Copper Doped Alkali Halides for Computed Radiography and Digital Imaging

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We report here the results of our x-ray fluorescence, photostimulated luminescence, and time resolved laser spectroscopy studies in KCl:Cu. This material seems to possess some desirable properties for being used as an imaging plate in computed radiography. This is a US government work. There are no restrictions on its use.

THE PHENOMENON of infrared stimulated emission in wide band gap materials has been known for quite some time.¹ The process involves excitation by infrared light after the materials are exposed to ionizing radiation. The resulting higher energy upconversion emission in the visible region has been used in infrared detection earlier. More recently, researchers called this optically stimulated luminescence (OSL) or photo stimulated luminescence (PSL) and found its use in radiology,^{2,3} radiation dosimetry,^{4,6} laser detection and discrimination^{7,8} and archeology.⁹ In order to have an efficient stimulated emission, the following two criteria must be fulfilled: (1) the materials used must be storage phosphors, that is, they must produce stable charge trapping on exposure to ionizing radiation and (2) optical stimulation of these irradiated phosphors at a later time can efficiently detrapp the charges and their recombination produce radiative transitions.

Double doping with various rare earth ion combinations were successfully employed for electron and hole trapping. Later it was found¹⁰⁻¹³ that F center type ionic defect centers can be exploited in charge trapping and stimulation of the charges at a later time during readout. Of all materials, BaFX (X = Cl, Br, I) are found to be the most successful materials which employ beneficial use of F-type defect centers produced during irradiation with ionizing radiation. Arguably, since the successful

use of F-centers as color center lasers, this material and phenomenon have found the most beneficial use of defect centers in any ionic crystal.

Although BaFX (X = Cl, Br, I) are widely used in computed radiography, these materials have definite limitations keeping the door open for further research to find more suitable materials for use in radiography in general and mammography in particular. It is imperative that any read out process that uses laser will restrict the resolution because of the internal reflection of the light beam and scattering, jitters, power instability and restriction in beam size of the laser used. However, many other parameters which also play important role in imaging such as luminescence decay and intrinsic luminescence efficiency can be improved with proper doping, host selections and appropriate stimulating energy. Blasse¹⁴ and Seggern¹⁵ have shown that both Y₂SiO₅: Ce, Sm and RbBr:Tl have a faster decay rate than BaFX (X = Cl, Br, I). More recently, Nanto¹⁶ has shown that a KCl:Eu can be a candidate for storage phosphor imaging plates for radiography. Bandyapadhyay et al¹⁷ have observed PSL in copper doped KCl and KBr. As an ongoing study in this material, we report some interesting results that have important implications in imaging.

EXPERIMENT

Single crystal of KCl:Cu used in this study was grown by the Czrokalski method in an inert atmosphere at the University of Utah Crystal Growth Laboratory. Copper in monovalent was introduced by adding 0.5 mole percent in the melt. Atomic absorption analysis showed that the samples contained only 5 to 10 percent of the copper added to the melt. The sample was x-irradiated around 30 kV. X-ray fluorescence was observed by exciting with x-ray and fluorescence was detected with a Princeton Instruments CCD detector with 1024 × 1024 array after the emission was dispersed through a Acton Research Spectra Pro 275 monochromator. Photostimulated emission was observed on exciting with ~530 nm light from conventional and laser sources. Time resolved spectrum was observed on exciting an unirradiated sample with 266 nm frequency quadrupled Q-switched Nd:YAG laser of pulse width 10 ns and energy 6 mJ. 266 nm

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laser light produced UV fluorescence in KCl of band gap ~ 8 eV. Emission was detected by an EG&G PARC model 1421 optical multichannel analyzer with silicon diode array cooled to -25 C. Time resolved measurements were made in the gated mode of the optical multichannel analyzer (OMA) with an EG&G PARC model 1304 pulse amplifier optically triggered from the exciting laser source.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1A shows x-ray induced fluorescence in KCl:Cu. Figure 1B shows PSL emission of x-irradiated sample excited by a 75w xenon lamp in conjunction with proper interference filter and stimulation spectrum of 400 nm emission. Figure 2A shows time resolved spectra at room temperature (RT) at different delay times of 0, 50 and 100 micro second. Figure 2B shows time resolved spectra at similar delay but at a lower temperature of 50 K.

