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Band-gap engineering in novel delafossite-type multicomponent oxides for photocatalytic degradation of methylene blue

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Keywords: Oxides Optical absorption Transition metals	A series of novel mixed oxides with honeycomb layered structure viz. delafossite-type $Na_3M_2SbO_6$ (where $M = Cu$; Ni; Cu, Ni; Cu, Ni, Co; Cu, Ni Co, Fe; Cu, Ni Co, Fe, Mn) were synthesized by a facile method. The synthesis involved heating of the metal precursors at 1100 °C followed by air quenching. The structure was analogous to that of $Na_3Ni_2SbO_6$ (space group: <i>C2/m</i>). The effect of increased entropy on the Jahn-Teller distortion effect, as previously reported in $M = Cu$ system, was evident from the X-ray diffraction (XRD)/Riet-veld structural analysis. The as-synthesized oxides showed photocatalytic activity as confirmed by the degra-

1. Introduction

Substitution of cations at specific sites in minor fractions has brought about vast improvements in traditional oxide systems over the ages. Rost et al. for the first time extended this concept to a new system of materials by substituting five or more than five cations [1]. (CoCuMgNiZn)O was synthesized by the substitution of multiple metal ions in the rock-salt structure [1]. Ever since, this has brought to light the synthesis of other oxides crystallizing in perovskite [2], spinel [3] and fluorite [4] structures. These compounds have exhibited several interesting functional properties leading to potential applications in the field of magnetic [5], electrochemical [6], dielectric [7] and energy storage [8].

A large number of layered oxides of transition and alkali metals have exhibited favorable properties as electrodes for rechargeable batteries [9]. superconductors [10], thermoelectric materials [11]. ion-conducting [12], intercalation [13], electrocatalytic [14] and photocatalytic [15] properties. In recent times, there have been multiple reports with the general layered structure of ABO₂ compounds where one-third of B³⁺ was partly substituted by X⁵⁺ cation. The general formula of such compounds changes to $A_3M_2XO_6$, where A (Li⁺, Na⁺), M²⁺ $(Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+} and Zn^{2+})$ and $X^{5+}(Bi^{5+}, Sb^{5+})$ [16–19]. Such a specific composition leads to a distinct M^{2+}/X^{5+} ratio in every layer.

Every XO₆ octahedron is thereby encompassed by 6 MO₆ octahedra to form a honeycomb structure. Na⁺ exists as another additional NaO₆ octahedron stacked between MO₆-XO₆ octahedral layer [18]. It is further observed that delafossite materials can exhibit optical band-gap tuning with the proper choice of dopants [20].

dation of methylene blue. This was correlated to a drop in the optical band-gap from 2.41 to 1.96 eV on

increasing the number of elements as well as its effect on the band energies are proposed here.

Band gap tunability has been exploited in the past for the engineering of visible light absorbing photocatalysts. Photocatalysis has obtained increased prominence in various applications e.g., water purification, owing to the abundant source of sunlight that is prevalent on the surface of the earth. There are several well-known techniques for band gap tuning, viz. site-specific substitution [21], heterostructure formation [22], nanostructured engineering [23], mixed metal oxides [24], defect concentration [25], optimization of mineralizing agent [26], and reduction in crystallite size by ball milling [27]. Owing to stability and cost effectiveness, TiO₂ is one of the most studied photocatalyst used for photo-degradation of various water pollutants [28]. However, visible light photocatalysts are more desirable when compared to TiO₂, which absorbs the ultraviolet rays from the solar spectrum owing to its wide band-gap. Thus, it is important to investigate the optical properties of other oxide materials, which can exhibit visible light photo-catalysis. Recently, Liang et al. reported an oxide system with the general form $NaXO_2$ (where X = Co, Rh, Ir) that exhibits suitable band edges for water

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Fig. 1. (a) XRD patterns of the synthesized oxide samples, (b) Rietveld refinement pattern of Na₃(CuNiCoFeMn)₂SbO₆, (c) colour of the compounds as a function of increasing number of elements.

splitting reaction [29].

