

Thermoluminescence in Pure and $\text{Nd}^{+3} + \text{K}^+$ Doped Lead Germanate Single Crystals

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Abstract— Pure lead germanate was grown by Zochralski's technique. $\text{Nd}^{+3} + \text{K}^+$ doped lead germanate was grown for comparative studies. Thermoluminescence studies were conducted on pure lead germanate and $\text{Nd}^{+3} + \text{K}^+$ doped lead germanate. Thermoluminescence in pure lead germanate single crystals (LG) and $\text{Nd}^{+3} + \text{K}^+$ doped lead germanate single crystals (DDLG) has been measured in terms of photomultiplier output current on Thermoluminescence Set Up. Thermoluminescence studies of LG revealed an increasing trend of Thermoluminescence output, with increasing temperature and sharp consistent maxima at 50°C and 100°C . TL studies of DDLG revealed a decreasing trend of Thermoluminescence output, with increasing temperature and a sharp consistent peak at 100°C and 120°C . It was further noted that doping increased Thermoluminescence output. Thermoluminescence in ferroelectric lead germanate was attributed to change in polarization with change in temperature and creation of defect states.

Keywords— lead germanate, thermoluminescence, doping, polarization, defect states.

I. INTRODUCTION

The process in which a material absorbs energy in one form or other and re-emits a fraction of it as a visible or near visible radiation is known as Luminescence. Thermoluminescence (TL) is interpreted as thermally stimulated release of an electron (or hole) from traps, into the conduction (or valance) band and its eventual radiative recombination with the hole (or electron) at the recombination center. Thermoluminescence can be sensitized in materials (which are originally not thermoluminescent) by means of irradiation.

Thermoluminescent detectors often use crystals that are purposely flawed by adding a small dopant portion or concentration of impurity to activate. However, there are some thermoluminescent detectors that can do away with the inclusion of an activator, but rely upon their own impurities and defects in the natural crystal. Upon heating, the trap is vacated and a TL photon is emitted.

Intrinsic shallow electron and hole traps can crucially influence thermoluminescence in perovskite materials. In particular, defects related to oxygen vacancies (V_o), always dissolved into these materials during crystal growth, have become a subject of intensive studies in the last few years.

Thermoluminescence in many perovskites is discussed based on radiative recombination of carriers freed from shallow traps with localized counterparts.

Thermoluminescence in Ferroelectrics

Many ferroelectric materials like BaTiO_3 , PbTiO_3 , KH_2PO_4 etc, exhibit thermoluminescence. Thermoluminescence is different in ferroelectrics than other materials because of the presence of spontaneous polarization. It is known that Thermoluminescence results due to the recombination of released charges from trap centers. The intensity of thermoluminescence depends upon the magnitude of these released charges. As temperature changes, polarization changes in lead germanate. This gives rise to the release of trap charges at the dipolar end. The subsequent recombination of which gives rise to thermoluminescence.

J.W. Gilliland Jr et al [1] reported TL studies on Rochelle salt and guanidine aluminum sulfate hexahydrate. Ferroelectric Rochelle salt and guanidine aluminum sulfate hexahydrate were irradiated with of Co^{60} gamma rays up to $3.5 \times 10^6\text{r}$ at liquid nitrogen temperature. They conducted the observations with a photomultiplier (PMT) tube. A glow peak at -61°C was found to yield by Rochelle salt.

M Aguilar [2] has studied Thermoluminescence of BaTiO₃ crystals. He has reported a study of the thermoluminescence (TL) of BaTiO₃ samples. The samples were X-irradiated at 20K. The value of dependence of TL on purity of crystal was studied. The change in the absorption spectrum with respect to thermal annealing was studied. Also its relation with TL peaks was obtained. Moreover, the spectral composition and kinetic order of all TL peaks was obtained. A discussion on the origin of thermoluminescence and X-ray induced luminescence in BaTiO₃ was reported.

QuanZhangetal [3] have reported thermoluminescence studies in ferroelectric (K_xNa_{1-x})NbO₃:Pr³⁺. The change in dopants were (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5). Dopants chosen were rare earth ions Pr³⁺.

Upon nm light irradiation, the samples showed strong red emissions at around 610 nm. The specimens showed a visible thermoluminescence when at 200 °C. They have discussed the mechanisms of thermoluminescence.

