Structural characterization, electrical and photocatalytic properties of α–and γ-Fe_2O_3 nanoparticles dispersed in iron aluminosilicate glass

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Abstract

The glass samples with the composition of $40Fe_2O_3$-xAl_2O_3-$(60-x)SiO_2$ were prepared by sol-gel method. The samples were characterized by XRD, 80 K ^{57}Fe Mössbauer spectroscopy, TEM, FTIR and impedance spectroscopy. In the glass samples with less than 10% alumina, fayalite and hematite were crystallized by addition of hercynite. Whereas nanoparticles of hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) doped with Al were confirmed with the increase of alumina contents (15% and 20%). The glass samples exhibit the electronic conduction which is explained by the polaronic conduction mechanism. It is noticed that the catalysts containing a mixture of hematite and maghemite nanoparticles showed higher photocatalytic degradation of Rhodamine B dye than those containing hematite alone. It is suggested from the characterizations of newly developed iron-containing aluminosilicate glass samples that the materials with several bandgaps and without dissolving itself should be developed in the future for water purification under visible light irradiation.

1. Introduction

Iron-containing silicate glass can be a good candidate for effective decontamination and mineralization of organic pollutants due to the electron transfer between Fe^{2+} and Fe^{3+} ions and the ratio of the Fe^{2+}/Fe^{3+} ions in the glass can be easily regulated by changing the composition. Furthermore, the concentration of mixed-valence iron ions has a strong influence on the electrical properties of the glass [1]. T. Nishida *et al*. revealed that fly ash waste containing silicate glass shows an electrical conductivity from 10^{-8} to 10^{-6} S cm^{-1} due to electron hopping from less distorted $Fe^{II}O_6$ octahedra to distorted $Fe^{III}O_4$ tetrahedra [2]. S. Frindy *et al.* reported that the graphene doped hematite nanoparticles resulted in higher photocatalytic activity [3]. Hematite (α-Fe_2O_3) is a suitable material for our purpose, to fabricate suitable material with high photocatalytic ability, chemical stability, and natural availability [4-6]. Furthermore, hematite is of particular fundamental interest as it transforms from an antiferromagnetic (AF) to a weakly ferromagnetic (WF) state at about 265 K, known as Morin transition (T_M) [7]. Due to this 90-degree spin reorientation, the magnetic hyperfine field (B_{int}) of AF, WF and especially quadrupole splitting (Δ) changes more intensely at T_M. It was reported that a large positive value of $\Delta = 0.37$ mm/s is observed for WF state at 80 K, which usually has a negative value of -0.19 mm/s at RT [8,9]. Because of this large difference, both the WF and AF phases can be separately identified from the fitting of ^{57}Fe Mössbauer spectra, therefore Mössbauer spectroscopy is a powerful tool to study Morin transition. Also, this technique is well suited for studying structures of glassy and crystalline materials, lattice imperfections, especially the structural behavior of iron in glasses [10-13]. It should be mention that the temperature (T_M) at which Morin transition takes place depends on several parameters such as the size of the particles, lattice defects (e.g., low crystallinity, vacancies), the substitution of foreign cations (e.g., Al^{3+}) and surface defects [14-17]. E.D. Grave *et al.* reported a pronounced effect of isomorphous substitution of Al^{3+} in hematite on the behavior of the Morin transition [18]. They concluded that the transition temperature TM lowers with increasing alumina content and transition region significantly broader with increasing alumina. T. Nishida *et al.* observed an excellent IR light-transmittance in aluminate glass and showed doping of alumina to silicate-based glasses could increase the photocatalytic activity under visible light [19,20]. Mysen *et al.* reported that substitution of alumina for silicate can affect the structure of the environment around iron [21].

In comparison to pure α-Fe_2O_3, it has been found that alumina doped or alumina modified α-Fe_2O_3 can increase the conductivity to a large extent [22]. Zhou *et al.* demonstrated that one-dimensional (1D) nanorods of hematite (α-Fe_2O_3) showed high photocatalytic activities in the degradation of RhB dye under visible-light irradiation [23].

The main purpose of this work is to investigate the effect of alumina on the electrical conductivity and photocatalytic ability of iron-containing aluminosilicate glass samples toward Rhodamine B (RhB). RhB is one of the major cationic dyes and not biodegradable in wastewater. The effects of operating parameters such as H_2O_2 dosage, catalyst dosage and initial dye concentration were evaluated. Furthermore, a relationship between the local structure and electrical conductivity properties of samples was investigated using XRD, 80 K ^{57}Fe-Mössbauer spectroscopy, TEM, FT-IR, impedance spectroscopy (IS) to detect new aspects of alumina addition to the glass samples.

