THERMO LUMINESCENCE DOSIMETRY OF SOME NATURAL MINERAL SAMPLES

BY

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A thesis submitted to the School of Postgraduate Studies, Ahmadu Bello University, Zaria, in partial fulfilment of the requirement for the award of the degree of Master of Science (M.Sc.) PHYSICS.,

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DEDICATION

To my dear wife Naomi and daughter MorHyel, for their patience.

DECLARATION

The author hereby declares that the report presented in this thesis is the result of the original research carried out by him under close supervision of Dr. B.W. Jimba and Dr. N. Hariharan. No part of this thesis has been submitted in any institution or organisation other than Ahmadu Bello University, Zaria, for the award of any degree. All sources of information utilised in this research are duly acknowledged.

15/5/94

Jackson J.Abafoni

CERTIFICATION

This M.Sc. thesis entitled "THERMOLUMINESCENCE DOSIMERTY OF SOME NATURAL MINERAL SAMPLES" by Abofoni J. Jackson, meets the regulation governing the award of Master of science (M.Sc.) degree in Physics of A.B.U., Zaria, and has been critically scrutinised and approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Natural mineral compounds of geologic origin usually contain diverse kinds of impurities, mechanical defects and imperfections lying in their forbidden energy levels. Some of these exhibit thermoluminescence (TL) characteristics when exposed to ionising radiation and heated at constant rate.

Natural minerals obtained locally (here in Nigeria) were ground into powder and thermoluminescence dosimetry properties were studied through artificial irradiation of the samples using Sr^{90}-Y^{90} B source at different dose levels. Using the Solaro Model 680 TLD reader, TL corresponding to a particular radiation dose can be obtained. The TL properties studied are based on the proposals for the International standards for TLDs. Tests required by international Atomic Energy Agency (IAEA) which are fading rate, dose versus response linearity, effect of ambient light and stability of dosemeters under standard climatic condition, and tests required by the International Electrotechnical Commission (IEC) which include batch homogeneity, detection threshold, stability of zero point, repeatability and residual TL, have been investigated.

The results obtained in this work are in partial agreement with the recommendations for the international standards for TLDs. Suggestions therefore, have been made on how to improve upon this present research in order to achieve the desired goal of producing dosimetric phosphors for use in various fields of radiation detection and measurements.

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CHAPTER ONE

1.0. INTRODUCTION

1.1 THE SUBJECT

The release of light in a crystalline material when it is heated at a constant rate is referred to as thermoluminescence (TL). This emission occurs when trapped charge carriers within the crystal are excited to higher energy levels, and then de-excite with release of optical radiation as thermoluminescence. This phenomenon is exhibited by both natural and synthetic materials and is utilised today in dose measurements (dosimetry).

Natural geologic minerals observed to be good thermoluminescence materials have been studied in the past (Becker, 1973) for use in solid state research, nuclear safety, medical dosimetry, archaeological and geological age determination. Due to complications from impurities and defects usually associated with natural samples, they are avoided in favour of synthetic materials (chemicals) in which choice impurities are used for doping. The impurities and imperfections (defects) in natural minerals however, varies from one location to another. In Nigeria, thermoluminescence properties of natural minerals available locally have not been studied in the past.

Using the test methods both for the tests required by International Atomic Energy Agency (IAEA) and International Electrotechnical Commission (IEC), (Azorin, *et al.* 1986), this research has proved the ability of some of these natural minerals to develop into possible dosemeters.

1.2 THERMOLUMINESCENCE MECHANISM

Charge carriers in a thermoluminescent material can absorb energy enough to be detached from the mother atoms and wander freely inside the materials. Natural thermoluminescent materials usually contain impurities and lattice mechanical defects which serve as traps to freely moving electrons. Those trapped are excited to higher energy levels when appropriate energy, equivalent to the trap depths is supplied. This is called stimulation., The electrons or holes could either be optically (photo stimulation) or thermally (thermal stimulation) stimulated. The probability P that an electron will escape from a trap of depth δE to a higher energy level at temperature T of the material is given by Boltzman equation.

$$P = s \exp(-\delta E/kT) \qquad ....1.1$$

where s is the frequency factor of the material and k is the Boltzman constant,

The energy supplied is equivalent to the energy difference between the two energy states which is same as

the trap depth. The return of the carriers to the ground level which is called annealing (or fading if it proceeds slowly) is associated with a release of energy most of which is thermal and result in minute increase of temperature of the sample (Becker, 1973). Part of this energy is released as thermoluminescence signal as carriers recombine at luminescent centres. If several traps of different depths are emptied, the recording of the light signal as a function of heating time or temperature, results in glow curve structure consisting of several glow peaks. Automated readout instrument which is linked to computer dose record keeping system is used for this work. Each glow peak represents a trap depth and the temperature at which a trap is emptied is the peak temperature. The glow curve and peak temperature are functions of thermoluminescent materials' pre-treatment, impurities concentration and heating rate.

1.3 THERMOLUMINESCENCE DOSIMETRY (TLD)

In thermoluminescence dosimetry, the means of excitation energy of electrons is ionising radiation. When such radiation passes through crystalline material, it generates free electrons, which can be trapped at defect and impurity sites in the crystal. Subsequent heating of the material results in emission of thermoluminescence signal whose intensity is proportional to the number of trapped electrons, hence to the energy absorbed from ionising

radiation since the last release of TL signal, (Johnson et al, 1967).

In thermoluminescence dosimetry, the dosemeters, which consists of TL materials (phosphors) in suitable forms are first irradiated, generally at ambient temperature, and at a convenient later time are heated in a readout instrument which is usually situated outside the radiation field. A TLD reader basically consists of a means of heating a thermoluminescent dosemeter and a means for measuring a constant fraction of the energy emitted by the dosemeter in the form of light, as it is heated. Natural radioactive elements present in the soil serve as ionising radiation sources to natural thermoluminescent phosphors which are mostly geological minerals and archaeological materials. Sometimes natural phosphors may be doped with radioactive elements, which still act as radiation sources to the host lattices.

Sources of natural ionising radiation of importance to natural TLD include trace impurities of Potassium, Rubidium and nuclides of the Uranium and Thorium decay series in the material and its surrounding, and also cosmic rays make reasonable impact. If the absorbed energy is divided by its rate of acquisition, the time which has elapsed since the last zeroing of the material or phosphor, can be calculated. This is the principle applied in thermoluminescence dating of materials, given by Aitken (1985).

Thermoluminescence is a two-way street, it can either tell us how long it has been since a phosphor was last heated, if assumptions about dose rates are made; or it can tell us how much radiation has been picked up in a given time. The 'how long?' is of value to geologists and archaeologists and 'how much?' is important in medical dosimetry, scientific research, personnel and environmental radiation monitoring.

1.3.1 Dosimetry Systems

There are several dosimetry systems available today for use in different fields of application, (Robertson, 1981). Currently developed systems are:

(a) Ionisation chamber

(b) Proportional counters

(c) Scintillation counters

(d) Chemical dosimetry

(e) Semiconductor counter

(f) Calorimetry

(g) Photographic method

(h) Solid state integrating dosimetry systems, which include:

(i) Thermoluminescence dosimetry (TLD)

(ii) Radiophotoluminescence (RPl)

(iii) Thermally stimulated exo-electron emission (TSEE)

(iv) Track etching.

Only four of these mentioned systems are frequently applied in medical dosimetry. These are TLD. RPL. ionisation chamber and photographic method (film badge).

1.3.2 Selection of TLD

Of the four commonly used dosimetry systems in medical dosimetry, TLD offers several significant advantages over the others. It has wide dose range, approximate tissue equivalent, re-usability, high phosphor stability under most climatic conditions and the availability of dosemeters in a number of configurations to suit special applications such as extremity dosimetry. Adoption of TLD over film badge and ionisation chamber in medical dosimetry has encouraged the design of new treatment planning in the field.

In the area of age determination, the TLD is found to be most accurate compared to track etching which have more disadvantages than the TLD (Becker, 1973). The TLD stands the most reliable because the materials to be dated serve as dosemeters. Though the natural phosphors used in TLD exhibit complex TL behaviour primarily caused by impurity contents of the phosphors, it is still preferred to other systems. The basic requirement for a phosphor to be datable by TLD system is that its TL signal be zero or small at the time the event to be dated occurred.

1.3.3 Characteristics of TLD System

The thermoluminescence dosimetry system has the following characteristics which distinguishes it from other systems.

(i) The TLD has minimum limitations on the dosemeter sizes.

(ii) Most of the known ionising radiations can be measured by TLD system and can successfully discriminate between different types

(iii) TLD has wide dose range and exhibit linear response versus dose relationship over 75% of the range in the developed phosphors (Robertson, 1981).

(iv) Near tissue equivalent achievable in medical dosimetry

(v) TLD is resistant to variations in climatic conditions such as temperature, pressure and humidity.

(vi) Long term retention of stored dose (good phosphor stability in stored energy).

(vii) The TLD system is reusable and provides the lowest cost per readout.

1.4 PREVIOUS WORK

Quantitative measurements of radiation exposure using thermoluminescence was first reported in the late 1940's by Daniels and his co-workers (McKinlay, [illegible] They studied the TL properties of alkali-halides some geologic minerals. They examined the glow peak structure of alkali-

halides and their isothermal fading and applied these to the measurements of ionising radiation exposure. The development of TL as practical method of ionising radiation dosimetry has proved a useful technique for variety of purposes in radiotherapy and radiological protection (Mckinlay, 1983).

There were however problems encountered when natural TLD was tested in these areas. The natural thermoluminescence materials were observed to exhibit abnormal TL behaviour which are blamed on complicated lattice mechanical defects and natural impurity contents (Becker, 1973). Radioactive impurities known to be common in natural thermoluminescence phosphors, contribute to the anomalous behaviour in TL sensitivity. Radioactive elements also damage the structure of the host lattices thereby rendering the material less sensitive as reported by Amin *et al.* (1985).

Natural TL phosphors are also known to fade (decay of TL signal at storage temperature) anomalously. This behaviour indicates the presence of shallow electron traps which require small amount of radiation dose to be filled during irradiation. These shallow traps are emptied at ambient temperatures, this behaviour is characteristic of natural materials. Good TLD phosphors have stable peaks at storage temperatures. Natural phosphors were replaced by

synthetic ones in which choice impurities are used as activators, because of their anomalous behaviours.

However, some natural phosphors of the fluorite family were studied from dosimetric point of view and partially satisfactory results were obtained by Schayes *et al.*, 1967. Further research on natural fluorite encouraged a firm, B.M.L.E. Brussels, Belgium, to introduce a commercial system based on natural fluorite (Becker, 1973). Efforts by many scientists to improve the dosemetric potentials of natural TL phosphors for application especially in medical dosimetry proved fruitless.

In chronological studies, the properties of natural TL are found most useful. It took almost two decades of intensive research to develop methods for routine dating applications with acceptable precession, since Daniels suggested the phenomenon of thermoluminescence in dosimetry. The problems of calibration in absolute dosimetry were earlier noted (Johnson *et al.*, 1967) but later, Aitken, 1985, Mejdahl and Wintle, 1984, were able to adopt appropriate techniques in TL dating processes. There's still uncertainty in the dose equivalent factor between natural radiations and common type of radiation used for calibration e.g. Co^{60}, Sr^{90}, Cs^{137}, AmBe. In the present state of research in thermoluminescence a satisfactory model explaining the TL emission of natural geologic minerals is still lacking. A step toward obtaining a more accurate dose

rate data for every TL dating material have been taken by Redhead (1987) when he developed dating equations that account for all TL contributions from radioactive elements and cosmic rays within and around the material. The contributions of this work is to determine other properties, if any, that would be studied to cause future improvement in use of natural TL materials.