In the present work, we report a novel strategy to effectively tune the band gap in delafossite systems. For this study, the synthesis of a new layered mixed oxide series Na₃(M)₂SbO₆ where M = (Cu); (Ni); (Ni, Cu); (Co, Ni, Cu); (Co, Fe, Ni, Cu) and (Mn, Co, Fe, Ni, Cu) has been carried out. The structural transition induced by substitution of Cu center with the systematic addition of metal-ions in Na₃Cu₂SbO₆ lattice has been probed using XRD analysis. Furthermore, the photochemical activity of these oxides has been investigated by decreasing the concentration of methylene blue in visible light illuminated aqueous solutions. Systematic studies of oxides exhibiting band gap tunability and photocatalytic activity have been investigated.

2. Experimental details

2.1. Synthesis of Na₃M₂SbO₆ by solid-state reaction

Na₃M₂SbO₆ was synthesized by solid-state reaction of stoichiometric amounts of Na₂CO₃.10H₂O, Sb₂O₅, CuO, NiO, Co(CH₃COO)₂, Fe₂O₃ and Mn(CH₃COO)₂.4H₂O. Co and Mn-oxides were formed by pre-heating the acetates. For the sake of brevity, the compounds will be abbreviated as Ni-I (Na₃Ni₂SbO₆), Cu-I (Na₃Cu₂SbO₆), CuNi [Na₃(CuNi)₂SbO₆], CuNiCo [Na₃(CuNiCo)₂SbO₆], CuNiCoFe [Na₃(CuNiCoFe)₂SbO₆] and CuNiCoFeMn [Na₃(CuNiCoFeMn)₂SbO₆].

The reaction for the synthesis of these multicomponent oxides are as follows:

$$3Na_2CO_3 + 4NiO + Sb_2O_5 \rightarrow 2Na_3Ni_2SbO_6 + 3CO_2$$

 $3Na_2CO_3 + 4CuO + Sb_2O_5 \rightarrow 2Na_3Cu_2SbO_6 + 3CO_2$

$$3Na_2CO_3 + 2CuO + 2NiO + Sb_2O_5 \rightarrow 2Na_3CuNiSbO_6 + 3CO_2$$

$$3Na_{2}CO_{3} + \frac{4}{3}CuO + \frac{4}{3}NiO + \frac{4}{3}CoO + Sb_{2}O_{5} \rightarrow 2Na_{3}Cu_{\frac{2}{3}}Ni_{\frac{2}{3}}Co_{\frac{2}{3}}SbO_{6} + 3CO_{2}$$

$$3Na_{2}CO_{3} + CuO + NiO + CoO + \frac{1}{2}Fe_{2}O_{3}$$

+ $Sb_{2}O_{5} \rightarrow 2Na_{3}Cu_{\frac{1}{2}}Ni_{\frac{1}{2}}Co_{\frac{1}{2}}Fe_{\frac{1}{2}}SbO_{6} + 3CO_{2} + \frac{1}{4}O_{2}$
$$3Na_{2}CO_{3} + \frac{4}{5}CuO + \frac{4}{5}NiO + \frac{4}{5}CoO + \frac{2}{5}Fe_{2}O_{3} + \frac{4}{5}MnO$$

+ $Sb_{2}O_{5} \rightarrow 2Na_{3}Cu_{\frac{3}{2}}Ni_{\frac{3}{2}}Co_{\frac{3}{2}}Fe_{\frac{3}{2}}Mn_{\frac{3}{2}}SbO_{6} + 3CO_{2} + \frac{1}{5}O_{2}$

The requisite powder mixtures (based on mole fractions as stated above) were ground for 15 min in a mortar and pestle for thorough mixing of the powder. The powder was subsequently transferred to a ceramic boat that was heated to a temperature of 1100 °C at a heating rate of 5 °C min⁻¹. It was isothermally held at 1100 °C for 2 h and subsequently air quenched on a stainless-steel plate.

