

# Preparation, Characterization and Photocatalytic Activity studies of $\text{Ag}^+$ , $\text{Cu}^{2+}$ and $\text{Sn}^{2+}$ -doped $\text{Li}_2\text{GeTeO}_6$ under Visible Light Irradiation

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Doping of cations into wide bandgap semiconductors is an effective method of increasing photocatalytic activity. This work aims to find out how dopant ions like  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  affect the structural, optical and photocatalytic properties of  $\text{Li}_2\text{GeTeO}_6$ . The parent  $\text{Li}_2\text{GeTeO}_6$  (LGTO) was synthesized by conventional solid-state method, whereas the  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$ -doped  $\text{Li}_2\text{GeTeO}_6$  were prepared by a simplistic ion-exchange method. Techniques such as XRD, FT-IR, SEM-EDS,  $\text{N}_2$  adsorption-desorption analysis, UV-Vis DRS, XPS, and PL were employed to examine the physico-chemical properties of the as-prepared materials and their photocatalytic activities on the degradation of methyl violet (MV) under visible light irradiation. The acquired photocatalytic activity results revealed that all doped samples displayed enhanced photocatalytic performance compared with parent LGTO. The Ag-LGTO had the best photocatalytic activity for MV degradation, with 68.6% degradation efficiency in 180 min of irradiation. Scavenging experiments were carried out to determine the role of various active species generated on the surface of Ag-LGTO during the photocatalytic degradation of MV. The reusability and stability of Ag-LGTO up to five cycles against MV degradation were also investigated. A photocatalytic mechanism for MV degradation over the Ag-LGTO sample was also proposed based on the findings described above.

## Introduction

Dyes and drug products, despite being used for specific tasks, have shown detrimental effects on the environment due to their continuous presence in water, air and soil. Textile and pharmaceutical industries and wastewater from normal households are the main sources of these contaminants [1-3]. These contaminants have to be removed to protect the water reservoirs. Although conventional water treatment methods such as activated carbon adsorption, coagulation/flocculation, reverse

osmosis, Fenton reagent, ozonation, use of chemicals ( $\text{NaOCl}$ , silica gel, Cucurbituril, etc.), use of peat and wood chips, etc. are available, they are either expensive or generate secondary pollutants or require complicated instrumentation [2]. Photocatalysis using semiconductors, one of the advanced oxidation processes (AOP), is suitable and extensively investigated. The advantages of photocatalysis are (a) use of renewable sunlight or visible light (b) low cost (c) mild experimental conditions (d) formation of harmless products (e) flexibility in destroying a variety of organic/inorganic contaminants and (f) minimum secondary waste generation [4].

Materials belonging to double perovskite types with the general formula  $\text{A}_2\text{BB}'\text{O}_6$  have attracted considerable attention, particularly when A-site cation is small, due to their remarkable structural and magnetic properties [5-11]. The structural flexibility of permitting transition metal ions at A and B sites with strong magnetic interactions and distortions in the structure leading to substantial spontaneous polarization makes them worthy of investigation. Compounds of type  $\text{Li}_2\text{MTeO}_6$  ( $\text{M} = \text{Zr}, \text{Hf}, \text{Ti}$ ), derived from  $\text{LiSbO}_3(\text{LiNbO}_3)$  by double substitution ( $2\text{Sb}^{5+} (2\text{Nb}^{5+}) \rightarrow \text{M}^{4+} + \text{Te}^{6+}$ ) have been studied for cation

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DOI: 10.5185/amlett.2022.031703

ordering phenomena at octahedral sites [5,6]. Recently, Zhao *et al.*, have studied the structural transformation of  $\text{Li}_2\text{GeTeO}_6$  crystallizing in corundum derived ordered ilmenite structure (ambient pressure, Rhombohedral R3) and high temperature, high pressure  $\text{LiSbO}_3$  derived  $\text{Li}_2\text{TiTeO}_6$  (orthorhombic Pnn2) and polar nature of these two phases, although P(E) and dielectric measurements do not show ferroelectric behaviour [7]. Though the structural, ordering and polar nature of  $\text{Li}_2\text{GeTeO}_6$  is investigated, its photocatalytic properties, to our knowledge, are not reported.

In general, the photocatalytic activity of pristine oxide semiconductors is less when compared to its doped composition or when combined with other metals/semiconductors. Many techniques have been used to improve the photocatalytic performance of oxide semiconductors, including elemental doping, noble metal deposition, and semiconductor coupling [12]. Doping transition metals into oxide semiconductors have been widely employed to improve their photocatalytic performance. It is well known that doping of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Sn}^{2+}$  ions in oxide lattices can result in the formation of impurity energy levels (Ag 4d, Cu 3d, and Sn 5s states) within the bandgap, lowering the bandgap energy and increasing visible light absorption [13,14]. As a result, doping of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Sn}^{2+}$  ions into  $\text{Li}_2\text{GeTeO}_6$  is expected to improve optical properties and thereby, photocatalytic activity. The structural and photocatalytic properties of pristine and  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Sn}^{2+}$ -doped  $\text{Li}_2\text{GeTeO}_6$  are reported in this paper.

## Experimental

### Materials

The analytical grade chemicals lithium carbonate ( $\text{Li}_2\text{CO}_3$ , 99%, SD Fine Chem.), germanium dioxide ( $\text{GeO}_2$ , 99.9%, Sigma-Aldrich), tellurium dioxide ( $\text{TeO}_2$ , 99.9%, Sigma-Aldrich), silver nitrate ( $\text{AgNO}_3$ , 99.9%, RFCL Ltd.), copper chloride ( $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ , 98%, Glaxo Laboratories), tin chloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , 98%, Sigma-Aldrich), and conc. HCl (SD Fine Chem.) were used as received. Laboratory-glassmade double distilled water was used for all the preparations.

