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Research Interests: Nanomaterials, Luminescent phosphors, Radiation dosimetry, Optoelectronics, Organic dye lasers, Optical gas detectors, Biosensors, Health physics, etc.

Editor-in-Chef: Journal of Luminescence and Applications, ISSN:ISSN: 2375-1045 (Online) Columbia International Publishing, USA, Website: http://jla.uscip.us.

- ✓ He has published more than 100 research papers in international peer reviewed journals of repute.
- ✓ He has produced ten Ph. Ds.
- ✓ He was instrumental in organizing many national and international conferences.
- ✓ He is recipient of IAAM Advanced Materials Scientist Award-2011.
- ✓ He is also Associate Editor, Advanced Materials Letters. He is also President, Luminescence Society of India (Delhi Cheaper).
- ✓ He has close association with Lebedev Physical Institute, Moscow and JINR, Dubna (Russia).
- ✓ His areas of interests include nanomaterials, luminescent phosphors, radiation dosimetry, organic dye lasers, gas detectors and optical sensors.

RESEARCH INTEREST

- ✓ Spectroscopy,
- ✓ Luminescence,
- ✓ Radiation dosimetry,
- ✓ Laser materials,
- ✓ Detectors and optical sensors,
- ✓ Sensors for space technology.

RESEARCH PROJECTS

- Response of TLD Materials to SHI" sponsored by Inter-University Accelerator Centre, New Delhi.
- "Development of X-ray radiation diagnostics equipment for investigation of the X-ray emission from laser and discharge produced plasma using TLD and X-ray storage phosphors", Indo-Russian ILTP Project sponsored by DST, Delhi and RAS, Moscow.
- "TLD Nanophosphors for Ion-Beam dosimetry" sponsored by Inter-University Accelerator Centre, New Delhi.
- "Development of Nanophosphors for Space Dosimetry" sponsored by ISRO at University of Pune.
- "Development of Gas Sensors for Polluting and Fire Extinguished Gases" sponsored by CFEES, DRDO, Delhi.
- "Modifications by SHI Beam in Wide Band Gap Semiconductor Nanoparticles for Their Applications as Multifunctional Materials" sponsored by IUAC, Delhi.
- Comparative Study of Some New Highly Sensitive Micro- and Nanocrystalline TLD/OSL Phosphors Using SHI sponsored by IUAC, Delhi.

BOOKS/MONOGRAPHS (AUTHORED/EDITED)

- One book entitled "TLD Nanophosphors: Synthesis, Characterization and Applications" under review and publications.
- Nanotechnology and Laser Induced Plasma, Proceedings, IRNANO- 2009.
- Nanomaterials and Nanotechnology, Eds. A. Tiwari and P. D. Sahare, VBRI Press,2011, ISBN: 978-81-920068-3-3.

SOME RESEARCH PAPERS

- An approach to produce single and double layer graphene from re-exfoliation of expanded graphite, CARBON, 49 (2011)
- Photoluminescence of Cu doped sponge-like porous ZnO nanoparticles synthesized via chemical route, AIP Conf. Proc. 1393 (2011) 63, doi:10.1063/1.3653610.
- Novel nanostructured zinc oxide ammonia gas sensor, AIP Conf. Proc. 1393 (2011) 219, doi:10.1063/1.3653688.
- Synthesis and Luminescent Properties of Li-doped ZnS Nanostructures by Chemical Precipitation Method, AIP Conf. Proc.,1393(2011) 253.

- Effect of Surface Defects on Green Luminescence from ZnO Nanoparticles, AIP Conf. Proc. 1393 (2011) 159,doi: 10.1063/1.3653658.
- Sensitization Of Mesoporous Silica Nanoparticles (MSNs) By Laser Grade Dye Acriflavin, Adv. Mater.Lett., DOI:10.5185 amlett.2012.icnano.172.
- Photoluminescence Study of Laser Grade POPOP Dye Incorporated into MCM-41, Adv. Porous Mater.1(2012) 1.
- Gas sensing behavior of Fluorescein sodium impregnated MCM-41 for Sulphur dioxide, Sensor lett.11(2013) 526, doi:10.1166/sl.2013.2830.

CONFRENCES ORGANIZED

- National Conference on Luminescence and its Applications 2003 in collaboration with National Physical Laboratory, New Delhi, India.
- International Conference on Luminescence and its Applications 2008 in collaboration with National Physical Laboratory, New Delhi, India.
- Indo-Russian Workshop on Nanotechnology and Laser Induced Plasma at the University of Delhi, Delhi, India in 2009.
- International Conference on Nanomaterials and Nanotechnology – 2011 (ICNANO-2009) at the University of Delhi, Delhi, India in 2011

Recent Trends in Solid State Dosimetry of High-Energy Radiation

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Delhi – 110007.

Summary:

- Introduction
- Review of the work on TLD and OSL phosphors
- Work done in our laboratory
- Advantages of the TLD phosphors
- Advantages of the OSL phosphors over TLDs
- Concluding Remarks

Introduction:

High-energy radiation is hazardous to living beings. The world has seen its horrifying effects after the nuclear bomb explosion in Hiroshima and Nagasaki in Japan during the World War-II. The people are still suffering due to its genetically mutated hereditary effects. The use of materials and equipments generating high-energy radiation for medical, diagnostic and research purposes, especially, X-ray machines, reactors and accelerators, radioactive materials always pose a threat. Recent major accidents at Chernobyl in Russia and Fukushima in Japan forced world leaders to think about the use of use of radioactive materials for weapons of mass destruction and look for ways to maintain peace and. People are finding more cleaner and alternative means and sources of energy.

The high-energy radiation, therefore, needs to be monitored not only for the radiation workers but for the people living in the high background radiation regions and even the common people, who are exposed to radiation during medical diagnostics and nuclear medicine.

There are different kinds of detectors available, e.g., gas filled detectors and counters, nuclear emulsions, streak cameras, semiconductor detectors, scintillators thermoluminescent detectors (TLD), optically stimulated luminescent detectors (OSLD). However, most of the former ones carry electronic gadgets with them and are not comfortable to handle during working. TLD and OSLD, therefore, became

Thermoluminescence (TL) is a simple and good technique for radiation dosimetry. There are several thermoluminescence dosimetry (TLD) phosphors commercially available. The advantages of the technique are:

i. No need of any electronic gadgets are needed during radiation monitoring.
ii. The size of the detector is very tiny and could be used as badges, I-cards, ornaments like, a ring, neckless, ear rings, etc.
iii. The instrumentation for taking readouts is very simple.
iv. The detectors (TLD materials) are generally nontoxic and easy to use.
v. The detectors are reusable and cost effective.
vi. The detectors could be coded and a large number of them could be processed simultaneously and the records could be maintained easily.
vii. Some of them are tissue equivalent and could be used in mixed filed also.
viii. Dosimetry of swift heavy ions, neutrons, alpha/beta/gamma rays is possible.

Some drawbacks of the TLD detectors:

The main drawback of these materials is that not many are low-Z (tissue equivalent, i.e., $Z_{eff.} \approx 7.4$) materials. Low-Z (tissue equivalence) materials are usually preferred in radiation monitoring for due to their energy independent TL response which makes them suitable for the dosimetry even in a mixed field. There are some tissue equivalent phosphors available commercially but they cannot be considered as ideal ones. For example, $CaSO_4$:Dy (TLD 900) is a sensitive but the shape of its glow curves change at high doses and on annealing to high temperatures adding inaccuries in mesurements. LiF:Mg,Ti (TLD 100) is considered to be a *'good'* one but suffers from some drawbacks, e.g., it is not relatively very sensitive material and has also very complicated glow curve structure, another improved one is LiF:Mg,Cu,P and is very sensitive but reusability is a problem, if heated beyond 523 K and if not the remaining deep traps add inaccuracies in measurements, This problem exists in CaF_2:Mn also. BeO doped with alkali ions is another highly sensitive tissue equivalent TLD phosphor but it is toxic and handling is a problem during synthesis and radiation monitoring. Therefore, either the existing materials are being modified suitably or new phosphor materials are developed.

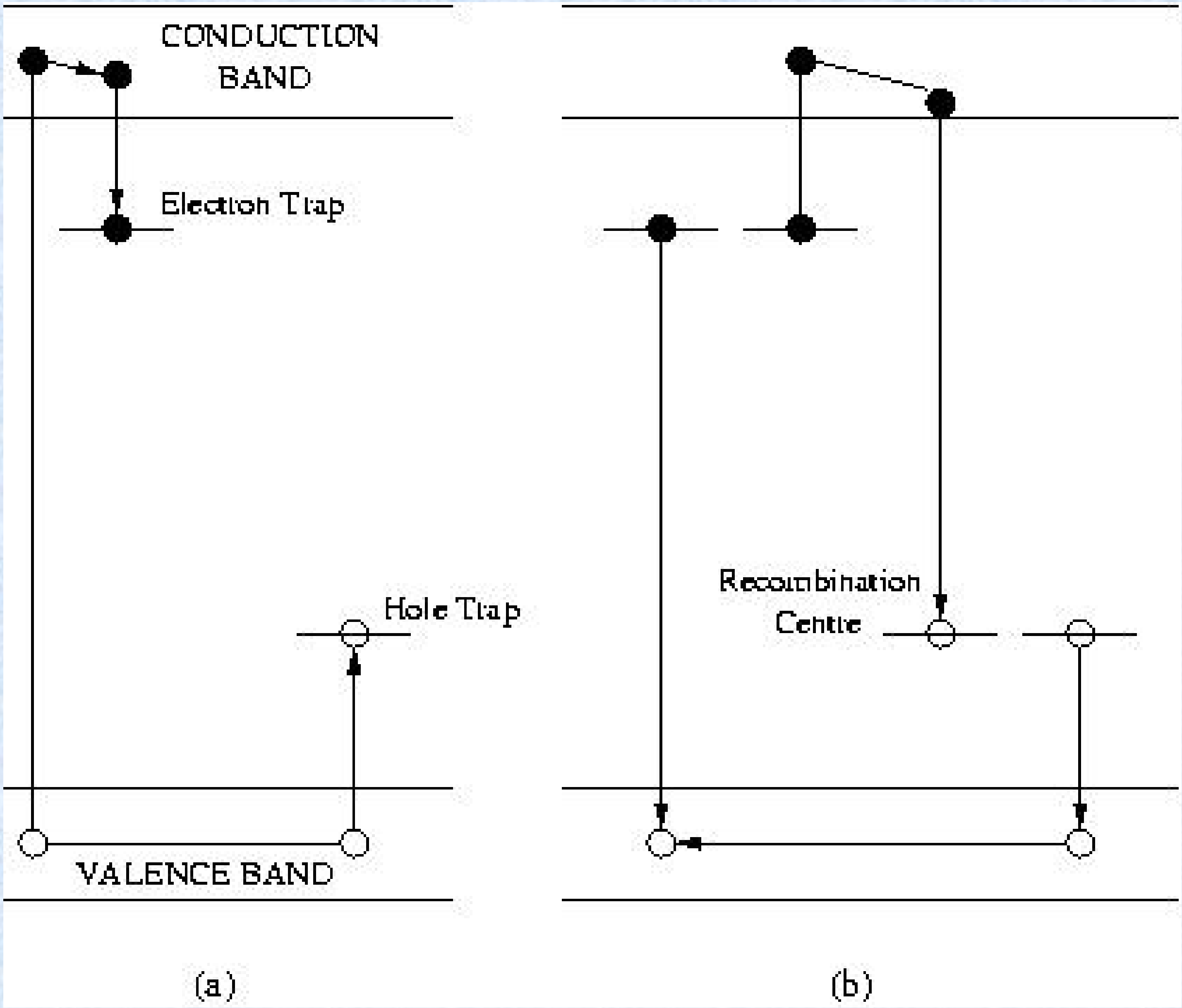
Various detectors used for the detection of High energy radiation:

- Nuclear emulsions
- Streak cameras
- Special uncoated photo-emulsions
- Semiconductor detectors
- Scintillators
- Thermoluminescent detectors (TLD)
- Optically Stimulated Luminescent (OSL) phosphors

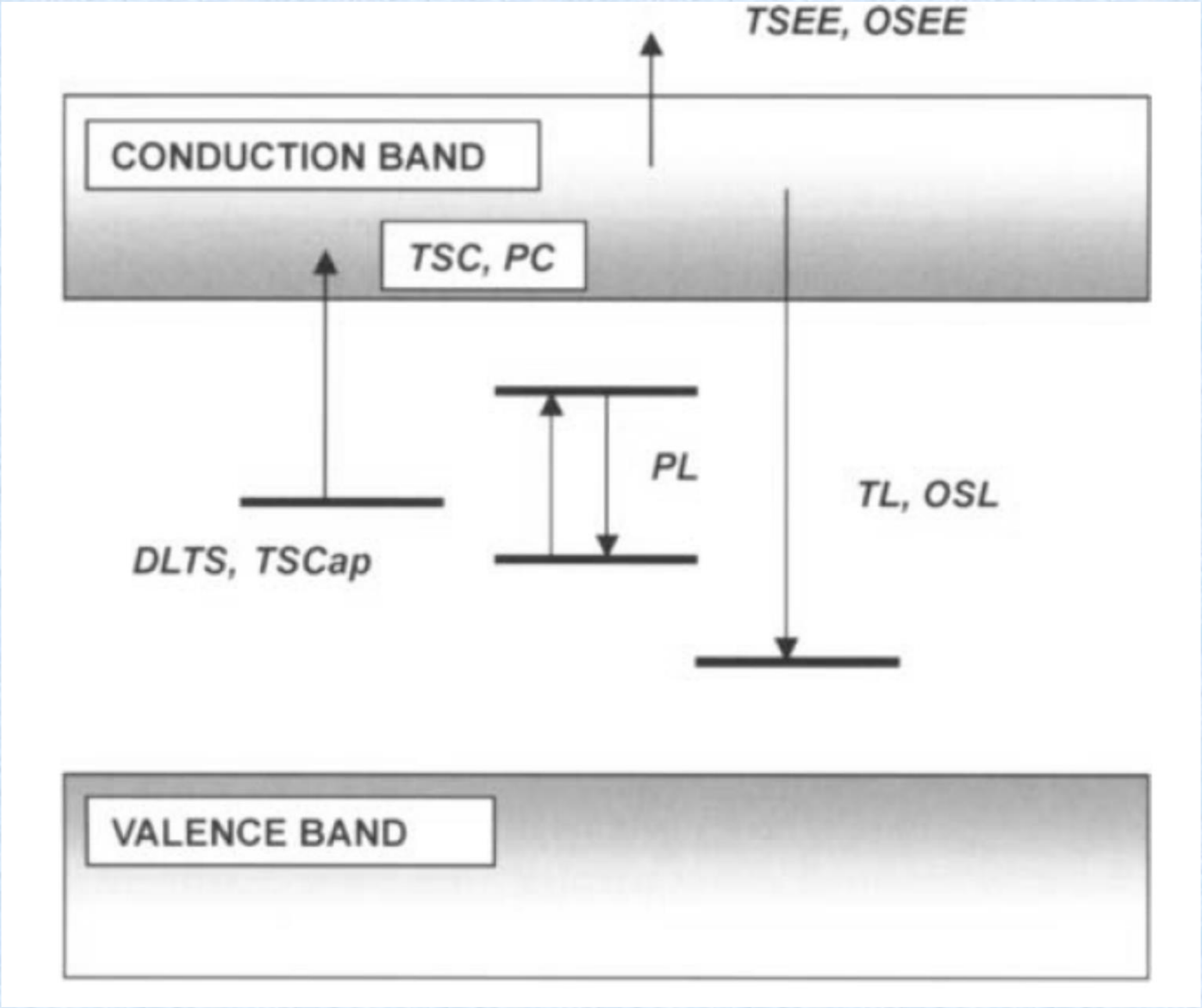
Advantages of the TLD/OSL Phosphors:

- Very small amount of the phosphor material is needed (~ few milligram - a gram)
- Could be used in any form i.e. powder, crystal, pellet, thin film, etc.
- Could be used as I-card, and ornaments as ring, necklace, bangle, etc.
- The phosphor material is usually nontoxic and easy to handle
- Instrumentation is very simple
- A large number of detectors could be coded and processed simultaneously
- Cost of the instrumentation and the detectors is low.

