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Self cleanliness of Er^{3+}/Nd^{3+} Co-do ped lithium niobate tellurite glass containing silver nanoparticles

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ABSTRACT

TEM image revealed the nucleation of Ag NPs with average particle size ≈3.5 ± 0.01 nm. The FTIR spectra displayed seven absorption bands which are assigned to different bonding vibrations of the glass network structures. Raman spectra are comprised of five peaks centered around 205.3 cm^{-1}–213.3 cm^{-1}, 354.6–356.9 cm^{-1}, 375.3–380.9 cm^{-1}, 622.8 cm^{-1} and 845.4–849.6 cm^{-1}. Water contact angle is found to increase with increasing of Ag NPs contents. Our systematic methods of glass preparation, characterization and functionalization with optimum NPs inclusion may be useful for preventing the transparency loss of the proposed glass system (modification of the self-cleaning behaviors).

1. Introduction

Nowadays self-cleaning glass received great attention due to its easy maintenance, low cost and time economy in terms of prevention and removal of surface pollutants in retaining the aesthetic appearance [1]. It finds broad array of applications such as optoelectronic device, microfluidic devices, biomedical science, ships, building, automotive, self-cleaning windows and solar panels [2–3]. Self-cleaning ability depends on the materials water contact angle which can be achieved by controlling the wettability of the surface [4]. The principle of self-cleaning process in materials surface is based on lotus-effect which includes the hydrophilic and hydrophobic attributes [2]. The advantage of these materials is that they can clean on their own depending on the action of water on the surface. The water contact angle determines the solid surface as hydrophilic is smaller than 90° and the hydrophobic is >90° [3]. The unique functionalities of lotus-effect of the natural organism were attributed to the combination of special micro/nano surface structures and low surface-free energy materials covering the surfaces [2,5]. On super-hydrophobic materials, water forms spherical-like droplets which can easily be cleaned by rolling off together with the dust and dirt. However, the super-hydrophilic materials surface forms a layer with low contact angle.

Glasses co-doped with two rare earth (RE) ions that provide large luminescence efficiency in many wavelength ranges are considered as useful host material [6]. Nowadays, there are developments in high power light source operating at eye-safe mid-infrared region (2–5 μm) useful for various applications such as biomedicine, laser surgery, optical amplifier for communication and remote chemical sensing [6–8]. The mid-infrared emission around ~3 μm can be obtained from several active ions which are Er^{3+} (2.7 μm), Dy^{3+} (2.9 μm) and Ho^{3+} (3.0 μm). Among these three elements, Er^{3+} shows an ideal luminescent center for 2.7 μm emission originating from its $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition. However, 2.7 μm cannot be efficiently obtained when Er^{3+} is singly doped in glass or crystal because of the Er^{3+} fluorescence lifetime of the laser upper level ($^4I_{11/2}$) is considerably shorter than the lower one ($^4I_{13/2}$). Therefore, the population inversion of 2.7 μm emission cannot be easily achieved. To overcome this problem, co-doping the glass with another RE as sensitizer such as Nd^{3+} is frequently adopted to create a desirable population inversion of Er^{3+} through the energy transfer process, which improved the 2.7 μm emission [8–9]. Moreover, there is a limit of high concentration of RE dopants beyond which the tellurite glass displays luminescence quenching through energy transfer between RE ions. In this view, we take an attempt to modify the overall properties of lithium niobate tellurite glass by co-doping with Er^{3+}/Nd^{3+}.

Glass containing Ag NPs reveals photocatalytic action, where dust and other impurities on the material's surface are easily carried away in the presence of sunlight. Silver at nanoscale is promising as an alternative water disinfectant because of its unique physiochemical properties and excellent antimicrobial action [10]. The application of Ag NPs is currently limited with strong plasmon absorption and enhancing the luminescence by plasmonic near-field enhancement in typical distance 1 and 10 nm [11]. Modification of Ag NPs in thin film materials influences the photo-catalytic activity of nanocrystalline photo-catalysts because of its distinct optical and electronic properties. Ag can trap the photo-

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generated electrons from the semiconductor and allow the holes to form hydroxyl radicals, resulting in the degeneration reaction. In addition, Ag can enhance the photo-catalytic activity by creating a surface plasmon (SP) mediated local electric field. The optical vibration of SP in Ag can make a reasonable enhancement in the electric field. Therefore, the increase in photo-catalytic activity is due to the change in surface properties via the creation of oxygen vacancies and the crystal defects [12]. Despite few researches the development of Ag NPs incorporated glass to achieve an efficient self-cleaning properties is still lacking [2,12–17]. Moreover, the correlation between self-cleanliness and structural alteration is not fully understood.

In this view, we prepare three LNT glass samples containing Ag NPs with of Er^{3+}/Nd^{3+} co-doping. These glass samples are further characterized using XRD, EDX, FTIR, Raman and VCA measurements to evaluate their self-cleaning behaviour. A correlation between self-cleanliness and structural properties is established.

2. Materials and methods

Glass samples (here after called TLNENA) of the form $(68 - x)TeO_2 + 15Li_2CO_3 + 15Nb_2O_5 + 1Er_2O_3 + 1Nd_2O_3 + (x)AgCl$ with $x = 1.0$, 2.0 and 3.0 mol% are synthesized using melt quenching technique. Table 1 enlists nominal compositions of the prepared samples and their codes. A 15 g batch of analytical grade raw materials of TeO_2 (Sigma-Aldrich 99.0%), Li_2CO_3 (Sigma-Aldrich 99%), Nb_2O_5 (Sigma-Aldrich 99%), Er_2O_3 (Sigma-Aldrich 99.9%), Nd_2O_3 (Sigma-Aldrich 99.9%) and AgCl (Sigma-Aldrich 99.0%) in the powder form are well mixed and placed in a platinum crucible before being melted at 950 °C for 30 min in an electric furnace. Upon complete melting and achieving the desired viscosity the molted fluid is quenched between two steel plates followed by annealing at 320 °C for 5 h. Finally, the furnace is switched off and allowed to cool down to the room temperature to reduce the mechanical stress that causes the embrittlement. Glass samples are cut into desired size and polished for further measurements.