### Preparation of $\text{Li}_2\text{GeTeO}_6$ (LGTO)

The parent  $\text{Li}_2\text{GeTeO}_6$  was prepared by a conventional solid-state method [7]. For a 5 g batch, the reactants  $\text{Li}_2\text{CO}_3$  (5% excess, 0.75 g),  $\text{TeO}_2$  (1.54 g) and  $\text{GeO}_2$  (1.02 g) were taken in a molar ratio of 1.05:1:1. The reactants were ground thoroughly for 1 h to a fine powder using acetone as a medium for homogeneous distribution of reactants. Finally, the powder was transferred into a porcelain crucible and placed in a muffle furnace. The reaction mixture was slowly heated to 500°C and kept at this temperature for 15 h. The sample was taken out, ground thoroughly and heated to 700 °C for 16 h. The sample was allowed to cool to room temperature naturally by power disconnection. A white solid was obtained.

### Synthesis of $\text{Ag}^+$ , $\text{Cu}^{2+}$ , and $\text{Sn}^{2+}$ -doped LGTO

A simplistic ion-exchange procedure was employed to synthesize of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$ -doped LGTO at room temperature. The preparation of ion-doped LGTO was as follows: For preparing Ag-doped LGTO, about 0.5 g of parent LGTO was added to a beaker containing 50 mL of  $\text{AgNO}_3$  solution (20% excess, 0.52 g) and magnetically stirred for 24 h. Then, the resultant wet solid was washed with water several times, filtered and dried at 80 °C overnight. For synthesizing Cu-doped LGTO and Sn-doped LGTO, the same procedure was followed with similar compositions. For simplicity, Ag, Cu and Sn-doped LGTO were abbreviated as Ag-LGTO, Cu-LGTO and Sn-LGTO, respectively.

### Characterizations

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku Miniflex 600 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 15 mA. The diffractograms were collected at a scan rate of 4°/min and a step size of 0.02° in the scattering angle range ( $2\theta$ ) of 10° to 80°. Fourier transform infrared (FT-IR) spectroscopy was measured using a JASCO IR-5300 spectrometer over the frequency range of 4000-250  $\text{cm}^{-1}$  in the form of KBr pellet support. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analyses were carried out on a HITACHI SU-1500 variable pressure scanning electron microscope (VP-SEM) equipped with an energy dispersive X-ray (EDS) analyzer. The surface area was determined by  $\text{N}_2$  adsorption-desorption isotherms at liquid nitrogen temperature (77 K) on a Micromeritics (ASAP2000) analyzer. Specific surface area was calculated by BET method. The samples were degassed at 200 °C for 2 h under vacuum to remove adsorbed impurities before measurement. UV-Vis diffuse reflectance spectroscopy (DRS) was recorded on a JASCO V650 UV/Vis spectrophotometer in the 200–800 nm wavelength using  $\text{BaSO}_4$  as the reference at room temperature. X-ray photoelectron spectroscopy (XPS) was performed on an AMICUS/ESCA 3400 (Kratos Analytical) spectrometer equipped with a monochromatic  $\text{Al-K}\alpha$  X-ray source (1486.6 eV). The C 1s peak was taken as an internal standard at 284.6 eV. Photoluminescence (PL) spectra were measured on a JASCO FP-8500 spectrofluorometer with an excitation wavelength of 280 nm.

### Photocatalytic activity studies

Methylviolet (MV) was degraded under visible light to evaluate the photocatalytic activity of synthesized samples. The photocatalytic activity was performed using Heber visible annular type photoreactor (model HVAR1234, Heber Scientific, India) under visible light irradiation using a 300 W tungsten lamp as the light source. A typical process is as follows: 50 mg of the sample was dispersed in 50 mL of MV ( $2.5 \times 10^{-5} \text{ M}$ ) solution in a cylindrical glass reactor. The suspension was aerated throughout the tenure to ensure the continuous supply of oxygen and kept in the dark for 60

min to attain adsorption-desorption equilibrium. After 60 min, about 5 mL of the suspension was collected. Subsequently, the remaining suspension was illuminated under visible light. The samples were collected at regular intervals of 30 min and the experiment was ended after 180 min of light irradiation. The collected samples were centrifuged to remove catalyst particles. The concentration of residual MV in the supernatant was measured using a JASCO V650 UV–Vis spectrophotometer. The amount of degradation was reported as  $C_t/C_0$  where  $C_t$  is the concentration of MV at each irradiated time and  $C_0$  is the concentration of the initial MV solution.

In addition to this, scavenger experiments were performed to detect the major reactive species generated in the photocatalytic process. The radical quenchers (2 mL of each) added to the photocatalytic system are benzoquinone (BQ, 2 mM), ammonium oxalate (AO, 2 mM) and isopropanol (IPA, 2 mM), respectively, for superoxide radicals ( $\cdot O_2^-$ ), holes ( $h^+$ ), and hydroxyl radicals ( $\cdot OH$ ). The above explained procedure was followed for these trapping experiments. To further investigate the formation of  $\cdot OH$  species, fluorescence experiments were conducted using terephthalic acid (TA) as a probe. For this purpose, 50 mg of the catalyst was dispersed in 50 mL of a 3 mM terephthalic acid solution that was diluted by NaOH aqueous solution (2 mM). The suspension was illuminated under visible light and the suspension was collected every 30 min, centrifuged and collected the supernatant. The fluorescence intensities of the generated 2-hydroxyterephthalic acid were measured on a Shimadzu RF-5301PC fluorescence spectrophotometer at an excitation wavelength of 320 nm.