Use of TLDs in different forms for radiation monitoring



A Simple Model For Thermoluminescence


TSEE, OSEE
CONDUCTION BAND
TSC, PC
PL
TL, OSL
DLTS, TSCap
VALENCE BAND

Commercially available and widely used TLD Phosphors

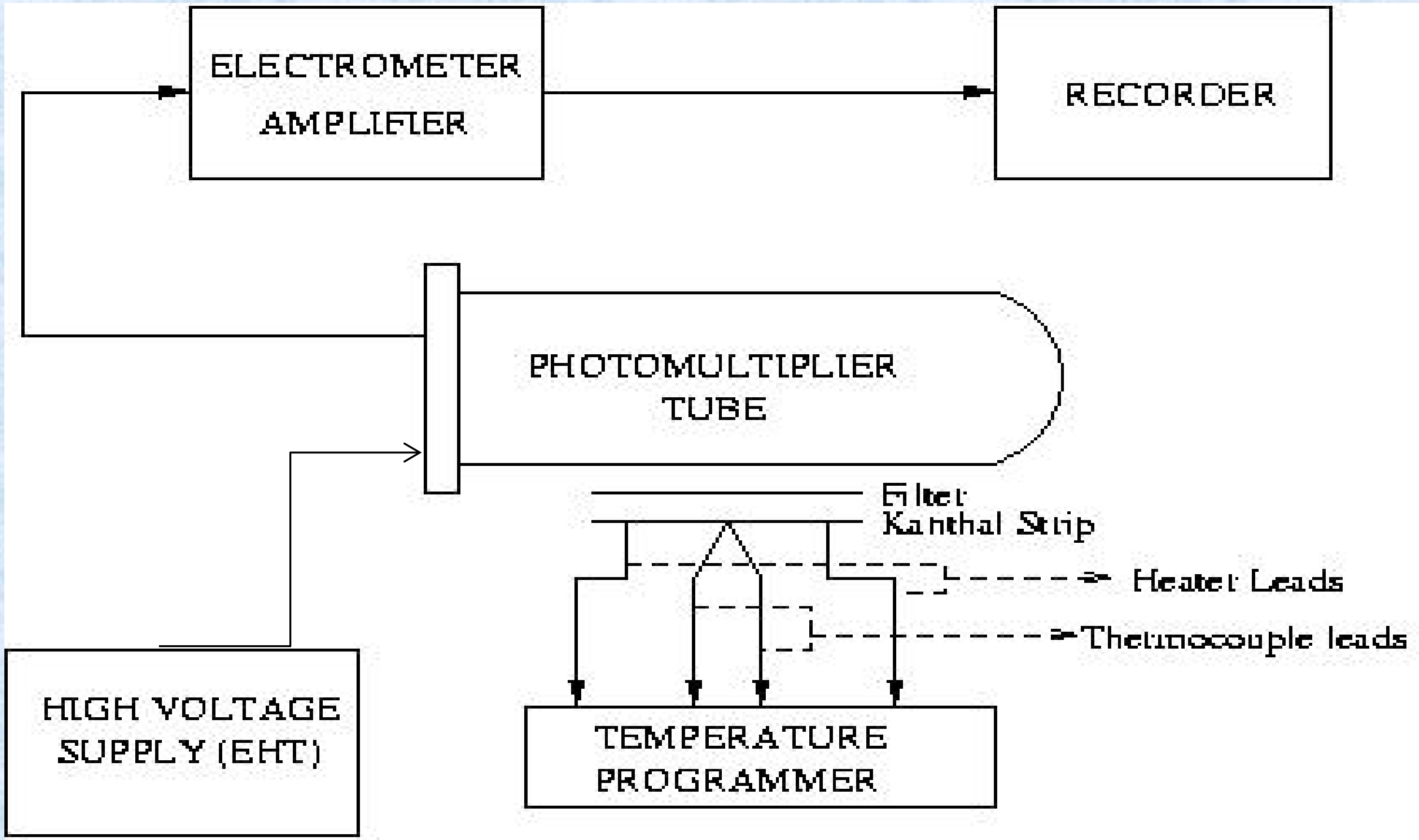
TLD Phosphor	Relative gamma ray sensitivity	TL emission spectrum (nm)	Dosimetric peak temperature (^0C)	Effective atomic number	TL fading of dosimetric peak at 25 ^0C
LiF:Mg,Ti	1	400	190	8.2	5%/month
LiF:Mg,Cu,P	30	360, 410	210	8.2	No fading in one month
$Li_2B_4O_7$:Cu	3	368	215	7.4	9%/month
$Li_2B_4O_7$:Mn	0.4	600	210	7.4	10%/month
MgB_4O_7:Dy	7	480, 570	210	8.4	<10%/month
$CaSO_4$:Tm	32	450	220	15.3	1-2%/month
$CaSO_4$:Dy	38	480, 570	220	15.3	1-2%/month
CaF_2:Mn	5	500	260	16	10%/month
CaF_2 (nat.)	23	380	260	16.3	3%/month
CaF_2:Dy	16	480, 570	200, 240	16	10%/year
Mg_2SiO_4:Tb	53	380, 552	195	11	3%/month
Al_2O_3:Si,Ti	5	420	250	10.2	5%/two weeks

New TLD Phosphors developed in our Laboratory:

TLD Phosphor	Relative γ ray sensitivity	TL emission spectrum (nm)	Dosimetric peak temp. (^{0}C)	Effective atomic number	TL fading of dosimetric peak
LiF:Mg,Ti (Com.)	1	400	190	8.2	5%/minth
LiF:Mg,Cu,P (Com.)	30	360,410	210	8.2	6%/month
$CaSO_4$:Dy (Ind. Dev.)	100	480,570	220	15.3	1-2%/month
$K_2Ca_2(SO_4)_3$	30	---	445	15.2	No appreciable
$K_2Ca_2(SO_4)_3$:Eu	500	420	145	15.2	<7%/month
$K_2Ca_2(SO_4)_3$:Eu,Ce	900	390	200	15.2	<6%/month
$K_2Mg_2(SO_4)_3$: P,Dy	300	480, 570	220	15.3	5%/month
K_3NaSO_4: Eu	600	420	220	15.2	6%/month
$NaKSO_4$: Eu	300	420	140	16	10%/month
$Mg_2B_4O_7$: Dy	230	480, 570	120	8.7	3%/month
$LiNaSO_4$: Eu	130	480, 570	145	16	10%/month
$Li_{0.7}Na_{1.3}SO_4$: Eu	300	425	145	11	10%/month
$BaSO_4$: Eu	300	420	250	10.2	5%/month
$Ca_{0.5}Ba_{0.5}SO_4$: Eu	500	410	210	17	5%/month

Some characteristics of a ideal TLD phosphor

1. It should be easily available and cost effective, so that it could be used by masses. It should be reusable as it makes cost effective
2. It should not be toxic as it is to be used by common people
3. Easy synthesis as it would make it cost effective
4. Highly sensitive to radiation as it would decide the minimum measurable dose limit
5. It should have wide dose response
6. The emission should lie in green region of visible spectra as most of the common photodetectors are more sensitive here
7. Simple glow curve structure and should not change with dose
8. The dosimetry peak should appear around 250 ^{0}C as at lower temperatures there is more fading but at higher temperature black body radiation makes it difficult to estimate low dose
9. Low fading as fading introduces inaccuracies in dose estimations
10. It should be preferably low-Z material to be used in mixed field



1 Figure 2.3: Block diagram of thermoluminescence glow curve reader.

Some drawbacks of the commercially available phosphors:

1. $CaSO_4$:Dy (TLD 900) is not a low-Z (tissue equivalent phosphor)

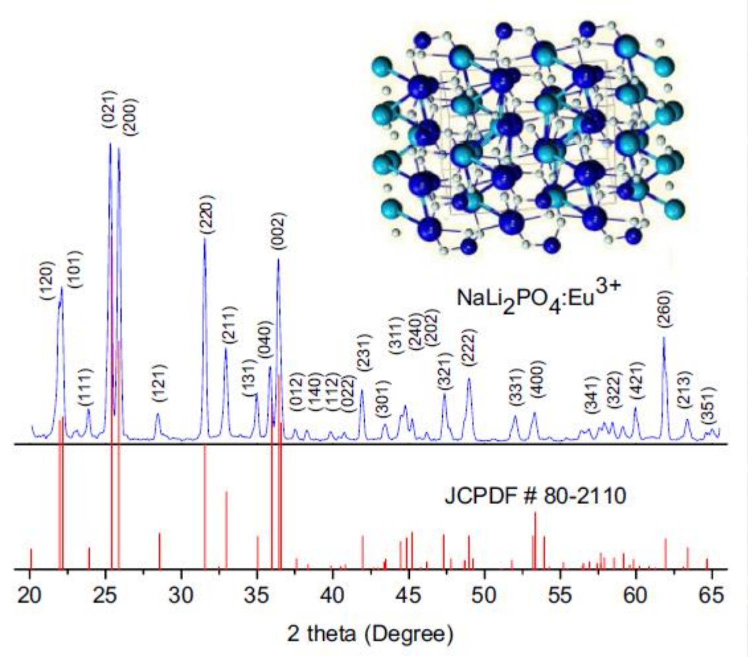
2. LiF: Mg,Ti (TLD-100) is a low-Z but not very sensitive. It also has very complicated glow curve structure.

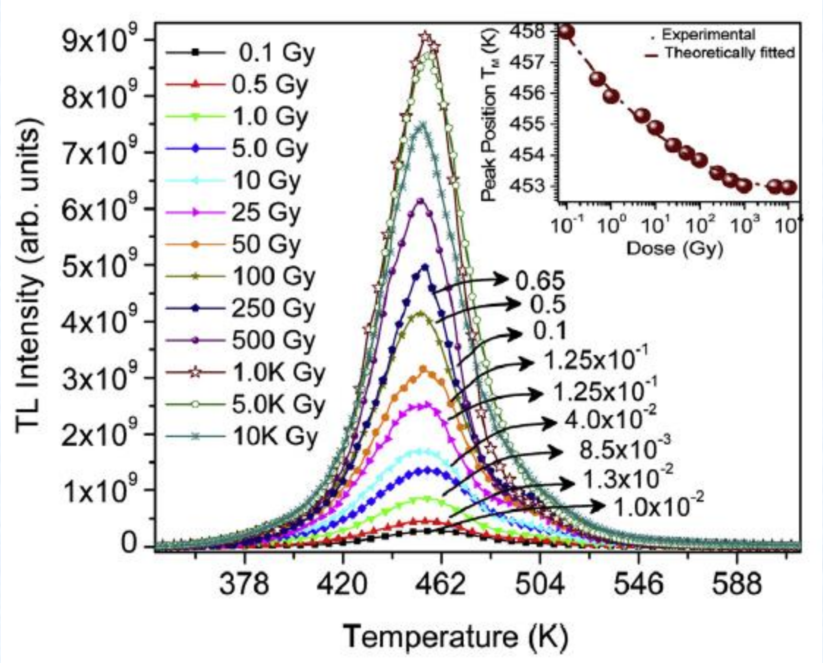
3. LiF:Mg,Cu,P (TLD-700H) is highly sensitive but need very precise heating during readouts as its sensitivity is affected greatly if it is heated 250 ^{0}C and cannot be reused

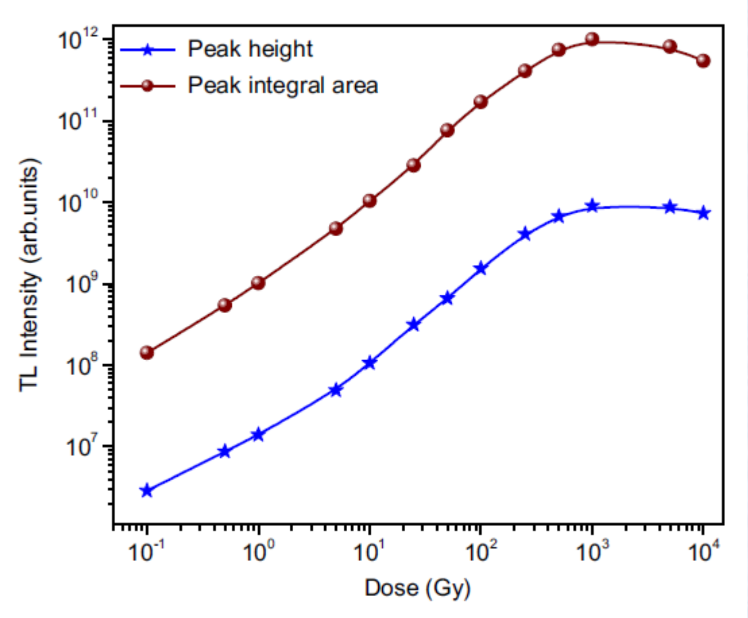
4. LiB_4O_7:Mn is also a tissue equivalent but not very sensitive as the TL emission lies in red region (600 nm)

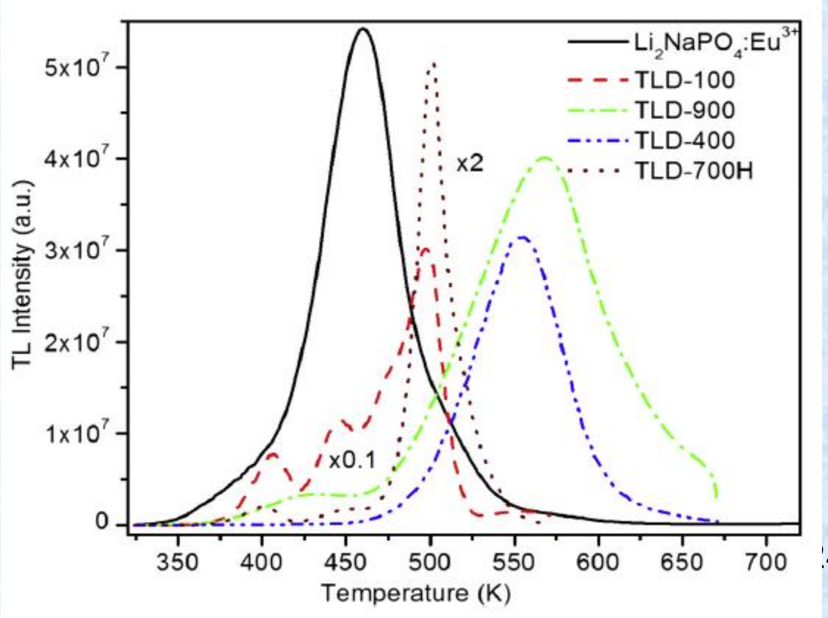
5. BeO:A (A = Li, Na, K) is highly sensitive, other good characteristics but it is toxic.

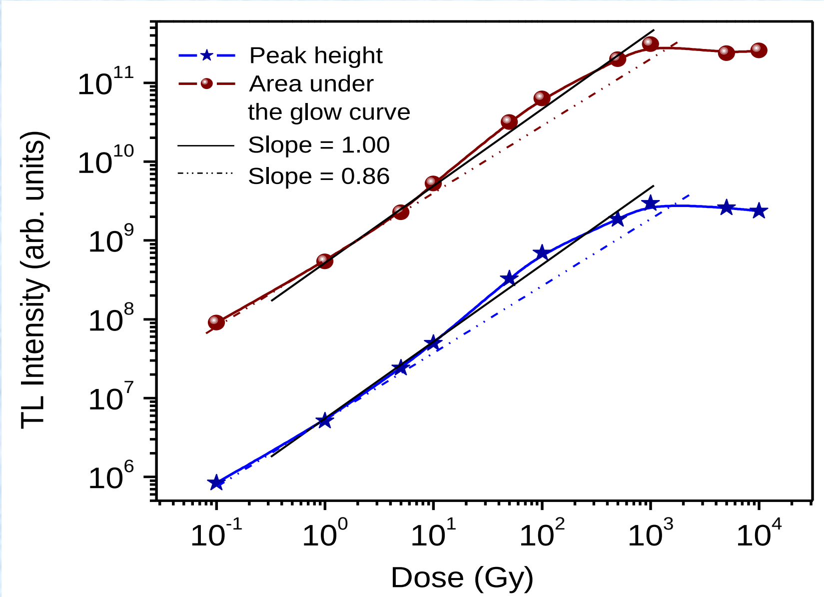
Dosimetric characteristics of a new $NaLi_2PO_4$:Eu TLD phosphor

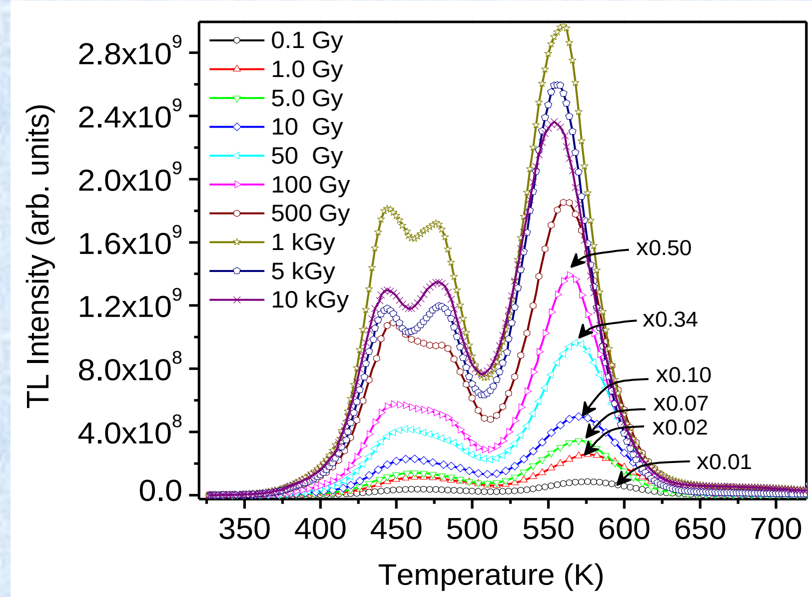


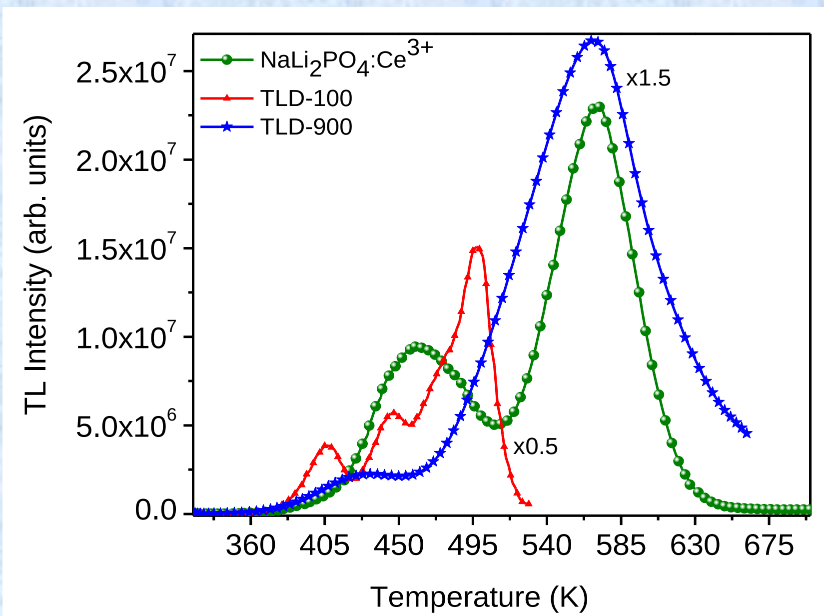


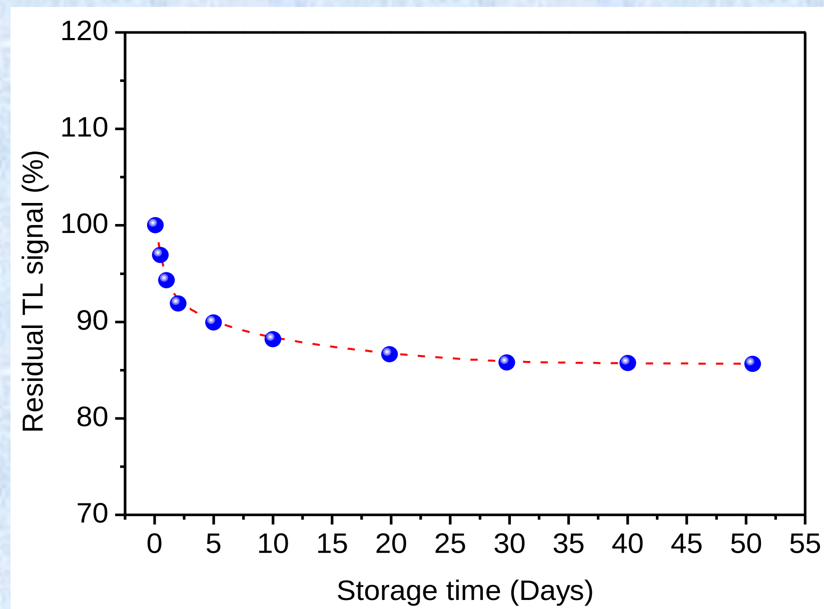












Dosimetric characteristics of a new $NaLi_2PO_4$:Ce TLD phosphor

Why Nanophosphors?