1.5 APPLICATIONS

The TLD system is utilised in some of the areas of application earlier mentioned in the following ways mentioned.

(a) Medical dosimetry

In medical dosimetry, there are two important areas of absorbed dose measurement.

(i) Clinical radiotherapy

The objective of radiotherapy is to deliver a prescribed absorbed dose to the area affected by the disease over a time interval and to minimise the spread of the absorbed dose to the surrounding tissue and other organs. The difficulties of accurately predicting treatment of absorbed doses by calculation have in the past lead to the development of *in vivo* measurement techn[illegible]s McKinlay (1983).

With the development of thermoluminescence as a practical method of ionising radiation dosimetry, its relevance in the field of clinical measurement was realised. McKinlay (1983) has stated that Brucer (Daniels *et al.* 1953) used some of Daniels' single crystals of Harshaw LiF to make internal *in vivo* measurement in cancer patients injected with radioactive material. It was successful and the patients just swallowed the crystals which were later on retrieved and readout after some days. Thermoluminescence dosimetry has proved a useful technique for a variety of purposes in radiotherapy, including the measurements of therapy machine output, beam uniformity checks, and the measurement of absorbed dose in phantoms and *in vivo* for both internally and externally applied fields. TL dosemeters give high precision, rapid retrieval of information using on site readers, good environmental stability, good water or tissue equivalence and wide range of sensitivities, (Mckinlay, 1983), compared to other dosimetry systems.

(ii) Radiological Protection

Diagnostic radiology is the largest contribution of exposures resulting from man-made collective dose contributions to both the somatic and the genetically significant dose equivalent. It is therefore desirable to reduce the exposure of patients to diagnostic x-rays to the minimum consistent with good diagnosis. Thermoluminescence dosimetry has proved to be a useful method in the comparison

of patients' absorbed dose from new techniques and from more traditional methods (Mckinlay, 1983). The TLD has more advantages over ionisation chamber in its application in diagnostic radiology.

The TLD system is therefore utilised in these areas today in most developed hospitals. Natural phosphors can however be analysed and produced to be equally effective as the synthetic phosphors in use today.

(b) Personnel and Environmental Monitoring

Individually monitored absorbed dose may serve to, ensure that dose-equivalent limits are not exceeded, limit the exposure of individuals and to provide supplementary information about work practices and dose trends. In the past individual doses have been monitored by film badge dosemeters but thermoluminescence dosemeters are now widely used. This is principally due to the availability of automated readout system which can be linked to compute dose record keeping system.

The exposure of radiation to the population is needed to be checked and monitored. As such environmental monitoring which is the measurement of radiation exposure from either cosmic and terrestrial radiation or from the controlled or accidental release of man-made radioactivity is necessary. There is often a requirement to measure the natural background exposure in a specific area, for example,

the measurement of cosmic radiation exposure in high altitude commercial aircraft (Becker, 1973) and the measurement of the radioactivity of soil for TL dating. The TLD is most appropriate and of convenience to perform such measurements.

(c) Thermoluminescence dating

In TL dating materials are assumed that in the distant past when they must have been heated or deposited will at that instant lose or record all the stored thermoluminescence in them. Any TL which the material now displays when later on heated would have resulted from irradiation of the material during the intervening period. If no artificial irradiation of such material occurred, the total TL is due to the absorbed dose from the radiations emitted by naturally occurring radioisotopes and cosmic rays. As discussed earlier, the sources of radiation doses in the ground are radioactive elements belonging to the uranium and thorium series, pottasium and rubidium impurities which are present in the soil matrix.

Taking the sedimentation of materials as an example, the principle of TL dating can be explained. The initial coming together of the sediments began at zero time. According to Singhvi *et al.*(1985); Wintle and Huntley (1979) suggested that the TL level in a natural sample be expressed as

$$I_{net} = I_o + I_a \qquad \ldots.1.2$$

i.e I_{net} is made up of I_o, the TL level present in the sample during the time of deposition and I_a is the TL level acquired since the time of deposition. In pottery firing I_o is zero since the material looses all the TL signal during firing.

Expressing the above equation in dose units

$$D(I_{net}) = D(I_o) + D(I_a) \qquad \ldots.1.3$$

where D(I) is the dose absorbed to generate a TL of intensity I. Determining the total annual effective absorbed dose then the TL age is given by

$$TL_{age} = \frac{D(I_a)}{\text{Annual Dose}}$$

$$= \frac{D(I_{net})}{aD\alpha + D + D\beta + Dc} \qquad \ldots.1.4$$

where a is the alpha efficiency factor and $D\alpha$, D, $D\beta$, and Dc, are annual dose from alpha, beta gamma and cosmic radiation respectively.

It has been reported by Mejdahl (1985) that most TL dating works done in the Nordic Laboratory for TL dating gave agreeable results, and in most cases comparable to those of radiocarbon dating. In some few cases the TL dating prove to be more accurate to the radiocarbon method. Young

samples present problems in TL dating because they do not generate enough TL signal and so result in non linear build up curves. The samples studied here therefore under appropriate calibration can be developed for application in this wise.

1.6 OBJECTIVES

Natural TL materials vary in impurity concentrations, radiation damage and lattice imperfections or defects from one location to another. These factors affects the TL sensitivity of phosphors. The geologic minerals (fluorites and calcites) the type studied in this work have satisfactory results among natural TL phosphors so far tested in other places e.g. Europe (Schayes *et al.*, 1967) and Aitken (1968). We are not aware that such tests were performed on natural minerals here in Nigeria. With the problem of radiation exposure on the increase, its imperative to develop dosimetry system especially TLD to monitor radiation workers. In this light therefore, this research work is aimed at identifying the potentials of natural minerals as good phosphors in the TLD system and suggest ways to improve on the development of such phosphors. Some of the fluorite minerals investigated have rapidly fading peaks at 100°C, reasonably stable at 150°C to 180°C and very stable peak at 240°C. This observation is in agreement with that obtained from Wolsendorf fluorite in Germany in 1958 (Becker, 1973).

CHAPTER TWO

2.0 THEORY

2.1 CRYSTAL STRUCTURE OF FLUORITES AND CALCITES

Read (1970) defined a crystal as a body bounded by surfaces usually flat arranged on a definite plan which is an expression of the internal arrangements of the atoms. Every crystal consist of certain atoms or group of atoms arranged in a three dimensional pattern which is repeated through out the crystal. The unit cell is the smallest complete unit of pattern and the whole crystal structure can be thought of as being built up of cells stacked together. To completely describe a crystal one has to define the positions of atoms (or molecules) inside the unit cell built on three vectors, a (i = 1, 2, 3) of arbitrary origin. All the atoms of the crystal will be obtained from the atoms of the unit cell by all the translations t, Robertson (1981).

$$\vec{t} = \Sigma \alpha_i \vec{a}_i \qquad \text{.....2.1}$$

where α_i represents all the positive and negative integers.

There are seven different shapes of unit cells, they include cubic, tetragonal, hexagonal, trigonal or

rhombhedral, orthorombic, monoclinic and triclinic cells. These cells are differentiated by the angles between their edges and or the lengths of the edges. The fluorite and calcite crystals studied in this work consists of cubic and hexagonal unit cell shapes respectively.

(a) Cubic System

In the cubic system all the axes of the unit cell are equal ie $a_1 = a_2 = a_3$ and are all at right angles (90°) to each other as shown in figure 2.1(a). The fluorite belongs to the galena type symmetry class in the cubic system and in fact it occurs as a simple cube, figure, 2.1(b).

The cube is a six faced solid bounded by faces which cut one axis and are parallel to the other two. Its Miller indices are given by 100 (front) $\bar{1}00$ (back) 010 (right) $0\bar{1}0$ (left) 001 (top) and $00\bar{1}$ (bottom). There are other forms of the galena type symmetry and they include rhombdodecahedron which has 12 rhomb-shaped faces, octahedron with eight equilateral triangular faces, tetrahexahedron, trioctahedron, trapezohedron and hexoctahedron are solids with more complicated faces.

The fluorite is an inorganic crystal with chemical composition CaF_2. The usual natural impurities

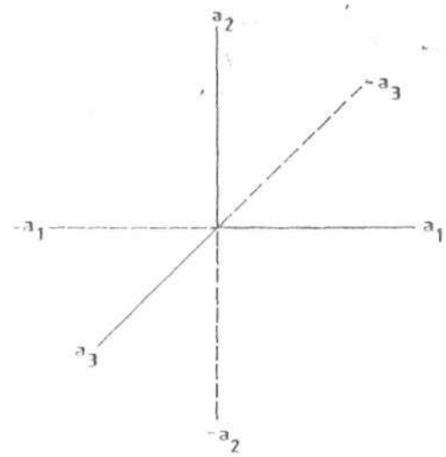


Fig. 2.1(a). The cubic axes.

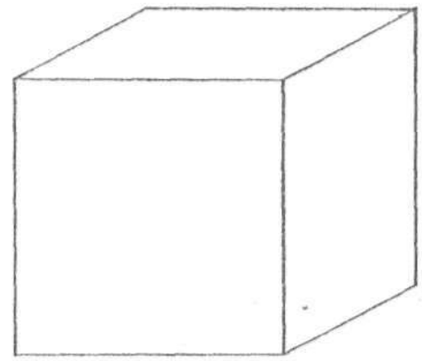


Fig. 2.1(b). Cubic crystal (fluorite).

associated with fluorites are the rare earth metal impurities, gadolinium Gd, dysprosium Dy, erbium Er, and terbium Tb, (Becker 1973). Manganese Mn and titanium, Ti are noticed to be the most prominent of the fluorite impurities. Rare earth trivalent impurities such as yttrium, Y act as electron traps in CaF_2:Mn while Mn act as hole trap, this suggestion was presented by Puite (1971).

(b) Hexagonal System

This system contains those crystals that have four axes. Three horizontal axes which are equal and at 120° to each other, with the fourth axis perpendicular to the plane containing the horizontal axes, as illustrated in fig. 2.2(a). The fourth axis is shorter than the others by about 15% in calcite (Read, 1970). The hexagonal system, unlike the cubic system is divided into two divisions, trigonal and hexagonal which are differentiated by their vertical axes symmetries, 3 fold and 6 fold respectively.

The calcite therefore belong to the trigonal division. Rhombohedron and scalenohedron are two forms of calcite crystals that exist naturally. The rhombohedron has 6 faces, each rhombo shaped. The perpendicular axis in the rhombohedron joins the two solid angles formed by the obtuse angle of the opposite rhombo faces as shown in

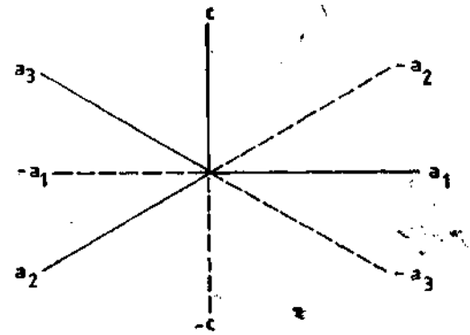


Fig. 2.2(a). The hexagonal axes.

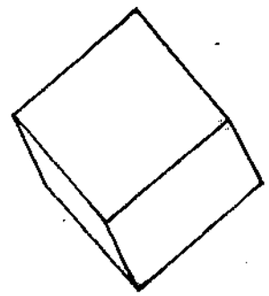


Fig. 2.2(b). Unit rhombohedron.

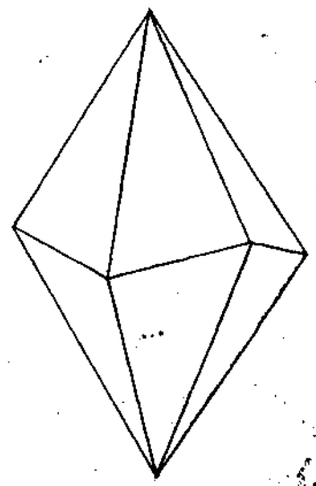


Fig. 2.2(c). A scalenohedron.

fig 2.2 (b). The general Miller symbol for rhombohedron is (h0hl) and diagram (b) shows a unit rhombohedron.