2.2. Characterization

Room temperature XRD data for all the synthesized samples were collected on a Panalytical X'Pert Pro instrument using Cu K_{α} radiation ($\lambda = 1.5405$ Å, current =30 mA, voltage =40 kV) for phase identification. UV–vis spectrophotometer (V-560, JASCO) was employed to estimate the band gap of the materials. Scanning Electron Microscopy (SEM) was used to identify the particle morphology and elemental distribution performed using Zeiss, Gemini-SEM 500.

2.3. Photocatalytic measurements

The photocatalytic performance of the synthesized catalysts was investigated by the degradation of organic dye. Methylene blue was selected as the candidate for the photocatalytic degradation. A stock solution of MB was prepared by dissolving 20 mg of dye in one liter of water. From the stock solution, 50 mL solution was taken in a beaker. 20 mg of catalyst was added to the solution. The contents were stirred in the absence of light for thirty minutes and subsequently exposed to

Table 1

Unit cell parameters of all the synthesized compounds.

Alloy	Lattice parameter			0	Unit cell	Pond con	
	a (nm)	b (nm)	c (nm)	р (°)	Volume (nm ³)	(eV)	Reference
Ni-I	0.5305	0.9171	0.5627	108.3	0.2599	4.29	[31]
Cu-I	0.5669	0.8845	0.5825	113.4	0.2681	2.62	[16]
Ni-I	0.5291	0.9157	0.5659	108.1	0.2605	NA	This work
Cu-I	0.5677	0.8863	0.5834	113.4	0.2695	NA	This work
NiCu (2 phases)	-	-	-	-	-	2.41	This work
NiCuCo	0.5326	0.9203	0.5649	108.4	0.2628	2.39	This work
NiCuCoFe	0.5324	0.9186	0.5742	108.4	0.2665	2.03	This work
NiCuCoFeMn	0.5319	0.9156	0.5757	108.2	0.2663	1.96	This work



Fig. 2. Crystal structure of (a) Na₃M₂SbO₆ and (b) Na₃(CuCoFeMnNi)₂SbO₆.

simulated solar irradiation. An Oriel 300 W solar simulator used in this study has an air mass filter AM1.0, that emanated radiation with power density of 128.3 mW cm⁻² [30]. Aliquots were collected at 15 min intervals of time to assess the drop in the concentration of MB in the solution. The solutions were poured into quartz cuvettes and UV–vis spectra were recorded by employing a Perkin Elmer Lambda 650 UV–vis spectrometer.

3. Results and discussion

3.1. Structural property of Na₃M₂SbO₆

Fig. 1(a) displays the XRD patterns of all the synthesized compounds demonstrating that they have crystallized in C2/m symmetry. The XRD pattern of Cu-I appears different from Ni-I possibly due to Jahn-Teller distortion in the former system as previously reported elsewhere [16]. The A₃M₂XO₆ compounds have been reported to adopt two different

crystal symmetry viz. C2/m [31] and $P3_112$ [17]. When M = Cu, a distorted monoclinic α -NaFeO₂ type lattice comes to prominence. The Cu²⁺ cation due to Jahn-Teller distortion exhibits 4 equatorial Cu-O bonds of 2 Å and two longer axial Cu-O bonds of 2.5 Å. When M = Ni, Co, Mg and Zn and X = Sb, the compounds prefer regular octahedral coordination instead of the distorted one as in the case of Cu [16]. However, such compounds with M = Ni, Co, Mg and Zn crystallize in a trigonal system and exhibit incomplete M/Sb ordering, which is evident from the low intensity of the superlattice lines. Such incomplete ordering permits the partial substitution of Sb^{5+} with M^{2+} and this, in turn, leads to Na^+ vacancies. Such vacancies in the lattice lead to Na⁺ conductivity, a feature that is absent in the case of Cu^{2+} sample [16]. However, it is worth noting that M = Ni, Co, Mg and Zn can result in the structure with C2/m symmetry [20]. However, the lattice parameters vary due to elongation along the c-axis due to Jahn-Teller distortion present in M = Cu system [16].