X-ray induced fluorescence shows strong emission peaking at 400 nm with a shoulder at 450 nm as shown in figure 1. Photostimulated emission after exposure to x-ray also exhibit similar emission. Strong photostimulation can be best observed on stimulating with 550 nm light. We observed photostimulated emission exciting with a 75 W xenon arc lamp, 532 nm laser light from a frequency doubled Nd:YAG laser and with 530 nm Argon ion laser light. However, we also observed a stimulation spectrum ranging from 500 nm to 650 nm with detection at 400 nm. Since there is an overlap of this stimulation band with shoulder of

the emission around 500 nm, it is advisable that photostimulation in this material is carried out by light of 530 nm or higher wavelength to avoid detection of stimulating light.

It is well known that rare-earth, or transition metal ions always introduce unwanted emission due to the presence of other impurity ions that enter the host lattice during doping in the melt. The dopant ions can also enter the material with different valence state resulting in more than one emission. In computed radiography, this unwanted emission due to either unknown impurities or due to the dopant ions in a different charge state can cause problems during the readout process, particularly if such emission is associated with slower emission decay. When x-ray imaging plates made up of such materials are read pixel by pixel during a readout process, slower decay from the previously read pixel can affect the image quality. In BaFX ($X = \text{Cl, Br, I}$), this detrimental effect has been known to cause a perennial problem.

In order to investigate this further in KCl:Cu, we studied time resolved laser spectroscopy at room temperature and at 50 K. As shown in Fig 3, that after a delay time of 100 micro second, no significant emission from either bands is observed. However, at 50 K, the 400 nm emission still persists after 100 micro second delay. This temperature dependence time resolved spectra clearly indicate that, at room temperature, copper emission is favored by phonon assisted decay. It is well known that the emission from the transition metal ions can be significantly influenced by photon-phonon coupling depending on the ligands and the host lattice

Fig 1. (A) X-ray induced fluorescence at RT in KCl:Cu. (B) PSL and stimulation spectrum.

Fig 2. (A) Time resolved spectra at different delay time at RT. (B) Time resolved spectra at different delay time at 50 K.

used. This property of photon-phonon coupling in transition metal ions have helped develop a new generation of four level solid state laser systems. Evidently, phonon assisted decay is observed in copper emission at room temperature as the decay rate becomes longer when the temperature is lowered to 50 K. The fast decay with the life time of emission on the order of few micro seconds at room temperature and the fact it produces strong x-ray fluorescence make this material attractive for use in computed radiography and digital imaging.

A detailed understanding about the origin of the ~ 450 nm emission band is also important as this may play non trivial role in the image quality. Our present study shows that at room temperature this emission does not produce any long lived fluorescence, a detrimental effect in image readout process as described earlier. Our preliminary study of photobleaching with laser light and x-ray photo electron spectroscopy (XPS) indicate that this emission may be due to the copper ions in divalent state. We plan to investigate the origin of this band further with different copper ion concentration in this material. It is also worth noting that readout

process in this material is very fast and photostimulation can essentially detrap the x-ray induced traps that participate in the imaging process. This is another very attractive feature of this material for use as x-ray imaging plates. It is well known that many storage phosphors are not properly cleaned after x-ray irradiation. The repeated exposure and readout process can produce 'ghost images' thereby causing spurious readings from the residual previous images.

SUMMARY

We have observed strong x-ray emission in KCl:Cu which have fast phonon assisted decay at room temperature. We, therefore, exhibit the advantage of using transition metal ions as dopant in photostimulable storage phosphors. Also the photostimulation process can efficiently clean this material for repeated use. A future study of DQE and MTF is planned for more relevant imaging information in this material once a good control of growth of a required size material with desirable concentration of copper ions is achieved.

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