Thermoluminescence in lead germanate

However, Thermoluminescence in ferroelectric materials, particularly lead germanate single crystals, has not yet been explored extensively. In our humble approach we have tried to explore and report thermoluminescence in pure and double doped lead germanate single crystals in this chapter on a very elementary basis.

II. METHODOLOGY

1) Experimental Setup

Thermoluminescence in pure lead germanate single crystals (LG) and Nd³⁺ + K⁺ doped lead germanate single crystals (DDLG) has been measured in terms of photomultiplier output current on Thermoluminescence Set Up (Figure 6.2) procured from Scientific Equipment & Services, Roorkee. The set up primarily consisted of i) High Voltage Power Supply ii) Digital Nanoammeter iii) a Photomultiplier tube iv) small furnace.

i) Power Supply(High Voltage)

The EHT power supply, EHT-11 consists of a stable power oscillator being controlled by an input signal. A step-up transformer is used for the output of this oscillator. The output was controlled with the help of transformer and then rectified and filtered. The power supply was varied continuously. It was further electronically regulated with a fully solid-state circuit which had low power consumption. The continuously adjustable power supply was used which had a range of 0 to 1500V.

ii) Digital Nanometer

The Digital Nanoammeter DNM-121 had an accuracy of +0.25 % for all ranges and consisted of 4-decade ranges with 100% circuit over-ranging. The unit was made suitable for current measurement in the range of 100 pA to 200 uA. The readings could be obtained on a 3/2-digit 7 segment LED display with auto polarity and decimal indication. The instrument used a FET input operational amplifier that offered very low input bias current, low offset voltage, low drift and noise.

iii) Photomultiplier Tube

A R C A 931-A photomultiplier tube was used for experimental purpose. A schematic diagram of the photomultiplier is shown in Figure 6.3. Light strikes a photocathode C and liberates electrons, the electrons are accelerated by a voltage E and focused upon an electrode, the dynode D₁, where each incident electron causes the emission of several secondary electrons. The same process is repeated at the dynodes D₂, D₃. The electrons from the last dynode stage are collected by a positive anode A and the current I_a is measured. If the gain of each stage (the number of electrons formed by secondary emission for each primary electron) is g and if n dynode stages are used, the total amplification is $A = g^n$.

The value of g varies with the voltage between successive dynodes and with the surface composition and the geometry of the dynodes from 0.5 to about 10.

The focusing of the electrons from one stage to the next can be accomplished with magnetic or electrostatic electron-optical systems. The gain and the sensitivity of the photomultiplier vary with the voltages applied to the dynode stage.

iv) Furnace

A small intact furnace, which could go up to 150°C, was employed for the experimental purpose. The furnace was square in shape. To avoid thermal losses while heating, the furnace was cemented compactly. The furnace had a small window on one of the sides, on which the mica sheet was pasted firmly. Any radiation could pass through this small window.

2) Experimental Procedure

A warm up time of about half an hour was given to the set-up, prior to the start of each run. Inside the furnace, a rod was provided on which one could mount the crystal. The crystal was mounted and adjusted to be exactly in front of a window, which was covered with a mica sheet through which the radiations could pass. In front of the window, the mouth of the photomultiplier tube was adjusted. The

photomultiplier tube had an adjustable window, which could be opened or closed to allow the inflow of the radiations coming out of the crystal. For taking measurements the crystal was mounted on the brass rod. The furnace was closed properly. The window of the photomultiplier tube was opened. The whole assembly was enclosed in a rectangular box. The whole box was covered with a black cloth so that no external light could enter the photomultiplier tube. A small hole was kept to insert the thermocouple. The thermocouple was inserted and placed just near the crystal, so that the exact temperature of the crystal could be monitored. The thermocouple, in turn, was connected to a microvoltmeter. A voltage of 800 V from the high voltage power supply was fed in to the photomultiplier tube. The Photomultiplier output was connected to a highly sensitive nano ammeter. Other parts of the furnace were perfectly insulated in order to avoid noise generation due to heat radiations. Thermoluminescence study was conducted for both, LG and DDLG from room temperature to 150°C, at an interval of 5°C. The study could be undertaken only upto 150°C, as the furnace could record a maximum temperature of 150°C. At each temperature interval, thermoluminescence readings were recorded without crystal (TL₁). The experiment was repeated for each temperature interval with crystal (TL₂). Thermoluminescence was evaluated using $TL = TL_2 - TL_1$. This was necessary to eliminate noise current. This procedure was repeated for all the crystals of LG and DDLG. A graph was plotted taking dTL on the y-axis and temperature in °C on the x-axis.

