Bi$_2$O$_3$–BiFeO$_3$ Glass-Ceramic: Controllable $\beta$-/γ-Bi$_2$O$_3$ Transformation and Application as Magnetic Solar-Driven Photocatalyst for Water Decontamination

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**ABSTRACT:** Glass and glass-ceramic materials containing photoactive and magnetic crystalline phases were prepared from Fe$_2$O$_3$ and Bi$_2$O$_3$ using the conventional melt method. All samples were characterized in terms of formed phases, morphological analyses, optical properties, and magnetic properties. Formation of the photocatalytic tetragonal $\beta$- and body-centered cubic $\gamma$-Bi$_2$O$_3$ phases along with the magnetic BiFeO$_3$ and Fe$_3$O$_4$ phases was revealed. However, the crystalline structure relied on the composition and the applied heat-treatment time. $\beta$-/γ-Bi$_2$O$_3$ transformation could be controlled by the heat-treatment time. The samples exhibited variable magnetic properties depending on their composition. All of the samples showed excellent absorbance in visible light with an optical band gap of 1.90–2.22 eV, making them ideal for solar-light-driven photocatalysis. The best performance was recorded for the sample containing equal amounts of Fe$_2$O$_3$ and Bi$_2$O$_3$ due to the formation of $\gamma$-Bi$_2$O$_3$/BiFeO$_3$ heterojunction in this sample.

**INTRODUCTION**

Water quality has been deteriorating and became the main issue in many countries. In an effort to combat the problem of water pollution, rapid and significant progress in water/wastewater treatment has been made, including photocatalytic oxidation. However, the practical application of photocatalytic oxidation is usually restricted by two main factors, namely, photocatalyst separation/recovery and the utilization of costly commercial lamps. A plausible solution to overcome these obstacles is to use magnetically separable solar-driven photocatalyst, such as bismuth ferrite (BiFeO$_3$).

BiFeO$_3$ belongs to multiferroic materials possessing electric, magnetic, and structural order parameters that yield simultaneous effects of ferroelectricity, ferromagnetism, and ferroelasticity in the same material. BiFeO$_3$ has magnetic properties and has the highest ferroelectric polarization. Usually, BiFeO$_3$ present in a rhombohedrally distorted perovskite (ABO$_3$) structure with the R3c space group. It was demonstrated as a fairly attractive visible-light photocatalyst for the photo-organic pollutant decomposition because of its narrow band gap energy (2.2 eV), superior magnetic properties, and excellent chemical stability. BiFeO$_3$ nanoparticles were used in the photocatalytic degradation of different dyes like methyl orange, rhodamine B, methylene blue, congo red, and reactive black-S as summarized by Ponraj et al. (2017). However, BiFeO$_3$ usually exhibits limited photocatalytic activity. Different strategies were employed to enhance its photocatalytic activity including doping with rare-earth metals, nonmetal, or metal dopants. Additionally, better charge carrier separation and higher photocatalytic activity could be achieved via the formation of heterojunction between BiFeO$_3$ and other semiconductors such as TiO$_2$, BiVO$_4$, CuO, and g-C$_3$N$_4$.