The importance of nanoparticles in the field of luminescence :

- They exhibit enhanced optical, electronic and structural properties.
- Efficient phosphors in display applications.
- Luminescent materials for biological labeling.
- Good TLD materials having many improved characteristics. Their responses to gamma radiation and ion beams have been studied and found suitable for the Dosimetry purpose.

In radiation dosimetry, very sensitive TLD Materials are:

1- $CaSO_4$:Dy .

2- LiF:Mg,Cu,P.

- Their sensitivity saturate at high exposures .

- On the contrary nanocrystalline powder of such materials, have been found to have a very wide range of TL linearity.

Dose Range of various phosphors

Chemical composition	Radiation	Maximum dose (fluence)		Ref.
		Nanophosphor	Traditional phosphor	
LiF:Mg,Cu,P	γ-Cs^{137}	20 kGy	10 Gy	Salah et al. (2007)
$BaSO_4$:Eu	48 MeV U^{3+} 75MeVC^{6+} 90MeVO^{7+}	10^{12} ions/cm^2	10^{10} ions/cm^2	Salah et al. (2008)
$BaSO_4$:Eu	γ-Co^{60}	7 kGy	10 Gy	Salah et al. (2009)
MgB_4O_7:Dy	γ-Co^{60}	5 kGy	10 Gy	Lochab et al. (2007)
ZnS:Cu	β-Sr^{90}	2 kGy	no data	Yazice et al. (2007)
α-Al_2O_3	β-Sr^{90}	30 kGy	10 Gy	Kortov et al. (2008a,b)
$K_3Na(SO_4)_2$	γ-Co^{60}	10^5 Gy	no data	Sahare et al. (2007)
$Ba_{0,97}Ca_{0,03}SO_4$:Eu	48 MeV U^{3+} 75MeVC^{6+} 90MeVO^{7+}	10^{12} ions/cm^2	no data	Lochab et al. (2008)
YAG	β-Sr^{90}	450 Gy	70 Gy	Rodriguez et al. (2005)

Data taken from V. Kortov, Radiat. Measur. 45 (2010) 512.

Extended Dose Range

- One could see very wide and extended dose ranges in case of TLD nanophosphors
- Kortov and Ustyantsev (Radiat. Measur., 2013) explained the higher radiation resistance of nanophosphors (which is also the reason for extended dose response) is due to efficient sinking and annihilation of defects at nanograin boundaries; as a result, accumulation of defects in nanomaterial is retarded.
- The existence of deeper traps also plays the role in extending the dose range.

- Brief Review of the Work Done in our Laboratory:

The nanophosphors developed in our laoratory

i. $K_2Ca_2(SO_4)_3$:Eu

ii. $K_2Ca_2(SO_4)_3$:Tb

iii. $LiNaSO_4$:Eu

iv. $CaSO_4$:Dy

v. LiF:Mg,Cu,P

vi. K_3NaSO_4:Eu

vii. $Ba_{0.97}Ca_{0.03}SO_4$: Eu.

✓ TL and PL studies were conducted on these phosphors.

✓ TL glow curves, particle sizes, morphology, Their TL response to gamma-rays irradiation, efficiencies, fading, reusability, etc. were studied. All the data is published.

Set-up for preparing samples by Co-precipitation method

$CaSO_4$:Dy Nanoparticles

[Numan Salah, P.D. Sahare, S.P. Lochab, Pratik Kumar (2005)]

Prepared by:

Precipitation method

$$(CH_3COO)_2Ca + (NH_4)_2SO_4 + Dy_2(SO_4)_3\,(0.1\,mole\,\%)$$

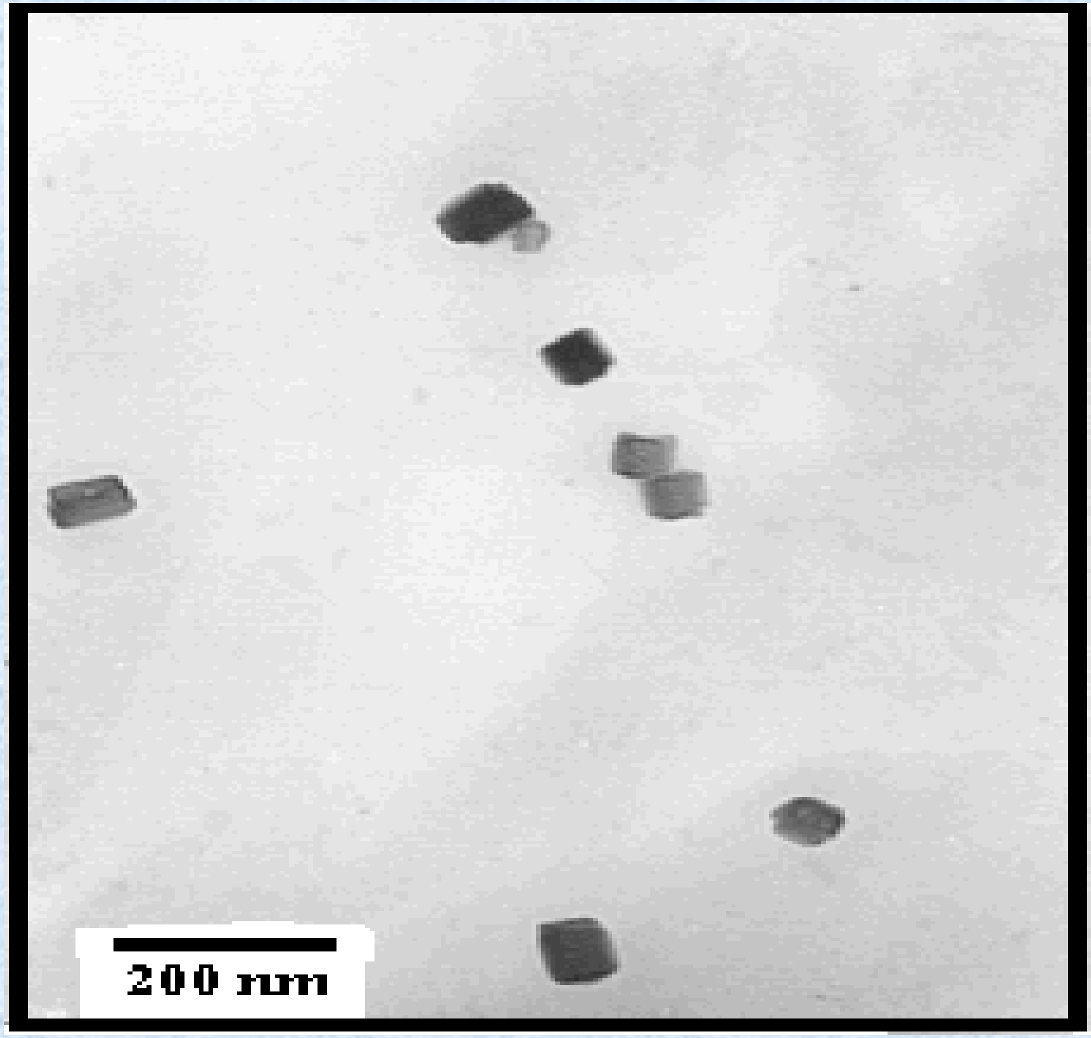
$$\xrightarrow{\mathrm{EtOH + H_2O}} CaSO_4 : Dy \downarrow + 2CH_3COONH_4$$

Studied for its :

XRD, TEM, TL, PL, GCCD.

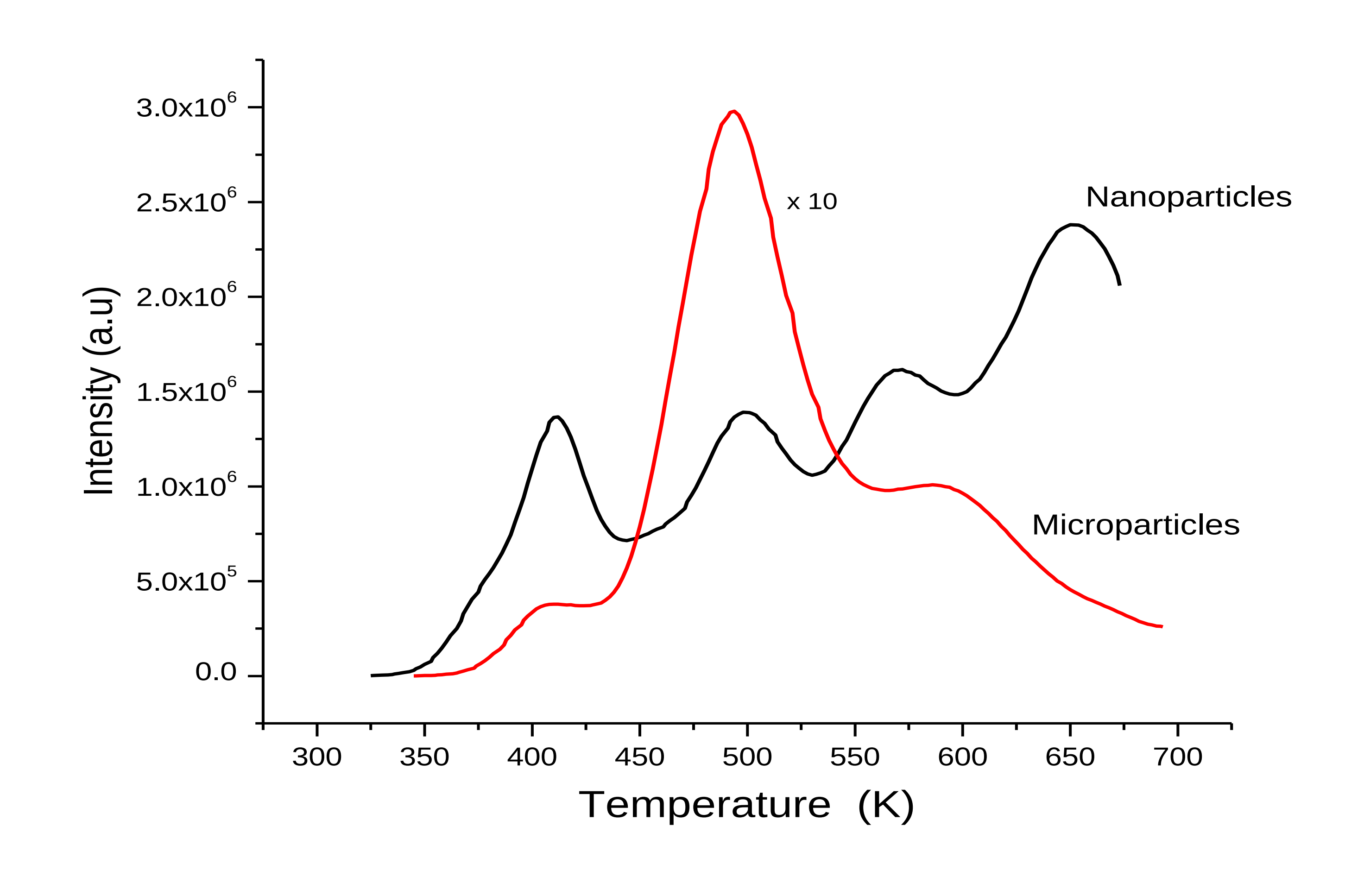
$CaSO_4$:Dy Nanoparticles

TEM photograph

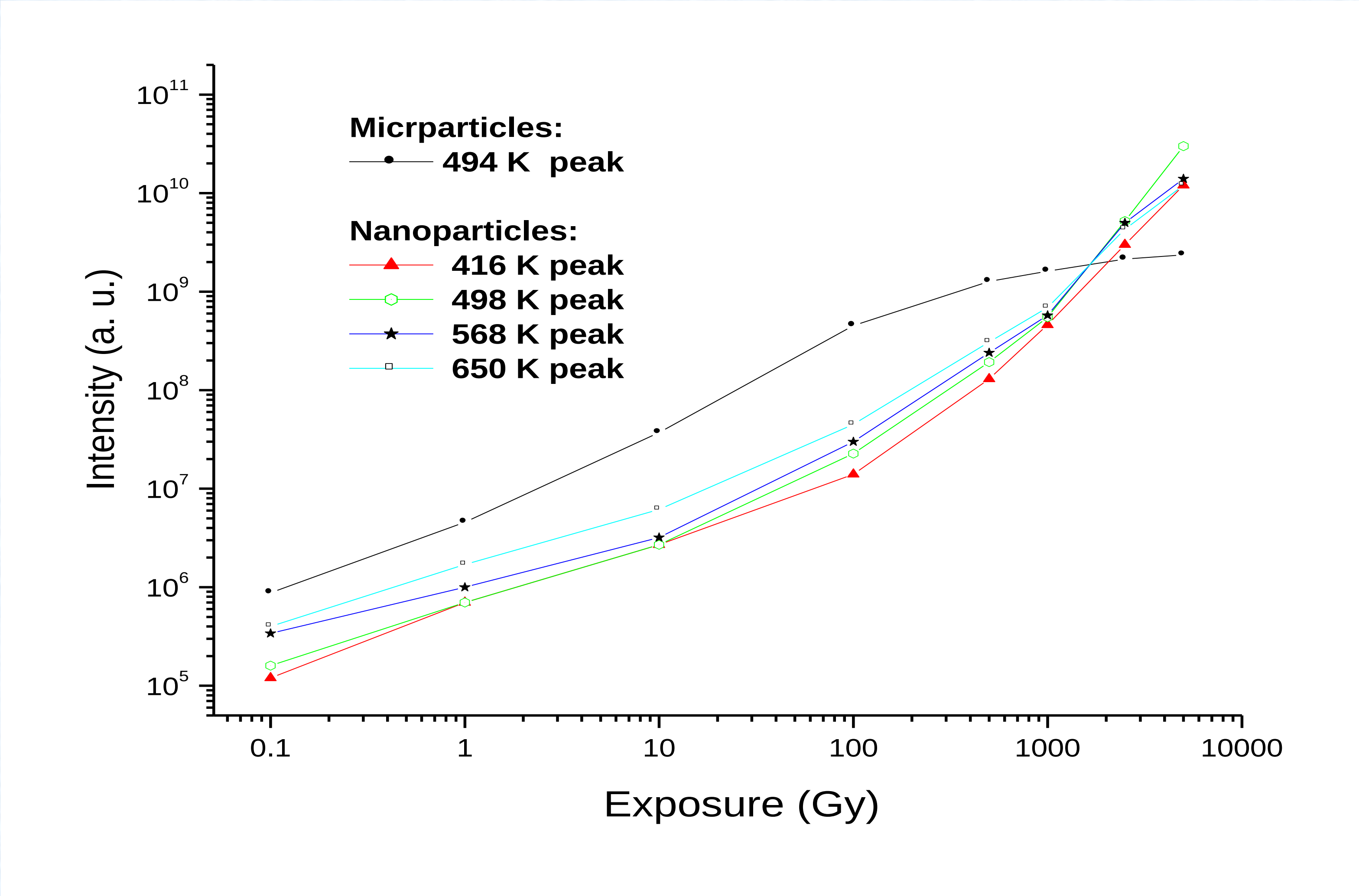


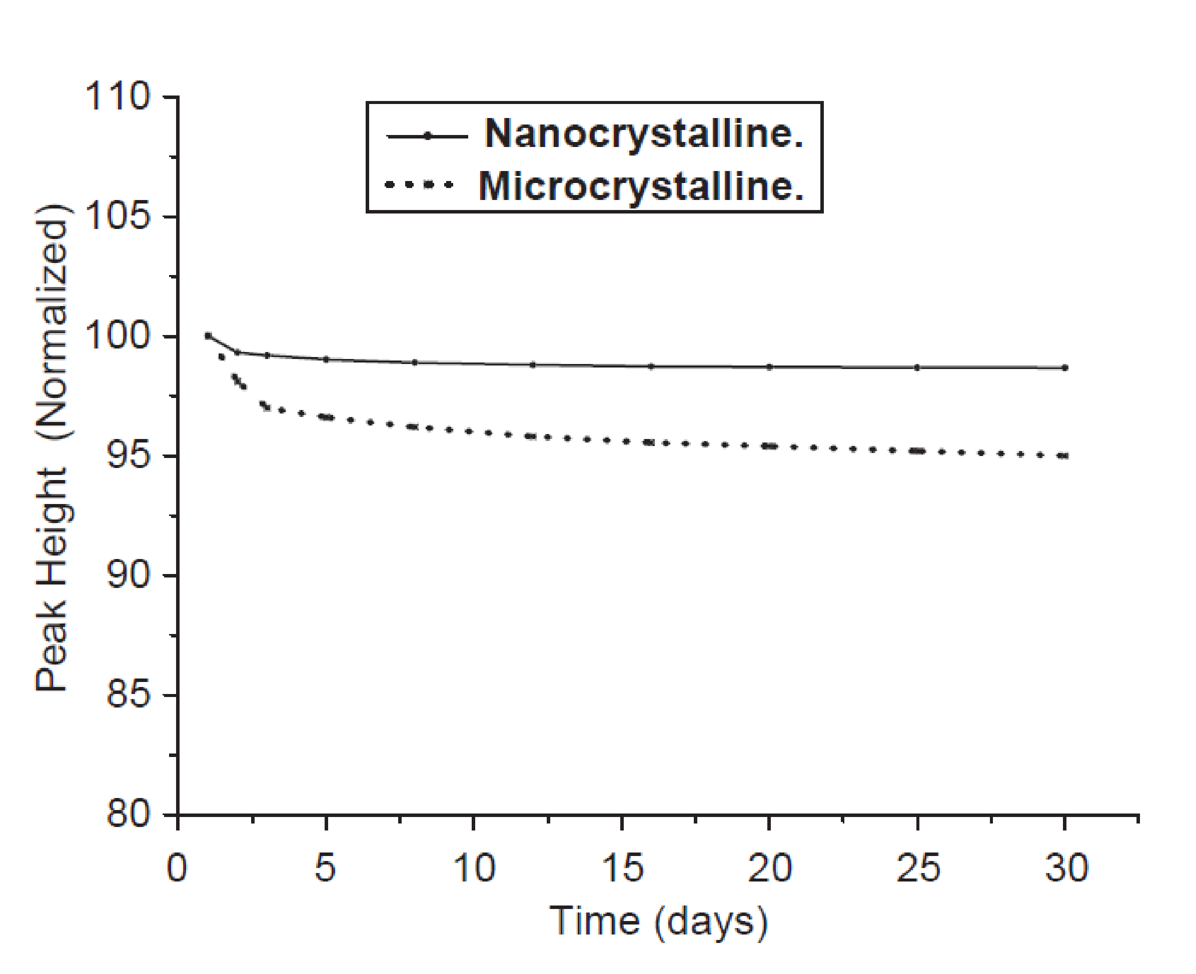
TL of $CaSO_4$:Dy micro- and nanocrystalline phosphor

(exposed to 10 Gy of γ-rays from Co^{60}).