III. RESULTS AND DISCUSSION

Figures 1 a, 1 b and 1 c show the thermoluminescence output of the LG crystals. Figures 2 a, 2 b and 2 c show the thermoluminescence output of DDLG crystals. Thermoluminescence studies of LG revealed an increasing trend of Thermoluminescence output, with increasing temperature and sharp consistent maxima at 50°C and 100°C. TL studies of DDLG revealed a decreasing trend of Thermoluminescence output, with increasing temperature and a sharp consistent peak at 100°C and 120°C. It was further noted that doping increased Thermoluminescence output.

It is well known that in an inherent crystal lattice, the outermost atomic electronic energy levels that are there are extended into uninterrupted allowed energy bands. The levels are then divided into energy regions those are forbidden.

The uppermost filled band is called the valence band. It is then divided by several electron volts. The lowermost empty energy band is called the conduction band. When a crystal is subjected to ionizing radiation, electrons get energized. They then move out of the valence band and jump to the conduction band.

All this process manages to leave a vacancy in the valence band which can be termed as a hole. It is to be noted that the electron and hole are free to roam throughout their individual bands. The presence of lattice defects or impurities, gives rise to discrete local energy levels within the forbidden region, between the valence and conduction bands.

These energy levels manage to localize electrons/holes. This process on subsequent heating and recombination causes an interesting process termed as thermoluminescence. Thermoluminescence can be defined as light emission which is possible because of thermal stimulation.

It is the energy difference between the conduction band and valence bands that is responsible for the temperature required to release the electron. This process by enlarge is able to yield thermoluminescence. It is a characteristic of the material used and differs from material to material.

Usually, so many localized electrons and holes are made. As you go on increasing the temperature of the crystal, the probability of liberating an electron from a trap is higher. This gives a periodicity in the graph such that the light that comes out will be feeble at low temperatures. It is then able to give a maxima at temperatures that is on a higher side. It then further and drops down to zero if there is a probability that no more traps remain that is electron laden. A glow curve is a curve or a graph where graph of the light that comes out as a function of time or temperature.

Thermoluminescence in ferroelectric lead germanate may be due to,

1. change in polarization with change in temperature.
2. creation of defect states.

Thermoluminescence results due to the recombination of released charges from trap centers. The intensity of thermoluminescence depends upon the magnitude of the released charges. As the temperature changes, polarization changes in lead germanate. This gives rise to the release of trap charges at the dipolar end. The subsequent recombination of which gives rise to thermoluminescence.

It is well known that the loss of lead and oxygen in lead germanate during growth leads to generation of vacancies

leading to enhancement in the formation of defect states. With increase in temperature, the probability of thermal excitation increases resulting in higher release of trap charges and hence higher TL is observed.

It is well known that homogeneity of the crystalline internal field is disturbed due to doping. Therefore, apart from the depth the crystalline field surrounding the defect states is also going to control creation of defect states, trapping of charges and release of charge mechanism. Because of this the nature of TL in doped crystals is going to be different in LG and DDLG. Shifting of the two temperatures at which peaks have been observed from 50°C and 100°C to 100°C to 120°C may arise due to change in the crystalline field. The very fact that peaks have shifted to higher temperature side suggests comparatively higher depth of trap level in DDLG as compared to LG.

The peaks correspond to temperatures at which maximum release of trap charges occurs. $\text{Nd}^{+3} + \text{K}^{+}$ double doping probably creates additional defect states and consequently generation of additional trap levels. This may lead in enhancing the magnitude of liberated charges in DDLG. The observed increase in thermoluminescence output due to doping hence may also be due to the increase in the density of traps as a result of doping.

IV. CONCLUSION

The fact that peaks have shifted to higher temperature side suggests comparatively higher depth of trap level in doped single crystal lead germanate as compared to pure lead germanate. $\text{Nd}^{+3} + \text{K}^{+}$ double doping in lead germanate single crystals probably creates additional defect states and consequently generation of additional trap levels.