Bismuth oxide (Bi$_2$O$_3$) is a good candidate for the formation of such heterojunction. This semiconductor has attracted great interest as a visible-light photocatalyst with a direct band gap ranging from 2 to 3.9 eV. Superior photocatalytic activity of Bi$_2$O$_3$ is principally attributed to the Bi–O layered crystal or special Bi–O polyhedron structures providing high surface area and more active sites. Additionally, the strong hybridization between Bi 6s 6p and O 2p electrons favors the mobility of photoinduced holes. Therefore, the photocatalytic activity of Bi$_2$O$_3$ relies on its crystalline structure and morphology. Usually, Bi$_2$O$_3$ exists in one of the polymorphs $\alpha$, $\beta$, $\gamma$, $\delta$, $\epsilon$, or high-pressure hexagonal phases. However, $\alpha$, $\beta$, $\gamma$, and $\delta$-Bi$_2$O$_3$ are the most predominant polymorphic forms. $\alpha$-Bi$_2$O$_3$ (monoclinic) and $\delta$-Bi$_2$O$_3$ (face-centered cubic) phases are stable at room and high temperature, respectively. Meanwhile,
\(\beta\)-\(\text{Bi}_2\text{O}_3\) (tetragonal) and \(\gamma\)-\(\text{Bi}_2\text{O}_3\) (body-centered cubic, BCC) phases are metastable, formed at high temperature, and usually transformed into \(\alpha\)-\(\text{Bi}_2\text{O}_3\) when the temperature is reduced.\(^1\)\(^2\)\(^3\) Among the different polymorphs of \(\text{Bi}_2\text{O}_3\), the \(\alpha\), \(\beta\), and \(\gamma\)-phases were demonstrated to possess high photocatalytic activity in the order of \(\alpha < \beta < \gamma\)-\(\text{Bi}_2\text{O}_3\).\(^1\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) The superior photocatalytic activity of \(\gamma\)-\(\text{Bi}_2\text{O}_3\) has been attributed to its disordered truncated octahedral \(\text{BiO}_5\) units providing more active sites and to its unique valence band structure.\(^1\)\(^7\)\(^8\)\(^9\)\(^10\)\(^11\)\(^12\) However, \(\beta\) - and \(\gamma\)-\(\text{Bi}_2\text{O}_3\) phases are metastable and cannot be obtained in pure form.

To the best of our knowledge, the photocatalytic behavior of the \(\text{Bi}_2\text{O}_3\)/\(\text{BiFeO}_3\) heterostructure has been studied a few times in literature. In these very recent publications,\(^2\)\(^2\)\(^3\) authors prepared this heterostructure using the costly nitrates precursors and monitored the change in characteristics of the developed glass-ceramic samples of different compositions that were prepared at different heat-treatment times. The collected XRD patterns are illustrated in Figure 2. Different crystalline structures were observed as summarized in Table 1. When equal amounts of \(\text{Bi}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3\) were used (i.e., BF samples), two major phases, tetragonal \(\beta\)-\(\text{Bi}_2\text{O}_3\) and \(\text{BiFeO}_3\) were observed in the as-prepared sample (Figure 2a). Heating this sample at 640 °C for 2 h resulted in the complete phase transformation from tetragonal \(\beta\)-\(\text{Bi}_2\text{O}_3\) to the body-centered cubic (BCC) \(\gamma\)-\(\text{Bi}_2\text{O}_3\) along with the formation of a new phase, \(\text{Fe}_3\text{O}_4\). These phases coexisted with the \(\text{BiFeO}_3\) phase that was already observed in BF as-prepared sample. The phase transformation from \(\beta\)- to \(\gamma\)-\(\text{Bi}_2\text{O}_3\) phase might be the result of the grain growth at the grain boundary or within the grains of \(\beta\)-\(\text{Bi}_2\text{O}_3\). Consequently, larger grains of \(\gamma\)-crystallites are formed after heat-treatment for 2 h due to the formation of \(\gamma\)-nuclei within the \(\beta\)-crystallites.\(^2\)\(^3\) This transformation could be additionally confirmed by the appearance of new peaks at 2\(\theta\) values of 24.95, 30.7, 33.22, 42, 52.92, and 62\(^o\), which recognized as the phase \(\gamma\)-\(\text{Bi}_2\text{O}_3\) (ICCD No. 1–74–1375). Increasing the heating time to 4 h caused, surprisingly, the partial reverse transformation from the \(\gamma\)-\(\text{Bi}_2\text{O}_3\) back to the \(\beta\)-\(\text{Bi}_2\text{O}_3\) phase (ICCD No. 1-75-0993), while the \(\text{BiFeO}_3\) and \(\text{Fe}_3\text{O}_4\) phases continue to exist. This backward phase transformation could be supported by the following two observations. First, the intensity of the peak at 2\(\theta\) = 31.92\(^o\) slightly increased after heating for 4 h and further increased after 10 h of heat-treatment. The second observation is that the intensity of the main peak of \(\gamma\)-\(\text{Bi}_2\text{O}_3\) at 2\(\theta\) = 27.96\(^o\) decreased gradually from the sample heat-treated for 4 h to that heat-treated for 10 h. This backward phase transition from \(\gamma\)- to \(\beta\)-\(\text{Bi}_2\text{O}_3\) might be due to the reformation of the disordered truncated octahedral units \(\text{BiO}_5\) and tetrahedral \(\text{BiO}_4\), which are the building blocks of cubic \(\gamma\)-\(\text{Bi}_2\text{O}_3\)\(^1\)\(^7\) after heating for a prolonged time. These results clearly demonstrate that the crystal structure of \(\text{Bi}_2\text{O}_3\) depends critically on the heat-treatment time.