## Results and discussion

### Powder XRD analysis

Parent LGTO was prepared by a high temperature solid state method while all the ion doped compositions were obtained through a simple ion-exchange method. All prepared samples were subjected to XRD analysis to ensure phase purity, crystalline nature, and the incorporation of transition metal ions into the parent LGTO. The powder XRD patterns of all the synthesized materials are shown in **Fig. 1(a)**, along with the typical JCPDS pattern for comparison. All of the diffraction peaks of parent LGTO are compatible with the Rhombohedral  $Li_2GeTeO_6$  pattern (JCPDS No. 89-8462, space group  $R\bar{3}(146)$ ), as illustrated in **Fig. 1(a)** [7]. The diffraction peaks of Ag, Cu, and Sn-doped LGTO samples were similar to those of parent LGTO and free from impurities indicating that the samples were of high purity. Using Scherrer's formula, the average crystallite size of the parent and doped samples was estimated based on the strongest peak at  $2\theta = 18.54^\circ$ . The crystallite size of LGTO, Ag-LGTO, Cu-LGTO, and Sn-LGTO were 45.6, 36.7, 42.8, and 39.97 nm, respectively. The diffraction peak at  $2\theta = 18.54^\circ$  corresponding to (0 0 3) plane was expanded and shown in **Fig. 1(b)**. Small but

finite shift in  $2\theta$  value was noticed in all doped LGTO compositions. LGTO has two polymorphs. When prepared at ambient pressure (AP, Rhombohedral  $R\bar{3}$ , designated as R-LGTO), it adopts ordered ilmenite type (corundum type) derivative with face sharing  $GeO_6$  and  $TeO_6$  octahedral units along the  $c$ -axis and face sharing octahedral layers in the  $ab$ -plane [7,15,16]. The high-pressure phase adopted  $Li_2TiTeO_6$  structure (Orthorhombic,  $Pnn2$ ) and was named as O-LGTO [7]. The present investigation deals with R-LGTO only. The Li ion occupies octahedral holes between the layers and both  $GeO_6$  and  $TeO_6$  octahedral share faces with  $LiO_6$  octahedral [17]. As shown in **Fig. 1(b)**, the diffraction peak of Ag-LGTO and Sn-LGTO at  $2\theta \approx 18.60^\circ$  corresponding to the (0 0 3) plane was displaced to lower  $2\theta$  angles, whereas Cu-LGTO was shifted higher  $2\theta$  angle when compared with parent LGTO. This observation is consistent based on the ionic size of the guest  $Ag^+$  (1.28 Å),  $Sn^{2+}$  (1.18 Å) and  $Cu^{2+}$  (0.73 Å) replacing  $Li^+$  (0.76 Å) sites for octahedral coordination. The lattice parameters of LGTO, Ag-LGTO, Cu-LGTO and Sn-LGTO are refined using the least-squares subroutine of the standard computer program package POWD, and the results are displayed in Table S1 (supporting information). It is noted that Ag-LGTO and Sn-LGTO have slightly higher lattice parameters and Cu-LGTO has lower lattice parameters than parent LGTO. This result indicates that the ions ( $Ag^+$ ,  $Cu^{2+}$ , and  $Sn^{2+}$ ) were introduced into  $Li^+$  sites in the LGTO lattice.

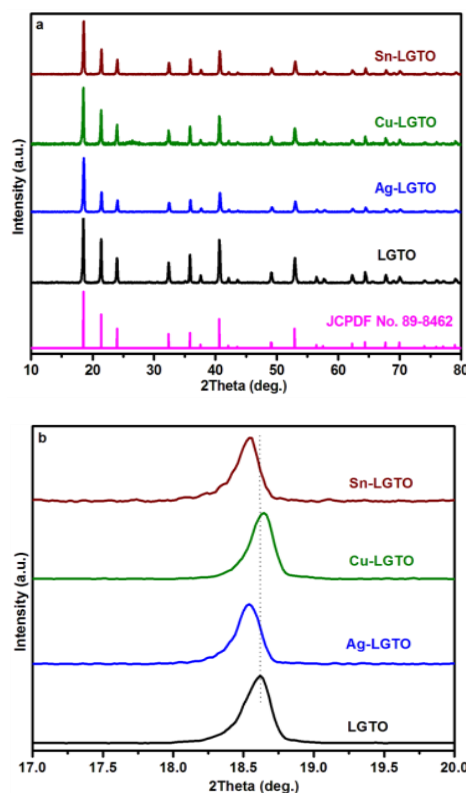


**Fig. 1.** (a) Powder XRD patterns of all catalysts (b) shift observed in the strongest diffraction peak for (003) plane ( $2\theta$  range  $17^\circ$  to  $20^\circ$ ).

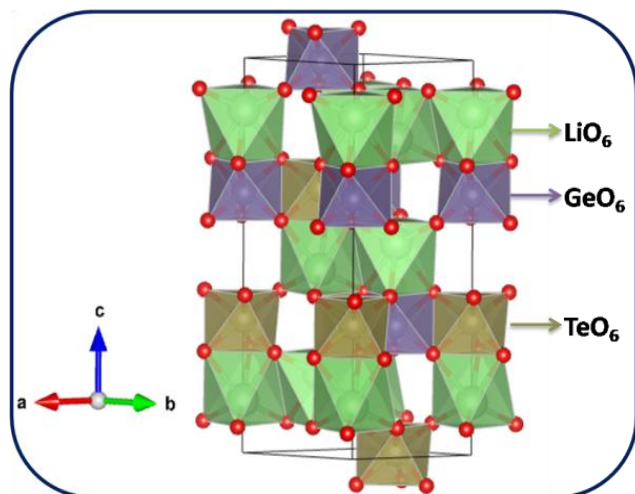


Fig. 2. Schematic representation of LGTO crystal lattice.

