Optical non linear characteristics of particles from natural resources

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Abstract. In these work some nano and micro particles such as granite, zeolite, diopside ferrous and sand glass which considered as waste or byproduct from mining industries. The micro and nano particles from natural resources were prepared by sieving and mixing with acidic solution at certain concentration, the particles are soaked and immerged in the acidic solution for long time to achieve reasonable hemogenity, sterring is done directly before measurements. The non linear characteristics of the prepared solution were measured by z-scan open apature technique. The results explained in terms of the composition and structure of the micro and nano particles. Granite particles does not introduce any emission due to compact structure, while zeolite, diopside ferrous and sand glass have significant non linear spectrum related to their structure. The research introduces new applications of the ceramics materials micro and nano particles in non linear optical devices. The research ends with conclusions and recommendation for future work in this new field of applications. The new techniques and the new materials selected in the current study have good non linear optical characteristics; these are promising for practical application. It can be used for various optical applications such as optical modulators, sensors and other optical protection applications.

1. Introduction

Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects[1],[2]. For example gold nanoparticles appear deep-red to black in solution. Nanoparticles of yellow gold and grey silicon are red in color. Gold nanoparticles melt at much lower temperatures (~300 °C for 2.5 nm size) than the gold slabs (1064 °C);[3] Absorption of solar radiation is much higher in materials composed of nanoparticles than it is radiation in thin films of continuous sheets of material. In both solar PV and solar thermal applications, controlling the size, shape, and material of the particles, it is possible to control solar absorption [3],[4]. other size-dependent property changes include quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super para magnetism in magnetic materials, which would appear the changes in physical properties[5],[6]. Ferromagnetic materials smaller than 10 nm can switch their magnetisation direction using room temperature thermal energy, thus making them unsuitable for memory storage [7],[8]. Nonlinear effects in electromagnetism had been observed as early as the late nineteenth century by Kerr, Röntgen, Kundt, and Pockels, and later by Raman in 1927 when he discovered spontaneous scattering of light into new wavelengths is passing through a transparent medium[9],[10]. the first observation of coherent nonlinear optical effects was made by Franken et al. (1961), who demonstrated second-harmonic generation of light in the crystal of quartz. This discovery propelled the field of modern nonlinear optics and initiated intensive research in materials science and crystal technology, figure 1 shows different applications of Non linear optical elements [11]. Non linear optical (NLO materials) has distinct crystal structure which is anisotropic with respect to electromagnetic radiation. It is the branch of optics that describes the behavior of light in nonlinear media, as a field of electromagnetic wave propagation, Media in
which the dielectric polarization $P$ responds nonlinearly to the electric field $E$ of the light\cite{12},\cite{13}. The nonlinearity is typically observed only at very high light intensities (values of the electric field comparable to interatomic electric fields typically 108 V/m) such as those provided by lasers. The fundamental aspects of nonlinear optical (NLO) materials and their role in modern communication were presented. NLO materials have distinct crystal structure which is anisotropic with respect to electromagnetic radiation \cite{14},\cite{15}.

Figure 1. Different applications of Non linear optical elements.

2. Experimental

2.1 Materials and methods
Preparation of nano and micro Ceramics Material (natural materials)
The micro- nano particles from natural resources (Granite, Zeolite, glass sand, diopside ferrous) were soaked for 100 hour in standard solution from distilled water with 30 % Sulphuric acid $H_2 SO_4$. Table 1 shows the relation between crystal structure and chemical composition for the micro and nano particles of ceramics materials used in the current study. The micro and nano particles were found as waste or by products during mining process. The particle size of waste material in this study was less than 0.125 mm. Figure 2 shows the apparatus use in mixing and preparation of samples.

Figure 2. The experimental apparatus for samples preparation.
Table 1. Chemical composition and structure of ceramics materials,

| Commercial name  | Composition                | Structure                                      |
|------------------|----------------------------|------------------------------------------------|
| 1. Granite       | SiO₂, Al₂O₃, K₂O, Na₂O₃,  |
|                  | CaO, FeO, Fe₂O₃, MgO, TiO₂,|                                                |
|                  | P₂O₅, MnO                  |                                                |
| 2. Diopside ferrous | SiO₂  |
|                  | Ca₉₂Fe₀₈ Al₁₄ Fe₃₃ Mg₅₃Si₂O₆|                                                |
| 3. Zeolite       | SiO₂, CaO, TiO₂, Na₂O, Al₂O₃,|
|                  | K₂O, Fe₂O₃, P₂O₅, MnO, SO₃ |                                                |
| 4. Sand glass    | SiO₂, Al₂O₃, Fe₂O₃, TiO₂, |
|                  | MgO, K₂O, Na₂O₃, CaO, Cr₂O₃|                                                |