TL response of CaSO4:Dy micro-and nanoparticles to γ - rays of Co60





Nanocrystalline.
Microcrystalline.
Peak Height (Normalized)
110
105
100
95
90
85
80
0
5
10
15
20
25
30
Time (days)

LiF:Mg,Cu,P nanocrystalline phosphor

[Numan Salaha, P.D. Saharea, and A A Rupasove (2006, in Press)].

Prepared by:

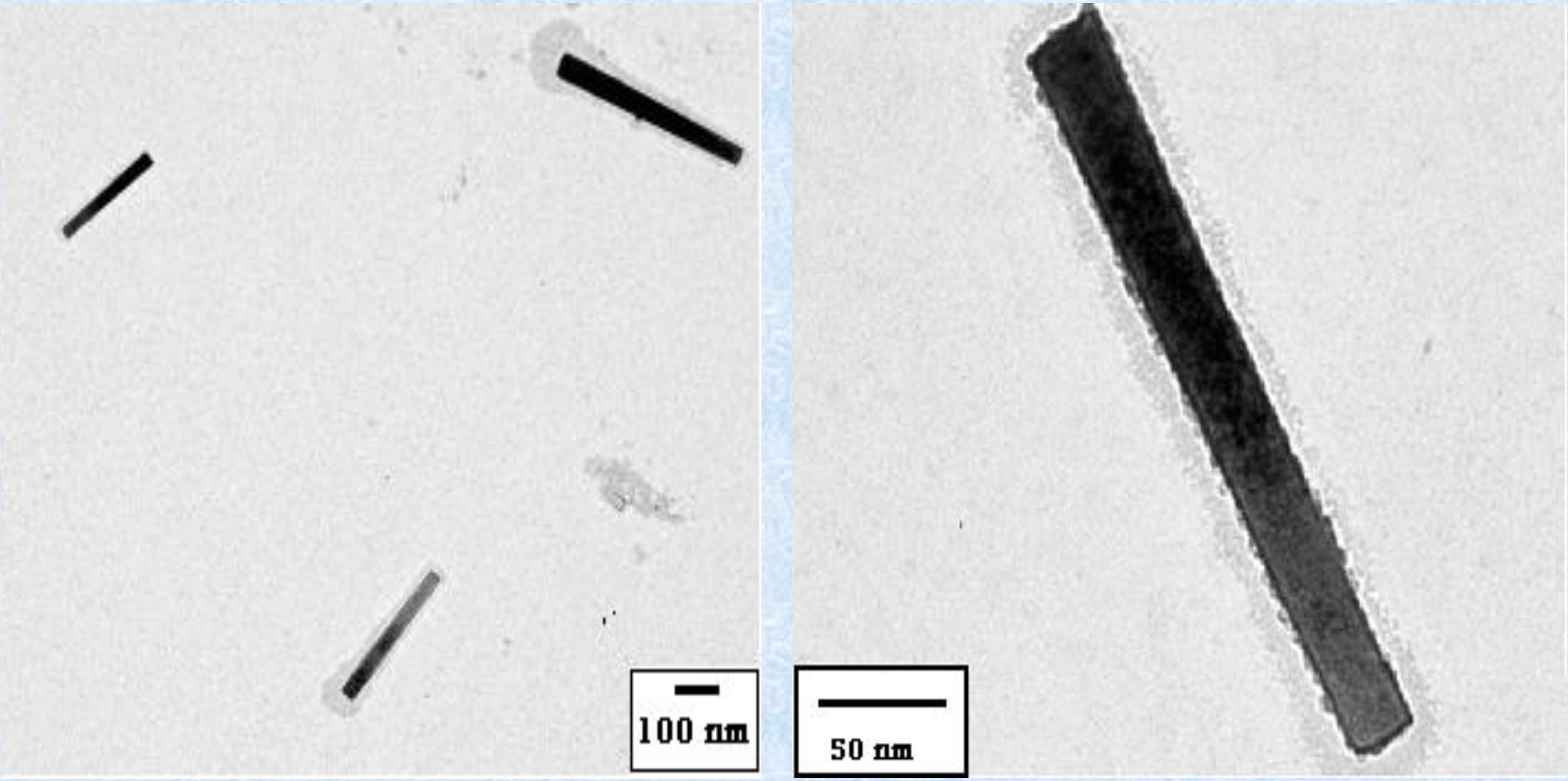
Precipitation method

Studied for its:

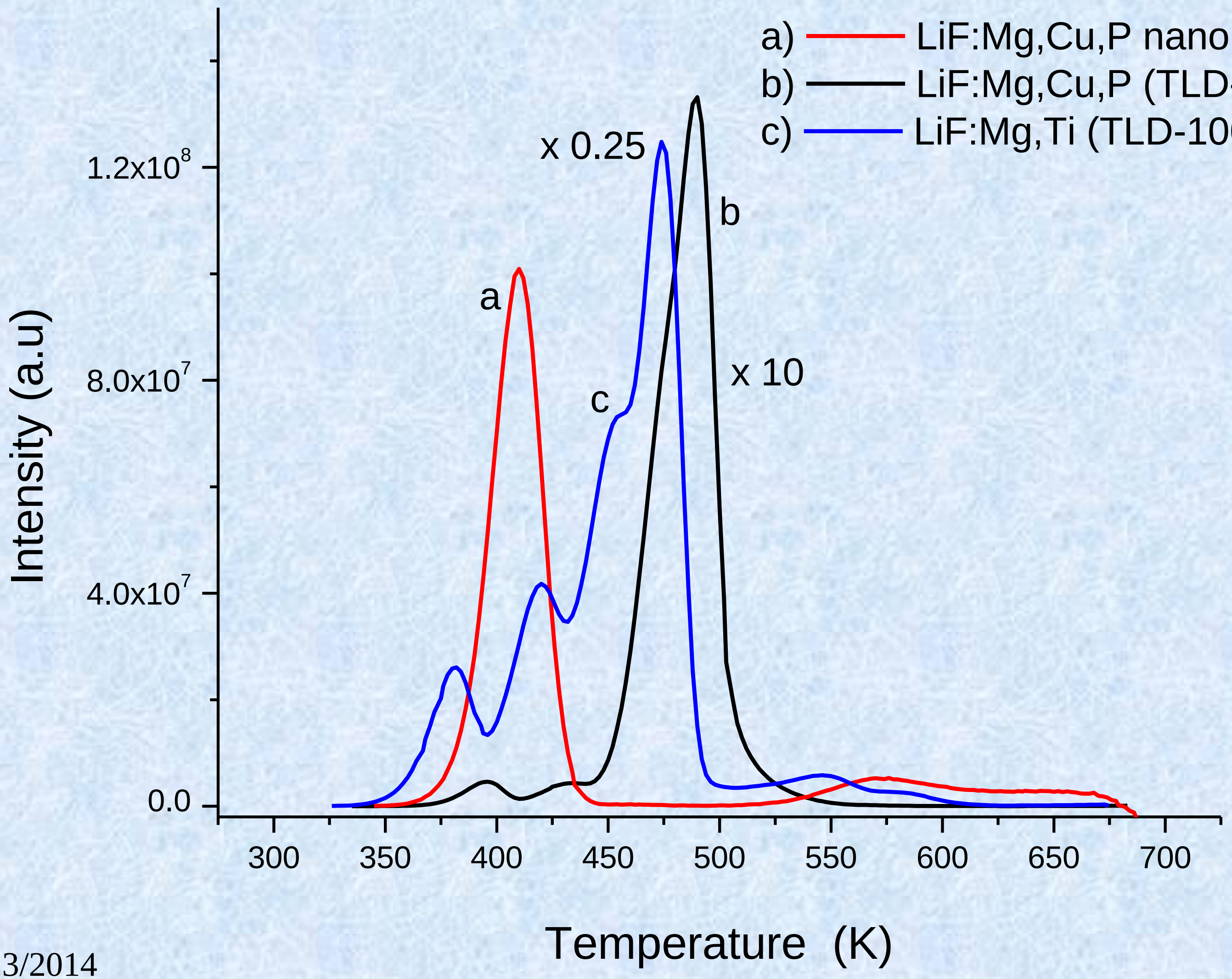
XRD, TEM, TL, PL, GCCD, etc.

LiF:Mg,Cu,P nanocrystalline.

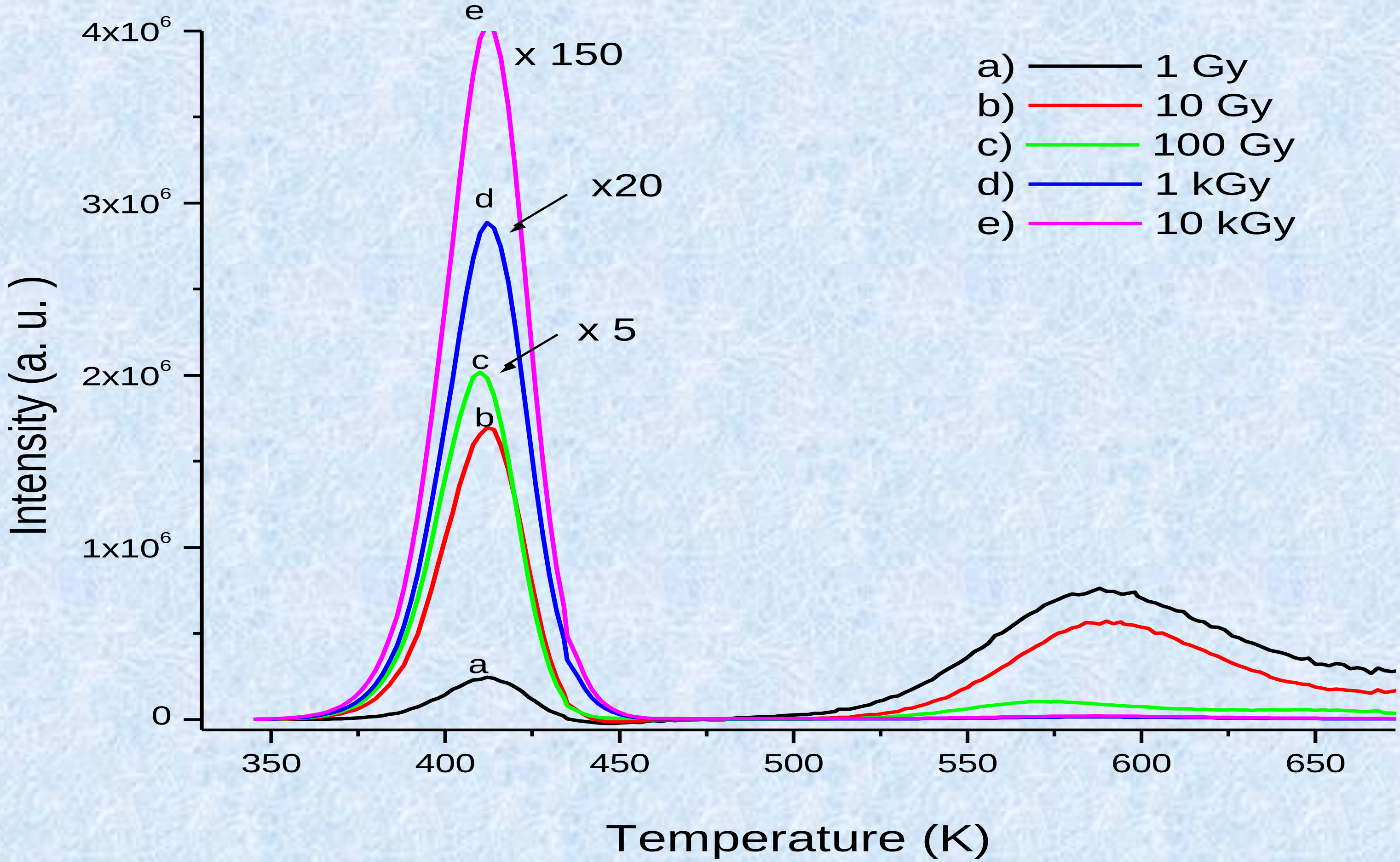
TEM images



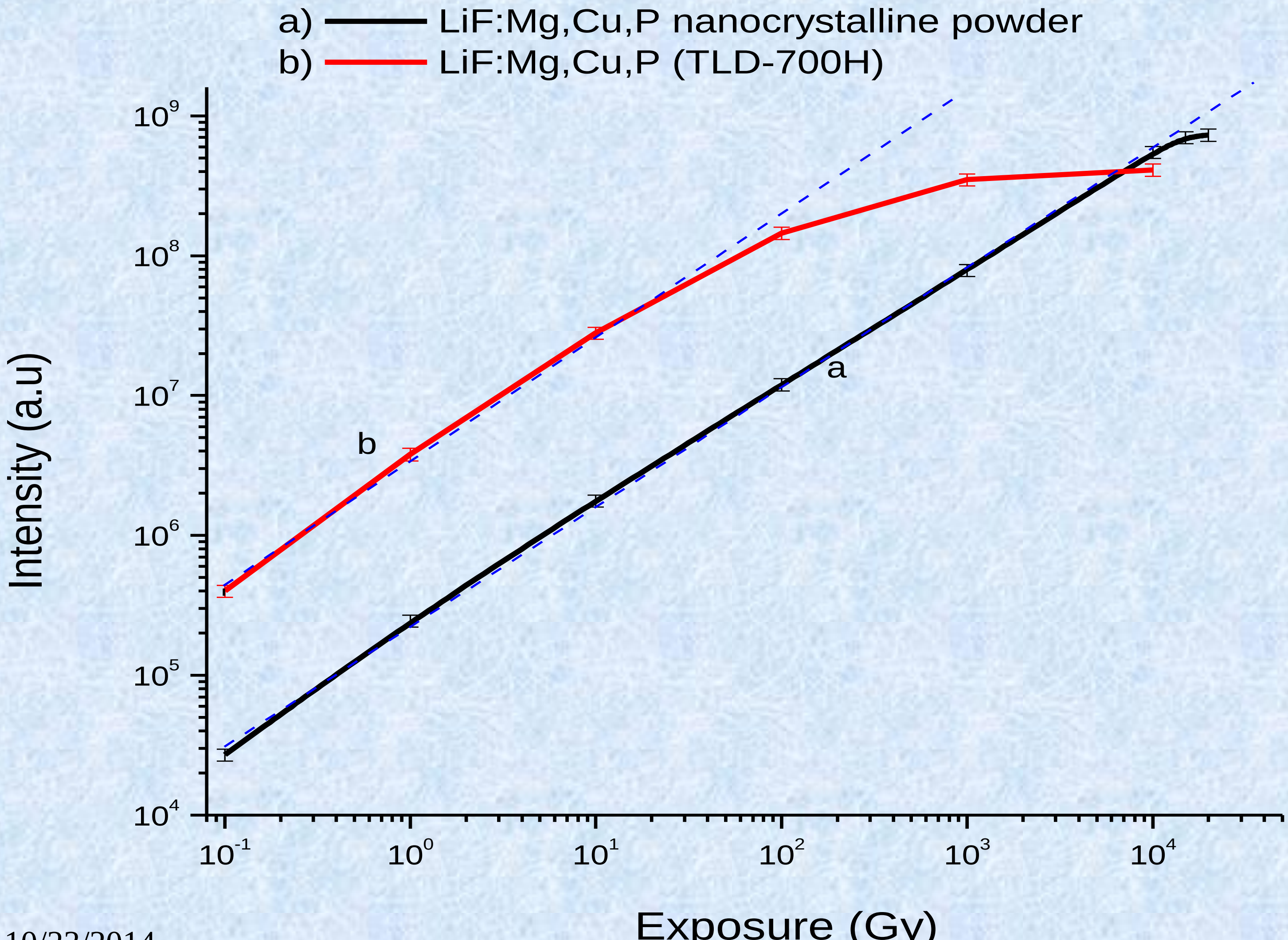
TL glow curve of LiF:Mg,Cu,P TL nanocrystalline powder



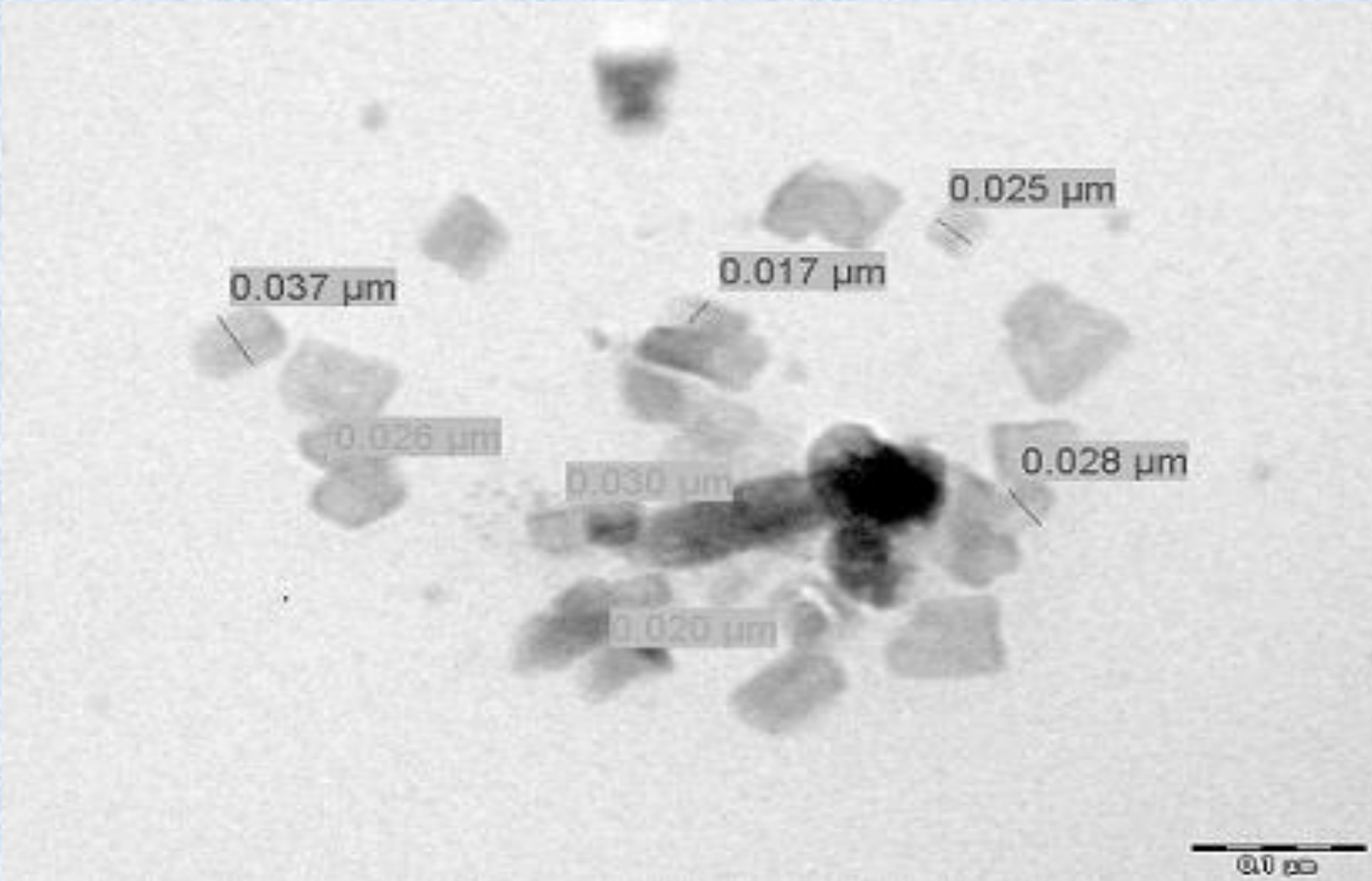
TL glow curves of LiF:Mg,Cu,P nanocrystalline exposed to various doses of γ –rays.