The scalenohedron is a solid bounded by twelve faces each face being a scalene triangle. The end edges are sharp and it zigzags around the middle of the crystal as shown in fig 2.2(c). Its general Miller symbol is (hkil). The natural calcite however occurs in various combinations of rhombohedral and scalenohedral (Read, 1970).

The calcite is an inorganic mineral with composition $CaCO_3$. It exist in variety of forms and metals such as manganese Mn, dysprosium Dy are common natural impurities of the calcite mineral. The type studied here is a compact, finely fibrous variety with satin like lustre

2.1.1 Description of Ionic Crystal

One or more electrons are given by an electropositive atom to a nearby electronegative atom. The result is the existence of ions of opposite signs, each ion surrounded by ions of opposite sign, which result in a strong electrostatic attraction. The equilibrium distance that is between these ions results from a balance between this attraction and repulsion of internal electronic shell of the ions.

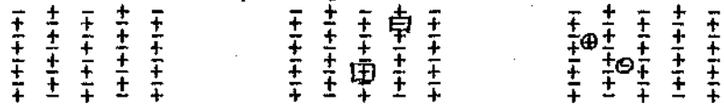
Equation 2.1 is not possible since atoms are not at rest. Thermal vibrations makes it impossible for equation 2.1 to be obeyed, An average position can be specified, referred to as atomic site, such that the distance δa between an atom and the site is always in a way that $\delta a/a$ (a is the nearest neighbour distance) is small and reaches a maximum of about one tenth (1/10) near melting point (Robertson, 1981). Both fluorite and calcite crystals are ionic in nature. The crystals' impurities also contribute to this electrostatic attraction and repulsion forces within the crystal. They distort the orientation of atomic sites greatly bringing defects.

2.2. ROLE OF DEFECTS IN NATURAL THERMOLUMINESCENCE

Any deviation in a crystal from perfect periodicity of atomic sites (equation 2.1) is an imperfection or defect. Defects in crystals are categorised according to their dimensions. Natural crystals have vacant atomic sites (Schottky defect) self interstitial (Frenkel defect) and presence of chemical impurity, which are regarded as point defects (dimensionless). Mechanical defects which results in dislocations (one dimensional) surface defects (two dimensional) and volume defects are also common in natural samples. Free surfaces of crystals pose the first and most unavoidable types of crystal

defects. Traps arising from defects in crystals are negative or positive ion vacancies which are regions of excessive positive or negative charge respectively. Inorganic crystals which form most groups of natural TL materials are good examples of this. Consider an inorganic crystal whose ideal structure is given by fig 2.3(a) and schottky and Frenkel defects, figures 2.3 (b).

Fig.2.3 Crystal Defects

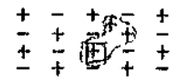


(a) Ideal crystal (b) Schottky defect (c) Frenkel defect

and (c) respectively. Both Schottky and Frenkel defects can occur at the same time in a crystal. If the inorganic crystal is doped with a divalent positive impurity, substituting for a positive ion, the concentrations of vacancies could be affected. To make up for the excess positive charge of the impurity ion, a positive host ion has to be removed from the structure. This means that each substitutional divalent positive impurity ion creates a positive ion vacancy. The concentration of the negative ion vacancies therefore decreases since at a finite temperature the equilibrium condition of a crystal is the state of minimum free energy.

The divalent cation impurity is a local positive charge and the cation vacancy is a local negative charge and these two attract each other forming complexes as shown in figure 2.4. dipole.

Fig.2.4 Vacancy-Impurity Complex



The vacancy-impurity complex is a dipole. The concentration and nature of hole and electron traps is thus greatly affected by the presence of impurity. Its important to know the type of impurity necessary to provide expected signal from any material. Natural samples are doped with diverse kinds of impurities which play vital roles in the TL properties of materials.

2.3 LUMINESCENCE PROCESS

Schulman (1967) has suggested that a more meaningful distinction may be based on the temperature dependence of the luminescence decay time. This was emphasised by Robertson (1981).

The decay time of the fluorescence process is strictly temperature independent being determined by the probability of the transition process. When the decay time depends on temperature then thermoluminescence process occurs. Excited electrons that are trapped in

metastable state can only escape when appropriate energy is supplied (optical or thermal). The path of the process is given as:

$$(E + \text{heat}) \longrightarrow E \longrightarrow (E + \text{photon})$$

where E is the metastable energy level, E is the conduction band (highest energy level) E the ground

level. De-excitation from metastable state to the ground level is forbidden (Becker, 1973). Figures 2.5 (a) and (b) shows the steps of thermoluminescence process. During irradiation the electrons absorb enough energy to be trapped in metastable state shown in figure 2.5 (a). There are three possibilities during irradiation of TL phosphors.

* At point (1) some electrons and holes after excitation get trapped.

* At point (2) some de-excite radiatively (fluorescence) or non-radiatively to the ground state (recombination).

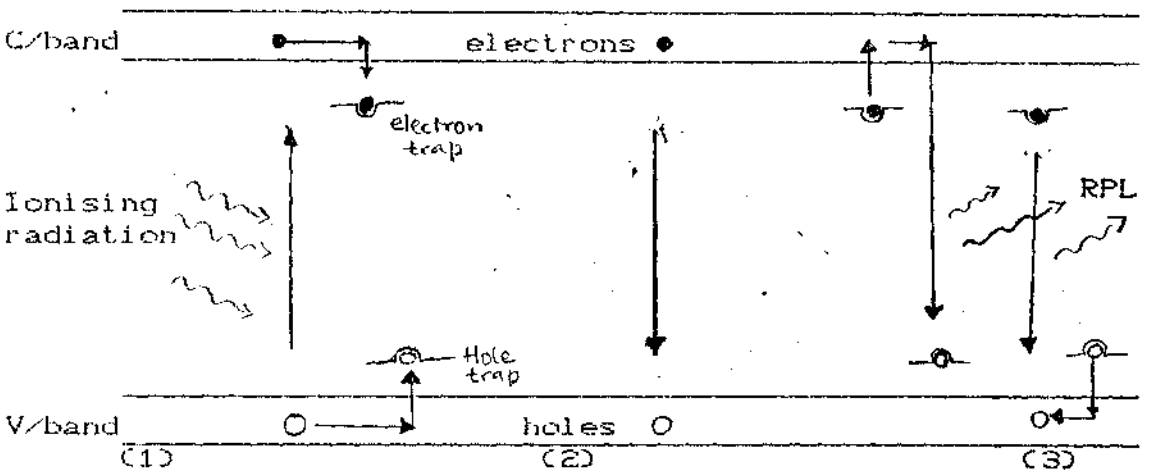


Fig. 2.5(a) Irradiation.

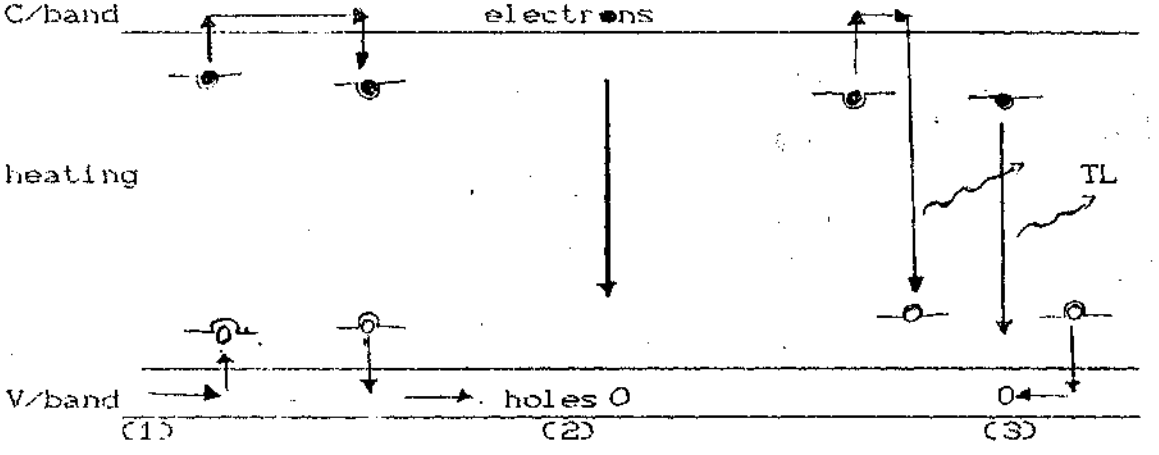


Fig. 2.5(b) Thermal stimulation

* At point (3) Radioluminescence is a possibility. Similarly, during heating the thermoluminescence process takes place as seen in figure 2.5 (b) and three possibilities results.

* At point (1) retrapping at defects and luminescent centres occurs.

* At point (2) radiative or non-radiative recombination.

* At point (3) TL signal is emitted as carriers recombine at luminescent centres.

2.4 THERMOLUMINESCENCE ANALYSIS

2.4.1 Thermoluminescence Kinetics

The first and second order TL kinetics describes the situation in which retrapping of liberated electrons may or may not occur. If retrapping of charge carries does not take place then the situation is described by first order TL kinetics. But if there exists retrapping with equal probability of recombination, then second order TL kinetics is used to describe the situation. Considering a phosphorescence process consisting of a single electron trap level and assuming all recombination events give

rise to TL emission, the general equation describing the trapped electrons' variation during time is given by

$$-\frac{dn}{dt} = n.s\ \exp(-E/kT)\left[1 - \frac{\sigma(N - n')}{\sigma(N - n) + n'}\right] \quad ....2.2$$

where n = trapped electrons concentration at time t (m^{-3})

n = trapped holes concentration at time t (m^{-3})

s = frequency factor (s^{-1})

E = Thermal activation energy (eV)

N = Trap concentration (m^{-3})

k = Boltzman constant

T = temperature (K)

σ = retrapping and recombination cross section ratio.

This equation was used by Levy (1985) and was also used by Bacci *et al.* (1989). The first and second order kinetics are both special cases of this equation. By assuming that retrapping does not occur, $\sigma = 0$, equation (2.2) reduces to:

$$-\frac{dn}{dt} = n\ s\ \exp(-E/kT) = n\ P \quad ....2.3$$

where $P = s\ e^{-E/kT}$.

If its assumed that retrapping is present with equal probability of recombination, $\sigma = 1$ and $n = n'$, then (2.2) becomes:

$$-\frac{dn}{dt} = \frac{n^2}{N}\ s\ \exp(-E/kT) = \frac{n^2 P}{N} \quad ....2.4$$

Solve equation (2.3) and (2.4) to obtain

$$n(t) = n_o \exp(-Pt) \qquad \ldots.2.5$$

$$\text{and} \quad n(t) = \frac{n_o}{(1 + Pn_o t/N)} \qquad \ldots..2.6$$

respectively. Where n_o is the number of trapped electrons at t=0. Let n_c be the number of electrons in conduction band. If the life time is less than that in the traps, then:

$$\frac{dn}{dt} = - \frac{dn_c}{dt} \qquad \ldots.2.7$$

The number of photons emitted per unit time (Intensity) at time t is I(t). If there's constant proportions of electrons in the conduction band that give rise to TL transitions then:

$$I(t) = - \alpha \frac{dn_c}{dt} \qquad \ldots.2.8$$

α is a constant (Robertson, 1981).

$$\Longrightarrow \quad = I(t) = - \alpha \frac{dn_c}{dt} = \alpha P n_o \exp(-Pt)$$

$$= \frac{\alpha n_o}{\tau} \exp(-t/\tau)$$

where $1/\tau = P$ and τ is the life time of a trapped electron. This means that the TL signal intensity decays exponentially. If there exists a trap distribution, the

number that till these traps initially with life time between τ and $\tau + d\tau$ is given by $n_o \tau d\tau$.