On contrary, mainly amorphous structure with low-intensity peaks belonging to the \(\gamma\)-\(\text{Fe}_2\text{O}_3\) phase was observed in the as-prepared sample with a high content of \(\text{Fe}_2\text{O}_3\) (coded GF (as-prepared) in Figure 2b) likely due to iron acting as a glass former, which led to increased glass stability and retardation of the \(\text{Bi}_2\text{O}_3\) crystallization. Thereby, only low-intensity peaks relevant to the \(\gamma\)-\(\text{Fe}_2\text{O}_3\) phase was observed in this sample. However, heat-treatment enhanced, to some extent, the crystallinity of the GF glass-ceramic samples. The heat-treated GF samples possessed \(\text{Fe}_3\text{O}_4\) and \(\gamma\)-\(\text{Fe}_2\text{O}_3\) phases were observed in the as-prepared sample (Figure 2c) due to the high content of \(\text{Bi}_2\text{O}_3\). Additionally, peaks at 12 and 23\(^o\) were detected in both GB and GF samples. These diffraction peaks do not match with any known crystal structure and may be due to the formation of new or mixed phases.

The prepared materials were intended to be used as magnetic photocatalysts. Therefore, the magnetic behavior of the prepared materials was assessed from the recorded vibrating sample magnetometer (VSM) hysteresis loops depicted in Figure 3. It is interesting to note that the magnetic properties were found to be significantly dependent on the starting ratio between \(\text{Fe}_2\text{O}_3\) and \(\text{Bi}_2\text{O}_3\) of the materials rather than the heat-treatment. For instance, all BF samples prepared at different heat-treatment times depict nearly the same hard ferromagnetic remanent magnetization (\(r\)) of 0.16 emu/g (Figure 3a). A plausible explanation is that BF samples (either the as-prepared or the corresponding glass-ceramics) contain the same crystalline magnetic phases. The heat-treatment changed the crystallinity of \(\text{Bi}_2\text{O}_3\), which is a nonmagnetic component. As a result, all BF samples exhibited the same magnetic behavior. In

![Figure 1. DSC trace of BF as-prepared sample.](https://dx.doi.org/10.1021/acsomega.0c01307)
Figure 3b, the GF as-prepared sample exhibited interesting superparamagnetic behavior of 1.4 emu/g saturation magnetization ($M_s$) with $H_c$ and $M_r$ values of 146 G and 0.17 emu/g, respectively. It is well-established that the decrease in particle size is usually accompanied with a surface spin disorder, and the coercivity may approach zero if the crystal size is small enough. Consequently, this may give an indication of the formation of magnetic nanocrystallites in this sample; in this case, $\gamma$-Fe$_2$O$_3$ phase. The heat-treatment caused the growth of these nanocrystallites and the formation of the magnetic Fe$_3$O$_4$ and BiFeO$_3$ phases along with the nonmagnetic $\beta$-Bi$_2$O$_3$ phase as presented in the relevant XRD patterns (Figure 3b). Accordingly, heat-treated GF sample showed ferromagnetic properties with $M_s$, $H_c$, and $M_r$ values of 0.45 emu/g, 529 G, and 0.12 emu/g, respectively.