2. Experimental

2.1 Sample preparation

Iron-containing aluminosilicate glass with the composition of $40Fe_2O_3$-xAl_2O_3-$(60-x)SiO_2$ (in mass%, $x = 0$, 10, 15 and 20), abbreviated as 40Fe*x*AlSi was prepared by sol-gel method. Chemical reagents of 1-propanol, 7.8 M HNO_3 and $Si(OC_2H_5)_4$ were stirred for 2 h at 80 ºC for hydrolysis and precondensation of Si precursor. The synthesis started with dissolving 6.07 g $Fe(NO_3)_3$•$9H_2O$ and appropriate amount of $Al(NO_3)_3$•$9H_2O$ in the reaction mixture. Then gradually added 7.25 ml of propylene oxide and stirred for 2 h. After the gelation, the mixture was aged at 80 ºC for 2 h and dried at 60 ºC for 1 day. The dried xerogel was heat-treated at 1000 ºC for 100 min.

2.2 Characterization methods

The structure characterization of the samples was done by means of X-ray diffractometry (XRD), ^{57}Fe-Mössbauer spectroscopy (80 K), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), whereas the electrical conductivity measurements were carried by Impedance spectroscopy (IS). Powder X-ray diffractograms of the samples were measured in Bragg-Brentano geometry using a Rigaku diffractometer with Cu-K_α radiation (λ=0.1541 nm) generated at 50kV and 300mA, and monocromator at room temperature. The XRD patterns were recorded between 2Θ=10° and 80° with an accuracy of 0.02° and a scan rate of 5° min^{-1}. The patterns were evaluated using the EXRAY peak searching software (developed by Z. Klencsar at the Eötvös and Padova University, 1996) and the ASTM X-ray Diffraction Data (PCPDFWIN ASTM cards) were used for identification of the phases. ^{57}Fe-Mössbauer spectra were measured in constant acceleration mode at 80 K, using a source of 925 MBq ^{57}Co(Rh) and α-Fe as a reference of zero velocity and velocity scale calibration. The source was mounted on the MVT-1000 transducer, which is connected by MDU-1200 driving unit of a WISSEL type spectrometer. The driving unit was connected to DFG-1200 digital function generator. The γ-ray transmitted through the sample was detected by a Xe gas proportional counter at a voltage of 2 kV provided by an ORTEC 556 High Voltage Power Supply unit. The signals were amplified by ORTEC 142 preamplifier and ORTEC 570 amplifier and then recorded by a multi-channel analyzer (MCA-7700, Seiko EG&G). The samples with a weight of 40 mg were homogeneously dispersed in a disk of 10 mm in diameter and sandwiched with aluminum foil to improve thermal conductivity, and fixed inside the sample chamber for decompression. The internal pressure of the sample chamber was about 10^{-5} to 10^{-6} hPa with a vacuum gauge (PKR 361). Using a CryoMini Compressor (SW115) made by ULVAC CRYOGRNICS INC, and a CryoMini-cold head (M310 type), the sample chamber was cooled to 80 K, and a temperature controller (9650-I- 1-1 (410-10)) was used to measure the temperature up to 300K. For some 80 K measurements, a JANIS-type helium cryostat was also used. Mösswinn 3.0i XP program was used to analyze the spectra obtained. This program uses Monte Carlo simulation to calculate the errors. TEM images were obtained using a JEM-3200FS Field Emission Energy Filter Electron Microscope operating at 300kV accelerating voltage. Infrared transmission spectra were obtained by KBr method using a Fourier transform infrared spectrometer (Spectrum Two, PerkinElmer Co., Ltd.). The measurement wavenumber region was from 4000 to 370 cm^{-1}, the resolution was 4 cm^{-1}, and the number of integrations was 10.

