCES - 48 batch). Subsequently he joined the Chemistry Division of BARC, Mumbai in Sept. 2005. He is involved in the development of catalyst for sulphuric acid decomposition reaction in thermochemical cycle for hydrogen generation by water splitting and photocatalytic water splitting. He has 2 publications in International journals and 6 publications in Symposia/conferences. He is a recipient of Best Paper Award conferred during ISMC-2006 for the paper titled “Studies for S-I Thermochemical Cycle for Hydrogen production”.

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ABOUT THE AUTHORS

Dr. (Ms.) Mrinal R. Pai joined BARC through Training School (40th Batch) after completing her Post graduation in Chemistry from IIT Delhi in 1996. She initiated her research activities in the field of catalysis with development of H₂ mitigation catalyst during year 1999 in Chemistry Division. She was awarded Ph.D degree in Physical Chemistry from Mumbai University in year 2005. Also, she gained experience in synthesizing fine powders of nano-size oxides/mixed oxides with spinels, perovskites and pyrochlore structures and characterizing them by various techniques for their prospective applications in pollution abatement, water splitting by photocatalysis and sulfuric acid decomposition reaction in S-I thermochemical cycle. There are sixteen publications in refereed international journals, several publications in symposium and conferences and invited talks to her credit.

Dr. Shyamala Bharadwaj obtained her B.Sc. Degree from Mumbai University in the year 1976 and joined the Department of Atomic Energy in the year 1977, after graduating from the 20th Batch of BARC Training School. Later she completed her Masters Degree and obtained Ph. D. in Physical Chemistry from Mumbai University. She has been working in the area of high temperature thermodynamics of nuclear as well as other refractory materials for the past 30 years. During the year 2000-2001, she worked as a Guest Scientist at the Juelich Research Centre, Juelich, Germany, where she was involved in the investigations of Solid Oxide Fuel Cell materials. Presently, she is heading the Fuel Cell Materials and Catalysis Section of Chemistry Division, BARC. Her current interests are in the field of Intermediate Temperature Solid Oxide Fuel Cells and generation of hydrogen by water splitting, by thermochemical and photocatalytic methods. She has more than 180 publications to her credit, with more than 75 publications in reputed international journals. She is a Ph.D. Guide of Mumbai University. She was Hon. Treasurer of Indian Thermal Analysis Society (ITAS) during 1996-2000 and is currently the Hon. Secretary of ITAS. She has been bestowed with NETSH-ITAS Award 2006, for her contribution in the field of thermodynamics and thermal analysis.