The GB as-prepared sample presents a linear magnetization-field strength ($M$--$H$) relationship with nearly neither $M_r$ nor $H_c$, which are typical characteristics of paramagnetic materials (Figure 3c). This would be expected, as this sample is mostly amorphous with a random arrangement of atoms. After heat-treatment for 10 h, the Bi$_2$O$_3$ and BiFeO$_3$ phases were developed in the GB glass-ceramic sample. The presence of these crystalline phases converted the GB glass-ceramic sample into a weak ferromagnetic material of very small $H_c$ and $M_r$.

To identify the morphology and the surface structure of the samples, imaging by field emission scanning electron micros-
copy (FE-SEM) was performed on the selected sample, BF. As Figure 4 demonstrates, the SEM image of the BF sample heat-treated at 640 °C for 2 h contains spherical particles embedded in a glassy matrix. However, after etching this sample for 150 s, the glassy matrix corroded, allowing a clearer appearance of the formed crystals as spherical particles in a homogeneous and uniform texture. In addition, some particles were diffrused with each other and precipitated on the surface in the form of rod-shaped particles (inset of Figure 4b). Evidently, increasing the soaking time to 10 h caused the growth of the granules (Figure 4c).

The optical properties of the as-prepared samples and the corresponding glass-ceramic samples were evaluated from the collected diffuse reflectance spectra. The absorption coefficient was calculated using the Kubelka–Munk equation (eq 1)²⁹  

\[
F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty}
\]  

where \(R_\infty\) denotes the reflectance of an infinite film and the function \(F(R_\infty)\) is equivalent to the absorption coefficient, \(\alpha\). The obtained absorbance spectra are presented in Figure 5.

The optical band gap (\(E_g\)) of the prepared samples could be determined by eq 2  

\[
(\alpha h\nu)^{1/n} = K(h\nu - E_g)
\]  

where \(\alpha\), \(h\nu\), \(E_g\), and \(K\) are optical absorption coefficient, photon energy, band gap, and a constant, respectively. \(n\) is a parameter related to the type of optical transition process in a semiconductor. That is, \(n = 1/2\) for direct transition, whereas \(n = 2\) for an indirect transition. Plotting \((\alpha h\nu)^{1/n}\) versus photon energy \((h\nu)\) (Tauc plot) gives the optical band gap \((E_g)\) by extrapolation of the linear part of this curve, as depicted in Figure 6. According to the presented data, the band gap energy of the prepared materials is in the range of 1.90–2.22 eV, confirming their absorption in the visible-light range (\(\lambda = 542–634\) nm). Additionally, it is noticeable that the heat-treatment time does not affect the optical properties in the case of the GB and GF samples. It only has a minor effect in the case of the BF sample where the band gap was red-shifted from 2.1 to 2.0 eV by applying the heat-treatment and conversion from glass to glass-ceramic.

Photodegradation Efficiency of the Prepared Samples. To assess and optimize the photocatalytic efficiency of the prepared materials, four main factors have been studied, namely, the composition, heat-treatment time, initial pH of the dye solution, and the etching of the glass-ceramic surface. Figure 7 illustrates the time variation of the dye concentration with simulated solar-light irradiation in the presence of the prepared materials. It is worth mentioning that the studied dye was not removed either by photolysis or adsorption in dark in these