Electrical properties were studied by impedance spectroscopy. Powder samples were pressed into cylindrical pellets having diameter 5 mm and thickness about 1 mm under a uniform load of 2 tonnes using a hydraulic press. For the electrical contact, gold electrodes 3.8 mm in diameter were sputtered onto both sides of disks using Sputter coater SC7620, Quorum Technologies. Complex impedance was measured using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer, Novocontrol Technologies GmbH & Co. KG, Germany) over a wide frequency range from 0.01 Hz to 1 MHz at room temperature (RT). The typical complex impedance plot consists of a single or multiple semicircles with the centers below the real axis. The equivalent circuit that represents each such depressed semicircle, with the center below the real axis is a parallel combination of a resistor (R) and constant-phase element (CPE). The CPE is an empirical impedance function of the type $Z_{CPE}^{*} = A(j\omega)^{-\alpha}$, where A and α are the constants. Experimental data were analysed by equivalent circuit modelling using the complex nonlinear least-square (CNLLSQ) fitting procedure. The values of the resistance obtained from the fitting procedures, R, and electrode dimensions (*d* is sample thickness and *A* is electrode area) were used to calculate the DC conductivity, $\sigma_{DC} = d/(R\times A)$.

The catalytic performance of the heat-treated samples was evaluated by the degradation of Rhodamine B dye aqueous solution (RhB_{aq}). At first, 40 mg of well-pulverized glass sample was added into 10 mL of RhB_{aq} with an initial concentration of 20 μM. Then, an appropriate amount of 0.2 M hydrogen peroxide was also added in the solution. UV-VIS spectra of RhB_{aq} before and after the photocatalytic reaction were measured by GENESYS^{TM} 10S UV-Vis spectrophotometer in which the visible light emitted by a metal-halide lamp with the wavelength region from 200 to 800 nm, the output power of 100 W and the intensity of 6 mWcm^{-2} on the sample surface. The dye concentration after each interval was measured using the UV–vis spectrophotometer at the wavelength of 554 nm.

3. Results and Discussion

3.1. Structural characterization

3.1.1. X-ray diffractometry

The evaluation of the XRD diffractograms for heat-treated 40Fe*x*AlSi glass samples was done by the help of EXRAY code (developed by Z. Klencsar in 1996) using PCPDFWIN ASTM cards [24]. Crystalline structure with sharp peaks ascribed to fayalite (Fe_2SiO_4, PDF No.: 72-0460), hercynite ($FeAl_2O_4$, PDF No.: 82-0594) and hematite (α-Fe_2O_3, PDF No.: 72-0469) phases could be detected for 40Fe*x*AlSi glass with '*x*' of 0 and 10. For 40Fe15AlSi and 40Fe20AlSi samples, besides quartz and hematite additional peaks attributed to maghemite (γ-Fe_2O_3, PDF No.: 39-1346) and sekaninaite ($Fe_2Al_4Si_5O_{18}$, PDF No.: 31-0616) phases were observed as shown in Fig. 1. The very broad halo patterns in each sample reflect the amorphous phase due to (alumino) silicate's 3D network. The identified crystalline phases can segregate into the glassy matrix during the heat treatment at different alumina content. Without alumina doping, fayalite dominates besides hematite. Upon 10% alumina addition the relative occurrence of fayalite decreases while hercynite and quartz appear beside the increasing amount of hematite. Above 15 wt% alumina doping hematite and maghemite are dominating together with quartz and sekaninaite, but the relative occurrence of the latter two phases is less in the 40Fe20AlSi sample.

By estimation, the crystallite size of maghemite and hematite, from their most intense reflections, using the Scherrer equation, ~8-9 nm and higher than ~16 nm were obtained, respectively. Therefore, it is concluded that γ-Fe_2O_3 and α-Fe_2O_3 have nanocrystalline characters and especially maghemite phase persists superparamagnetic nature. These behaviors can be well verified by Mössbauer spectrum and literature data for Al substituted maghemite from the work of daCosta *et al.* [25,26]. It was also stated in their study that the relative intensity of Al substituted maghemite in the XRD pattern is much less than its real occurrence in the phase composition. Our corresponding Mössbauer spectra indicate much more relative fraction of maghemite (Table 1) than that observed in the XRD measurement. Accordingly, Al-substituted maghemite was found in both 40Fe15AlSi and 40Fe20AlSi samples. Al^{3+} ions can be primarily incorporated into the silicate network owing to their network former ability. The heat treatment of alumina doped samples results in Al-substitution in hematite, too. This is clearly demonstrated by the 80 K Mössbauer spectra of 40Fe15AlSi and 40Fe20AlSi samples, which will be discussed in detail in the next section. Furthermore, the above fact is also supported by the change found in the XRD crystallite size from ~29 nm (15% Al) to ~17 nm (20% Al). The crystallinity of the hematite was improved up to 15 wt% alumina. Higher alumina substitution retards crystal growth. It indicates a lattice strain relief by a low concentration of small Al cation in the octahedral position. A similar trend of the crystallite sizes has been observed in the previously reported research of XRD peaks as a function of Al^{3+} in the hematite structure [27]. Since maghemite is isostructural with magnetite, the occurrence of magnetite cannot be excluded entirely based on the analysis of the XRD diffractogram. However, for the XRD patterns of 40Fe15AlSi and 40Fe20AlSi samples, nano magnetite could only be fitted with an unusual lattice parameter of 0.8329 nm instead of common 0.8392 nm according to the most accepted standard (ASTM card No 85-1436).