The CuNi compound exhibits a combination of two monoclinic systems viz. Cu-I and Ni-I systems. With the incorporation of a third element (Co), the XRD pattern of CuNiCo adopts a structure similar to that of Ni-I albeit with a difference in the peak intensities at around $2\theta \sim 35^{\circ}$. This brings forth the idea that when the mole fraction of Cu in the M lattice site is ~0.33, the system adopts the centrosymmetric structure that corresponds to M = Zn, Ni, Co, etc. Thus, the presence of Jahn-Teller distortion (as observed in M = Cu) leading to a change in the lattice parameter along the c-axis is no longer exhibited [16]. In the case of CuNiCoFe and CuNiCoFeMn (Fig. 1b) systems, the peaks were identical to that observed for Ni-I. The compounds with increasing M exhibited a marked difference in powder colour as shown in Fig. 1(c).

The estimated lattice parameter and unit cell volumes are shown in Table 1. The lattice parameter of Ni-I and Cu-I alloys are markedly different along the b axis. However, the values obtained are very similar to that of Ni-I [31] and Cu-I [16] reported in the literature (Table 1). It is also worth noting that the unit cell volume increases with the increased entropy in the system and there is a distortion observed in the unit cell (in comparison to the parent structure) as shown in Fig. 2. The honey-comb stacking sequence can be confirmed by superlattice reflections at $2\theta \sim 20^{\circ}$ as shown in Fig. 3. The presence of these peaks, namely (020), (110) and ($\overline{1}$ 11), can be observed in the zoomed region of the XRD patterns as shown in Fig. 3. These additional peaks are generated due to stacking defects along the c-axis in the monoclinic unit cell [17].

The Rietveld refinement pattern of the CuNiCoFeMn oxide crystallizing in C2/m symmetry is shown in Fig. 1(b). The refinement was carried out using the parameters reported by Yuan et al. [31]. The red hollow circles represent the experimental pattern, the black line denotes the fitted profile, the blue line denotes the difference plot and the green sticks represent the Bragg positions.

The polyhedral view showing the honeycomb lattice is displayed in Fig. 4. This is in good agreement with the literature reports on $Na_3M_2SbO_6$ [17,18]. The addition of several elements can lead to phase segregation and the formation of multiple oxide phases. Therefore, the distribution of the elements was investigated by performing elemental analysis in the CuNiCoFeMn compound as shown in Fig. 5. It was



Fig. 3. Zoomed in portion of the XRD patterns exhibiting superlattice reflections. While Na₃(CuNi)₂SbO₆ exhibits peaks corresponding to both Na₃Cu₂SbO₆ and Na₃Ni₂SbO₆ phases, Na₃(CuNiCo)₂SbO₆, Na₃(CuNiCoFe)₂SbO₆ and Na₃(CuNiCoFeMn)₂SbO₆ exhibit peaks similar to that observed in Ni system.



Fig. 4. Polyhedral view showing the presence of honeycomb lattice in $Na_3(CuCoFeMnNi)_2SbO_6$. The honeycomb sequence is shown by a white hexagon in the polyhedral view. The SbO₆ octahedron is covered by 6 MO₆ octahedra to form the honeycomb sequence.

observed that all the elements were distributed uniformly in the sample, indicating the presence of a single phase.

The diffused reflectance spectra were recorded for these samples to estimate the band gap as there is a clear indication of colour change (Fig. 1c) with an increase in the entropy of the sample. It may be noted

that the existing set of rules that are used to calculate the ΔS_{config} tends to overestimate the values. This happens if the oxide system is considered as completely random, similar to that in high entropy alloys. In any oxide, the multi-element substitution is accounted for in a single lattice site. Thus, atoms existing at other lattice sites do not contribute to any sort of mixing and hence should not be accounted for in the ΔS_{config} calculations. Recently, Parida et al. have shown that the calculation of ΔS_{config} employing sublattice model is a more accurate technique [3]. The details of the calculations are shown in Table 2.