### Table 1. Crystallization Characteristics of the Studied Glasses

| sample code | heat-treatment time | crystallized phases (ICCD No.) |
|------------|---------------------|-------------------------------|
| BF         | as-prepared 2 h     | T β-Bi\(_2\)O\(_3\) (01-78-1793); BiFeO\(_3\) (01-74-2016) |
| BF         | as-prepared 4 h     | BCC γ-Bi\(_2\)O\(_3\) (01-74-1375); BiFeO\(_3\) (01-74-2016); Fe\(_3\)O\(_4\) (01-88-0866) |
| BF         | as-prepared 10 h    | T β-Bi\(_2\)O\(_3\) (01-78-1793); BiFeO\(_3\) (01-74-2016); Fe\(_3\)O\(_4\) (01-89-0951) |
| GF         | as-prepared 2 h     | Fe\(_3\)O\(_4\) (01-89-0951); T β-Bi\(_2\)O\(_3\) (01-78-1793); BiFeO\(_3\) (01-74-2016); Fe\(_3\)O\(_4\) (00-039-1346) |
| GF         | as-prepared 4 h     | Fe\(_3\)O\(_4\) (01-89-0951); T β-Bi\(_2\)O\(_3\) (01-78-1793); BiFeO\(_3\) (01-74-2016); Fe\(_3\)O\(_4\) (00-039-1346) |
| GB         | as-prepared 2 h     | Bi\(_2\)O\(_3\) (03-065-3319); BiFeO\(_3\) (01-74-2016); α-Fe\(_2\)O\(_3\) (01-85-0987, 01-88-2359) |
| GB         | as-prepared 4 h     | Bi\(_2\)O\(_3\) (03-065-3319); BiFeO\(_3\) (01-74-2016); α-Fe\(_2\)O\(_3\) (01-85-0987, 01-88-2359) |

Figure 3. VSM hysteresis loops of the as-prepared samples and the corresponding glass-ceramic samples: (a) BF, (b) GF, and (c) GB.
experiments. According to Figure 7, it is noticeable that the degradation rate was influenced significantly by the composition and time of heat-treatment; in other words, by the crystalline structure. For a better comparison, the achieved dye removal after 6 h of irradiation was compared in Figure 7d. The highest removal percentage was observed mainly in the BF sample that was heat-treated for 2 h. This BF sample is composed mainly of the photoactive $\gamma$-Bi$_2$O$_3$ and BiFeO$_3$ phases according to the XRD analysis (see Figure 2a). This metastable $\gamma$-Bi$_2$O$_3$ was reported to be the most active polymorph among the Bi$_2$O$_3$ polymorphs because of its unique valence band structure, surface defects, strains, and reconstructions.\textsuperscript{16,17} Additionally, BiFeO$_3$ is the second crystalline phase of this sample, which also has photocatalytic activity, as illustrated by other researchers.\textsuperscript{5,22,30} It is worth noting that the combination between these two phases in one material should reinforce the photocatalytic activity due to the formation of heterojunction that enhances the accumulation of charge carriers in BiFeO$_3$\textsuperscript{31} as depicted in Figure 8. Other BF samples contain the $\beta$-Bi$_2$O$_3$ phase of lower photocatalytic activity, leading to a lower performance for the degradation of the RY160 dye.

Surprisingly, the amorphous GB as-prepared sample showed a slightly lower photodegradation efficiency than that of the BF sample heat-treated for 2 h but higher than those of other samples. Consequently, it can be deduced that this sample might contain very tiny photoactive crystals, which could not be detected by the XRD analysis. These crystals provide a sufficient number of active sites for the photodegradation of the RY160 dye. Other samples showed lower activity, which can be attributed to the formation of the less photoactive crystalline phases such as $\beta$-Bi$_2$O$_3$, Fe$_2$O$_3$, and Fe$_3$O$_4$. Therefore, this study supports the fact that stabilization of the metastable $\gamma$-Bi$_2$O$_3$ can provide excellent photocatalytic material.

To further understand and correlate the phase composition to the photocatalytic activity of the different prepared materials, BiFeO$_3$ and Bi$_2$O$_3$ phases were quantified and the results are displayed in Figure 9.

Among the different BF samples, the ratio of BiFeO$_3$ was the lowest in the as-prepared sample. Nevertheless, after heat-treatment for 2 h, an appreciable amount of BiFeO$_3$ phase was formed. Further heat-treatment for 4 and 10 h caused a reduction in the amount of BiFeO$_3$ phase. Contrary, the heat-treatment time had an insignificant effect on the BiFeO$_3$:Bi$_2$O$_3$ ratio in the GB, and GF glass-ceramic samples. For the GF group, all samples had comparable amounts of Bi$_2$O$_3$ and BiFeO$_3$ phases. Keeping in mind the low photocatalytic activity of pure BiFeO$_3$ illustrates the low photocatalytic activity of GF glass-ceramic samples. On the other hand, all GB glass-ceramic samples showed the BiFeO$_3$ ratio of about 24%. This ratio is smaller than that of the corresponding BF samples, explaining the lower photocatalytic activity of the GB group relative to that of the BF group.

