THERMOLUMINESCENCE DEPENDENCE ON THE WAVELENGTH OF MONOCHROMATIC UV-RADIATION IN Cu-DOPED KCl AND KBr AT ROOM TEMPERATURE

A. Pérez-Rodríguez, T. Piters, R. Aceves
R. Rodríguez-Mijangos, R. Pérez-Salas

Departamento de Investigacion en Física
Universidad de Sonora
Apartado Postal 5-088 Hermosillo, Sonora, 83190, Mexico

E-mail: rperez@cifus.uson.mx

Abstract

Thermoluminescence (TL) dependence on the UV irradiation wavelengths from 200 to 500nm in Cu’-doped KCl and KBr crystals with different thermal treatment has been analyzed. Spectrum of the TL intensity of each material show lower intensity at wavelengths longer than 420nm. The TL intensity depends on the irradiation wavelength. Structure of the TL intensity spectrum of each sample is very similar to the structure of its optical absorption spectrum, indicating that at each wavelength, monochromatic radiation is absorbed to produce electronic transitions and electron-hole pairs. Thermoluminescence of materials with thermal treatment at high temperature shows electron-hole trapping with less efficiency. The results show that Cu-doped alkali-halide materials are good detectors of a wide range of UV monochromatic radiations and could be used to measure UV radiation doses.

Keywords: Thermoluminescence, ultraviolet radiation, alkali halide, uv-detectors
1.- INTRODUCTION

Thermoluminescence is a technique very useful to measure irradiation dose in materials. Actually, it is the mostly used for dosimetry applications. In addition, it provides us with an important tool to analyze and characterize the kinetics of recombination of different types of defects induced by irradiation in materials. For example, it has been used to study the F center participation in the electron-hole (e-h) recombination [Murty and Murty 1974; Delgado 1983; Manam and Rao 1990].

Nowadays, it is being used to study the formation of traps in the presence of nanoparticles. Nanoparticles can be formed and found in different environments such as glasses or crystals. It is known that CuX (X halogen ion) nanostructures can be self-structured in alkali halide hosts showing size effects. Optical absorption spectra of CuX nanoparticles and CuX bulk are very similar, but the former are shifted to higher energies as nanoparticles size decreases. In the case of CuX nanoparticles, their size depends on the annealing of the crystal. These materials absorb radiation in the 200 to 400 range [Haselhoff and Weber 1998]. Cu⁺ doped alkali halide crystals show an absorption band in the 230-280nm range which has been assigned to the electronic transitions of the Cu⁺ ions. While in the region of 300 to 400nm, absorption band is associated with the band-to-band electronic transitions of copper halides nanoparticles. On the other hand, the effects of X-ray irradiations at room temperature on KCl:Cu were studied by Delgado [1983]. He show that non-irradiated samples excited with UV light has two main emission bands at 400 and 420 nm, ascribed to isolated Cu⁺ ions and copper aggregates, respectively, and similar bands appear in the thermoluminescence spectra. F and M bands induced during irradiation show annealing steps simultaneously to the glow peaks. They indicate that the irradiation induced Cu⁻ and Cu⁰ centers can be electrically compensated by anion vacancies, and suggest that irradiation induces impurity aggregation as well as anion interstitial aggregation. These results lead them to assume that thermal release of interstitials may excite isolated Cu⁺-ions and copper aggregates, either through energy transfer from F + H recombination or by H+α → Vk, Vk + Cu⁰ reactions.

In another work, Li et al. [2005], found that KCl:Cu⁺ powder sample, after being exposed to non-monochromatic UV light, shows near ultraviolet blue luminescence by stimulation with F-light. They assume that Cu⁺ does not change into Cu²⁺ by UV irradiation. Thus, Cu⁺ ions do not act as hole traps, while anion vacancies act as electron traps. Once UV excited sample is stimulated, electron from F center combine with hole trapping center or Vₖ center, and cause subsequent energy transfer to Cu⁺ ion. Then, the characteristic emission
attributed to $d$-$s$ transition of Cu$^+$ in lattice occurs. PSL analysis on X-irradiated KCl:Cu crystals carried out by Bandyopadyay [1999] indicated that KCl:Cu is an efficient PSL material for X ray irradiations. Induced phenomena by ultraviolet irradiation such as the spectral hole burning and the electron-hole pair formation have been observed in crystals with nanoparticles exposed to excitation of laser light in the UV region [Masumoto and Ogasawara, 1999].

In this work, thermoluminescence induced by irradiations with UV light has been extended to the 200-500 nm spectral region in KCl:Cu$^+$ and KBr:Cu$^+$ crystals. For both materials, the TL intensity as function of the irradiation wavelength is compared with the optical absorption spectra allowing us to relate the emission TL intensity with absorption centers.