2.2 Z-scanning method
Z-scan is a single beam technique developed by Sheik Bahae to measure the magnitude of nonlinear absorption as well as the sign and magnitude of nonlinear refraction in these measurements in the current study using the standard single beam technique. The signs and values of nonlinear absorption coefficient and nonlinear refractive index were determined by the open aperture z-scan technique. In our measurements, a Q-switched 532 nm (2.33 eV) frequency doubled Nd:YAG laser (Continuum) characterized by pulse duration of 6 ns was employed. The pulse repetition rate was set at 1 Hz to reduce the possible thermal accumulative effect. The laser energy was remain constant. below the optical breakdown threshold for the samples investigated. Care must be taken to prevent material optical breakdown and irreversible changes produced by laser radiation. the beam passing through the sample is inblocked (S=1) and all the transmitted light is recorded as a function of z., measurements were performed by placing the sample (liquid solution contain particles) in a quartz cuvette of thickness 3mm . The samples were placed at the focus of the lens with the focal length 15 cm. Figure 3 shows the experimental set up used in this work. The Z-scanning method of the recording device and the test process are not complicated, but this method provides very rich information about the tested object [14],[15].
Figure 3. The z-scnn technique used in this work

2.3 Theory explain Z-scan aperture

Open aperture z-scm and reverse saturable absorption (RSA) positive nonlinear absorption $\beta$, $\beta>0$, ESA>GSA

Saturable absorption (SA), Negative Non linear absorption $\beta$, $\beta<0$, ESA<GSA

$$T(z,S=1) = \sum_{n=0}^{\infty} \frac{(-\beta I_{eff})^n}{(m+1)\sqrt{1+\frac{z^2}{z_0^2}}}$$  \hspace{1cm} (1)

$$L_{eff} = \frac{1-e^{-\alpha L}}{\alpha}$$  \hspace{1cm} (2)

Non linear refraction (NLR) $n=n_0+n_2I$ \hspace{1cm} (3)

Non linear absorption (NLA) $\alpha(I)=\alpha_0+\beta I$ \hspace{1cm} (4)

$$\beta=\sum \beta_i$$  \hspace{1cm} (5)

Positive nonlinear refractive index (V-P), $n>0$
\[ T(x,\Delta \phi_0) \approx 1 - \frac{4\Delta \phi_0}{(x^2 + 9)(x^2 + 1)} \]  

(6)

Negative nonlinear refractive index (P-V), \( n_2 < 0 \)

\[ \Delta T_{P-V} \approx 0.406(1 - S)^{0.25} \left| \Delta \phi_0 \right| \]  

(7)

\[ \Delta \phi_0 = kI_0 n_2 L_{\text{eff}} \]  

(8)

\( \alpha \) The low intensity absorption coefficient

\( n_2 \) refractive index (The third-order nonlinear refractive index)

\( n_0 \) The linear index of refraction

\( n \) The refractive index in the presence of nonlinearity

\( \beta \) The two-photon absorption coefficient

\( I \) Intensity of incident laser radiation

\( \phi \) the on-axis phase shift

\( L_{\text{eff}} \) the effective interaction length

\( S \) the aperture linear transmittance

\( \chi \) the constant of proportionality known as the linear susceptibility.

\( L \) interaction length

\( E \) electric field

\( P \) induced polarization

\( \varepsilon \) Dielectric constant

3. Results and discussion

3.1 The new topic in this work can be summarized in two main points:-

First using insulated ceramics material in the powder form as nonlinear materials almost all previous work does not study this type of insulated materials.

Second preparation of the material as hinged particles in acidic solution at specific concentration solution phase measurement is often used to get information on microscopic nonlinearities. In the fluid phase, anisotropic molecules also exhibit another kind of nonlinearity, not observed in the case of inorganic semiconductors or salts, that is achieve flexibility for optimization of nonlinear optical response and necessary for studying non linear characteristics of material under fabrication.

3.2 Nonlinear properties of the samples

They were confirmed using open aperture Z-scan technique. Dependence of nonlinear optical properties on laser excitation energy is detected for different chemical composition and crystal structure Table 2 shows the Z-scan results for different ceramics materials prepared in acidic solution at the same volume percent and the same concentration of acid 30\%(battery water).

| Solution type | Composition       | Additive volume % | Effect      |
|---------------|-------------------|-------------------|-------------|
| 1             | Battery water     | 0                 | null        |
| 2             | Battery water     | Granite           | %\%        |
| 3             | Battery water     | Diopside ferrous  | %\%        |
| 4             | Battery water     | Zeolite           | %\%        |
| 5             | Battery water     | Sand glass        | %\%        |

From the above table, the physical origins of NLO phenomena can be categorized as either structural or compositional. Here structural refers to light-induced structure changes, There is no change in light-
induced chemical reactions, there is no significant difference in chemical composition between the
generated ceramics material under study all of the have silicate origin SiO\textsubscript{2} besides some other
oxides\cite{5,9}. The significant difference between the selected ceramics materials under study were in
the crystal structure which leads to change of electronic density, average interatomic distances,
molecular orientation, phase transition, the difference in the crystal structure as shown in the table (1)
leads to change in the non linear optical characteristics of the materials as shown in the following
curves.