The structure of LGTO is similar to the ordered ilmenite form of  $\text{NaSbO}_3$  (Fig. 2). In the typical  $\text{NaSbO}_3$  (ilmenite) structure, the alternating layers of edge-sharing  $\text{SbO}_6$  are interleaved with  $\text{NaO}_6$  octahedra in an ordered fashion [18]. The  $\text{SbO}_6$  octahedra are in one plane without any deviation. The structure of LGTO was refined by Woodward *et al.* [19]. Although the structures of  $\text{NaSbO}_3$  (Ilmenite) and LGTO are similar, a major difference exists in these two structures: In LGTO, the Ge and Te octahedra are no longer in plane but displaced by about 0.2 Å, which is a consequence of the difference in size and/or charge between  $\text{Ge}(4+)$  and  $\text{Te}(6+)$  [19]. The Li ions have octahedral coordination and share edges with  $\text{GeO}_6/\text{TeO}_6$  octahedra.

#### FT-IR analysis

The presence of functional groups on the surface of the synthesized samples is examined by FT-IR analysis. The obtained results are shown in Fig. 3. The absorption band positions of all the doped samples are comparable to those of the parent LGTO; however, there are differences in the intensities. The absorption peak at  $470\text{ cm}^{-1}$  indicates symmetric stretching vibration of  $(\text{Li/Te})\text{-O}$  in  $\text{LiO}_6/\text{TeO}_6$  octahedral units [20,21]. Two strong bands in the range of  $560\text{-}580$  and  $710\text{-}730\text{ cm}^{-1}$  correspond to  $(\text{Te/Ge})\text{-O}$  stretching and bending vibration modes in  $(\text{Te/Ge})\text{O}_6$  octahedra, respectively [21,22]. The small band observed at  $\sim 1,085\text{ cm}^{-1}$  is due to  $\text{M-OH}$  bending vibrations on the surface of catalysts [14]. The broad absorption band in the region  $3300\text{-}3400\text{ cm}^{-1}$  is associated with  $\text{O-H}$  stretching vibration, while the band at  $1635\text{ cm}^{-1}$  is related to  $\text{H-O-H}$  bending vibration of adsorbed water molecules [23]. It is well known that the presence of  $\text{O-H/H-O-H}$  species is vital for photocatalytic degradation reactions because they can combine with photo-generated holes on the catalyst surface to produce hydroxyl radicals [24]. It is pertinent to note that the intensity of IR bands corresponding to  $\text{O-H/H-O-H}$  species is more for ion doped samples than parent LGTO, especially in Ag-LGTO. Thus, there are more  $\text{-OH}$  groups

on the surface of Ag-LGTO, which could lead to the generation of more hydroxyl radicals and hence expected to show higher photocatalytic activity.

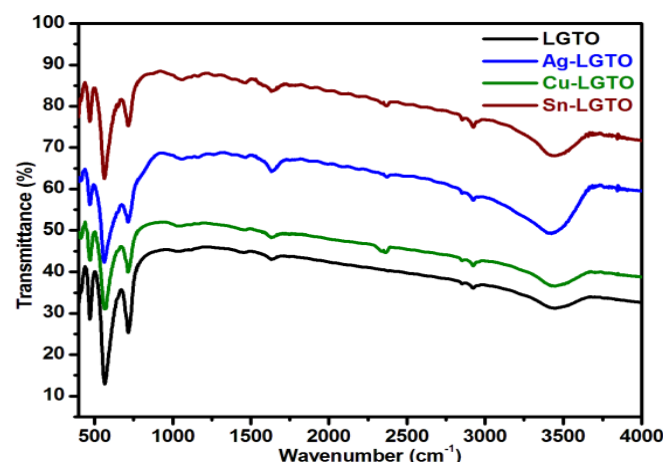


Fig. 3. FT-IR spectra of all catalysts.

#### SEM-EDS studies

SEM analysis was used to investigate the surface morphology of LGTO, Ag-LGTO, Cu-LGTO and Sn-LGTO samples, and the results are depicted in Fig. S1 (supporting information). According to the SEM images, all of the samples were mostly irregular-shaped discontinuous lumps with a considerable aggregation. In addition, some rod-shaped particles with a diameter range of  $2.5\text{-}4.2\text{ }\mu\text{m}$  can be seen in all samples. The morphology of parent LGTO did not change upon doping with  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Sn}^{2+}$  ions. The elemental composition of all the samples was examined by the EDS analysis (Fig. S2; supporting information). As shown in the EDS spectra, the existence of Ge, Te, and O elements in all the samples was confirmed, while Ag, Cu, and Sn elements were identified in Ag-LGTO, Cu-LGTO, and Sn-LGTO samples, respectively (Fig. S1). The absence of Li element in EDS spectra is owing to lithium low atomic mass [25]. Absence of peaks corresponding to impurities confirms the phase purity of all the samples.