3.2. Photocatalytic property of Na₃M₂SbO₆

Band gap (E_g) of the synthesized materials were estimated by employing Kubelka-Munk equation, which is given as [32]:

$$(\alpha h\nu)^{\frac{1}{n}} = A \ (h\nu - E_g)$$

where, A is a constant, n depends on the nature of electronic transitions and α is the absorption coefficient. Considering, n = 1/2 for allowed interband transitions, the direct energy gap (E_g) was evaluated. Extrapolating the straight line towards x-axis for CuNi, CuNiCo, CuNi-CoFe and CuNiCoFeMn the calculated direct band gap from above relation was found out to be 2.41, 2.39, 2.03 and 1.96 eV, respectively (Fig. 6). The optical band gaps of the compounds are lower than that reported for Cu (2.62) or Ni (4.29) systems [20]. Band gap of these compounds decreases continuously from 2.41 eV to 1.96 eV and this could be ascribed to the presence of impurity states which are responsible for inducing an allowed or non-allowed transition in the compound [33].



Fig. 5. SEM elemental mapping showing uniform distribution of all the elements in Na₃(CuNiCoFeMn)₂SbO₆.

Entropy calculation for the synthesized compounds.					
Sample	$\Delta S_{ m config}$				
CuNi	$-R\left(rac{3}{12}(0)+rac{1}{12}(0)+rac{6}{12}(0)+rac{2}{12}\left(rac{1}{2}lnrac{1}{2}+rac{1}{2}lnrac{1}{2} ight) ight)$				
CuNiCo	$-R\left(\frac{3}{12}(0)+\frac{1}{12}(0)+\frac{6}{12}(0)+\frac{2}{12}\left(\frac{1}{3}h\frac{1}{3}+\frac{1}{3}h\frac{1}{3}+\frac{1}{3}h\frac{1}{3}\right)\right)$				
CuNiCoFe	$-R\left(\frac{3}{12}(0)+\frac{1}{12}(0)+\frac{2}{12}(0)+\frac{2}{12}\left(\frac{1}{4}ln\frac{1}{4}+\frac{1}{4}ln\frac{1}{4}+\frac{1}{4}ln\frac{1}{4}+\frac{1}{4}ln\frac{1}{4}+\frac{1}{4}ln\frac{1}{4}\right)\right)$				
CuNiCoFeMn	$-R\left(\frac{3}{12}(0) + \frac{1}{12}(0) + \frac{6}{12}(0) + \frac{2}{12}\left(\frac{1}{5}ln\frac{1}{5} + \frac{1}{5}ln\frac{1}{5} + \frac{1}{5}ln\frac{1}{5} + \frac{1}{5}ln\frac{1}{5} + \frac{1}{5}ln\frac{1}{5} + \frac{1}{5}ln\frac{1}{5}\right)\right)$				

The valence band maximum (VBM) and conduction band minimum (CBM) are calculated for all the oxides (Fig. 7a) using the technique as followed in [29]. The energy position corresponding to the reduction potential (H^+/H_2) and oxidation potential (H_2O/O_2) of water are also shown in Fig. 7(a). For a compound to exhibit water-splitting reaction,

Table 2

the CBM should be more positive than -4.5 eV and the VBM should be more negative than -5.5 eV. As for example, layered CuRhO₂ with CBM and VBM close to these values exhibit water-splitting reaction [34]. Additionally, it was predicted that NaXO₂ type compounds can exhibit photocatalytic properties [29]. Thus, the VBM and CBM positions were



Fig. 6. Tauc plot for (a) Na₃(CuNi)₂SbO₆ (b) Na₃(CuNiCo)₂SbO₆ (c) Na₃(CuNiCoFe)₂SbO₆ (d) Na₃(CuNiCoFeMn)₂SbO₆. The linear portion of the curves are interpolated to estimate the band gap values.

calculated for the oxides and were compared with Na₃Ni₂SbO₆ and Na₃Cu₂SbO₆. Based on these calculations, it can be predicted that the oxides can possibly exhibit water splitting applications. In the present study, MB degradation was employed for studying the photocatalytic activity of the oxides.