The above analyses of X-ray diffraction patterns are well consistent with the corresponding Mossbauer and TEM results.

3.1.2. ^{57}Fe Mössbauer results

Fig. 2 and Table 1 shows the Mössbauer spectra at 80K and data of heat-treated 40Fe*x*AlSi samples with *'x'* of 0, 10, 15 and 20. In the absence of Al^{3+} ($x = 0$), the spectrum showed two paramagnetic doublets and a sextet, first doublet due to Fe^{2+} microenvironment with isomer shift, δ of $1.26_{\pm 0.01}$ mm s^{-1}, quadrupole splitting, Δ of $2.97_{\pm 0.01}$ mm s^{-1} and absorption area, A of 80 % indicating a precipitation of fayalite (Fe_2SiO_4) [28] and another doublet due to $Fe^{3+}(T_d)$ with δ of $0.19_{\pm 0.02}$ mm s^{-1}, Δ of $0.49_{\pm 0.03}$ mm s^{-1} and A of 10 %, which can be associated with $Fe^{3+}(T_d)$ being in the glassy state. The sextet is the fingerprint of hematite with δ of $0.47_{\pm 0.01}$ mm s^{-1}, Δ of $0.36_{\pm 0.01}$ mm s^{-1} and hyperfine field, B of $52.6_{\pm 0.08}$ T [29]. The high content of fayalite in 40Fe0AlSi is due to the reducing effect of organic compounds, which is commonly observed in heat-treated xerogels prepared from TEOS [30,31]. The results of this analysis are well consistent with that derived from the room temperature spectrum and also with the phase composition obtained from the XRD analysis, however, the 80K spectra are able to supply more accurate data for the relative occurrence of the individual components. In 40Fe10AlSi sample, the Mössbauer spectrum includes a sextet due to hematite with δ of 0.45$_{\pm 0.01}$ mm s^{-1}, Δ of 0.21$_{\pm 0.01}$ mm s^{-1} and B of 51.6$_{\pm 0.07}$ T and two doublets both due to fayalite with δ of 1.24$_{\pm 0.01}$ mm s^{-1}, Δ of 2.96$_{\pm 0.01}$ mm s^{-1} and A of 59 % and to hercynite ($FeAl_2O_4$) with δ of 1.02$_{\pm 0.01}$ mm s^{-1}, Δ of 1.85$_{\pm 0.02}$ mm s^{-1} and A of 19 %. The decrease of the hyperfine field value of the sextet in comparison to that of 40Fe0AlSi spectrum is indicative of the Al-substitution of hematite due to alumina doping. On the other hand, the Mössbauer spectra of 40Fe15AlSi and 40Fe20AlSi samples were optimally decomposed into two doublets and three sextets. First doublet is due to Fe^{3+}(T_d) with increasing δ from 0.23$_{\pm 0.01}$ mm s^{-1} to 0.36$_{\pm 0.01}$ mm s^{-1} and Δ from 0.74$_{\pm 0.01}$ to 0.96$_{\pm 0.01}$ mm s^{-1}, respectively. The other small intensity doublet with δ of 0.84$_{\pm 0.01}$ mm s^{-1}, Δ of 1.98$_{\pm 0.01}$ mm s^{-1} for 15% alumina doping is attributed to Fe^{2+} microenvironment in sekaninaite, which was identified in these samples by XRD. In addition to the above-mentioned components, from the magnetically split components, two sextets were attributed to Al-containing hematite and one sextet to Al-containing maghemite. The spectrum obtained in Fig. 2(c) and Fig. 2(d), clearly shows the splitting of hematite spectrum into two components (sextets), which occurs in the case when Al is substituted into small particle size hematite leading to the depression of Morin temperature and coexistence of weak ferromagnetic and antiferromagnetic phases of hematite. The sextet having higher hyperfine field (B) ensues from antiferromagnetic phase (AF), while the with lower B from the weakly ferromagnetic phase (WF). The deviations in hyperfine field values between the 40Fe15AlSi and 40Fe20AlSi samples can indicate differences in the Al content of the samples. The hematite spectrum composed of the two sextets in spectra of 40Fe15AlSi and 40Fe20AlSi undoubtedly evidences the occurrence of Al-substituted hematite in these samples. These results indicated that the Morin transition in hematite