So $$I(t) = \alpha \int_0^\infty n_o \tau / \tau e^{-t/\tau} d\tau \quad \ldots.2.9$$

This is a condition of first order TL kinetics, assuming all electrons are released without retrapping and contribute to TL signal. For the condition of retrapping, the equation is given by:

$$I(t) = \alpha \int_0^\infty n_o^2 (1 + n_o \tau t / N\tau)^{-2} d\tau \quad 2.10$$

2.4.2 Glow Curves

The method of glow curves was first proposed by Usbach in 1930 but achieved extensive use due to Randall and Wilkins in 1945 (Robertson, 1981). This work is based on the glow curve theory of Randall and Wilkins.

We consider defects which give rise to single trap depth in the natural phosphors. If the ground state energy is E and at certain time t the temperature of the phosphor is T(K) with a single trap containing n electrons, then the energy distribution of the electrons within the trap is described by equation (1.1).

$$P = s\exp(-E/kT)$$

where P, s, E, kT are as previously defined. The intensity of the TL glow depends on the rate of photon emission hence on the rate of release of electrons from traps and their rate of arrival at luminescent centres.

$$I(t) = -\alpha dn/dt = \alpha nP = \alpha nsexp(-E/kT)$$

If the phosphor is heated at a particular rate,

$$Q = dT/dt$$

Then
$$-dn/dt = \frac{dn}{dT}.\frac{dT}{dt} \qquad .....2.11$$

$$= -Qdn/dT \qquad .....2.12$$

Using equation (2.3),

$$dn/dT = -1/Q*nP$$

whose solution is given by

$$n(t) = n_o exp \int_{T_o}^{T} -P/\alpha \, dT, \qquad ....2.13$$

and

$$n(t) = \alpha n_o P exp \int_{T_o}^{T} -P/\alpha \, dT, \qquad ....2.14$$

for the fist order kinetics. Suppose retrapping occurs then

$$I(t) = \frac{\alpha n_o P}{(1 + \int_{T_o}^{T} P/\alpha dt)^2} \qquad ....2.15$$

Equations (2.14), and (2.15) represents TL curves which are obtained through numerical integration of each. They give a bell shaped curve with maximum intensities at characteristic temperatures (Peak). Here a relationship between E and maximum T can be obtained if maximum derivative with the respect to temperature of I(t) is taken . Equation (2.14) give

$$EQ/k(T^*)^2 = P \qquad \ldots.2.16$$

T is maximum temperature, also (2.15) gives

$$EQ/2k(T^*)^2\{1 + \int_{T_o}^{T^*} P/Q \, dT\}^{-1} = P \qquad \ldots.2.17$$

(2.16) and (2.17) differ by

$$\tfrac{1}{2}(1 + \int_{T_o}^{T^*} P/Q dT)^{-1}$$

which is equal to $\frac{n_o}{2n^*}$ (Robertson, 1981),

where n^* represents the number of electrons left in the trap at T^*. The main difference between first and second order TL kinetics is that, in the later, greater fraction of the light is produced at temperature above the peak temperature because the retrapping effectively delays the release of electrons. Second order kinetics apply when the concentration of traps is comparable or greater than the concentration of luminescent centres, as the later

increases, the probability of retrapping decreases and the curve of second order kinetics moves closer to the curve of first order kinetics. The integrated light sum A under the glow curves is give by

$$A = \int_0^\infty I dt = \int_0^\infty -\alpha^{dn}/_{dt} dt = \int_{n_o}^0 \alpha dn = \alpha n_o \qquad 2.18$$

This shows that A is proportional to the initial number of trapped charges and is independent of read out cycle as long as α remains constant. This is calculated by the readout instrument and displayed together with the glow curve structure.

2.4.3 Decay of the Glow Curves

The release of trapped electrons at storage temperature before readout is called fading. Fading is a fundamental problem in the development and maintenance of dosemeters. Several factors contribute to the fading rates of TL Phosphors. These factors vary from one TL material to another and they include trap depth, total energy stored and storage conditions (temperature, humidity, pressure). It is therefore necessary to study the stability of stored signal in each phosphor and the various reasons responsible for instability, be known and if possible be corrected.

The half-life ($t_{\frac{1}{2}}$) of a particular trap, and by association, a particular glow peak, is defined as the time for the number of trapped carriers to fall to half of its original value

$$t_{\frac{1}{2}} = 0.693/s.\exp(-E/kT) \quad ....2.19$$

With E and s known, one will know at what temperature T is the peak most stable.

2.4.4 Dose Versus Response Relationship

The linear dependence of the light sum of the radiation dose is an important property of thermoluminescence dosimetry system. For most phosphors, at relatively low value of absorbed dose, the relationship is linear,(McKinlay, 1983).

$$A = zD + B \quad ....2.2$$

where A is the integrated light sum for an absorbed dose D. z is the TL emitted per unit absorbed dose, and B is the background signal of an unirradiated phosphor.

For most natural phosphors, a sublinear relationship results at low dose levels. At high dose levels a supralinear relationship is noticed with eventual saturation. Since the dose-response here are sublinear, in the expansion:

$$e^{-x} = 1 - x + x^2/2! - x^3/3! + ...$$

x is small and so a quadratic polynomial is used to represent the early build up curves. The polynomial is given as

$$A = A + Bx + Cx + ... \qquad ....2.21$$

where A is the integrated light under the curve, x is the dose absorbed and A, B, C, are constants.

2.4.5 Phosphor Repeatability

When a single measurement is performed repeatedly, there exist a certain degree of regularity which is displayed in a pattern closely approximated by normal distribution. This displayed pattern demands that, for such measurements to be repeatable, 68% of the data observed should fall within one standard deviation of the mean, and about 95% should fall within two standard deviations from the mean. If this condition is not met then the measurement is not repeatable, (John Freund, 1973).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 DESCRIPTION OF MINERALS

A mineral is defined as a substance having finite chemical composition and atomic structure and formed by the inorganic processes of nature (Read, 1970). The mineral solids are usually associated with a particular portion of the earth's crust, the rocks, in which they are deposited. There are two groups of mineral deposits, those formed at the same time as the associated rocks, syngenetic deposits and those formed later than the enclosing associated rocks, epigenetic deposits. The two categories of minerals studied in this work differ in both physical and chemical properties.

(a) Fluorite

This mineral as said earlier is an alkali-halide and exist as replacement deposits associated with other minerals such as galena, blende, quartz, barytes e.t.c. Its deposition formation is epigenetic of the endogenetic mineral deposit type. The endogenetic mineral deposit here is hydrothermal (50 -500°C) (Read 1970). Which is a process by which metals of economic values are dissolved and transported by heated water of great chemical activity and eventually deposited

either in cavities, fissures or between grains of sediments, during a final stage of magma consolidation.

(b) Calcite

Calcite is associated with sedimentary rocks, rocks formed by deposition of material arising from physical and chemical decay (caused by weathering agents such as frost, rain, ice, running water and chemical reaction) of pre-existing rocks at the earth's surface. The mineral deposit type here is exorgenetic which results in chemical-organic deposits. They are formed by precipitation of material from solution or organic processes. Carbonate (-CO) deposits results from accumulation of fragments consisting of calcium carbonates, calcite of shells, corals, e.t.c. while calcareous algae precipitate calciun carbonate that make thick beds in certain formations (Read, 1970). The calcite studied here is of the finely fibrous variety which mostly occur in veins and crevices of rocks of the sedimentary type.

3.1.i Source

All the samples studied in this work have been collected from Plateau, Benue and Bauchi States of Nigeria. The fluorites were found in hydrothermal veins and in cavities of igneous rocks and of limestone and marble in Ashaka and Akwana Arufu, areas of Bauchi and Benue States respectively (College of Preliminary Studies, Geology

Laboratory, Yola). The calcites also are obtained from veins and crevices of sedimentary rocks both in Ashaka and Jos in Bauchi and Plateau States.

3.2 INSTRUMENTATION

A commercial TL reader has been used in this research work. The model is the Vinten Solaro System which mainly consists of model 680 TLD reader, a visual display unit (VDU) and Keyboard. The system is designed to meet the requirements of TLD applications including research. An external anneal oven and phosphor irradiator with attached Sr^{90}-Y^{90} β- Source (β energies 0.61 and 2.2 MeV with half life 28 years) were also used for pre-irradiation annealing and artificial irradiation respectively.

3.2.1 System Operation

(a) The Oven

External pre-irradiation anneal at 300°C for eight (8) hours was done using an automated electrical oven designed with an inbuilt programme for heating samples at any rate to a temperature not more than 500°C. The oven was programmed to heat the ground sample from room temperature 26°C to 326°C in one hour, at this temperature, it stayed for eight (8) hours after which it is cooled back to room temperature in another hour. The samples were thus annealed.

(b) Irradiator

The irradiator machine used here is capable of irradiating group of dosemeters to the same dose over a wide dose range. Its fitted with fixed radiation source (Sr^{90}-Y^{90} β- source in this case). The system is designed to accommodate 30 dosemeters at a time on a turn table which turns at a constant speed. When the turn-table rotates the dosemeters pass directly under the radiation source. The rotation, being at a constant speed, enables the dosemeters to receive the same dose per pass under the source. The number of times the dosemeters pass under the source is pre-set by means of a count-down revolution counter. The radiation source used has an activity of 37mBq and is shielded with perspex to absorb high energy beta emitting minimal bremsstrahlung, and then with lead, to reduce the radiation dose rate on the surface of the irradiation to a safe level. All samples intended for irradiation are mounted on the turn-table before operating the machine to a required number of revolutions.

(c) Model 680 TLD Reader

The Solaro model 680 TLD reader is very easy to operate. All user interface and status indication are presented on the VDU and operator control is exercised via the keyboard. The model has two identical light measurement systems, stations A and B, which could be used unchangeably.

These consists of a photomultiplier tube (PM tube), current to pulse converter (CTPC), ratemeter, internal light source reference, digital to analogue converter, soft wire control and high voltage supply unit, each.

A sample to be read is inserted via a drawer opening and a mechanical device positions the heater to heat the sample under the control of heating regime established by a pre-set heating table. The light signal is detected by the PM tube. This signal is converted to pulse by CTPC, which is counted and integrated over the read time. This gives the raw counts. The real TL signal, background noise from the heated phosphor and dark current signals from light measurement systems make up the raw count, which is corrected by the reader using a calibration factor pre-set in the system. The glow curve, signal intensity and the corrected reading are displayed after readout on the monitor through a software manoeuvre.

3.3. METHOD

3.3.1 Sample Preparation

Measurement with loose powder was adopted in this research work, Through it has disadvantages such as sensitivity variations with particle size due to light scattering, and inconveniences involved in handling powdered samples, its preferred because of its simplicity.

Materials are ground into coarse grain powder to minimise the effects of grinding (triboluminescence) on the TL sensitivity. Finer grains aid contributions of natural alpha radiations, complicating the TL sensitivity of these phosphors. Efforts have been made to reduce complexities arising from phosphor grinding in this case. Using coarse grain powder also reduces the electrostatic charges noticed in fine grain powdered samples as they stick to each other and the container bringing further inconveniences in powder handling.

All samples were weighed on heating trays before any measurement. The heating trays supplied with the Solaro TLD system are designed to hold powder phosphors during irradiation and readout.

