Oxidation and Photo-Eged Studies of Graphen-Like Two Dimentional Arsenic-, Germanium Sulfide Crystalls and Nanostructured Glasses

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Arsenic sulphide minerals are found naturally and have been used as artists' pigments since prehistoric times. Orpiment As_2S_3 gives a yellow pigment and realgar As_4S_4 usually gives an orange-red. Recently by macro FT-Raman and energy-dependent micro-Raman spectroscopy we found the light-induced structural changes in glassy As-S system with realgar inclusion [1,2]. New observed features in the Raman spectra of As-S glass are related to transformations of As_4S_4 molecules. Being initially in the structure of glassy closed and connected with glassy network only by weak Van der Vaals forces α (β)-As_4S_4 molecules are transformed into pararealgar p-As_4S_4 form during laser illumination. The effectiveness of transformations depends mainly from photon energies used for irradiation but transformation tendency observed for all used photon energies ranged from 1.65 to 2.54 eV. Our findings are multidisciplinary and may have a significant value to play in disciplines such as natural resources, prehistoric artistic expression, archaeology, art history and chalcogenide photonics. Based on our finding of light-induce realgar-paraleargar transformation the additional related investigations [3] also found realgar degradation by different halogen lamps and a LED lamp, used in museum exhibitions are helpful to describe the photo-degradation processes in pigment[4].The light remains unique because it can neither be eliminated nor completely controlled. The red colour of the pigment based on realgar α-As_4S_4 on exposure to light transformed to pararealgar p-As4S4 that exhibits yellow colour. Based on our investigations, the light necessary for viewing a work of art with realgar pigments, can damage the artwork starting from with photon energies equal 1.65 eV with relatively high intensities 10^2 W/cm^2. Process of light induces polymorph transformation on air is accompanies with formation arsenolite As_2O_3 and finally lead to whitening of realgar. The process is not completely clarified so far. Based on SRPS, XPS and surface enhance Raman

and PL spectroscopy studies we found some photo-aged processes occurring on the surface of amorphous As_2S_3 film for chalcogenide photonics. In energy dependent luminescence in orpiment, realgar and glassy As-S with realgar inclusion we have found evidence of As_2O_3, As_2O_5 formation and PL band typical for substance known in general formula $As_2O_3xH_2O$. Last is show that is why the illuminated places with realgar in high humidity condition can by wet. May be this finding help to give answer why some places on paintings "dry". The positions of PL bands in excitation-dependent photoluminescence of aged and freshly fractured g-$GeS_2(T_iV_j)$ prepared with different rate of quenching (V_j) and melt temperature (T_i) are compare and analyse together with Raman PL , XPS spectra of GeS, β-GeS_2 . Excitation-dependent PL spectra of g-$GeS_2(T_iV_j)$ exhibit increasing intensity up to E_{ex} = 2.75 eV . For this E_{ex} the strong broad green band centred at 2.37 eV appear. Such behaviour of PL spectra of β-GeS_2 is typical for GeO_2 with quartz-like structure.

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