#### Surface area (BET) analysis

The photocatalytic performance of semiconductors is strongly depending on the surface area. Surface areas of as-prepared samples are determined from the  $\text{N}_2$  adsorption-desorption isotherms using the BET method. Compared with the parent LGTO, the surface area was increased from 8.59 to 18.26, 13.32 and  $16.58\text{ m}^2/\text{g}$ , respectively, indicating that the doping of Ag, Cu and Sn ions can effectively improve the surface area of the parent LGTO. The increase in surface area in doped samples may be attributed to the decrease in the crystallite size. Noticeably, the highest surface area of Ag-LGTO sample suggests that it may provide more active sites for the MV dye molecules degradation and thereby achieving higher photocatalytic activity.

### UV-Vis DRS studies

The UV-Vis DRS analysis was used to determine the optical absorption properties of the as-synthesized samples in the range of 200–800 nm (**Fig. 4**). As shown in **Fig. 4**, all samples exhibited two absorption bands at 242 and 315 nm in the UV region, which can be ascribed to the ligand-to-metal charge transfer transitions. The parent LGTO exhibits an absorption edge at around 315 nm and has no absorption in the visible region. However, the absorption edge showed an obvious red-shift when  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  ions were doped into the parent LGTO lattice. This red-shift in the absorption band can be attributed to the formation of impurity levels within the bandgap of LGTO after the incorporation of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  ions. Furthermore, the absorption intensity in the visible region was remarkably enhanced. It is well-known that enhanced light absorption leads to the formation of more electron-hole pairs, which is beneficial to improve the photocatalytic activity of the catalysts [26]. A change in the color of the sample from white (parent LGTO) to black (Ag-LGTO), dark grey (Cu-LGTO) and light brown (Sn-LGTO) also provided supportive information regarding the red-shift of the absorption edge (**Fig. 3(b)**). Based on the Kubelka-Munk function (not shown), the bandgap energy of the LGTO sample was calculated to be 3.93 eV. It is observed that absorption edge tailing towards visible light is more pronounced in Ag-LGTO, Cu-LGTO, and Sn-LGTO, and hence attempts to estimate the band gap energy were not strived because this could lead to inaccurate results. The catalyst, Ag-LGTO shows higher visible light absorption and expected to exhibit relatively higher photocatalytic activity.

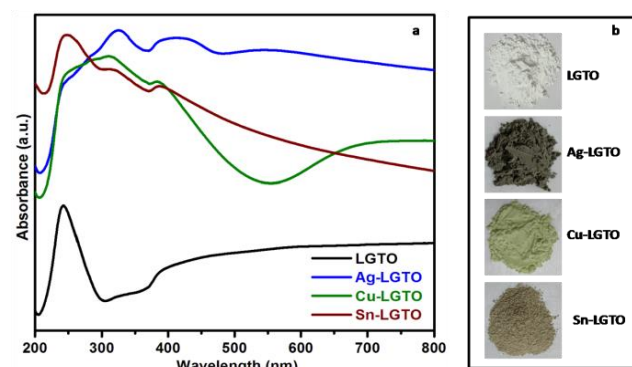


**Fig. 4.** (a) UV-Vis DRS plot and (b) colors of all catalysts.

### XPS analysis

The XPS measurements were performed to investigate the chemical composition and oxidation states of the elements in the synthesized samples. The survey scan XPS spectra of all the samples are shown in Fig. S3 (supporting information). As shown in Fig. S3, the parent LGTO shows the presence of Li, Ge, Te and O elements, while Ag, Cu, and Sn elements are found in Ag-LGTO, Cu-LGTO, and Sn-LGTO, respectively, along with Li, Ge, Te, and O. This result indicates that Ag, Cu, and Sn ions were successfully

doped into the LGTO lattice, as validated by the EDS analysis. The high-resolution XPS spectra of the Li 1s, Ge 3d, Te 4d and O 1s in LGTO and Ag 3d in Ag-LGTO, Cu 2p in Cu-LGTO and Sn 3d in Sn-LGTO are shown in **Fig. 5** and Fig. S4, respectively. The high-resolution XPS spectrum of the Li 1s revealed a strong peak at 53.1 eV (**Fig. 5(a)**), confirming that Li has an oxidation state of  $1^+$  [27]. The Ge 3d XPS spectrum (**Fig. 5(b)**) displays a broad peak at 33.6 eV, matching the Ge  $3d_{5/2}$  core level, corresponding to  $\text{Ge}^{4+}$  oxidation state [28]. In **Fig. 5(c)**, the two characteristic peaks of Te 3d are located at 576.6 and 587.4 eV, corresponding to the Te  $3d_{5/2}$  and Te  $3d_{3/2}$ , respectively, which indicates that Te is in the oxidation state of  $\text{Te}^{6+}$  [29]. The O 1s XPS spectra of the LGTO sample are shown in **Fig. 5(d)**. It is seen that the O 1s peak can be deconvoluted into two peaks located at 530.39 eV and 531.18 eV, indicating that there exist two oxygen states in the samples. The lower binding energy peak (530.39 eV) corresponds to lattice oxygen (OL) and the higher binding energy peak (531.18 eV) is usually ascribed to and surface hydroxyl species (OS) respectively [14,30]. In the Ag 3d XPS (Fig. S4a; supporting information) profile, two peaks at 367.4 and 373.6 eV can be assigned to Ag  $3d_{5/2}$  and  $3d_{3/2}$ , respectively. This result implies that Ag has an oxidation state of  $+1$  [31]. As for the Cu 2p (Fig. S4b; supporting information), two notable characteristic peaks at 933.4 and 953.5 eV can be endorsed to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively. Two satellite peaks at 942.5 and 962.5 eV are also visible, indicating the presence of  $\text{Cu}^{2+}$  in the Cu-LGTO sample [32]. The characteristic peaks at 486.6 and 495.2 eV (Fig. S4c; supporting information) correspond to Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$  spin-orbit components, which confirmed the presence of  $\text{Sn}^{2+}$  in the Sn-LGTO material [14]. The XPS results confirmed the doping of  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  ions into the LGTO lattice and have a good consistency with XRD.