Granite samples immersed in the acidic solution, the compact structure without any
significant interatomic distances in the structure prevent any transmission of light so all the incident
light was absorbed, granite cover prepared by the technique developed in this work can be used as
optical filter or optical protection to protect the sensitive detectors from the action of high power
Lasers. So the development of optical devices protecting eyes from laser radiation optical filters work
at all wavelengths as result of high attenuation of the transmission in the nonlinear regime and
complete beam decay happen, the new technique marked by high thermal and chemical stabilities
beside low cost The available protecting devices are optical filters, which don't transmit radiation at
specific laser wavelengths. The new devices made from granite particles immersed in acidic solution
can overcome the main disadvantages in the common filter which can be mentioned in the same
points. The filters may become transparent at high input intensity because of saturation of absorption.
The optical damage phenomena also may be occurs.

The open aperture z- scan of the acidic solution H\textsubscript{2}SO\textsubscript{4} with 30% was shown in figure (4). There is
Gaussian beam distribution appear with maxmum value at 50mm and minimum values at 0-
100mm, the solution does not introduce any nonlinear characteristics so it is ideal as media for
preparation of new particles from ceramics materials, it allows the determination of nonlinear
behaviour of the immersed particles without any confusion.

![Figure 4. Open aperture z-scan for acidic solution (H\textsubscript{2}SO\textsubscript{4} 30% concentration).](image)

Saturable absorption (SA) can be observed clearly in figure (5) where the open aperture z-scan for
zeolite particles imerged in the standard solution used in this work (H\textsubscript{2}SO\textsubscript{4} with 30% concentration)
the amount of particles were determined to be 20% volume percent \cite{14}. Saturable absorption (SA)
where the absorption coefficient decreases with increasing intensity, saturable absorption can occur when the cross-section of excited state less than the ground state cross section. Zeolite solution on glass covett measured by Z-scan technique, it is recorded saturable absorption beak at 38mm and other beak can be recorded at 55mm but as less value of normalized transmission.

The second-order nonlinear optical interactions can occur only in non centrosymmetric crystals that is happened in crystals that do not display inversion symmetry. Since liquids, gases, amorphous solids (such as glass), and even many crystals display inversion symmetry. The solution prepared in our work has inversion symmetry and suitable for second -order nonlinear optical interaction. Third-order nonlinear optical interactions can occur for both centrosymmetric and noncentrosymmetric media [13] so it is can occur in the solution prepared in our study range. In other words the new technique developed in this work is suitable for second and third order non linear optics.

Figure 5. Open aperture (z-scan) for zeolite nano and micro particles at volume fraction 20%.

In figure (6) The measured nonlinear refractive index and absorption coefficient of the diopside ferrous solution on glass covett by Z-scan technique was recorded. It is observed saturable absorption (SA) at 40mm and a transition from saturable absorption to reverse saturable absorption at 50mm and 60mm with decrease in normalized transmission. reverse saturable absorption (RSA), where the absorption coefficient increases with increasing intensity. RSA can occur when the absorption cross-section of excited states exceeds the ground state cross section. The behaviour is re-reverse to saturable absorption(SA) at 70mm, The complex behaviour of the diopside ferrous is related to the existance of some compounds mixed with the original structure such as Illite-2M1 (NR), Actinolite,Hematite and Montmorillonite[1],[3]. The electronic structure change is the distribution of electrons at different electronic states. The nonlinearity can be enhanced by several orders of magnitude by sacrificing response time and absorption loss.
Figure 6. Open aperture (z-scan) for diopside ferrous micro and nano particles with volume fraction 20%.

Reverse saturable absorption (RSA) can be observed clearly in figure (7), the nonlinear behaviour of sand glass emmerged in standard acidic solution (H$_2$SO$_4$ 30%), with volume fraction 20%.

Figure 7. Open aperture z-scan for sand glass micro and nano particles at 20% volume fraction.

When the absorption cross-section from excited state is larger than that from the ground state, the transmission of the system will be less under intense laser fields. The normalized transmission exhibits a small one valley with respect to the focus at ($z = 50$mm), implying that the RSA plays a primary role for the nonlinear properties of material. Sand glass introduce special pure and simple behaviour when
comparing this with the behaviour introduced by other ceramics materials under study. the behaviour of sand glass can be explained in terms of the purity and transparency of the crystal [8].

3.3. Disadvantages of the new technique
The new technique has only one disadvantage that the concentration of solution is inhomogenous due to precipitation of particles under their weights. The future research will be developed to overcome this disadvantage.

3.4. Advantages of the new technique
1) Abundant and low cost achieve economic version of non linear optical material
2) Avoid effects occurs in resonant NLO interactions due to the absorption of light and the generation of phonons.
3) Avoid thermal effect
4) Suitable for different applications
5) Suitable for second order and third order non linear phenomenas

4. Conclusions
1. Development of new type of materials from natural resources suitable for optical non linear characteristics
2. The new techniques and the new materials selected in the current study have good non linear optical characteristics; these are promising for practical application. It can be used for various optical applications such as optical modulators, sensors and other optical protection applications.
3. Granite particle prepared by the technique mentioned in the current work can be used as optical protect and/or optical filter which can overcome the disadvantages in the common filters or protection devices.
4. Open the way to the study of new nonlinear optical effects and the introduction of new concepts, and find and develop materials presenting large nonlinearities and satisfying at the same time all the technological.

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