3.3.2 Thermoluminescence Dosimetry Study

For phosphors to qualify as good TL dosemeters, they should pass tests based on the proposals of international standard for TLDs. Detailed tests methods both for the test required by the International Atomic Energy Agency (IAEA) which include fading, dose versus response linearity, stability under standard climatic conditions and requirements of International Electrotechnical Commission (IEC) which are batch homogeneity, detection threshold, stability of zero point, repeatability and residual TL, in addition to the general requirement of glow curve structure,

have been regarded. This glow curve structure given by bo+ relations (2.14) and (2.15) follows from the assumption given by (1.1). The residual glow corresponding to a given trap will thus also follow the same law, hence glow curve structure when several traps are emitted.

Some of the recommended test were not performed due to some technical constraints encountered. However, the following were studied.

(i) Glow curve structure.

(ii) Linearity.

(iii) Repeatability

(iv) Fading rate

(v) Residual TL

(vi) Minimum detectable signal

The relative photon energy dependence of these natural phosphors could not be determined because the constituent elements of the phosphors are not yet determined.

3.3.2.1 Natural TL (NTL)

Powdered samples after weighing were read without any pre-read heating (anneal) or irradiation. This provides the NTL resulting from natural irradiation by radioactive elements and cosmic rays from the surrounding matrix, which

has been cumulative over the years. The area under th resulting glow curve with peak at characteristic temperatu gives the magnitude of the TL signal. Its hardly feasible that a phosphor will exhibit TL properties without characteristic glow curve structure.

3.3.2.2 Artificial TL (ATL)

After every background measurement (NTL), the phosphors were then artificially irradiated using the Sr^{90}-Yb^{90} β-source for different radiation doses. The magnitude of the TL signal was noted for every exposure and since the TL signal is proportional to radiation energy absorbed, a linear relationship between dose and response was expected. However a sublinear relationship was obtained which could be attributed to the low dose level of the samples.

3.3.2.3 Fading

The stability of the stored TL signal was studied at room temperature for each phsophor. All samples earlier studied were annealed at 300°C for eight (8) hours each, This process helped to eliminate the natural TL present in the samples. Some of the samples gave high background reading even after annealing at such a high temperature for a long time. No appropriate annealing procedures were investigated for these samples, as such this annealing method adopted must have left some of the samples sensitized while others lost their sensitivities.

A particular dose was given to each phosphor and a short term fading for maximum of 1146 minutes monitored for some samples. In this study though, only the lower temperature peaks were observed for level at 0.33 mSv (Co^{60} gamma source equivalent). High temperature peaks were avoided because of high degree of spurious TL exhibited at such temperatures.

3.3.2.4. Repeatability

Repeatability was studied by irradiating and reading each of three phosphors in a cycle repeated twenty (20) times. This test describes its re-usability and was performed only for one of the promising samples. The spread of the TL responses was observed. The graph that shows the behaviour of responses have been obtained.

3.3.2.5. Residual TL

This test gives the effect of previous irradiation on the samples. Specific dose was given to the phosphors and were read out. After 60 minutes the same phosphors were read again and the magnitude of TL signal was compared to the background equivalent.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 GLOW CURVE STRUCTURE

The naturally irradiated samples (powdered form) were readout without prior heating. Lower temperature peaks were studied to avoid too much complications arising from spurious TL noticed in high temperature readouts due to chemiluminescence. Spurious TL is usually suppressed by an Oxygen free Nitrogen which is not used here because of the nature of the samples used. Effects of spurious TL at low temperature are minimal and is decided to be overlooked in this study. Table 4.1 shows the details of the phosphors studied.

Comparison of results with that of a synthetic phosphor (LiF:Mn,Ti) in a disc form, shows a close resemblance as illustrated in the figures (4.1a, b, c). Some of the samples especially calcites gave very poor TL response after external anneal at 300°C for eight hours. The background TL dropped to a very low level. Ash C_2 and Pla C_2 which before heating gave poor TL response compared to the rest, became irresponsive even after dose of 167mSv (^{60}Co gamma radiation equivalent) was given to the phosphors. This might suggest that the samples could be pure and have negligible impurity and defect levels. The other calcites Ash C_1 and Pla C_1 show

Table 4.1: Details of the Natural Phosphors

No.	Phosphor	Location	Mineral	TL-response	Peak-Temp (°C)
1	Ben F_1	Akwana Arufu	Fluorite	good	150
2	Ben F_2	"	"	"	"
3	Ash F_1	Ashaka	"	"	100-150
4	Ash F_2	"	"	"	"
5	Ash C_1	"	Calcite	moderate	180-200
6	Ash C_2	"	"	poor	250
7	Pla C_1	Jos	"	good	200
8	Pla C_2	"	"	poor	250

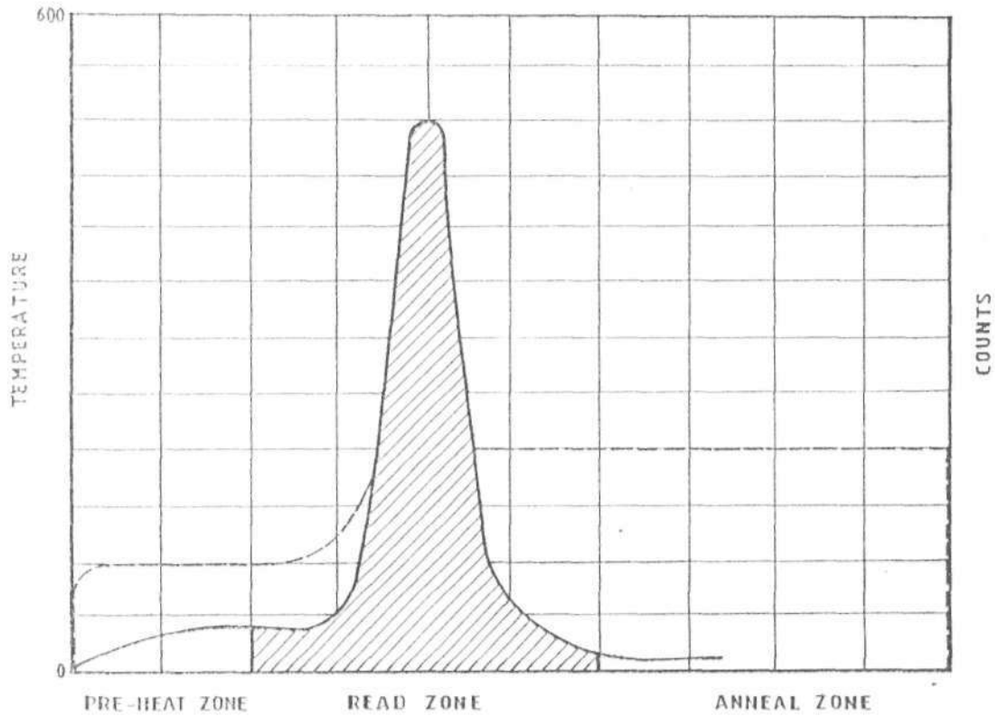


Fig. 4.1(a). A glow curve structure of a calcite sample.

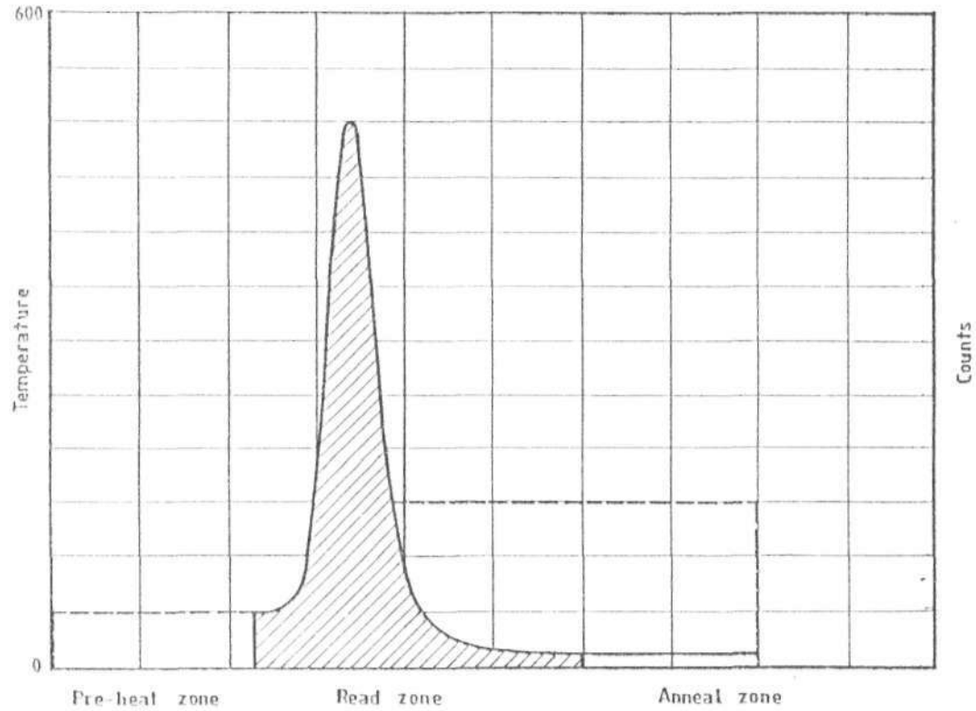


Fig.4.1(b). A glow curve structure of a fluorite sample.

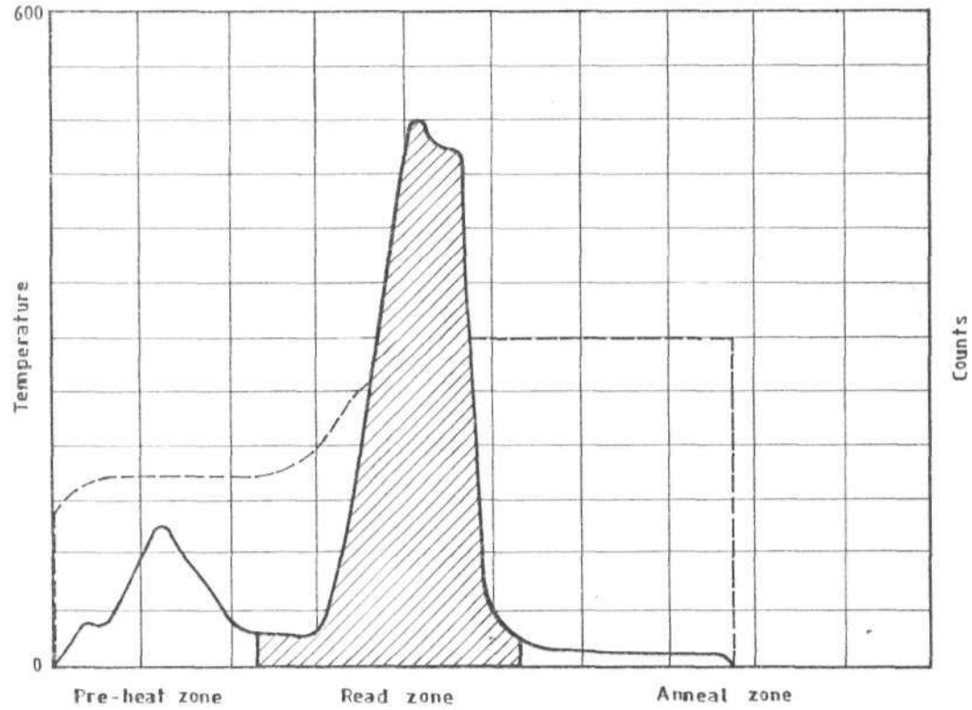


Fig. 4.1(c). A glow curve structure of synthetic LiF ; Mn, Tl dosimeter .