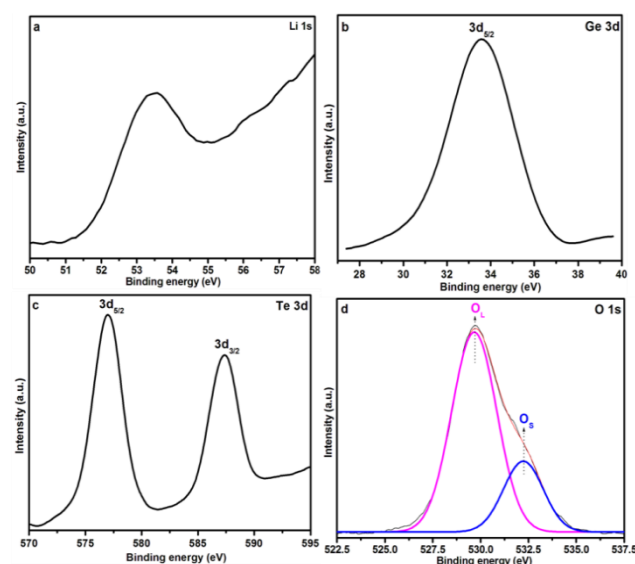


**Fig. 5.** High-resolution XPS spectra of (a) Li 1s, (b) Ge 3d, (c) Te 3d and (d) O 1s of LGTO.

### PL spectroscopy

Most photocatalytic studies have examined and confirmed the significance of bandgap towards the better activity of photocatalyst. The bandgap is a crucial factor that determines the electron-hole pair recombination rate. After the photoexcitation process, the separation of electron-hole pairs is mandatory for the photoreaction to occur. Photoluminescence (PL) spectroscopy can be used to qualitatively measure the electron-hole pair recombination rate. The PL signal originates from the recombination of electron-hole pairs. Thus, the intensity of PL signal is proportional to electron-hole recombination rate. The PL emission spectrum of as-prepared samples at an excitation wavelength of 280 nm is shown in **Fig. 6**. The decreased intensity of the signal around 425 nm for doped samples suggests the lowered electron-hole pair recombination rate, indicating the effect of dopants introduced into the parent LGTO lattice structure. Among all the doped samples, Ag-LGTO has least intensity. Thus, the Ag-LGTO catalyst has shown higher electron-hole pair separation, which is beneficial to enhance the photocatalytic performance.

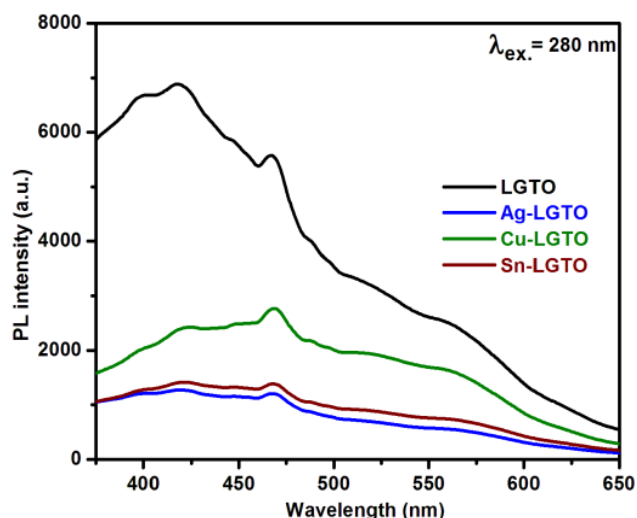


**Fig. 6.** Room-temperature PL emission spectra of all powder catalysts ( $\lambda_{\text{ex}} = 280 \text{ nm}$ ).

### Photocatalytic activity studies

The as-prepared samples LGTO, Ag-LGTO, Cu-LGTO and Sn-LGTO were evaluated for photocatalytic degradation studies on methyl violet (MV) dye. It is a persistent and carcinogenic dye and widely used in dyeing textiles, printing, and as pH indicator [33]. Biological and chemical methods of removal of MV have their shortcomings. This study presents a comprehensive degradation and mechanism of MV degradation in the presence of photocatalyst under the irradiation of visible light. Figure S5 (supporting information) depicts the temporal changes in the concentration of MV as a function of irradiation time under visible light irradiation in the presence and absence of catalysts. Clearly, the characteristic absorption peak

intensity of MV at 563 nm over Ag-LGTO was decreased faster than that of other samples with increased reaction time. The changes of  $C_t/C_0$  vs. time ( $t$ ) of all the photocatalysts are plotted and shown in **Fig. 7(a)**. The percentage of MV degradation in the absence of catalyst is about 9% indicating the photo-stable nature of MV dye. Further, the degradation percentage of the MV over the catalysts, LGTO, Ag-LGTO, Cu-LGTO and Sn-LGTO, is 37.8%, 68.6%, 44.8% and 56.5%, respectively. The ion doped samples have shown better photocatalytic activity than parent LGTO which is in accordance with PL results. Among the ion doped compositions, Ag-LGTO sample exhibits better degradation efficiency. In general, the dye degradation process is considered as a pseudo-first order reaction and is written as