TL response curve of LiF:Mg,Cu,P nanocrystalline to γ -rays of ^{137}Cs.

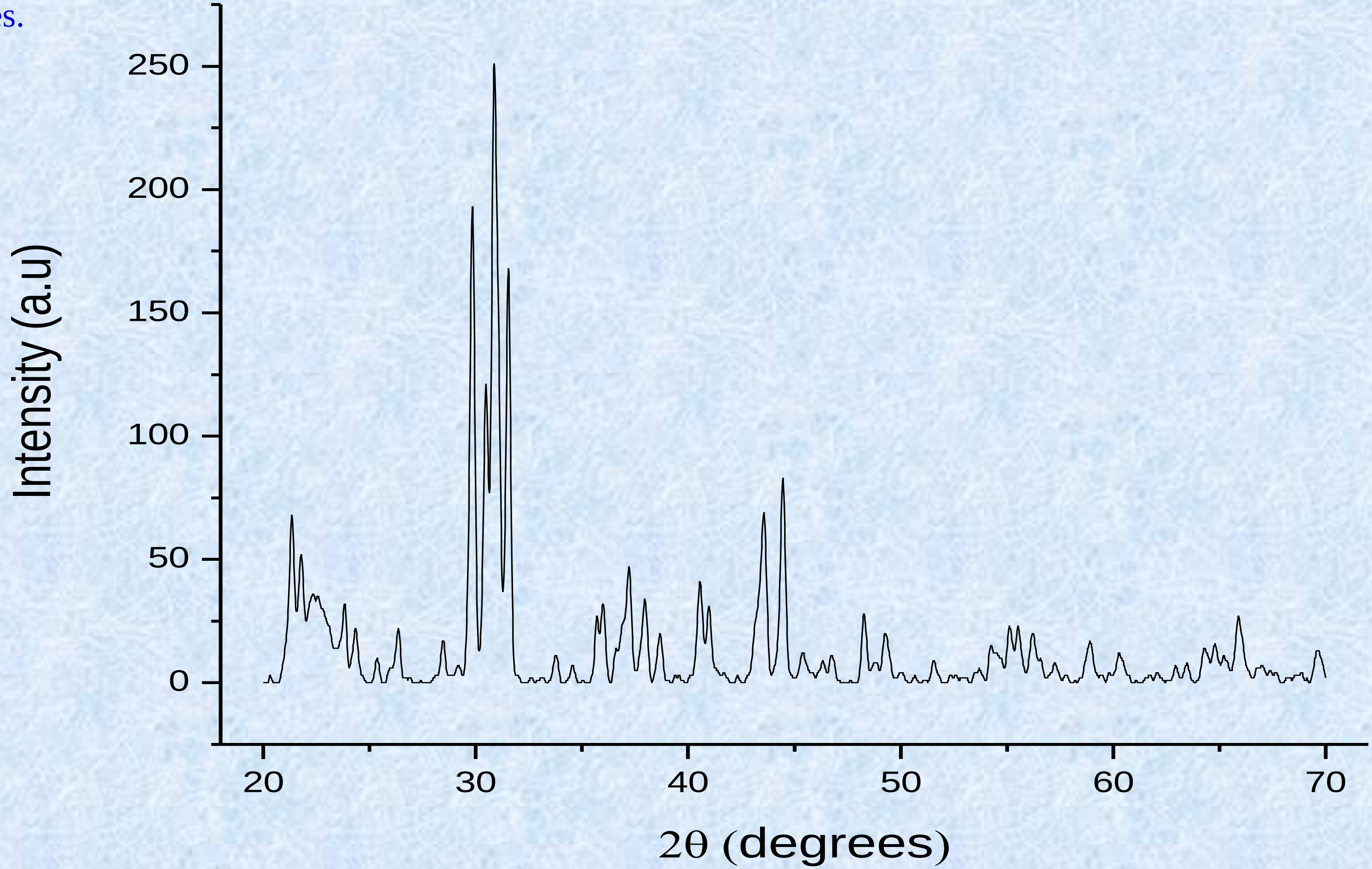


$K_3Na(SO_4)_2$:Eu nanoparticles.



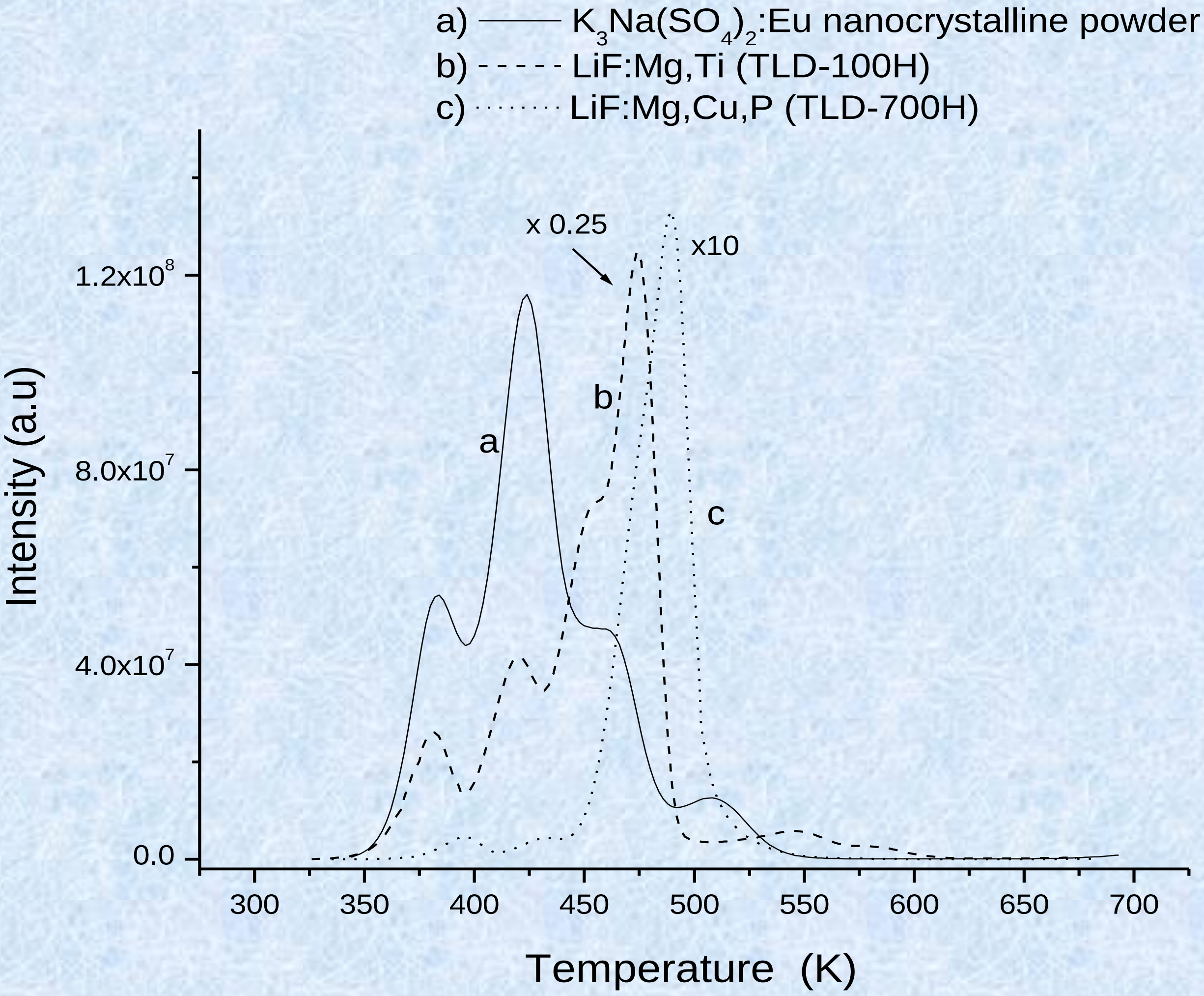
TEM images of K3Na(SO4)2:Eu nanoparticles.

$K_3Na(SO_4)_2$:Eu nanoparticles.



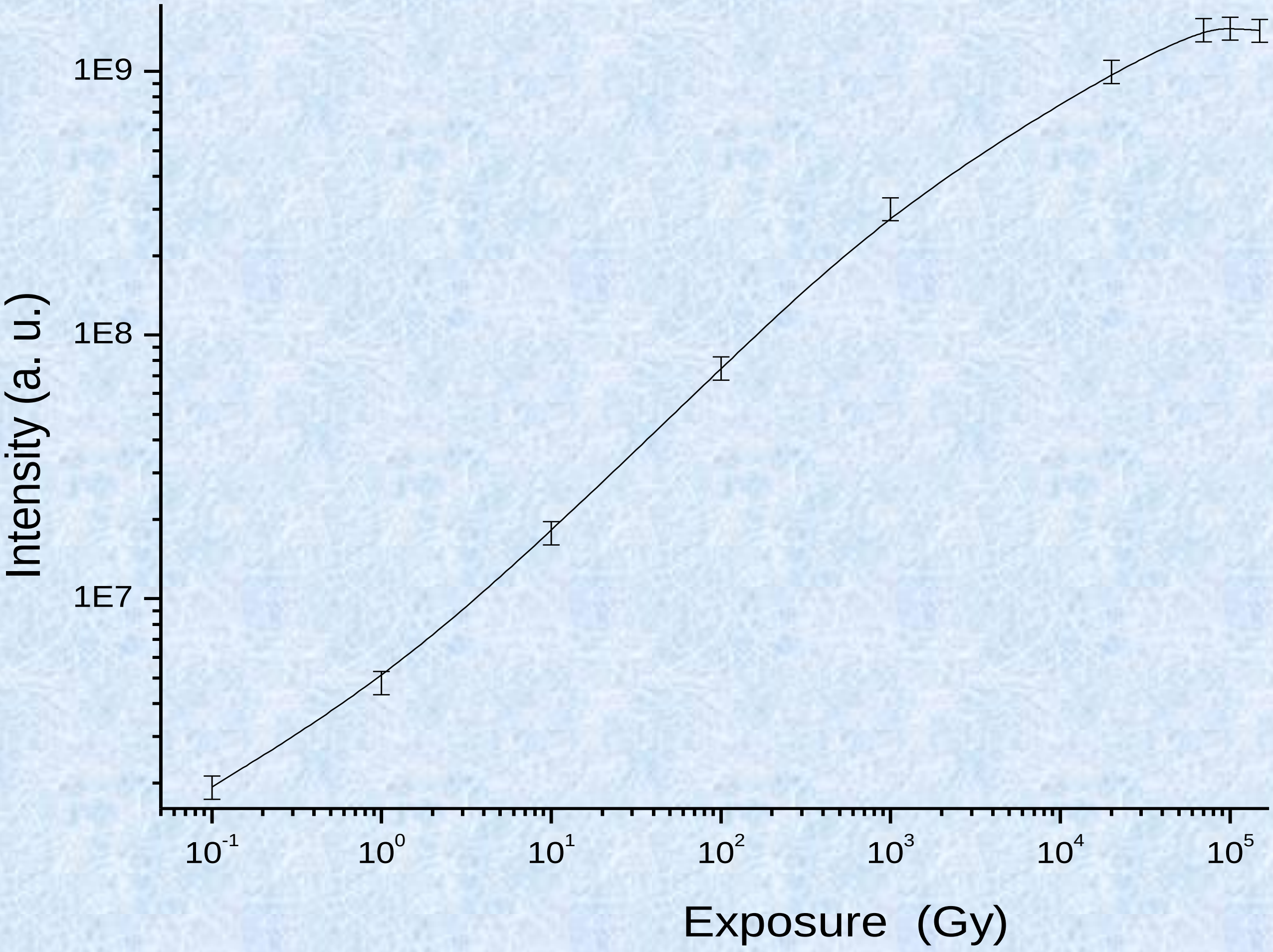
X-Ray diffraction pattern of K3Na(SO4)2:Eu nanocrystalline powder.

$K_3Na(SO_4)_2$:Eu nanoparticles.



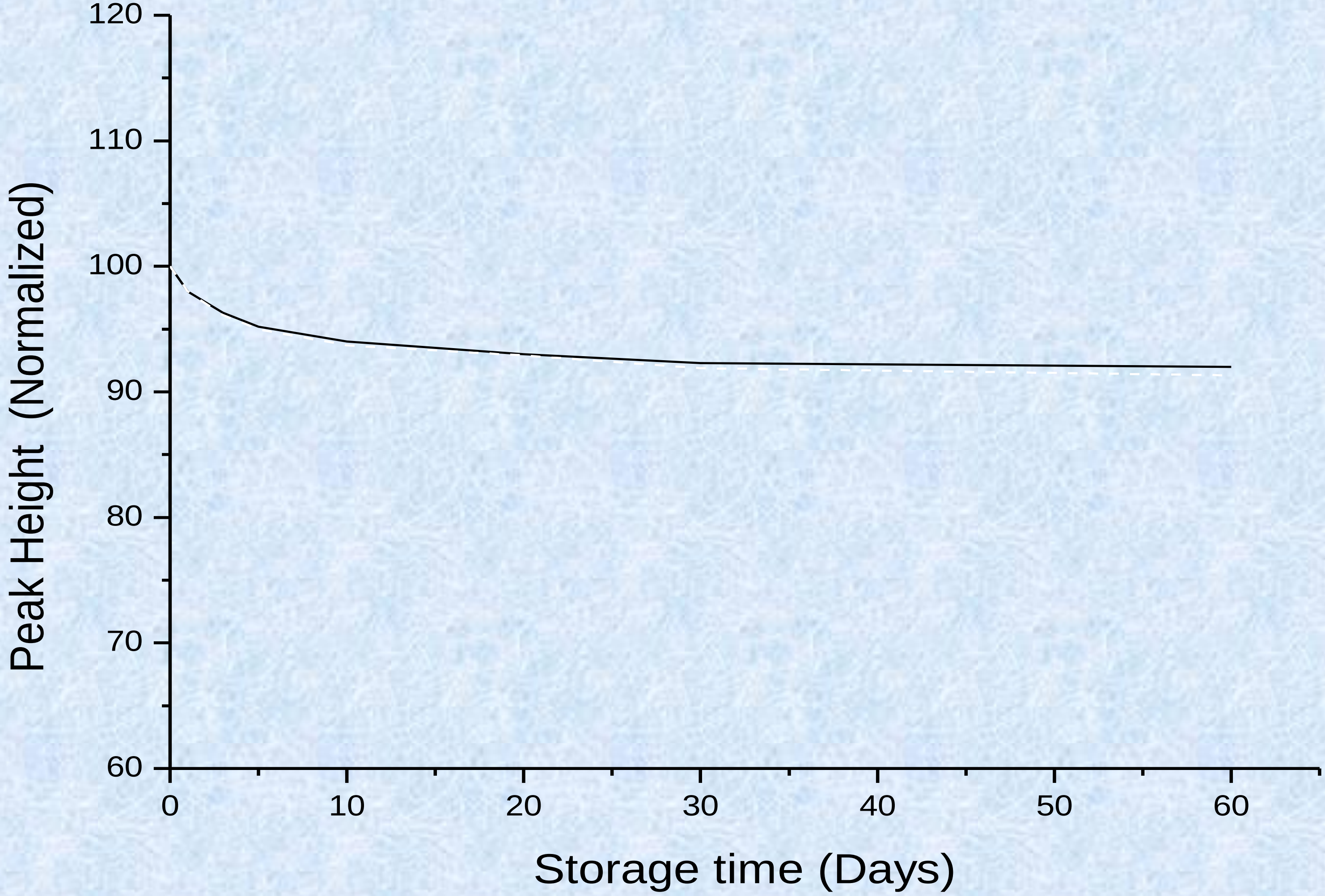
Typical TL glow curve of K3Na(SO4)2:Eu nanocrystalline powder exposed to100 Gy of γ-rays from a 60Co source. TL glow curves of LiF:Mg,Cu,P (TLD-700H) and LiF:Mg,Ti (TLD-100) phosphors are also shown for comparison.