(α-Fe_2O_3) phase occurs when the Al_2O_3 content '*x*' reaches 15 or exceeds it. These results are in very good agreement with the previously reported for Morin transition in alumina-substituted hematites at 80 K [32-36].

The third sextet with broad lines and with *B* of $48.1_{\pm 0.09}$ T as well as *B* of $49.7_{\pm 0.09}$ T for 40Fe15AlSi and 40Fe20AlSi, respectively, reflects the Al substituted nano maghemite phase revealed by the corresponding XRD analysis. The assignment of this component was also based on the excellent correspondence of both 80K and room temperature Mössbauer parameters with those obtained for Al-substituted nano maghemite studied extensively by daCosta *et al.* [37,38]. Furthermore, the relaxation changes observed between the 80K and room temperature Mossbauer spectra reflect well the superparamagnetic nature of Al-substituted nanomaghemite in good correspondence with the crystallite size estimated from XRD. On the other hand, *B* for maghemite spectra obtained in this study increased with more alumina substitution (x=20). This happens when substituted Al for Fe in maghemite tends to occupy the A sites [39,40]. Batista *et al.* confirmed the maximum Al substitution in maghemite would be approx. 18.3 mol% (B = 49.70 T) [41], which is very close to the value estimated in our study. The Mossbauer analysis also revealed that the relative occurrence of Al-substituted maghemite is considerably higher in the case of the highest alumina substitution (x=20) than in the case of lower alumina doping (x=15). The precipitated phases obtained through Mössbauer results are in excellent agreement with those obtained by XRD analysis. The qualitative phase determination is more straightforward from the XRD, while the quantitative occurrence of individual phases can be determined more accurately from the 80K Mossbauer spectra.

3.1.3. TEM results

The TEM micrographs of heat-treated 40Fe*x*AlSi glass samples are shown in Fig. 3. A low-magnified TEM image [Figs. 3(a) and 3(b)] shows small dark particles embedded in the amorphous phase (see arrows), indicating the presence of crystallized phases in the glass matrix. It can be observed from these images that the number of crystallized species increased after the insertion of alumina in the samples, which is consistent with the results obtained from XRD measurements. Most of the particles have a spherical shape present with a large distribution in the range of about 25–190 nm. The crystal appears thicker at lower alumina substitution Fig. 3(b) but become increasingly thinner with higher substitution Fig. 3(c) owing to the smaller size of Al^{3+} ions than that of Fe ions [27]. The high-magnified TEM images [Figs. 3(d), 3(e) and 3(f)] illustrate the lattice fringes at distances of about 0.18 nm, 0.29 nm and 0.22 nm, which match well with the crystal facet of fayalite (151), hematite (104) and maghemite (222) respectively. These results indicated that the crystal size and architecture of the crystalline phases formed depend on the glass composition, particularly on alumina concentration.