2. MATERIALS AND METHODS

KCl:Cu and KBr:Cu crystals were grown using the Czochralski method. Copper was added in the melt as CuCl in concentrations of 0.2 and 0.5 mol%, respectively. Crystals were stored by more than two years at room temperature (RT) assuring the formation of small aggregates. Samples were cleaved from the blocks. If samples were not subjected to a thermal treatment are designated as “as grown” samples. The light source was a 450W Xe lamp. Light was passed by a Kratos-Oriel monochromator system. Monochromatic light in the 200 - 500nm range was used for irradiating the samples. Each irradiation was done during 30s. TL measurements were obtained with a RISO OSL/TL-DAS-15 system in the range of 30-400°C at a heating rate of 5°Cs$^{-1}$. Optical absorption spectra were measured with a Lambda 19 Perkin Elmer spectrophotometer. Some samples were heated at 500°C during 25 min in order to know the effect of less aggregate content in the TL measurement. These samples are called “quenched” samples.

3. RESULTS

For each material, the first glow curve was obtained for 200nm then for 210nm and so on until 500nm. Each TL glow curve was measured immediately after cooling and irradiating the sample. In each running, a persistent luminescence with intensity lower than the TL
signal was observed but removed before to do the analysis of the TL intensity. Figure 1 show typical TL glow curves of KCl:Cu and KBr:Cu samples, respectively. In all the measurements the most intense glow peaks have appeared between 50 and 250°C. The TL glow curve of KCl:Cu irradiated by 230nm is composed by at least two glow peaks at 70°C and 150°C (Fig. 2a) being the later the most intense. A similar glow peak composition appeared in the glow curves of KBr:Cu. In this case, the glow peaks appear at 115 and 145°C. For shorter wavelength irradiations the glow curves show an additional shoulder at 180°C.

Figure 1.- Thermoluminescence glow curves of samples irradiated 30 s with ultraviolet light.
On the other hand, to assure that TL is related with nanostructures, samples were heated at 500°C during 25 min in order to dissolve some nanostructures. Typical optical absorption spectra of as grown and freshly quenched samples non-irradiated are displayed in Figure 2.

The absorption band around 254 of KCl:Cu and 265nm of KBr:Cu are assigned to the 3d-4s electronic transition of Cu⁺, while those bands at lower energies correspond to CuX aggregates. It is noted that the Cu⁺ absorption increases with the thermal treatment given at 500°C, indicating that Cu⁺ ions are separated from the aggregates or nanoparticles.
The relative TL efficiency spectra are portrayed in figure 3. Each point corresponds to the area of a glow curve from 50 to 250°C. These spectra were does not take into account the lamp spectrum. In these figures the optical absorption spectra of the corresponding crystals are included in order to distinguish the type of centers participating in the recombination process.

A high correlation is observed in these spectra. It can be seen that there is formation of e-h pairs in both the spectral region of isolated Cu$^+$ ions optical absorption and the nanoparticles absorption range. In the former, there is a photoionization of Cu$^+$ ions and in the second one, ionization occur inside the nanoparticles. TL of quenched samples resulted with lower intensity than that observed in as grown samples.
4.- DISCUSSION

It can be seen that the copper content in the crystals produce the 254 and 265nm in KCl and KBr, respectively. These bands have been ascribed to the 3d10 – 4s electronic transitions of ions which occupy potassium sites. Additional bands are found between 280 and 420nm associated to CuX aggregates including nanostructures of CuX. Heating the samples at 500°C, during long periods of time, causes that intensity of the Cu⁺ bands increases while the bands of aggregates decrease. Before heating the as grown sample contains some aggregates. And after heating, Cu⁺ ions of these aggregates are converted in “free ions” leaving fewer aggregates or decreasing the size of aggregates, and increasing the Cu⁺ isolated ions population. In spite of the temperature effects in the stability of the aggregates, the creation of defects persists. It suggests that Cu⁺ ions absorption is shown only when such ions are outside the CuX aggregates. Also it is observed that both photons in the Cu⁺ absorption region and photons of the aggregates absorption region produce e-h pairs. This lead us to think that there are two type of e-h creation centers with different ionization energy. One is located around isolated Cu⁺ ions, while the other is found inside the CuX aggregate.

The results described earlier show some differences with those reported by Delgado [1983] and Li et al. [2005] because these authors do not take into account absorption of aggregates in the 300-400nm spectral region. On the other hand, the photoionization induced in nanoparticles has been observed in NaCl:Cu using a laser line as irradiation source [Masumoto and Ogasawara, 1999].

The low TL intensities in samples with high temperature treatment indicate that as grown samples has less difficulty to form e-h pairs. To explain this result, it is assumed that first must exist a composite capable of absorbing a low ionization energy and secondly the ionization products must find the traps where they can be stabilized.

According with the above results, KCl:Cu and KBr:Cu are sensitive to a very broad region of the UV electromagnetic spectrum due to the presence of embedded CuX aggregates, and this do them good candidates for dosimetric applications for UV radiation.
Cu$^+$ ions and CuX aggregates as its changes induced by high temperature treatments has been related with the thermoluminescence intensity response in copper doped KCl and KBr. The thermoluminescence signal is observed in a wide UV range including the absorption of Cu$^+$ ions and CuX aggregates. According with the results, these materials are sensitive to a very broad region of the UV electromagnetic spectrum due to the presence of embedded CuX aggregates, and can be considered as good candidates for dosimetric applications.

Acknowledgments

This work has been partially supported by projects 123952 of CONACyT and PIFI-2009 y P/MAA-2008-18 of Universidad de Sonora.

REFERENCES