$K_3Na(SO_4)_2$:Eu nanoparticles.



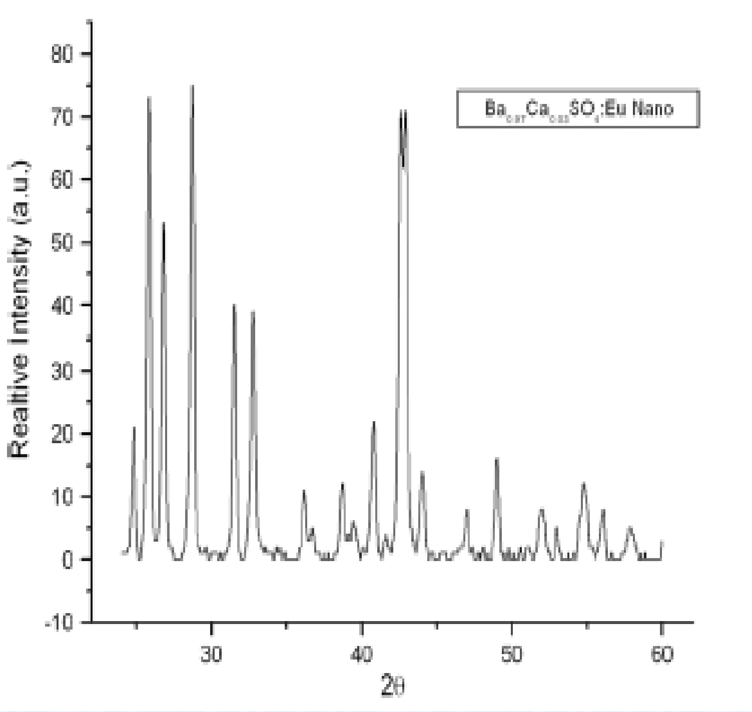
TL response curve of K3Na(SO4)2:Eu nanocrystalline powder to γ -rays of 60Co.

$K_3Na(SO_4)_2$:Eu nanoparticles.



Fading in K3Na(SO4)2:Eu nanocrystalline powder.

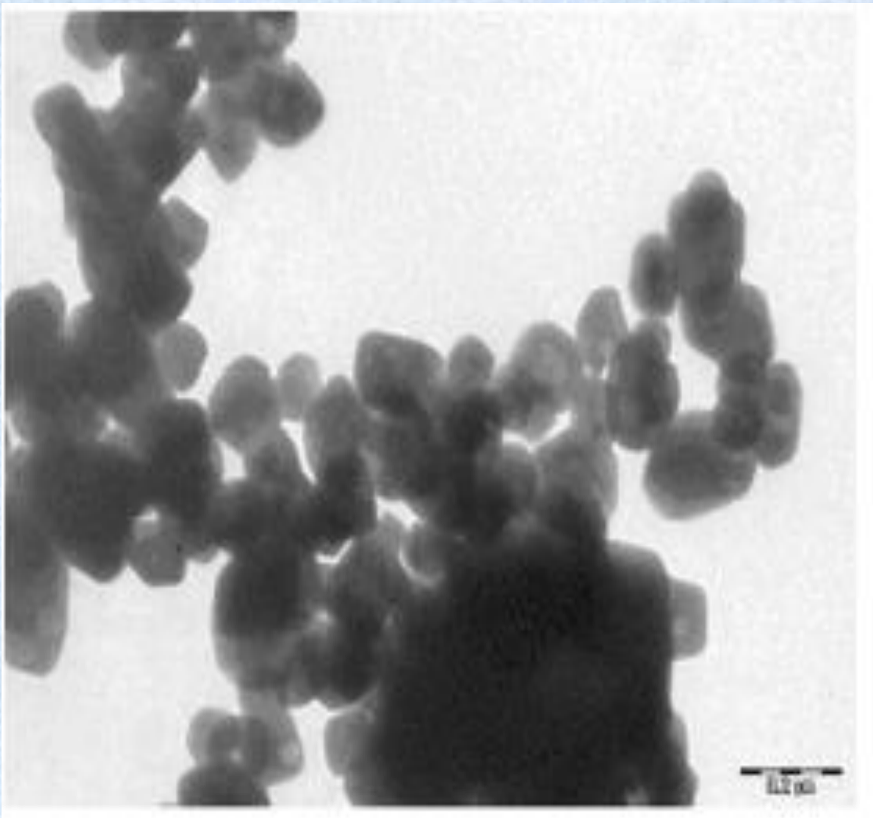
Nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$: Eu



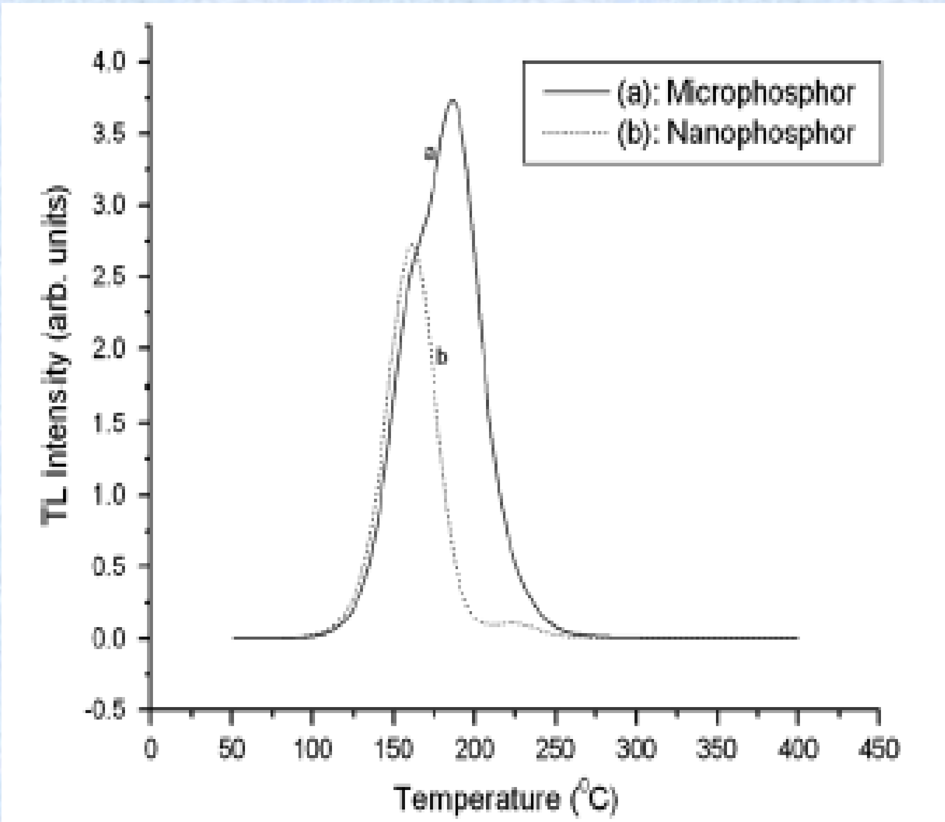
X-ray diffraction pattern of nanophosphor Ba0.97Ca0.03SO4 : Eu.

Preparation: Barium chloride and calcium chloride were taken according to formula ratio (0.97 Ba and 0.03 Ca) and the impurity $EuCl_2$ (0.2 mol %) dissolved in water. To control the size of particles to be produced on precipitation, ethanol was added to the solution. Further ammonium sulfate was added drop wise to the solution until the precipitation was complete. The precipitate was filtered out and washed several times with distilled water. The nanophosphor was finally obtained by drying the precipitate at 90 .C for 4 h.

Nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$: Eu

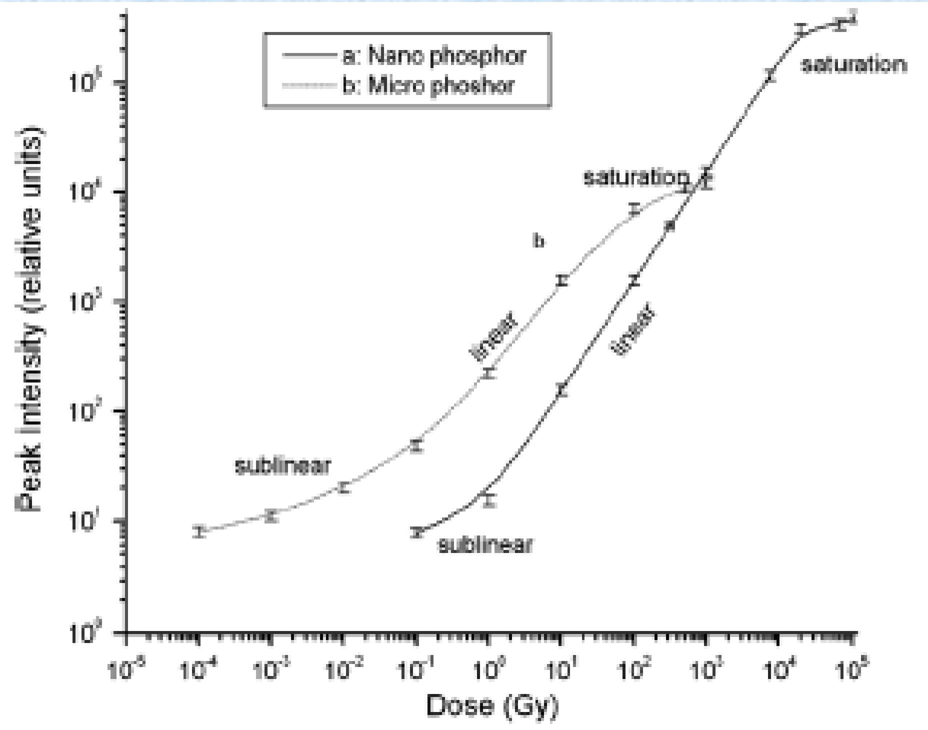


TEM photograph of nanophosphor Ba0.97Ca0.03SO4 : Eu.

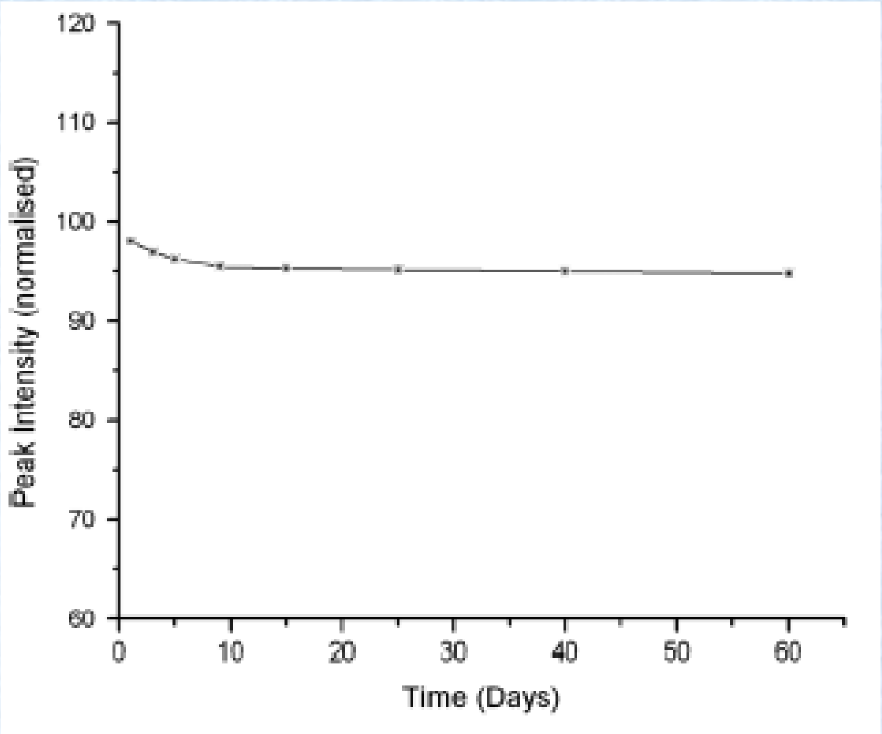


TL glow curves of micro- (curve a) and nano- (curve b) crystalline Ba0.97Ca0.03SO4 : Eu irradiated to a gamma dose of 10 Gy.

Nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$: Eu



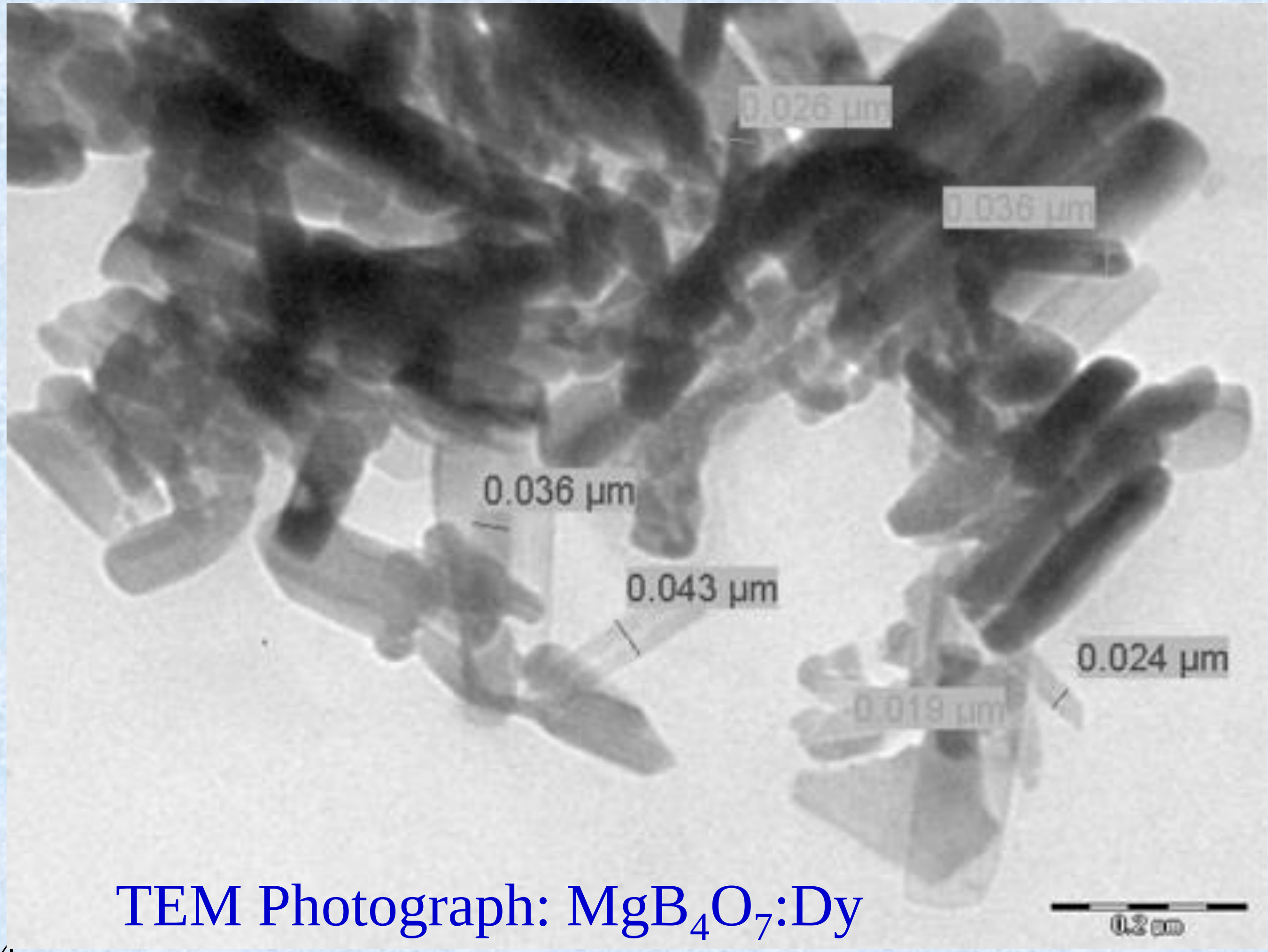
TL response of micro- and nanocrystalline $Ba_{0.97}Ca_{0.03}SO_4$: Eu.



TL Fading curve of $Ba_{0.97}Ca_{0.03}SO_4$: Eu.