$$-\ln \frac{C}{C_0} = kt$$

In this equation,  $C_0$  and  $C$  are concentrations of MV dye at 0 and  $t$  min, respectively;  $k$  is pseudo first order rate constant. The kinetics plots for photodegradation as a function of irradiation time are depicted in **Fig. 7(b)**. The calculated rate constant from the slope of linear fitted data for LGTO, Ag-LGTO, Sn-LGTO, and Cu-LGTO is 0.0023, 0.0064, 0.0032 and 0.0045  $\text{min}^{-1}$ , respectively. Thus, the higher rate constant observed for Ag-LGTO shows higher activity against MV degradation. It can be inferred that the photocatalytic degradation efficiency of the LGTO was substantially enhanced by doping, especially with  $\text{Ag}^+$  ions. The improved photocatalytic efficiency of Ag-LGTO can be due to the higher visible light absorption ability and lower recombination rate of photogenerated electron-hole pair, as confirmed by the above UV-Vis DRS and PL results.

The role of generated superoxide radicals, hydroxyl radicals and holes in the degradation mechanism is crucial [34]. To investigate the contribution of these radical species, scavenger tests were conducted over the Ag-LGTO sample. The scavengers such as ammonium oxalate (AO), benzoquinone (BQ) and isopropyl alcohol (IPA) were employed to trap holes, superoxide radicals and hydroxyl radicals respectively. The experimental results revealed that the degradation, which was 68.6% in the absence of any scavenger, has dropped to 14.3% (AO), 27.5% (BQ), and 31.6% (IPA) in the presence of scavengers (**Fig. 7(c)**). The decrease in photodegradation in the presence of scavengers is due to the trapping of reactive species that are responsible for the degradation. These results indicate that the combinational effect of all the  $\text{h}^+$ ,  $\text{O}_2^-$  and  $\text{OH}^\cdot$  species has a significant contribution towards the degradation of the MV dye molecules, affirming the deduced mechanism for photodegradation.

In addition to scavenger tests, the formation of hydroxyl radicals during the photocatalytic degradation process is justified by the terephthalic acid probe experiment. The hydroxyl radicals generated during photo-irradiation experiment are trapped with terephthalic acid to

produce 2-hydroxy terephthalic acid, which presents a strong fluorescent signal around 425 nm. The results obtained for terephthalic experiment in the presence of Ag-LGTO are shown in Fig. S6 (supporting information). As shown in this figure, a clear increase in the intensity of the PL signal with the time of irradiation is noticed, suggesting an increase in the concentration of the hydroxyl radicals with irradiation time. Meanwhile, the hydroxyl radical concentration of all the as-prepared samples at 120 min of irradiation time was also examined using the same process (Fig. 7(d)). As shown in Fig. 7(d), the concentration of hydroxyl radicals is in the order LGTO < Cu-LGTO < Sn-LGTO < Ag-LGTO, substantiating their order degradation efficiencies.

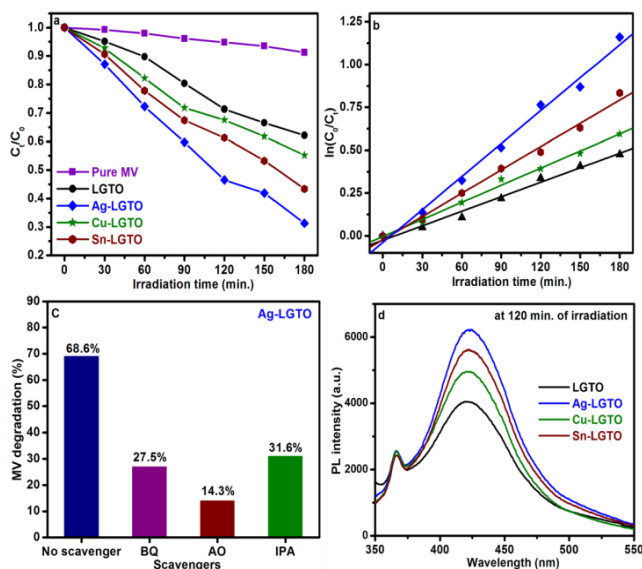


**Fig. 7.** (a) Degradation efficiency (b) kinetic curves for the photocatalytic degradation of MV of all catalysts under visible light irradiation (c) effects of different scavengers on the photocatalytic degradation of MV in the presence of Ag-LGTO (d) fluorescence spectra of all catalyst suspensions in the TA solution for 120 min of irradiation ( $\lambda_{ex.} = 320$  nm).

### Mechanism of photoactivity of MV over Ag-LGTO

Based on the obtained results, the probable photocatalytic mechanism for the MV degradation by Ag-LGTO is shown below: When the Ag-LGTO sample was irradiated with the visible light, electrons in the valence band (VB) excited to the conduction band (CB) with the same number of holes left in the VB. The photoinduced electrons on CB react with the dissolved oxygen ( $O_2$ ), generating the superoxide radicals ( $\cdot O_2^-$ ) by the reduction process. Some of these  $\cdot O_2^-$  radicals are neutralized with protons to form  $HO_2^\cdot$  species, which react among themselves and form  $H_2O_2$  and  $O_2$  species. Finally, the  $H_2O_2$  decomposes to form  $\cdot OH$  radicals [35]. Meanwhile, some of the holes in the VB could react with  $OH^-$  or  $H_2O$  to produce reactive  $\cdot OH$  radicals. As a result, the holes,  $\cdot O_2^-$  and  $\cdot OH$  radicals, can decompose the MV dye molecules into harmless degradation products.