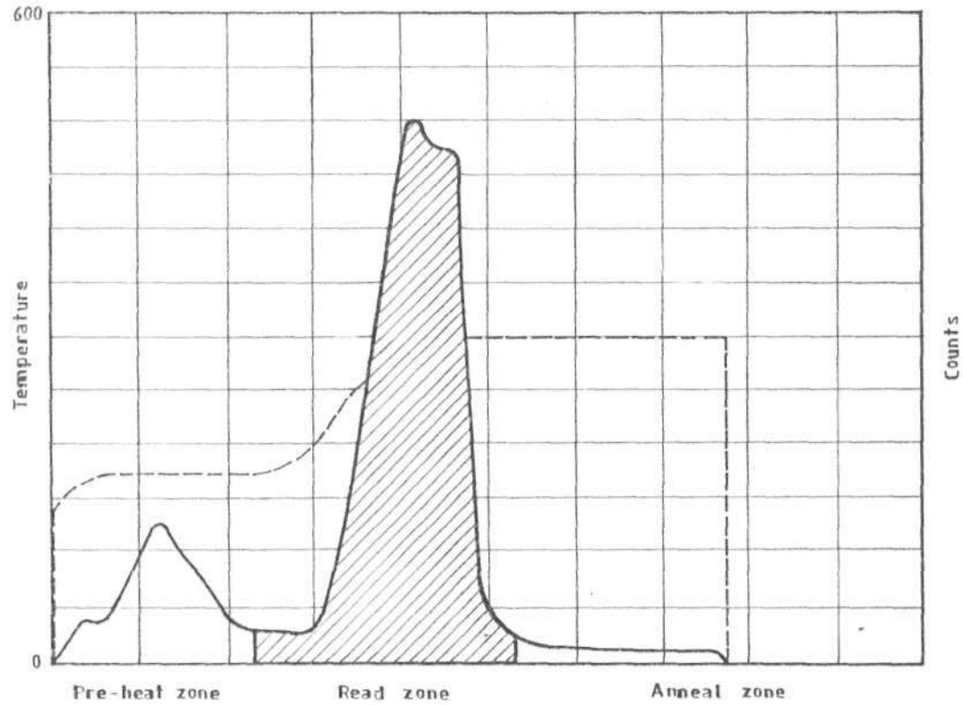


Fig. 4.1(c). A glow curve structure of synthetic LiF ; Mn, Tl dosimeter .

low level of response at the chosen peak temperature (200°C).

The fluorites however, showed good TL response at 150°C peak temperature even after heating. Though these minerals belong to the same groups they differ in their TL properties even if equal weights are used. Table 4.2 shows some characteristics of the glow peaks. The half-life of each peak determined theoretically seem not to agree with experimental values. This is expected because the theoretical values are obtained by considering only single trap concentrations. The difference may therefore arise due to the trap distribution that occurs in the natural samples.

4.2 DOSE VERSUS RESPONSE LINEARITY

The response versus dose relationship for these phosphors is sublinear. The corresponding TL response for every exposure, is not linear. The sublinear relationship may partly be attributed to the low dose level in the samples which might have had their traps filled completely at certain times. A fitting programme has been used to obtain new equations using the least square criterion. A second order polynomial (equation 2.21) have been used and the respective coefficients obtained as shown in table 4.3. below. The sublinearity is seen from the nature of coefficient of x^2 in the sample. The polynomial is given as

$$\text{Area} = A + Bx + Cx^2 \quad \text{where } x = \text{dose.}$$

The fitted curves are shown in figures 4.2 .

Table 4.2: Glow Peaks' Characteristics

Phosphor	Peak temp. (°C)	Trap Depth, E (eV)	Frequency factors, s (s^{-1})	Peak half-life
Ben F_1	150	0.97	$4.76 * 10^{11}$	7.6 hrs
Ash C_1	200	1.23	$9.60 * 10^{12}$	1.0 yr
Ben F_2	120	0.83	$5.87 * 10^{10}$	11.6 min
Ash F_1	110	0.76	$2.91 * 10^{10}$	4.8 min
Ash C_2	180	1.12	$3.52 * 10^{12}$	33.7 hrs
Pla C_1	190	1.17	$6.60 * 10^{12}$	51.6 days
Ash F_2	160	1.02	$9.10 * 10^{11}$	27.4 hrs.

Table 4.3: Coefficients of the Second Order Polynomials

	Coefficients A	B	C
Ben F_1	-5.138	6.439	4.485
Ash C_1	1.981	2.100	-1.744
Ash F_1	1.641	6.057	1.326
Ash C_2	-2.553	6.012	-7.010
Pla C_1	1.111	4.238	-3.293
Ash F_2	-1.781	1.057	-1.669

The coefficient C is less than zero ($C<0$) for all sublinear curves and greater than zero ($C>0$) for all supralinear curves

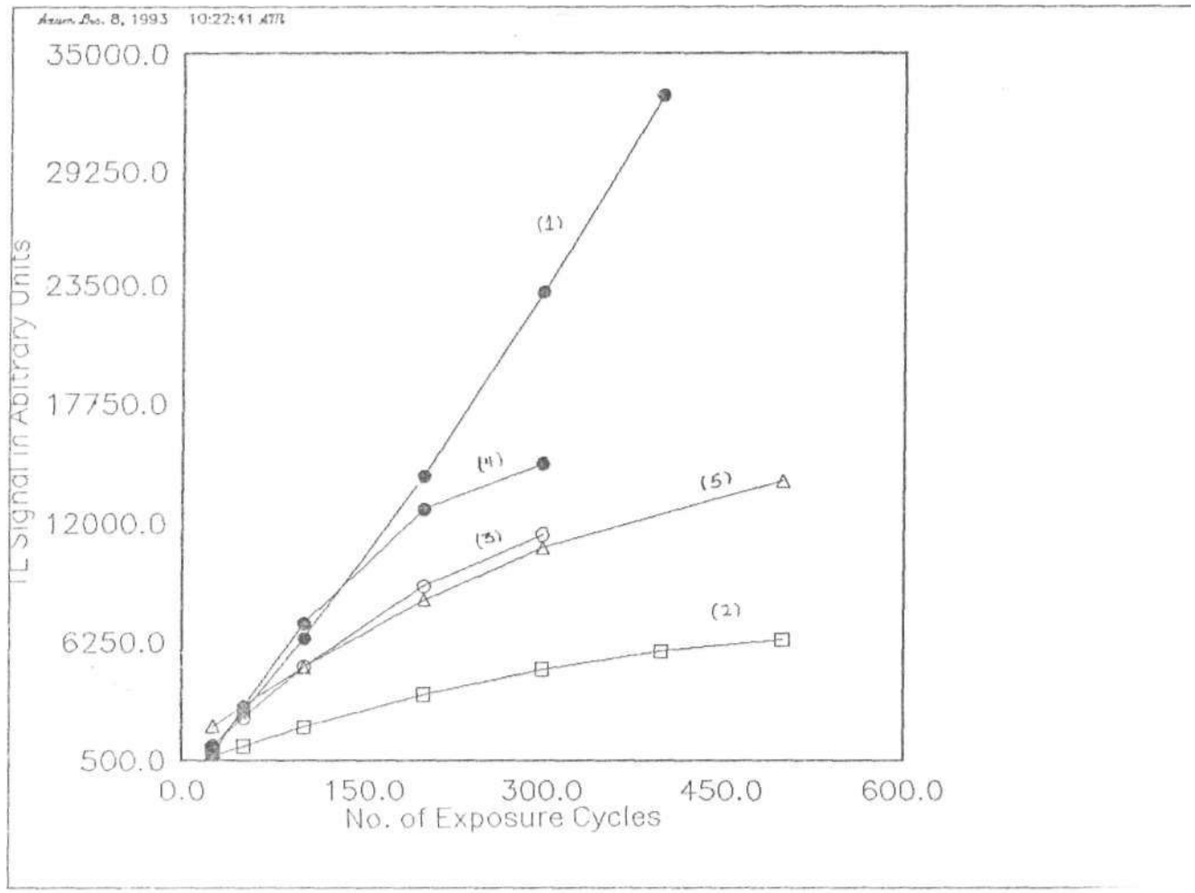


Fig. 4.2. Dose vs. response relationship, (1) $BenF_1$, (2) $AshC_1$, (3) $AshC_2$, (4) $AshF_2$, (5) $PlaC_1$.

4.3 ISOTHERMAL DECAY

Short term fading at room temperature of 27°C for the glow peaks were investigated for all the samples. The lower temperature peaks for each of the phosphors were studied at 150°C for fluorites and 200°C for the only calcite. The other calcites did not respond to the artificial irradiation in the low dose range utilised in isothermal fading observation. The short term fading was studied for maximum of 1146 minutes with a close monitoring of the first 120 minutes at intervals of 10, 20, and 30 minutes respectively. Table 4.4. shows the percentage loss of TL signal after 10, 120, 930, and 1146 minutes.

Some of the samples for which half-lives have been obtained theoretically (Ash C_1 , Ash C_2 , Ash F_1), have not been monitored because of their poor responses. Ash F_1, on the other hand exhibited abnormal behaviour of peak rebuilding instead of decaying. The fading rates for the samples are shown in figure 4.3.

4.4 SPECIAL STUDIES

One of the promising samples Ben F , was selected for further investigation regarding the quality of phosphors. Of the numerous tests recommended by IEC, re-usability and residual TL were studied and the following observations made.

Table 4.4 Decay of the TL - peaks in Percentage

Phosphor	10 min.	120 min.	930 min.	1146 min.
Ben F_1	12.8	66.1	70.8	*
Ben F_2	42.0	66.3	*	66.8
Ash F_2	4.8	42.5	62.6	*
Pla C_1	11.4	64.4	*	67.3

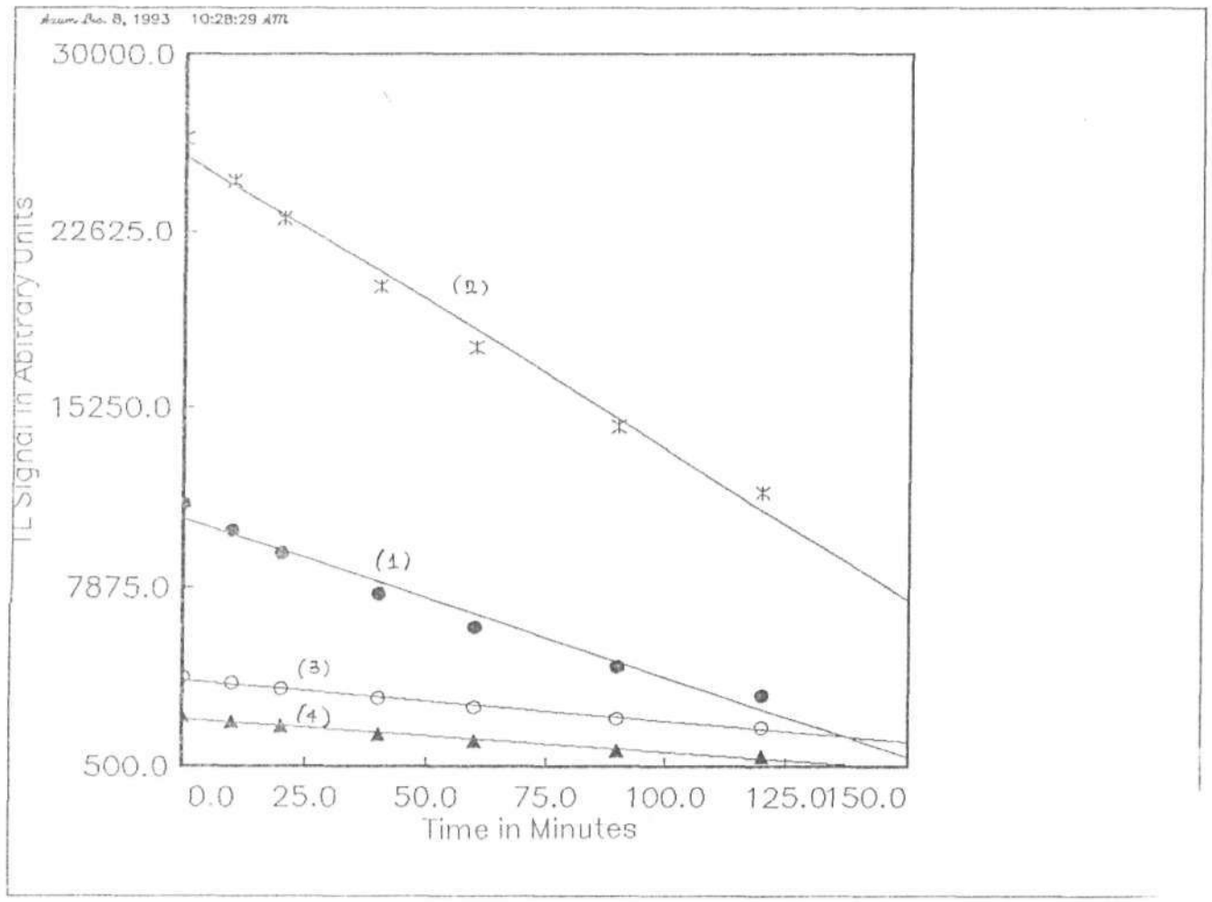


Fig: 4.3 Isothermal decay, (1) $BenF_1$, (2) $BenF_2$, (3) $AshF_2$, (4) $PlaC_1$.