MgB_4O_7:Dy

P. D. Sahare, ety al., phys. stat. sol. (a) 204 (2007) 2416.

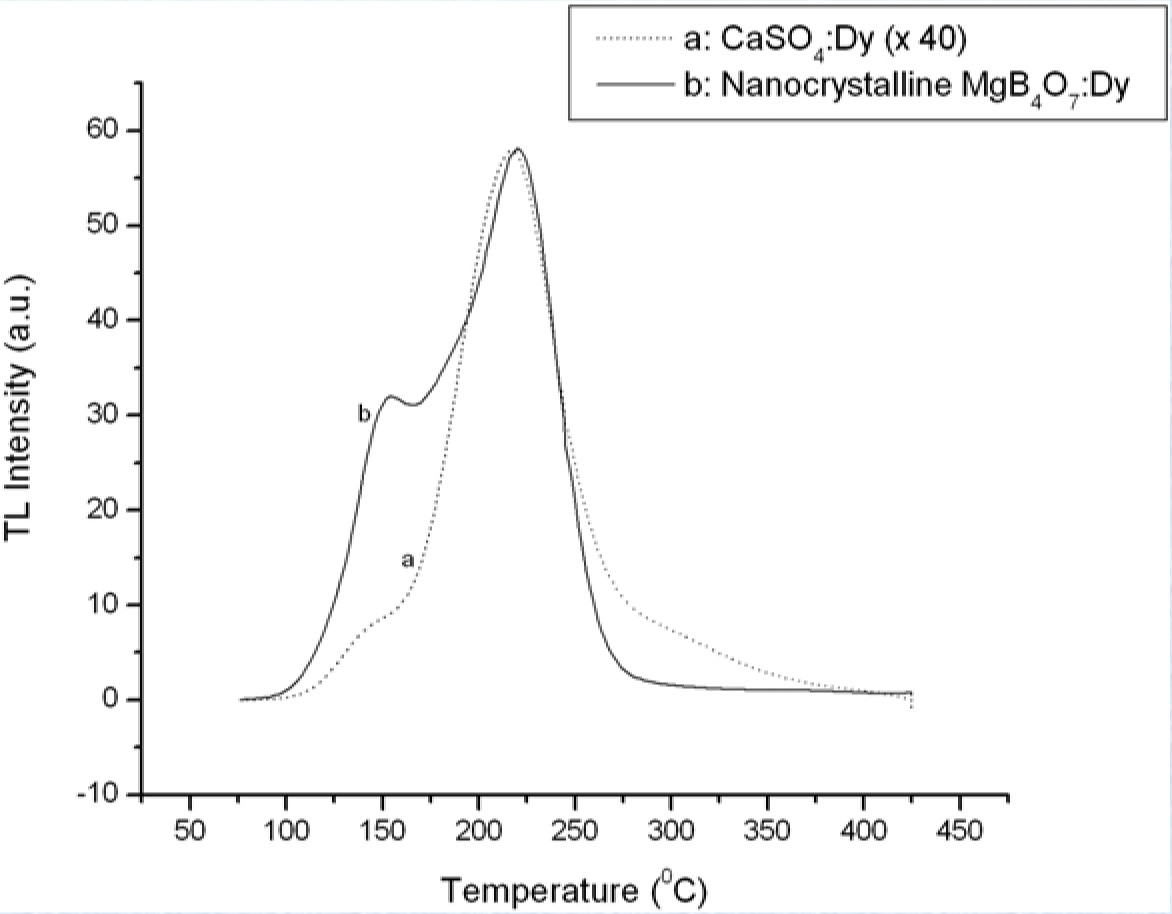


TEM Photograph: MgB_4O_7:Dy

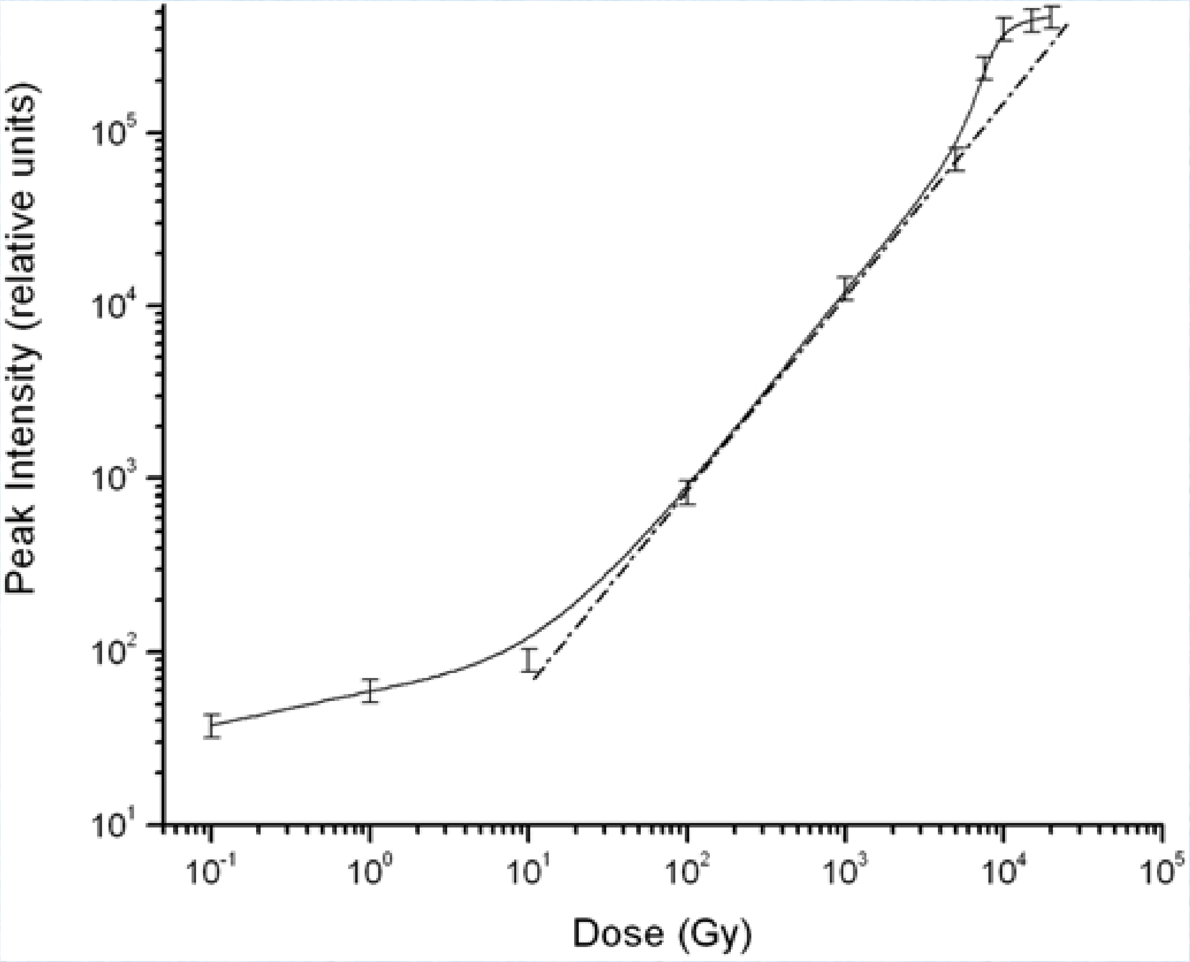
Synthesis:

The samples were synthesized by combustion method where commonly available materials like urea and ammonium nitrate work as fuel and oxidizer respectively.

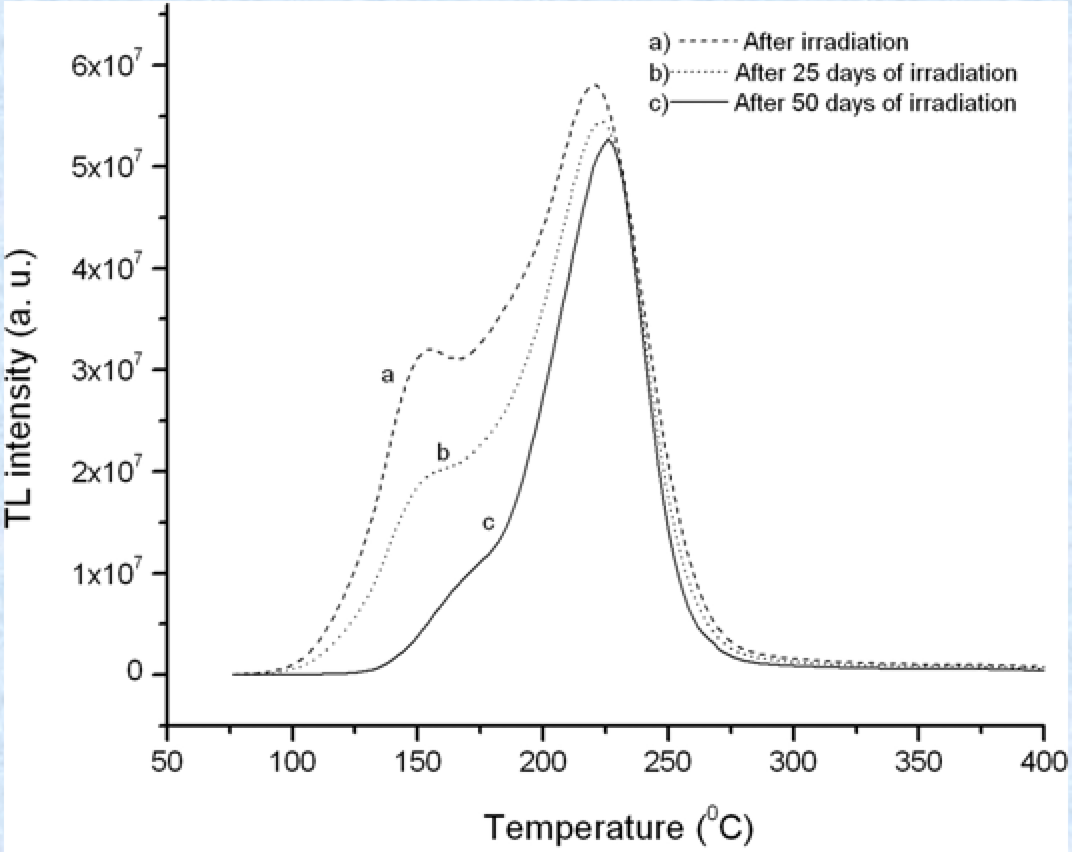
- The starting mixture, with a molar ratio of
- $Mg(NO_3)_2$:H_3BO_3:NH_4NO_3:Urea = 1.0:3.2:10.2:10.2,
- Appropriate amounts of $DyCl_3$ (0.1 mole%)
- Introduced in a muffle furnace preheated to 550 °C.



Comparison with $CaSO_4$:Dy TLD Phosphor



Dose Response


a) After irradiation
b) After 25 days of irradiation
c) After 50 days of irradiation
TL intensity (a. u.)
6x10^7
5x10^7
4x10^7
3x10^7
2x10^7
1x10^7
0
a
b
c
50
100
150
200
250
300
350
400
Temperature (°C)

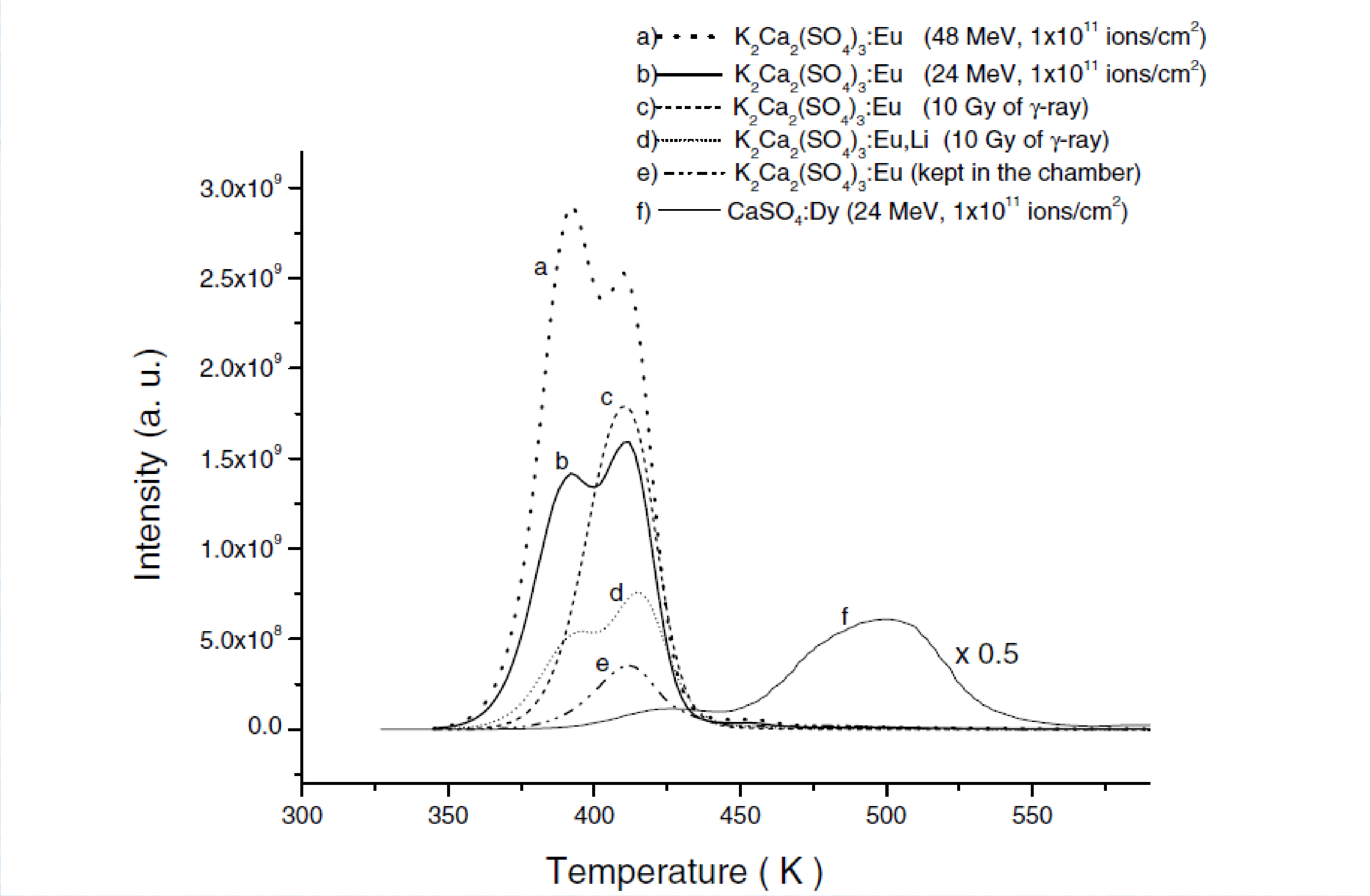
Fading

Application of TLD nanophosphors for Ion-Beam Dosimetry:

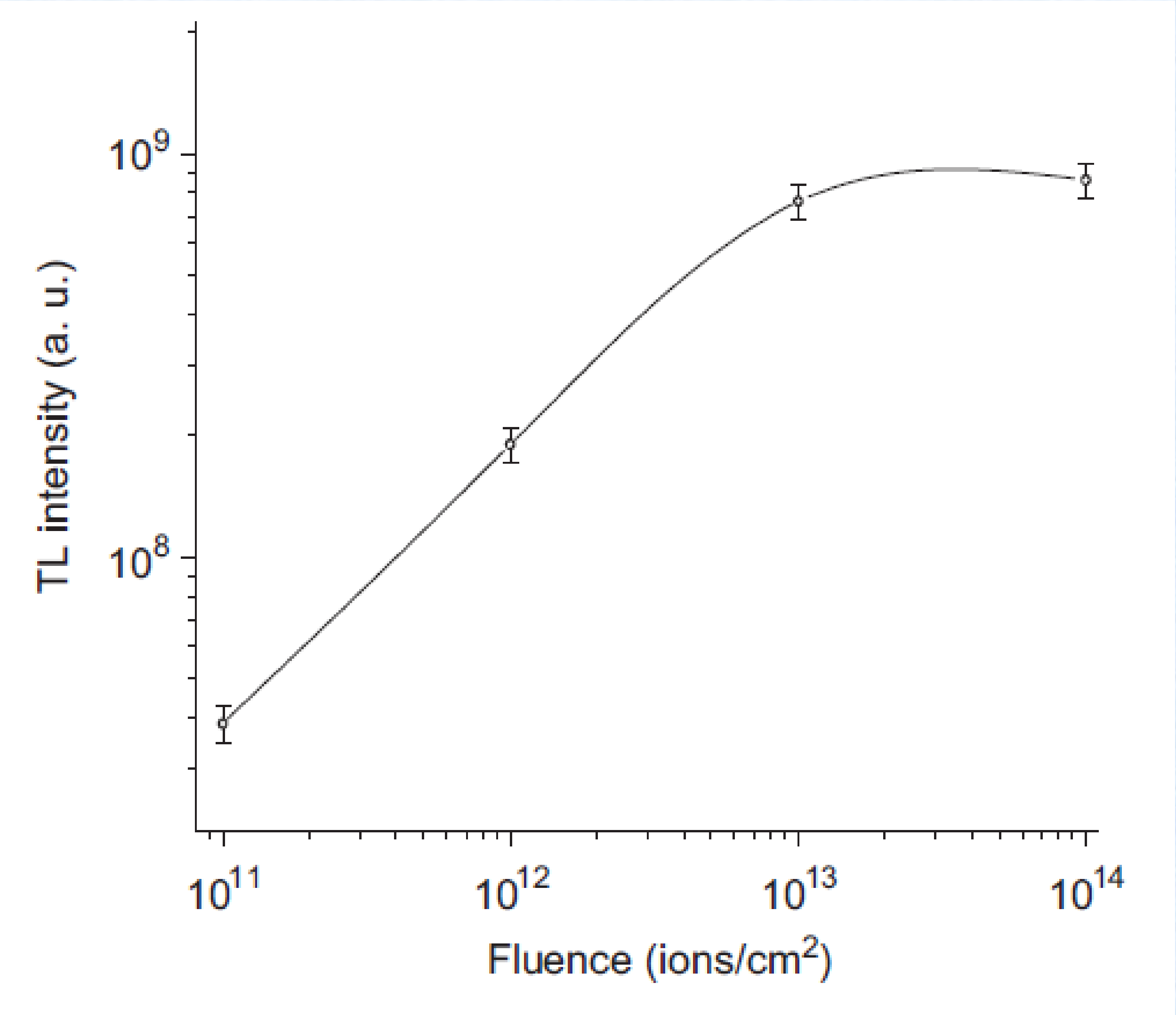
- TLD phosphors could also be used for the estimation of the fluence (no. particles/cm^2) of the ion beam.
- But it has been found that there is a possibility of ion implantation in the phosphor material during irradiation.
- The range is also limited as the phosphors saturates early
- TLD nanoparticles have found to be better option for such dosimetry

Numan Salah, Radiat. Phys. Chem. 80 (2011) 1

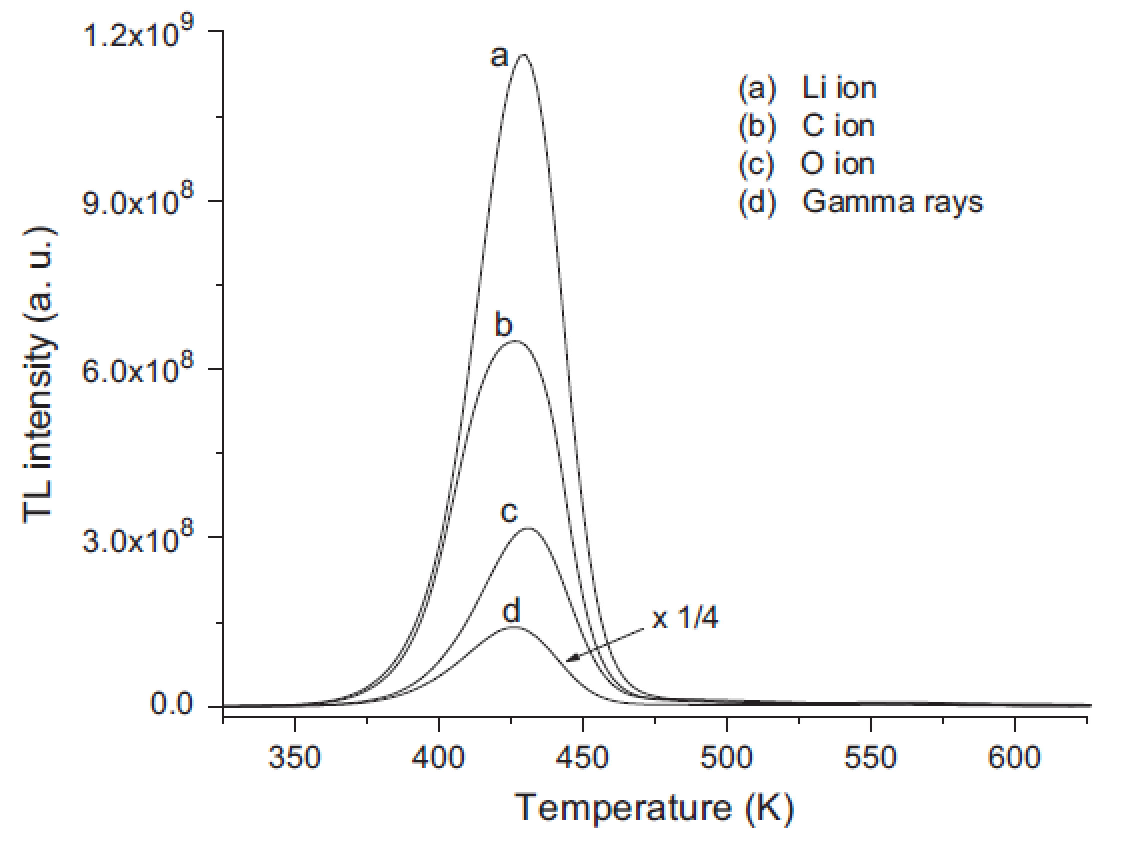
A case of Glow curves of $K_2Ca_2(SO_4)_3$:Eu (bulk) showing Li ions implantation during ion beam irradiation.