3.1.4. FT-IR

Fig. 4(A) shows the Fourier transform infrared (FT-IR) spectra for the heat-treated 40Fe*x*AlSi glass samples in the frequency range (400–4000 cm^{-1}). In order to obtain the precise position of the bands, FT-IR spectra of all investigated glasses were deconvoluted, see Fig. 4(B). The strong band around 470 cm^{-1} in all the glasses is ascribed to the vibrations of Si-0-Si [42] and Fe-O vibrations of hematite units [43]. No significant change was observed in the 470 cm^{-1} band with the increase of alumina content in the composition. This suggests that probably there is no significant change in the intertetrahedral angle of O-Si-O [11,44]. The band at 545 cm^{-1} can also be attributed to $Al_{(octa)}$-O stretching vibration. The bands at 872 cm^{-1} and 948 cm^{-1} are ascribed to fayalite and to bending vibration of Si(OH) [45,46]. The strong and broad absorption band at 1090 cm^{-1} can be assigned to antisymmetric stretching vibrations of bridging oxygens present in SiO_4 units [47]. As shown in Fig. 4(B), the addition of Al_2O_3 into the 40Fe*x*AlSi glass lead this strong peak shift towards lower wavelength from 1090 to 1075 cm^{-1}. Al_2O_3 acts as a network former and can introduce into silica network in octahedral coordination. The absorption peak at 1632 cm^{-1} mainly originated from Al–O non-bonded in the silicate network and Fe–O bonds [48]. The sharp bands at 2857 cm^{-1} and 2926 cm^{-1} are attributed to the stretching vibration of C–H in the CH_3 and CH_2 groups [49] which disappeared in alumina containing samples. The broad absorption, again typical for amorphous materials, around 3400 cm^{-1} is ascribed to both OH stretching vibrations of structural hydroxyl groups and H_2O vibrations [50]. With the known fact the frequency of the valence-stretching vibrations is inversely proportional to the atomic mass, it was expected that the substitution of aluminium for silicon would cause an increase in the frequency (atomic mass of silicon > that of aluminium). This band is identical to those found in this region in the spectra of silica polymorphs and alkali aluminosilicates. These results confirm that the skeleton of 40Fe*x*AlSi glass is composed of mainly silica and partly alumina, the iron oxide NPs are typically distributed in the amorphous matrix.

3.2. Electrical properties

3.2.1. Impedance analysis

Maghemite has the same spinal ferrite structure as magnetite and the former can be considered as Fe^{2+}- deficient magnetite. The difference between the phases of γ-Fe_2O_3 and Fe_3O_4 is revealed in their electronic structure and, consequently, electrical properties. The conductivity of Fe_3O_4 is 1-10 Ohm^{-1} m^{-1}, whereas, for γ-Fe_2O_3, it has a value lower by 7-8 orders [51]. For this reason and the investigation of the effect of Al_2O_3 on the conductivity in the iron-silicate glass, we carried out impedance spectroscopy measurements. Fig. 5 shows the impedance spectra at room temperature for 40Fe*x*AlSi with '*x*' of 0, 10, 15 and 20. From the impedance plots, we can see that all four samples have similar shape and consist of two overlapping semicircles: one dominant one and the beginning of the second one which is not fully formed. The initial step in the interpretation of the impedance plot is to choose an appropriate equivalent circuit model and then to estimate the parameters of the chosen model. The CNLLSQ procedure and commercial Z-view fitting software were used [52]. The corresponding equivalent circuit used for fitting of the experimental data and obtained fitting parameters for heat-treated 40Fe*x*AlSi glass samples at room temperature are shown in Fig. 5 and given in Table 2, respectively. According to the appropriate equivalent circuit model used, various processes can be identified and separated based on the order of magnitude values of obtained fitting parameters (capacitance/resistance) [53,54]. The proposed interpretation refers to ceramics, but it can be used for other similar solid materials. The complex impedance spectra of 40Fe20AlSi are described by two equivalent circuits connected in series. The semicircle at higher frequencies corresponds to the sample bulk which is the glass matrix, circuit R1-CPE1, whereas the semicircle at low frequencies determined by an equivalent circuit, R2-CPE2, is related to the gran or/and grain boundary from the multiple crystalline phases in obtained partially crystallized the sample.