The SEM and EDX analysis of the glass sample are performed on a JEOL: Variable Pressure-Scanning Electron Microscope (VP-SEM) and Electron Dispersive X-ray (EDX) Oxford X-Max 50 mm, respectively. The amorphous nature of glass samples is verified using X-ray diffraction (XRD) (Siemens Diffractometer D5000), equipped with diffraction software analyser with Cu Kα radiation ($\lambda = 1.54$ Å) operating at 40 kV and 30 mA. The XRD data of powdered samples are collected in the range of $2\theta = 5$–90^o at scanning rate of 0.05^o/s. Transmission Electron Microscopic (TEM) imaging is performed using Philips CM12 operated at 200 kV in confirming the existence of AgCl NPs in different sizes, shapes and distribution in the glass matrix. Infrared spectra in the wavenumber range of 400 to 4000 cm^{-1} are recorded using the Perkin-Elmer Spectrum GX FT-Infrared Spectrometer are recorded. A fine glass powder was mixed homogenously with anhydrous potassium bromide (KBr) powder with the ratio of 1:100 mg before being compressed at 120 MPa to form transparent disc pellet of diameter 1 cm with resolution of 0.8 cm^{-1}. Raman analysis is performed using Confocal Horbia Jobin Yuon Model HR800 UV spectrophotometer with laser power of 1000 mW in the spectral range of 200 to 2000 cm^{-1}. The water contact angle is measured using Video Contact Angle System (VCA Optima) over the angular range of 0 to 180°.

To determine the self-cleaning ability of these glass samples, the surface wettability is measured using the static contact angles. The wettability of an ideal flat surface in terms of water contact angle yields [3]:

$$\cos(\theta_Y) = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \quad (1)$$

where γ_{sg}, γ_{sl} and γ_{lg} represent the interfacial tension of solid-gas, solid-liquid and liquid-gas, respectively.

Table 1
Nominal compositions and codes of Er^{3+}/Nd^{3+} co-doped LNT glass containing Ag NPs.

Glass code	Nominal composition (mol%)					
	TeO_2	Li_2CO_3	Nb_2O_5	Er_2O_3	Nd_2O_3	AgCl
TLNENA1	67.0	15.0	15.0	1.0	1.0	1.0
TLNENA2	66.0	15.0	15.0	1.0	1.0	2.0
TLNENA3	65.0	15.0	15.0	1.0	1.0	3.0

3. Results and discussion

3.1. Glass appearance

The colour of Ag NPs embedded in Er^{3+}/Nd^{3+} co-doped LNT glass is found to change from pink to darker pink with increasing Ag NPs contents. The samples are transparent and non-hygroscopic. During the process of heating, Te^{3+} has been oxidized to Te^{5+} and trapped in the glass matrix [18,19]. The change in glass colour indicates the successful incorporation of Ag NPs inside the amorphous matrix. Ag NPs embedment in the glass system occurred during the melting process through thermally assisted oxidation-reduction process. The melting temperature of AgCl is about 455 °C, Ag^+ ion is form by dissociating the Cl atom at about 500 °C where Cl^- is transformed to chlorine gas and evaporated. During thermal reduction process, Ag^+ gains an electron to form Ag^0. Finally neutral Ag^0 atoms agglomerate via Ostwald ripening to form Ag NPs. The thermal reduction pathway can be viewed as [20]:

$$Ag^+ + e^- \rightarrow Ag^0 \quad (2)$$

The reduction process involved between Te^{3+} and Ag^+ is likely view below [21]:

$$Te^{3+} + 2Ag^+ \rightarrow Te^{5+} + 2Ag^0 \quad (3)$$

3.2. SEM and EDX analysis

Fig. 1 shows the typical SEM image of TLNENA1 with nanosize probe taken from selected area in the glass sample to detect the existence and distribution of Ag NPs. The examined particles consist of a number of smaller objects of micrometers in size. The image clearly reveals the formation of isotropic and homogeneous glass. The structures of NPs are not evident due to limitation associated with the magnification. In addition, the NPs are formed deep inside the bulk matrix. The problems of sample charging caused and wash out the details on SEM picture. The

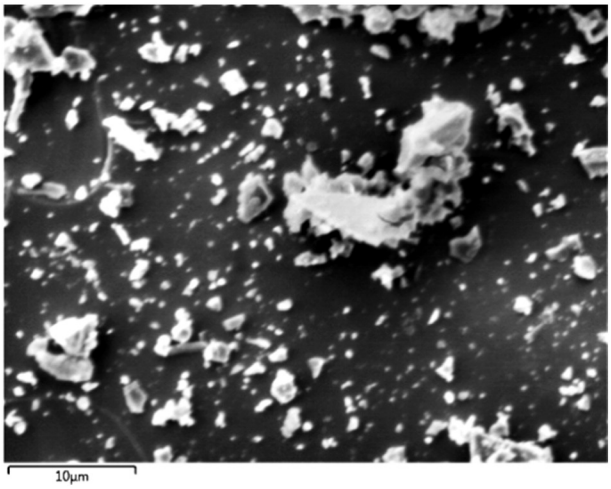

Fig. 1. SEM image of TLNENA1 glass.

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