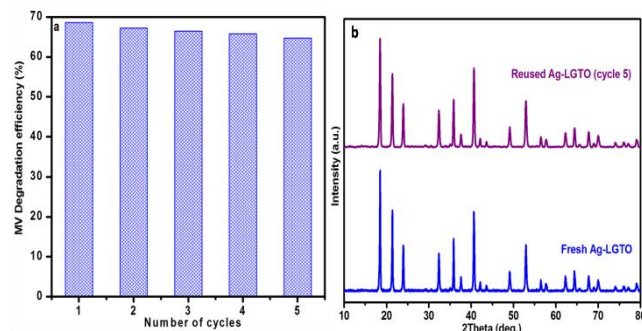
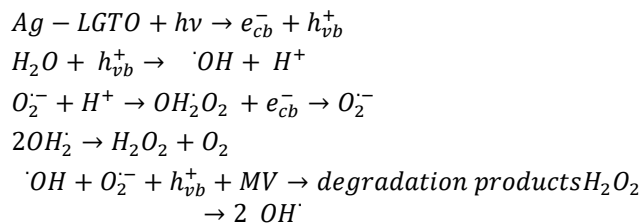


**Fig. 8.** (a) Cycling test for the photocatalytic degradation of MV in presence of Ag-LGTO (b) XRD patterns of fresh and reused Ag-LGTO catalysts.

To examine the reusability and chemical stability (including phase changes if any) of the photocatalysts, a recycling experiment was performed up to five cycles and the catalyst was subjected to XRD analysis. The catalyst employed in the first cycle, was separated, washed and used in the second cycle with fresh batch of dye solution. The procedure was repeated up to five cycles and the catalyst at the end of the fifth cycle was examined by XRD measurement. The recyclability experiment has shown considerable concordance in the percentage of dye degradation after each photodegradation experiment. The decrease in the percentage of degradation after five cycles of degradation was negligible. The powder XRD of the sample after fifth cycle of photodegradation was same as before indicating its chemical stability and did not undergo any phase changes. Therefore, the Ag-doped LGTO possess an excellent reusability and stability for photocatalytic degradation under visible light irradiation and can be employed for dye degradation experiments.

### Conclusion

The parent  $Li_2GeTeO_6$  and  $Ag^+$ ,  $Cu^{2+}$ , and  $Sn^{2+}$ -doped  $Li_2GeTeO_6$  samples have been successfully synthesized by solid state and facile ion-exchange methods, respectively. The doping of  $Ag^+$ ,  $Cu^{2+}$  and  $Sn^{2+}$  ions into the LGTO lattice was confirmed from (i) the shift in  $d$ -lines in XRD patterns, (ii) EDS analysis and (iii) XPS studies. The optical properties of parent  $Li_2GeTeO_6$  are tuned by doping of  $Ag^+$ ,  $Cu^{2+}$ , and  $Sn^{2+}$  ions with the introduction of impurity levels within the bandgap. Doping of these ions into  $Li_2GeTeO_6$  lattice has resulted in the visible light absorption. The photocatalytic activity of all the samples was evaluated by the degradation of MV dye under visible light irradiation.

The experimental results showed that the degradation efficiency of MV dye was enhanced substantially for all the doped samples than parent  $\text{Li}_2\text{GeTeO}_6$ . Among all the catalysts, the Ag-LGTO exhibited the highest photocatalytic performance and is attributed to the increased visible light absorption and lower electron-hole recombination rate. The scavenger experiments indicated that the  $\cdot\text{OH}$ ,  $\text{h}^+$  and  $\text{O}_2^-$  were participated in the photodegradation process. Further, the generation of hydroxyl radicals during photocatalysis was also verified from terephthalic acid experiment. In addition, the stability experiment shows that the Ag-LGTO photocatalyst is stable and can be reused at least up to five cycles.

### Acknowledgements

VK thanks to University Grants Commission (UGC), New Delhi for providing the Senior Research Fellowship (SRF; Registration No. 1211789). PV would like to express his gratitude to the CSIR, New Delhi for the award of Research Associate fellowship (File No. 21(1115)/20/EMR-II). MV thanks CSIR, New Delhi for the award of Emeritus Scientist (File No. 21(1115)/20/EMR-II).

### Author's contribution

Vaishnavi: Synthesized the materials, performed the experiments, and prepared the first draft; Venkataswamy: Conceived the plan, performed the experiments, data analysis, and took the lead in writing the manuscript; Manasa: performed the experiments and interpreted the data; Ramaswamy: Performed and interpreted the SEM-EDS analysis; Hima Bindu: Synthesized the materials, performed the experiments; Sudhakar Reddy: Formal analysis and performed the experiments; Vithal: Interpreted the results, supervision, project administration, resources, funding acquisition, and discussed and finalized the manuscript with the co-authors.

### Conflicts of interest

The authors of this work declare no conflict of interest.

### Supporting information

Detailed information about the structural parameters, SEM images, EDS patterns, XPS survey spectra, high resolution XPS spectra of Ag 3d, Cu 2p and Sn 3d, temporal absorption spectra of MV and fluorescence spectra using terephthalic acid over Ag-LGTO were given in the supplementary data.

### Keywords

$\text{Li}_2\text{GeTeO}_6$ , doping, ion-exchange, optical properties, photoluminescence.

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#### Graphical abstract

Ag-doped  $\text{Li}_2\text{GeTeO}_6$  showed the higher photocatalytic activity towards the MV degradation owing to the higher surface area, enhanced visible light absorption and reduced recombination rate of photogenerated electron-hole pairs compared to other catalysts.