3.2.2. Electrical conductivity

Fig. 6, shows the conductivity spectra for 40Fe*x*AlSi with '*x*' of 0, 10, 15 and 20. It is noted at higher frequencies there is dispersion, and at lower frequencies conductivity goes to plateau. It means frequency-independence and corresponds to the total resistance from impedance spectra. In our samples, DC plateau is not formed and therefore the values of the fitting parameter R obtained from modelling along with sample geometry were used to determine the total DC conductivity as shown in Table 3. The lowest conductivity was observed in 40Fe0AlSi, in which the main crystalline phase is fayalite (only Fe^{2+} ions). It is reported that the total amount of iron such as Fe^{2+} decreases and the conductivity rises after introducing Al^{3+} in iron-containing silicate systems [55-57]. In our study, a significant rise in DC conductivity from $\sigma_{DC} = 4.46\times10^{-11}$ to $\sigma_{DC} = 1.20\times10^{-10}$ $(\Omega\ cm)^{-1}$ is present after introducing Al^{3+}, e.g., in 40Fe*x*AlSi with '*x*' of 10. The observed increase could be related to the presence of hercynite ($FeAl_2O_4$) and hematite (α-Fe_2O_3) phase confirmed by XRD and Mössbauer analysis. It is known that hercynite is the member of the spinel group with the formula $A^{2+}B_2^{3+}O_4$, which contains both $Fe^{2+}(T_d)$ and $Fe^{3+}(O_h)$ ions [58]. Electronic transport occurs via small-polaron hopping (SPH) mechanism where conduction takes place by electron hopping from Fe^{3+} to Fe^{2+} ions [59-62]. Additionally, the conductivity mechanism in hematite can also be understood within the SPH model. The electrical properties are controlled by the defects present in the hematite structure [63]. In particular, the presence of oxygen vacancies leads to two excess electrons and formation of Fe^{2+} sites. As a result, presence of iron ions in mixed valance states (Fe^{3+}/Fe^{2+}) results in the increase of polaron concentration and therefore, the overall DC conductivity enhancement. With further increase of alumina content in 40Fe15AlSi and 40Fe20AlSi glass samples, DC conductivity increases. In these two samples crystallization and formation of α-Fe_2O_3, γ-Fe_2O_3 and sekaninaite ($Fe_2Al_4Si_5O_{18}$) was observed in the glass matrix. The increase in DC conductivity for '*x*' 15 to 20 can be explained due to the strain developed in the lattice of Fe_2O_3 due to the small size difference of the dopant (Al^{3+}). Such strain is anticipated to increase conductivity. Furthermore, Al-substituted α-Fe_2O_3 has a smaller volume than pure α-Fe_2O_3 with a decrease in the Fe-Fe separation distance; hence Fe-d wave-function overlap would be increased and facilitate carrier hopping [64]. It is noted that there is no significant increase in electrical conductivity as alumina increase from '*x*' 15 to 20. This could be related to the deposition of alumina on the grain boundaries or the surface of hematite particles, creating a barrier for interparticle electron transport. Also, it is shown in XRD, the crystallite size of α-Fe_2O_3 decreases when the Al-substitution increases from '*x*' 15 to 20.

The values of DC electrical conductivity, presented in Fig. 7, correspond to the range $\sim 10^{-11} - 10^{-10}$ $(\Omega\ \mathrm{cm})^{-1}$. They are in the reference range for iron-doped aluminosilicate glasses at room temperature [65,66]. The evaluated DC conductivity variation with alumina for 40Fe*x*AlSi glasses are shown in Fig. 7. These results indicate that by adding alumina more crystalline phases appear which enables the formation of continuous conduction pathways for the uninterrupted polaronic transport which leads to an increase in DC conductivity as iron is present in mixed valance states in these phases.

3.3 Photocatalytic properties

3.3.1 Photodegradation

The photocatalytic activity of the heat-treated 40Fe*x*AlSi glass samples with '*x*' of 0, 10, 15, 20 was investigated by monitoring the photodegradation of the dye, rhodamine B, under visible light exposure in the presence of H_2O_2 additive. Fig. 8(A) shows the photodegradation curves obtained. All of the samples showed the decomposition of RhB in the photocatalytic reaction tests under visible light exposure. Measurements were made without visible light-exposure as well. In these measurements, the degradation rates were very low in comparison to the light-on experiments as shown in Table 4. This further proves the photocatalytic activity in 40Fe*x*AlSi.

Pseudo-first-order rate constant (*k*) of the RhB decomposition was estimated using the following equation, *i.e.*,