(a) Re-usability

The effect of repeated irradiation with fixed dose and TL readout was investigated. Three samples were tested 20 times each. As stated earlier, n a repeatability tests results are expected to be such that 68% fall within one standard deviation from the mean and 95% fall within two standard deviations from the mean before the samples involved be re-usable. In the test performed here ,90% of the samples fall within one standard deviation from the mean. This clearly shows that Ben F_2 is re-usable.

(b) Remaining TL Signal

The effect of previous irradiation on the residual TL is tested using three samples of Ben F_1 phosphor. The mean and standard deviation of signal magnitude after irradiation with fixed dose is obtained. The respective value of the detection threshold was also obtained, with mean and standard deviation. The level of TL remaining is still high as shown from the ratio of the standard deviation

$$\sigma_1 / \sigma_2 = 1.35 \pm 0.59 \qquad \ldots.4.1$$

with σ_1 as the standard deviation from the mean of TL signal magnitude of the irradiated sample. And σ_2, the standard deviation from the mean of TL signal of the un-irradiated sample, (Azorin *et al.*, 1986).

4.5 DISCUSSION

4.5.1 Thermoluminescence low Curves.

The glow curve structure exhibited by these natural samples following the requirement for every TL phosphor and the areas under these curves corresponds to the natural TL intensity for each sample. Though several factors affect the quality of TL glow in every sample, it was not difficult to judge the TL sensitivities of these phosphors. The two groups of phosphors studied, namely flourites and calcites, have several glow peaks at different characteristic temperatures ranging from 150°C ± 12 to 300°C ± 15 for the calcites and 100°C ± 10 to 240°C ± 12 for flourites. Prominent among the factors affecting the TL glow quality is spurious TL contributions due to the following factors:

(i) Triboluminescence.

Energy imparted to powdered samples during grinding results in a luminous glow during readout. This glow is called triboluminescence and characteristic of natural mineral phosphors. There is however, means of minimising this effect adopted in this research work, through coarse grain production. The grain sizes used in this work falls within the range of 80 µm to 200 µm and have minimised the effect of triboluminescence greatly. The use of inert gas in the readout volume can also reduce this effect greatly.

(ii) Chemiluminescence.

This is the light emitted during heating process due to chemical reactions. The major chemical reaction in question is the reaction of oxygen with the dosemeter surface, oxidation, (Robertson, 1981) during heating. Usually, this effect is controlled by flushing the readout volume with an inert gas (nitrogen or argon) which removes any oxygen from the readout area. The inert gas (Argon) or nitrogen flow process could not be adopted here because of the condition of the powdered samples investigated which were not protected.

Efforts have, however, been made to reduce the effect of chemiluminescence on the sensitivities of these natural phosphors by studying only peaks at low temperatures. The flourite samples obtained from the Benue trough Ben F_1 and Ben F_2 were heated at 25°C per second. This fast heating rate was noticed to affect the glow peak temperature position. The glow peaks obtained at 150°C appeared good for the study The area under the curves increases with increase in radiation dose during irradiation. Though some of the fluorites obtained from Ashaka, Ash F_1 and Ash F_2 show similar peaks under the same heating conditions. The fluorites also have a much lower temperature peak at 100°C but was not used for investigation.

The calcites on the other hand were heated at the 25°C per second showed reasonable peaks at about 200°C which was found stable enough for the studies. They also have low temperature peaks at 150°C but highly unstable. So only the 200°C peak was used for further analysis.

With appropriate annealing procedure the calcite phosphors could exhibit interesting TL properties which might be found very useful.

4.5.2 Linear Relationships

Though for aged samples, the electron traps contributing to the TL signal generally became filled, and the simplest physically realistic model (the first order kinetic) describing dose response leads to a saturating exponential form Huntley *et al.* (1987). There are other samples for which the dose-response curves are only some what sublinear over the range of useful doses as in this case. So in the expansion.

$$e^{-x} \approx 1 - x + x^2/2! - x/3! + \ldots\ldots\ldots$$

x is small and sufficiently accurate extrapolation and error analysis can be obtained by using a quadratic polynomial to represent the early build up curves, (Berger, 1987). The second order polynomial is found appropriate here because the sublinearity was noticed for low dose levels. A fitting programme has been used to fit the dose versus

response data using the quadratic polynomial. It should be noted that the dose versus respond relationship was studied before the samples were annealed.

4.5.3 Annealing

Variations in glow curve structures were noticed in these samples when they were subjected to 300°C heating for 8 hours. This process, which was intended to eliminate low temperature peaks and spurious TL resulting from visible and/or ultraviolet light was fruitful in the case of fluorites. The long high temperature anneal was not however necessary for the calcites which suffered from sensitivity loss after the process. Only one of the calcite samples Pla C_1 was found promising throughout all the investigations even at low dose levels. This is a display of the complexity associated with natural phosphors. Annealing could remove sensitization in heavily irradiated phosphors and yet annealing is used to enhance sensitivity of such phosphors (Hwang, 1972). Its therefore appropriate that annealing procedure be developed for phosphors so that they can appropriately be annealed.

The fluorites, however, proved sensitized after the annealing process, They displayed the normal peaks at the characteristic temperature even before irradiation. While Ben F_1, Ben F_2, and Ash F_2 showed normal response to radiation doses after annealing, Ash F_1 showed anomalous

behaviour. Appropriate annealing process is also necessary for the fluorite samples to minimise irregularities.

4.5.4 Self-Dose

One of the samples Ash F_1 portrayed the characteristics of TL build up even when not exposed to artificial irradiation. The annealing of phosphors is known to increase their sensitivities, but does not always lead to high build ups. Natural phosphors are sometimes doped with radioactive elements which serve as radiation sources within the crystals. Sometimes such build ups are attributed to the radioactive impurities present in the phosphors. The fading properties of sample Ash F_1 could not be studied because of this problem. As the sensitivity of this phosphor might have increased considerably, laboratory light can also contribute to the TL build up.

4.5.5 Glow Peak Stability

The glow curve structure affects the stability of the stored signal with respect to time and storage temperature. For long storage of trapped carriers at normal working temperatures the trap depth E needs to be large, the frequency factor(s) below; (Robertson, 1981). In phosphors with complex trap structure the stability of stored signal depend not only on fading effects but also on migration and aggregation of traps at storage temperatures (Booth *et al.*, 1972; Johnson, 1974). This phenomenon can counteract fading

which sometimes leads to increase in stored signals as in the case of Ash F_1 .

The lower temperature peaks studied in this work are noticed to be unstable at higher dose levels. The isothermal fading rates of four of the samples Ben F_1 , Ben F_2 , Ash F_2, and Pla C_1 revealed this. Assessment of the signal loss after 120 and 930 minutes for Ben F_1 which are 66.1% and 70.8% respectively, shows that the decay was slower at this stage, loosing only 4.7% in 810 minutes. The decay is much slower in Ben F_2 when it lost 66.3% in 120 minutes and 66.8% in 1146 minutes, that is loosing 0.5% in 1026 minutes. When this values are compared to what the same samples lost in the first 10 minutes, there's sharp drop in decay rates as the dose levels reduces. So the stability of the peaks is indeed influenced by the magnitude of stored energy.

4.5.6 Special Studies on Ben F_2

(a) Re-usability: Variations in sensitivity with repeated readout cycles and with no external anneal is measured with standard deviation 19%. Initially the sensitivity was low but later increased with readout cycles. The inconsistent variation in sensitivity is not unconnected with the uncertainties in the behaviour of natural samples. After series of irradiation and heating, sensitization of the phosphors occurred and the level of residual TL increased after each cycle.

A decrease in sensitivity at a low rate 0.4% per cycle is however noticed in phosphors undergoing repetitive readout Robertson (1981). In a similar investigation with synthetic $CaSO_4$:Dy by Azorin *et al.* (1986) measurement with 7.5% standard deviation was obtained. The graph of figure 4.4 shows uneven spread of TL response around the most frequent value in the measurement. This spread shows that the increase in sensitivity is lower than its decrease. So phosphors generally get de-sensitized with re-use.

(b) Remaining TL Signal

The TL signal remaining after irradiation of the phosphor, with 0.02 mSv (^{60}Co gamma equivalent) and left for 1 hour before readout was noticed to be high. The standard deviation from the mean values of the initial background signal and the later signal is compared with that obtained by Azorin, *et al.* (1986) for $CaSO_4$:Dy performance test study. The mean values however disagree and its attributed to the action of chemiluminescence which continually increased with exposure and heating of the same sample.