After the addition of the photocatalysts to the MB solution, the visible colour change was observed (Fig. 8). The photocatalytic studies were carried out by observing the change in concentration of MB solution in the presence of simulated sunlight. The peak corresponding to 660 nm was monitored to check the degradation activity of MB in the presence of the photocatalyst. Fig. 9 depicts the photo-degradation spectrum of MB as a function of increasing time. The concentration profile is plotted as C/C_0 where C_0 is the concentration of MB solution after 30 min and Ct is the concentration of solution after time t. After stirring the solution for 30 min in dark, the degradation was less than 20 % for all the photocatalysts. During this interval, the material gets adsorbed on the surface of the catalyst and an adsorption-desorption equilibrium is attained. Owing to the large grain size of the oxide samples, there is very little adsorption activity of the photocatalyst. From Fig. 7b, it can be observed that C/C_0 of MB follows the order NiCu < NiCuCo < NiCuCoFe. However, upon moving to NiCuCoFeMn, the C/C₀ value drops slightly. The ln C₀/C plots are shown in Fig. 7c which confirm that all the photocatalysts exhibit pseudo first-order kinetics. With an increase in the number of elements there is a systematic increase in the rate constant in the order NiCu $(2.73 \times 10^{-3} \text{ min}^{-1}) < 10^{-3} \text{ min}^{-1}$ NiCuCo (3.89 \times 10 $^{-3}~$ min $^{-1}) <$ NiCuCoFe (3.99 \times 10 $^{-3}~$ min $^{-1}).$ However, NiCuCoFeMn exhibits a slightly lower rate constant of 3.32×10^{-3} min⁻¹. Thus, it can be concluded that although there is an improvement in the rate constant with increased entropy in the system, the proper

choice and number of elements are crucial for oxides to exhibit photocatalytic properties.

4. Conclusions

In the present study, a series of novel delafossite-type $Na_3M_2SbO_6$ (where M = Cu; Ni; Cu, Ni; Cu, Ni, Co; Cu, Ni Co, Fe; Cu, Ni Co, Fe, Mn) compounds were successfully synthesized. All the compounds adopted the *C2/m* symmetry. The as-synthesized oxides showed photocatalytic activities. This was due to a decrease in the optical band-gap and changes in the band energetics caused by the increase in the entropy of the system. The results indicate that HE-approach can be employed in tailoring the optical band gap in ABO₂ type mixed oxides.

CRediT authorship contribution statement

Anirudha Karati: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft, Writing - review & editing. Tripta Parida: Investigation, Writing - review & editing. Jyoti Gupta: Investigation, Writing - review & editing. Harish Kumar Adigilli: Investigation, Writing - review & editing. Pramod H. Borse: Supervision, Writing - review & editing. Joydip Joardar: Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 7. (a) VBM and CBM energy levels of oxides, (b) change in concentration of MB as a function of time for various catalysts and (b) pseudo first order relation between $\ln (C_0/C)$ vs time.



Fig. 8. Degradation of MB solutions upon photocatalysis by using $Na_3(NiCuCoFeMn)_2SbO_6$. The solutions exhibit a gradual fading of colour as a function of increasing exposure time.



Fig. 9. UV-vis plots showing MB degradation for (a) Na₃(CuNi)₂SbO₆, (b) Na₃(CuNiCo)₂SbO₆, (c) Na₃(CuNiCoFe)₂SbO₆ and (d) Na₃(CuNiCoFeMn)₂SbO₆,

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