Correlating the results of the phases quantification and the photocatalytic activity indicates that the enhancement of the
photocatalytic activity is ruled not only by the formation of the Bi₂O₃−BiFeO₃ heterojunction but also by the ratio of BiFeO₃:Bi₂O₃ phases. Changing the BiFeO₃:Bi₂O₃ phases ratio has a considerable effect on the photocatalytic activity. The BF 2 h sample achieved the highest photocatalytic activity, indicating that the optimum ratio of BiFeO₃:Bi₂O₃ phases in this composition is 34/66.

Figure 5. Kubelka–Munk transformation of the diffuse reflectance UV−vis spectra of the different as-prepared samples and the corresponding glass-ceramic photocatalysts: (a) BF, (b) GF, and (c) GB.

Figure 6. Tauc’s plot of the prepared samples: (a) BF, (b) GF, and (c) GB samples.
It is well known that the pH of the medium is a key factor in photocatalytic efficiency. Photodegradation of the RY160 dye was performed at different initial pH values to define the optimum pH of the photocatalytic reaction. The obtained results are depicted in Figure 10. The point at zero time corresponds to the normalized dye absorbance after the dark adsorption period. The photocatalytic degradation of the RY160 dye was possible only under acidic pH conditions because of the preferred adsorption of the dye on the photocatalyst surface under this condition. Therefore, more dye molecules can be attacked by the reactive oxidizing species that are photogenerated at the photocatalyst surface. The highest photodegradation rate was obtained at pH 3, with the pseudo-first-order rate constant of 0.90 ± 0.03 min⁻¹ (R² = 0.99). However, at pH 5, the rate constant dropped significantly to the value of 0.19 ± 0.02 min⁻¹ (R² = 0.90). Therefore, pH 3 can be considered as the optimum value for the degradation of the RY160 dye using the BF sample heat-treated at 640 °C for 2 h as a photocatalyst.

To improve the photocatalytic activity, the glass component was etched from the surface of the BF sample heat-treated at 640 °C for 2 h using an aqueous solution containing 0.2% HF and 0.2% HNO₃ for 150 s. Figure 11 compares the adsorption and photocatalytic performance of the nonetched and etched samples. The point at zero time corresponds to the normalized dye absorbance during the dark period. In contrast, the enrichment of the surface photoactive crystalline phases on the expense of glassy matrix could accelerate the photodegradation rate of the RY160 dye by
starting ratio between Fe$_2$O$_3$ and Bi$_2$O$_3$ of the materials rather highly dependent on the heat-treatment time. The magnetic ± to 1.42 treated at 640 °C for 2 h at different initial pH values [50 mL of the 10 mg/L RY160 dye solution and 2 g/L of photocatalyst].

![Figure 10. Photocatalytic degradation of the RY160 dye using the BF sample heat-treated at 640 °C for 2 h at different initial pH values.](image)

The performance could be enhanced by carrying out the photodegradation experiment at pH 3 and after etching the surface of this sample.

![Figure 11. Photocatalytic performances of the BF sample heat-treated at 640 °C for 2 h before and after etching.](image)

CONCLUSIONS

Glass-ceramic materials containing the highly photoactive metastable β- and γ-Bi$_2$O$_3$ phases with BiFeO$_3$ were successfully prepared using the traditional melt technique. The XRD analysis of these materials revealed the formation of different crystalline phases of Bi$_2$O$_3$ and iron oxide depending on the chemical composition of the parent glass and the heat-treatment schedule applied to develop the corresponding glass-ceramic. Remarkably, the transformation between β- and γ-Bi$_2$O$_3$ phases was highly dependent on the heat-treatment time. The magnetic behavior was demonstrated to be significantly dependent on the starting ratio between Fe$_2$O$_3$ and Bi$_2$O$_3$ of the materials rather than the applied heat-treatment. The calculated optical band gap energy of all prepared materials confirmed their high absorptivity to visible light. Photocatalytic activity tests for the degradation of the RY160 dye illustrated that the sample containing equal starting amounts of Fe$_2$O$_3$ and Bi$_2$O$_3$ and heat-treated at 640 °C for 2 h exhibits the best performance due to the formation of the γ-Bi$_2$O$_3$/BiFeO$_3$ heterojunction in this sample. The performance could be enhanced by carrying out the photodegradation experiment at pH 3 and after etching the surface of this sample.