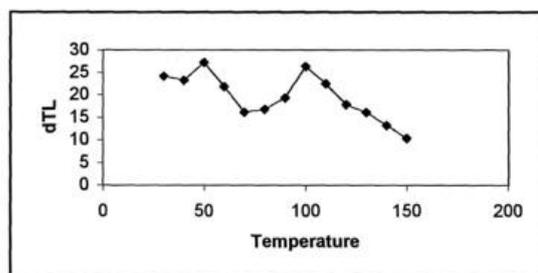


Figure 1a
Dimension of the sample (0.372cm x 0.306cm x 0.302cm)

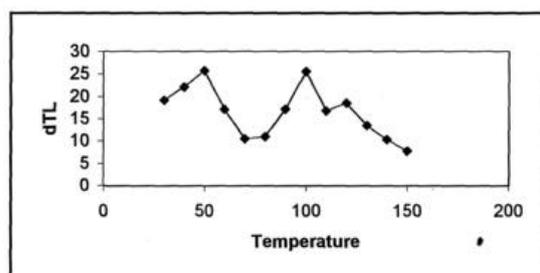


Figure 1b
Dimension of the sample (0.482cm x 0.370cm x 0.307cm)

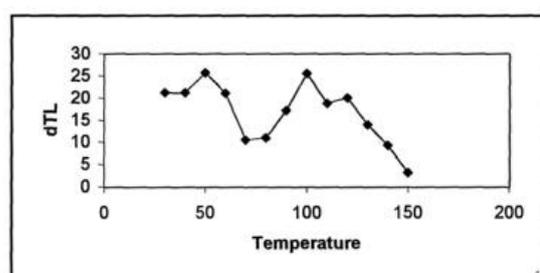


Figure 1c
Dimension of the sample (0.432cm x 0.338cm x 0.206cm)

Thermoluminescence in Pure ferroelectric lead germanate single crystal

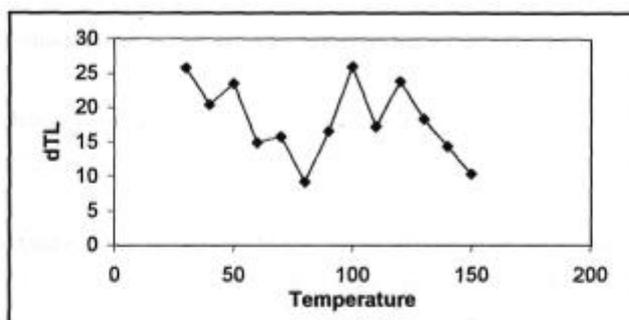


Figure 2a
Dimension of the sample (0.529 cm x 0.345 cm x 0.355cm)

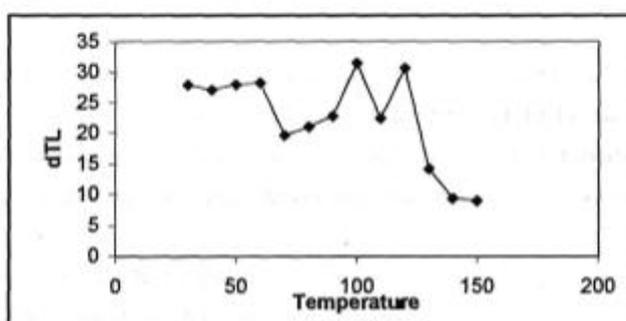


Figure 2b
Dimension of the sample (0.507 cm x 0.394 cm x 0.333cm)

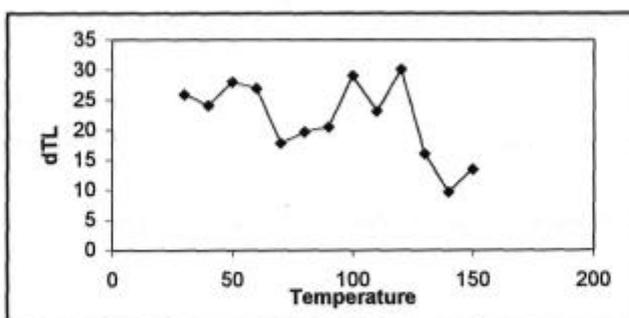


Figure 2c
Dimension of the sample (0.557 cm x 0.405 cm x 0.354cm)

Thermoluminescence in $\text{Nd}^{+3} + \text{K}^+$ doped ferroelectric lead germanate single crystal

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