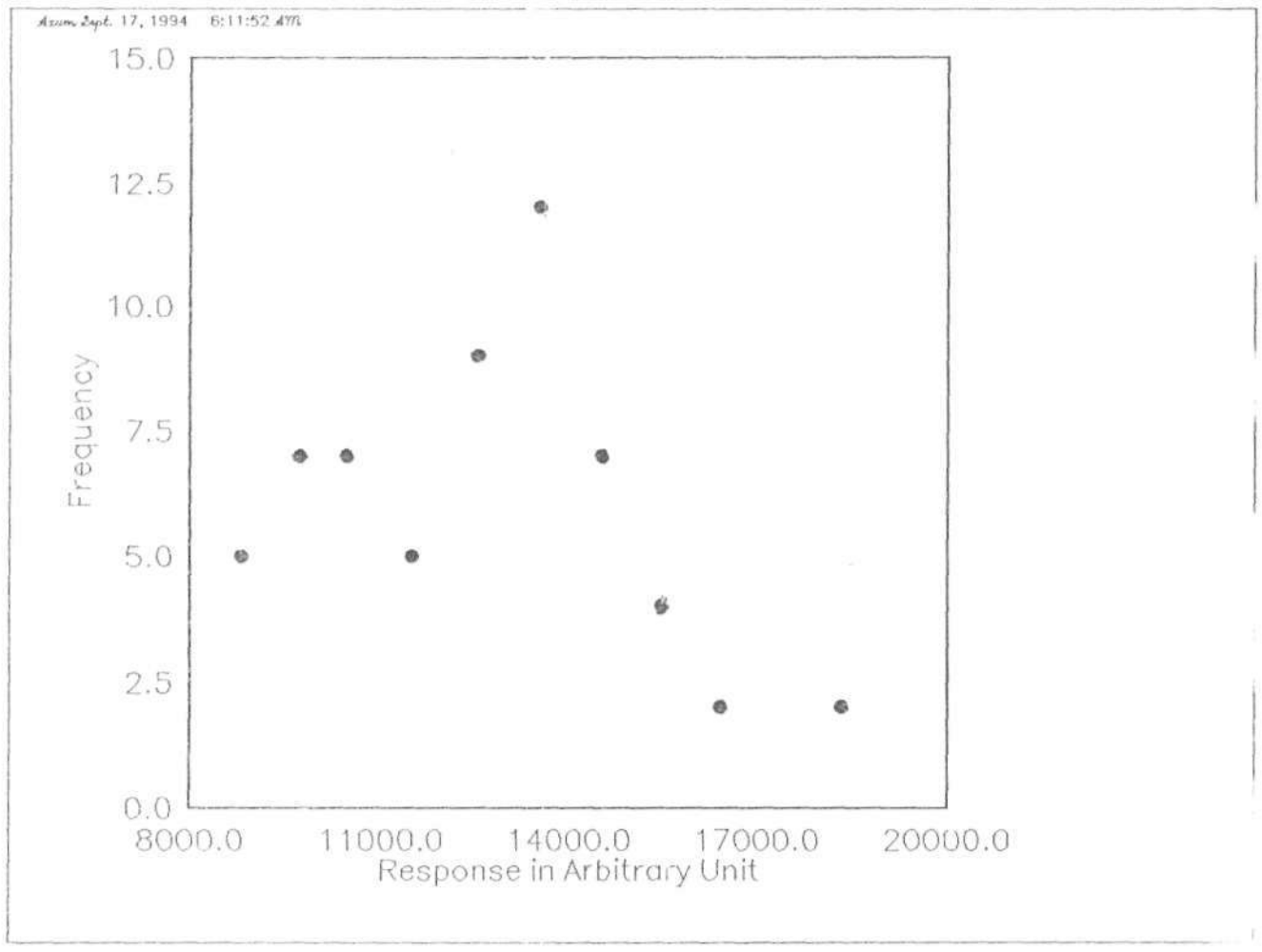


Fig. 4.4: Repeatability Curve

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

The result presented in this research is in accordance with the primary objective which concentrates on the identification of TL potentiality in natural minerals locally available. The studies, however are not detailed at all stages due to the technical constraints encountered. The observations therefore are mostly in partial agreement with those expected from TLD materials, natural or synthetic, as reported by other researchers.

The TLD systems generally have limitations which are either practical or inherent. Some of these limitations can be rectified with further research and development.

Though not all the recommended tests by IAEA and IEC were performed, those left out were because the facilities necessary were not available at the time of this research. It is believed that the test would be possible at least to provide steps for further analysis. In the area of glow curve structure for example all the samples have shown the expected characteristic behaviour under the required observation conditions. For confirmation, other samples were tested and were found incompetent even in the exhibition of the characteristic behaviour. Other tests such as linearity in dose versus response relationship, stability of stored

signal and re-usability, were fairly in agreement for natural phosphors studied under such harsh conditions.

The dose versus response linearity test performed did not reveal the expected behaviour of general TL phosphor because of the sublinearity shown due to low dose levels. Most of these samples require high dose levels for linear relationship to be observed. From what is obtained however, There is clear indication that they could exhibit the required linearity at appropriate dose levels.

In the test for stability of stored signal, The result shows that all the samples are most stable at low dose levels. This behaviour is normally expected because the traps are filled up with high doses, with carriers requiring little stimulation to escape from the traps. If the rate of decay can be established for each phosphor, it can be possible to tell dose content at any point in time regardless of the level of exposure.

The high TL remaining after readout, which was observed in one of the samples, means that the phosphor should undergo certain treatments such as adequate annealing procedure and elimination of irrelevant impurities present inside the sample that might enhance TL effeciency. The readout process should be adequately adopted to ensure that all traps empty the charge carriers in every readout.

Although substantial progress was made in identifying TLD potentials in the local natural fluorites and calcites in this research. Some difficulties were encountered in the measurement and must have to be overcome to achieve an appreciable standard to pass conclusive deductions. These difficulties include:

(a) Measurement With Loose Powder

The phosphors were not able to provide good and conclusive results in most areas of tests due to the presence of spurious TL all the time. In TLD measurements, during readouts, care has to be taken of most physical factors that may contribute substantially to the increase or decrease of TL intensity. Using loose powder in TLD measurements however is not alien but usually done by packing the powder in a plastic material that is resistant to high temperature (Robertson, 1981). While loose powder is encapsulated in plastic material, solid dosemeters are made into discs, pellets or rods. In all TLD measurements, inert gas (nitrogen or argon) is used in the readout volume to reduce the effect of spurious TL arising from chemiluminescence discussed earlier. In this work, the inert gas was not used because the powdered phosphors used were not protected and it was feared that the powder could be blown off by the gas. Efforts made earlier to produce pellets that can fit in the TLD reader failed after discovering that the smallest pellet produced (the size of a

Fenegan tablet, about 5mm in diameter) was too large for the method recommended. So, since the use of the inert gas was made optional in the model 680 TLD reader, it was decided that the tests be performed under this condition, utilizing every chance of minimising spurious TL.

(b) Climatic Conditions not Standardised

All measurements are expected to be done under possible standard climatic conditions especially for research purposes. Environmental factors are noticed to affect the TL sensitivity, stability, precision and minimum detectable absorbed dose. Fluctuations in ambient storage temperature was not controlled and it is expected that phosphors are not to be heated above ambient temperature. Those affected by humidity were not protected during storage or measurement, and this can influence the TL sensitivity.

Their responds to normal ambient levels of ultraviolet and visible radiation were evident but there was no possible protection from ambient light for the phosphors at the time of this work. The effects in this case are twofold: The production of light induced TL signal and the phototransfer and subsequent retrapping of trapped charge carriers, McKinlay (1983). This last effect can in some phosphor result in increased fading while in others increase in TL sensitivity. This means that the complexity of natural

phosphors is enhanced by exposure to ambient light. For effective result these factors must be controlled.

5.1 RECOMMENDATIONS

Of the several samples used for this work, fluorites from the Benue Valley (Akwana Arufu) show fair agreement with recommendation for international standards for TLDs in some tests. The special studies performed on Ben F_2 sample reveals this and it is the recommendation of this research that this particular sample should be properly analysed for further research and development.

To achieve the desired goal in developing natural phsophors as dosemeters to be used in the TLD system, it is recommended that the following steps be taken to improve on the research.

(A) Phosphor Handling

To minimise the possible uncertainties in precision and re-usability associated with phosphor handling, it is important that a particular form of dosemeter be adopted throughout the measurements. One should also bear in mind that the TL sensitivity of a dosemeter is directly proportional to the mass of active phosphor present. In the solid dosemeters where matrix (binder) is used in making them, are should taken that the phosphor and binder are mixed in correct proportions. No part of the phosphor should

be lost during measurements in the case of powdered samples. The surfaces of the solid dosemeters, should be kept smooth as they contribute in TL sensitivity. When powdered samples are used. The weights of the phosphors should be monitored with every measurement so that TL variation with weight should be obtained. Powder dispensers should be employed in the research with powdered phosphor, This will help in obtaining a fixed grain size range.

(b) Proper Annealing Procedure

A correct and proper annealing procedure should be developed for each of the phsophors. This will provide good ground to monitor the TL behaviour of the natural samples which might have suffered radiation damage for the long period they stayed irradiated in the soil. Its noted that annealing can enhance the sensitivity of heavily irradiated phosphor and conversely de-sensitize such a heavily irradiated phosphor. Such complex characteristics are exhibited by most natural phsophors. With correct knowledge of temperature level responsible for these changes, one can predict what to obtain at what temperature.

(c) Chemical Contents

The Chemical constituents of the natural samples should be known and if possible proper washing technique be adopted to reduce irrelevant impurities. With this process, the relative photon energy dependence of the phosphors could be

obtained which could be a property of the constituent elements of the samples. The mass energy absorption coefficient of the TL phosphors is a function of the photon energy and depends on photon absorption and other interaction processes taking place in the phsophor lattice, such as Compton scattering, photoelectric effect, pair production, etc.

The TL phosphor has to respond to radiation in the same manner as the medium in which the dose is to be measured. In this case, this will be possible only if the ratio of mass energy absorption coefficient of the phosphor and that of the medium does not vary with photon energy (McKinlay, 1983).

REFERENCE

Aitken, M.J. (1968) Low level environmental radiation monitoring using natural calcium fluoride, Proceeding on Second International Conference on Luminescence Dosimetry, Standford CONF. 680920.

Aitken, M.J. (1985) **Thermoluminescence Dating.** Academic press, London.

Amin, Y.M. and Durrani, S.A. (1985) A Spectral Study of Thermoluminescence from Natural Zircons, **Nuclear Tracks Radiation Measurement.** Vol. 1,2.

Azorin, A. Guteierrez, A. and Niewriadomski, T. (1986) "Performance tests of a $CaSO_4$:Dy based thermoluminescence personal dosemeter," **Radiation Protection Dosimetry,** 17, 53-56

Bacci, C., Fasso, A., Furetta, C., and Rispoli, B. (1989) "Some theoretical observations on the behaviours of thermoluminescent response as function of storage, irradiation and temperature", **Nuclear Tracks Radiation Measurement**, vol. 16, No 4, 235.

Becker, K. (1973) **Solid State Dosimetry,** CRC Press Inc. Cleveland, Ohio, U.S.A.

Berger, G.W., Lockhart, R.A. and Kuo, J. (1987) "Regression and error analysis applied to the dose - response areas in thermoluminescence dating" **Nuclear Tracks Radiation Measurements**, vol. 13,

Huntley, D.J. (1987) Thermoluminescence response to alpha and beta irradiations, and age determinations when the high dose response is non-linear, **Radiation effects.**

Hwang, F.S.W., (1972) "Evaluation of the thermoluminescence dating technique applied to smoky quartz", Journal of Geophysical Research, Vol. 77,

John, F., (1973) **Modern Elementary Statistics**, Prentice Hall International, Inc., London.

Johnson, N.M. and Blanchard, R. L. (1967) "Radiation dosimetry from the natural thermoluminescence of fossil shells" **The American Mineralogist**, 52, 1297-1310

Levy, P.W. (1985) Recent development in thermoluminescence kinetics, **Nucl. Tracks Radiat. Measurement**, Vol. 10.

McKinlay, A. F. (1983) **Thermoluminescence Dosimetry**, Adam Hilger Limited, Bristol, GB.,

Mejdhal, V. (1985) "Thermoluminescence dating based on feldspars" **Nuclear Tracks Radiation Measurements**, Vol. 10, No. 1-2.

Puite, K.J. (1971) Trapping centres in CaF_2:Mn from thermoluminescence and thermally stimulated exoelectron emission measurements in undoped and Mn doped CaF_2 samples. Procd. of third Intern.Conf. on Luminescence Dosimetry. Danish AEC.

Read, H.H. (1970) **Ruttey's Elements Of Mineralogy**, George Allen and Unwin Limited, London, GB.

Readhead, M. L. (1987) "Thermoluminescence dose rate data and dating equations for the case of disequilibrium in the decay series" **Nuclear Tracks Radiation Measurement**, vol. 13.

Robertson, M.E.A. (1981) **Identification And Reduction Of Errors In Thermoluminescence Dosimetry Systems**, D.A. Pitman Limited, Weybridge, Surrey, G.B.

Schayes, R. (1967) Thermoluminescent properties of natural Calcium Fluoride, Luminescence Conf., 650637.

Schulman, J.H. (1967) Theory of Luminescence, Amelinckx.

Singhvi, A.K., and Mejdahl, V. (1985). "Thermoluminescence of Dating Sediments" **Nuclear Tracks Radiation Measurements**, vol. 10, 137-161