EXPERIMENTAL SECTION

Materials. Reagent grades bismuth oxide (Bi$_2$O$_3$) and iron(III) oxide (Fe$_2$O$_3$) were purchased from Loba Chemie Company (India). The reactive yellow 160 (RY160) dye was supplied by a local dyeing factory. The chemical structure of this dye is presented in Figure 12.

![Figure 12. Chemical structure of the RY160 dye.](image)

Preparation of Glass-Ceramic Samples. Glass samples of different compositions were prepared using the conventional melting method. The samples’ codes, chemical compositions, and temperature of preparation are illustrated in Table 2. Briefly, a 100 g batch was melted in an electrical furnace (Nabertherm, Germany). The batch was swirled repeatedly to ensure the homogenization of the molten. Then, the molten was poured on a preheated mold. The cast samples were annealed in another preheated furnace to remove any stress in the cast sample. Finally, the samples were crushed to fine powders before assessing their photocatalytic activity.

Characterization of the Prepared Samples. The thermal behavior of the as-prepared samples was investigated using DSC analysis. The DSC traces were collected using a STD Q600 instrument (TA Instruments Company) at a 10 °C/min heating rate under nitrogen atmosphere (30 mL/min). α-Al$_2$O$_3$ was used as the reference material in this analysis. Crystalline phases developed in the glass-ceramic samples were identified from the XRD patterns obtained by an Empyrean XRD diffractometer (Malvern Panalytical Company). The XRD analysis was performed using Cu Kα (1.54060 Å) radiation in the 2θ range of 10–70° with 0.0260 step size and 18.87 s scan step time. The microstructure was examined for the intact specimen and for samples etched for 150 s in aqueous solution containing 0.2% HF and 0.2% HNO$_3$. A field emission scanning electron microscope FE-SEM (Philips XL30 model) was used for this purpose. Magnetic properties were assessed by vibrating sample magnetometer (VSM, Riken Denshi BH-55) at room temperature. UV–vis diffuse reflectance spectroscopy (DRS) was used to study the optical properties. DRS spectra, within the range of 200–1000 nm, were recorded by a JASCO spectrophotometer (model V570, Japan) using BaSO$_4$ as the reference material.

Photocatalytic Activity Tests. Photocatalytic activity of the samples prepared at different conditions was evaluated by the degradation of the RY160 dye under simulated sunlight. Irradiation system (model UVACube 400) was purchased from Honle UV Technology Company (Germany). This system is equipped with a halogen high-pressure lamp (model SOL 500) emitting light of a spectrum comparable to that of the natural sunlight. The emitted light passes through a filter (model H2) with a cutoff at 295 nm. In typical photocatalytic experiments, 2 g/L of the material under investigation was suspended in 50 mL of the 10 mg/L RY160 dye aqueous solution. The suspension was first agitated in dark before starting the irradiation. The reaction temperature was kept constant at

~1.5 times, specifically from $k = 0.90 \pm 0.03$ min$^{-1}$ ($R^2 = 0.99$) to $1.42 \pm 0.16$ min$^{-1}$ ($R^2 = 0.93$) for nonetched and etched samples, respectively.
20 °C by means of a chiller (Julabo FC400). During the reaction course, 3 mL of aliquots was withdrawn from the reaction medium at different time intervals and filtered through a 0.22 μm filter (Agilent) before the analysis. Variation in the dye absorbance was monitored spectrophotometrically using Jasco V630 spectrophotometer (Japan).

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### Notes

The authors declare no competing financial interest.

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