$$\ln(C_t/C_0) = -kt, \qquad (1)$$

where C_0 is the concentration of RhB_{aq} before photocatalytic reaction test (=20 μM). Values of k for RhB decomposition calculated from Fig. 8(B) for the blank and annealed 40Fe*x*AlSi glass samples are shown in Table 4. The best sample was 40Fe15AlSi yielding the highest pseudo-first-order rate constant of 14.89×10^{-2} min^{-1}, which is more than thrice of the reported uniform α-Fe_2O_3 nanocrystals ($k = 4.38 \times 10^{-2}$ min^{-1}) synthesized by the hydrothermal method [67]. The reason for the high degradation rate is the coexistence of the Al-substituted α-Fe_2O_3 and γ-Fe_2O_3 nanoparticles in the sample 40Fe15AlSi. Fig. S1 in the Supporting material shows the proposed mechanism for the photocatalytic degradation of RhB by α-Fe_2O_3/γ-Fe_2O_3 nanoparticles and hydrogen peroxide in visible light, which is summarized as the two bandgap energies of hematite (2.02 eV) and maghemite (2.03 eV) are contiguous, but they have different band positions. Accordingly, hematite has a conduction band level at −0.62 V and a valence band level at +1.40 V, while maghemite has two band levels at −0.08 and +1.94 V, respectively [68,69]. In their mixture, the electrons from the conduction band of hematite would move to the conduction band of maghemite, which results in an effective electron separation and transformation within the iron oxides. Consequently, the photo-induced electron reduces Fe^{3+} to Fe^{2+} which further reacts with H_2O_2 to produce hydroxyl radicals, OH• and these radicals then react with the dye and fasten the photocatalytic degradation process. In addition, such interaction of bands helps to reduce the probability of electron-hole recombination. Therefore, it is concluded that the photodegradation of RhB dye is probably caused by a successful combination of electronic structures of the phases of hematite and maghemite.

Fig. 9(a) shows the effect of H_2O_2 concentration on the degradation rate of RhB. The degradation rate of RhB increased from 80.0% to 92.7% with the H_2O_2 concentration ranging from 0.1 M to 0.2 M. This is determining because the amount of hydroxyl radicals increased with the increasing of H_2O_2 concentration. But the degradation rate of RhB decreases to 88.3% when the concentration of H_2O_2 is up to 0.4 M. Previous studies showed that excess amount of H_2O_2 is a disadvantage to the removal of organic pollutants due to the hydroxyl radical scavenging effect [70,71]. Thus, 0.2 M of H_2O_2 concentration is the best choice in our experiment.

Fig. 9(b) shows the effect of catalysts dosage on the photodegradation of RhB by 40Fe15AlSi. The results indicate that the degradation of RhB was significantly influenced by the dosage of the catalyst. A large enhancement in dye decomposition was observed when the catalyst dosage was increased from 1.0-4.0 g/L. It is mainly because of the increase in the number of active sites on the catalyst surface as well as the free hydroxyl radicals generation [72]. Also, more catalyst amount could increase the adsorption of RhB due to the oxygen-containing functionalities on the surface of the catalyst, leading to the rapid degradation of RhB. In this experiment, the degradation rate of RhB reached 92.7% at a catalyst dosage of 4.0g/L in 3h.

The effect of initial concentrations of RhB on its degradation was shown in Fig. 9(c). However, when the RhB concentration was relatively low (10 and 20 μM), the degradation rate constant was quite similar (0.147 and 0.148 min^{-1}), indicating no significant concentration effect on the degradation of RhB at lower concentrations. It is because of the sufficient amount of ·OH generated during the reaction. However, when the RhB concentration increased from 20 to 40 μM, the degradation rate decreased significantly ($0.038\ \mathrm{min}^{-1}$), which suggested that a high RhB concentration had a negative effect on the degradation kinetics of the RhB in the reaction system due to the limited yield of ·OH radicals. Furthermore, large amounts of dye molecules presented in solution block light utilization, thereby reducing the degradation rate [73]. The stability and reusability of the photocatalyst were evaluated by recycling the reactions for the degradation of RhB over 40Fe15AlSi glass sample. In each test, the solid catalyst was separated from its suspension via centrifugation and oven-dried at 60 ºC for 8 h. The decomposition rate of the catalyst still remained a high value (86%) after reusing it five times, offering the potential for practical applications. Fig. 10 shows that RhB degradation decreases gradually during five successive runs.

4. Conclusion

Electrical conductivity and photocatalytic ability of the glass samples obtained were found to strongly depend on the structural modifications. XRD and Mössbauer analysis confirmed Al-substituted hematite and maghemite nanoparticles in the heat-treated (alumino) silicate matrix. The crystallite size value depended on Al^{3+} substitution indicating that crystal growth is particularly influenced by alumina content as confirmed by TEM measurements. The presence of various crystalline phases that contain iron ions in mixed-valence states favors the formation of continuous pathways for uninterrupted polaronic transport which enhances an increase in DC conductivity. The addition of alumina could increase the Fe_2O_3 content (i.e., at the expense of fayalite), which further enhances the photodegradation rate constant. It is suggested from the characterizations of newly developed iron-containing aluminosilicate glass samples that the materials with several bandgaps and without dissolving itself should be developed in the future for water purification under visible light irradiation.

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