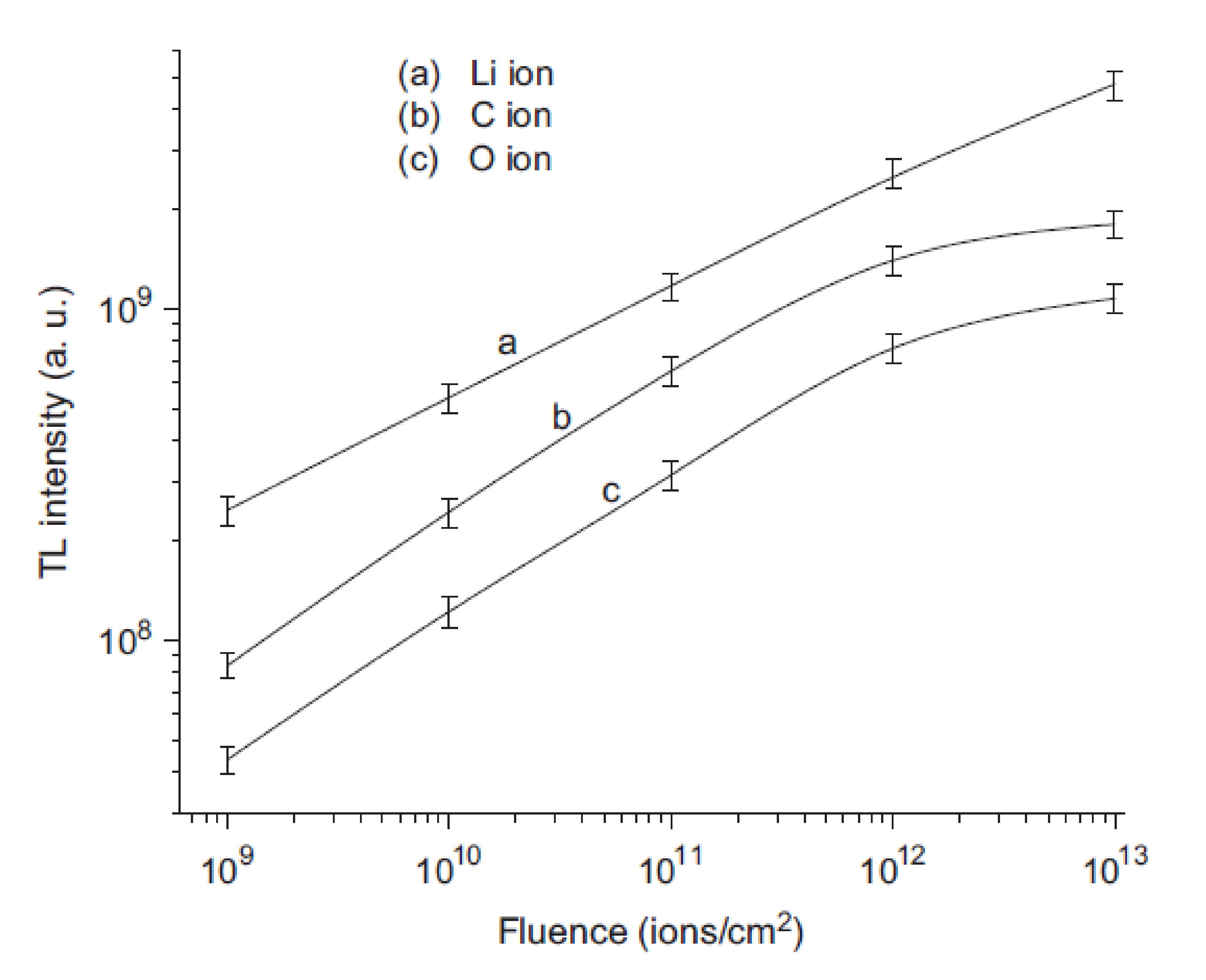
Glow curves of K2Ca2(SO4)3 : Eu exposed to 1 × 10^{11} ions/cm^2 of ^{7}Li ion beams. Glow curves of $K_2Ca_2(SO_4)_3$:Eu and $K_2Ca_2(SO_4)_3$:Eu,Li irradiated with *γ* -rays are also shown.



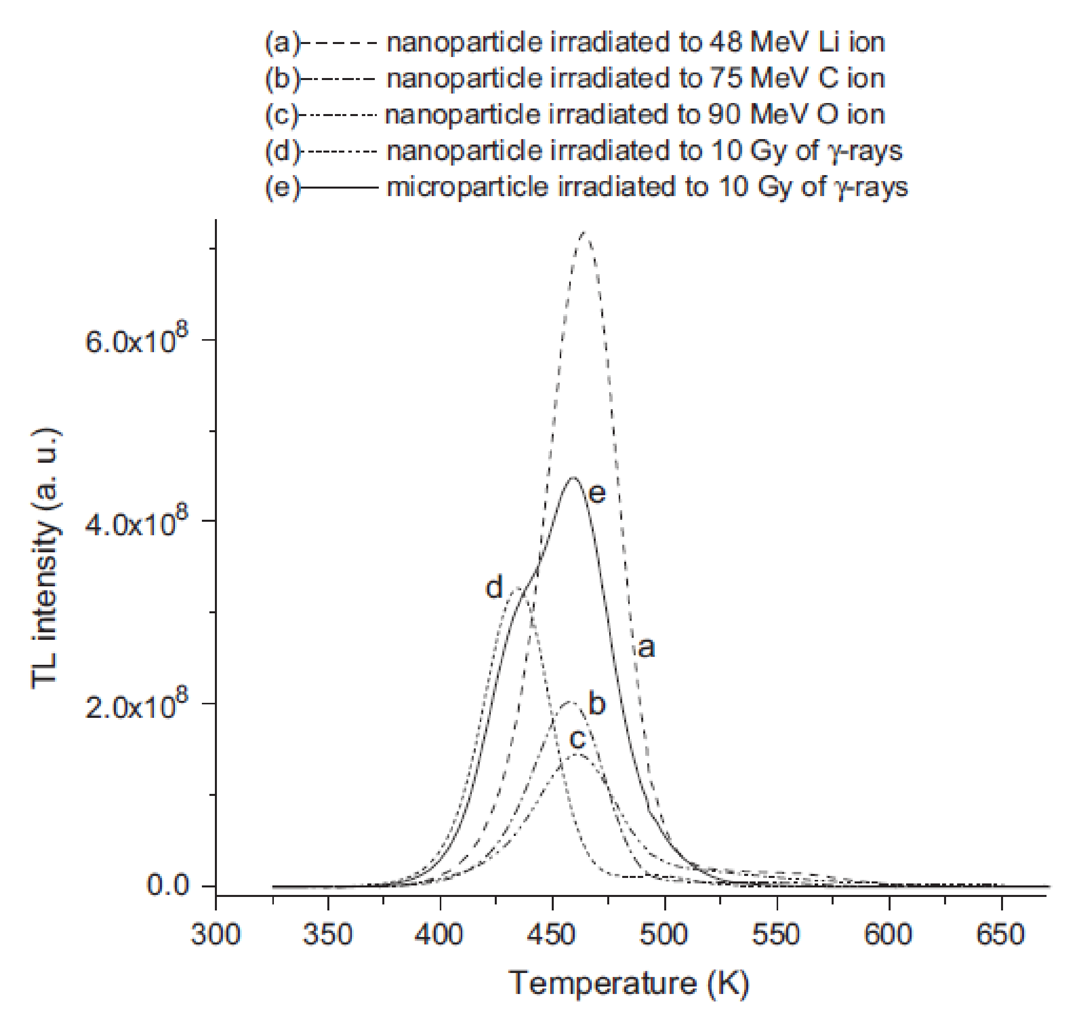
TL response after irradiation to ^{7}Li ion beam of 48 MeV energy



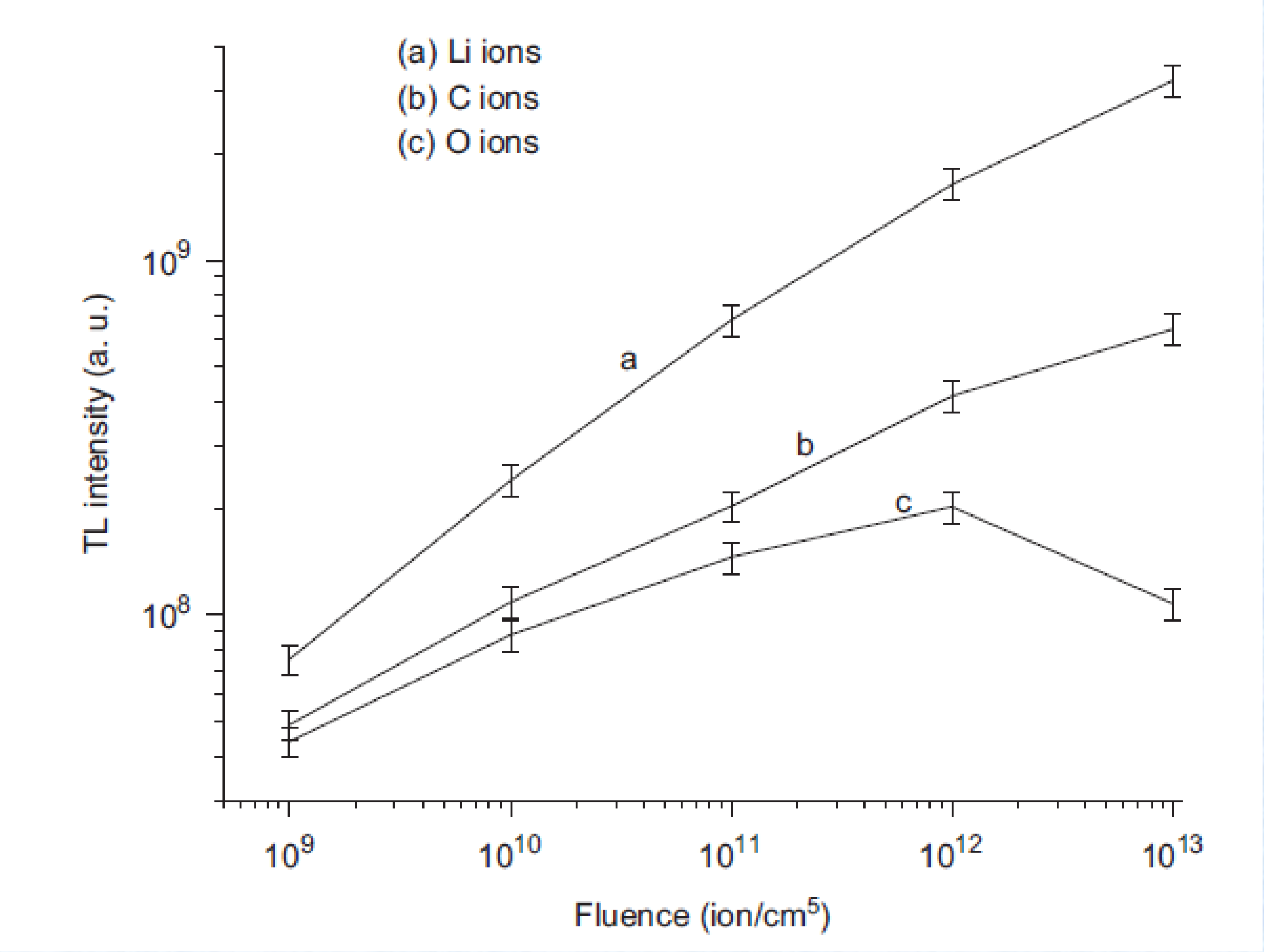
TL glow curves of $K_2Ca_2(SO_4)_3$:Eu nanocrystalline Samples to 48 MeV Li^{3+}, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams



TL response of TL response curves of $K_2Ca_2(SO_4)_3$:Eu nanocrystalline Samples to 48 MeV Li^{3+}, 75 MeV C^{6+} and 90 MeV O^{7+} ion beams



Typical TL glow curves of $Ba_{0.97}Ca_{0.03}SO_4$:Eu nanocrystalline sample exposed to $11x^{11}$ ions/cm^2 of 48 MeV Li,75 MeV Cand 90 MeV O ion beams.



TL response curves of $Ba_{0.97}Ca_{0.03}SO_4$:Eu nanocrystalline sample exposed to $11x^{11}$ ions/cm^2 of 48 MeV Li,75 MeV Cand 90 MeV O ion beams.

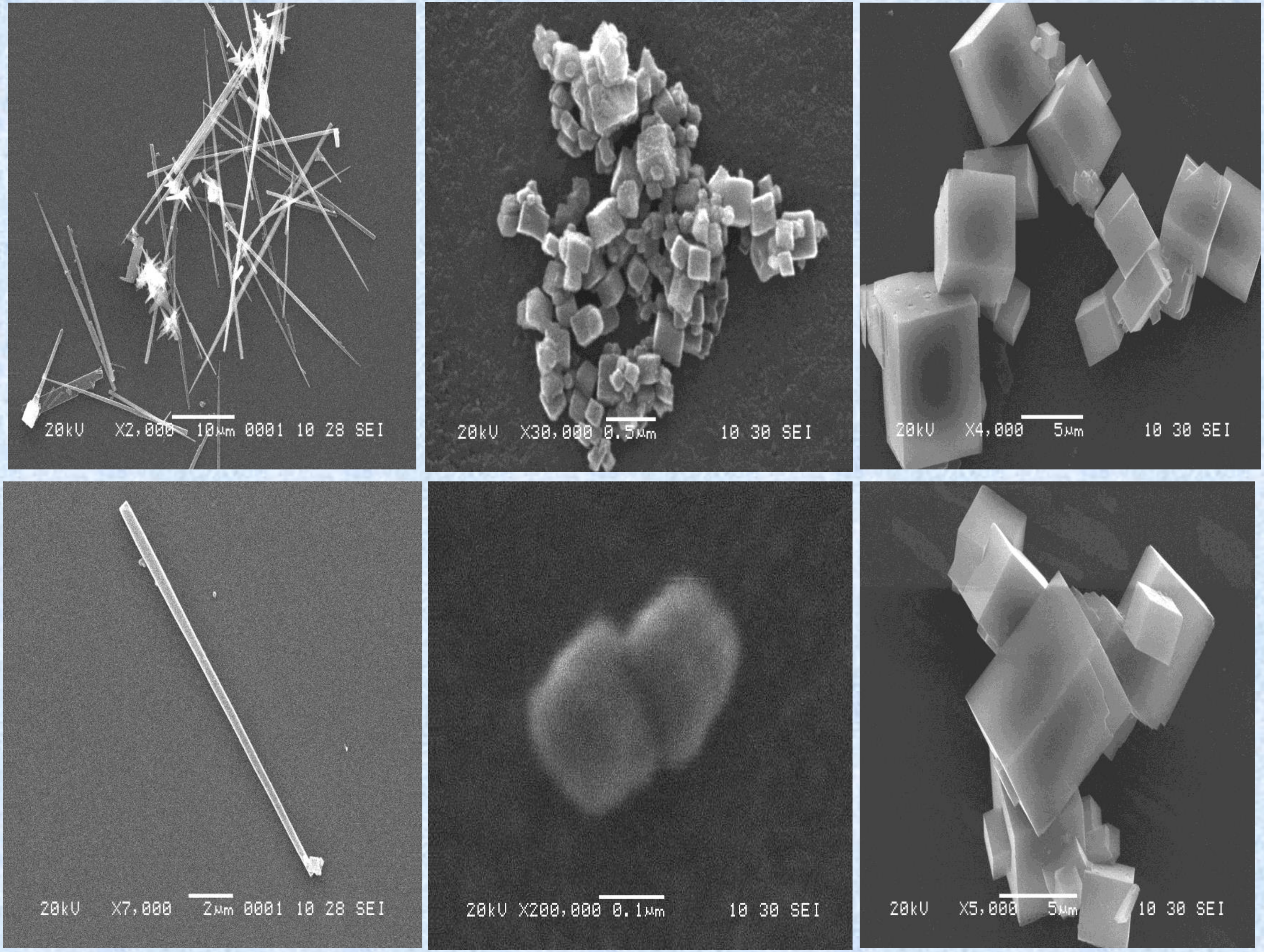
The issues related to the application of the TLD nanophosphors for the dosimetry of high-energy radiations:

1. It has been found that the TL glow curves/sensitivity of a phosphor may change with the shape and size/morphology of the nanoparticles. Therefore, utmost care needs to be taken while synthesizing the material.
2. There is not much studies available about the toxicity on inhaling of the nanoparticles available. Therefore, proper care should be taken while synthesis and handling. They may be used in the form of pellets as TL dosimeters.

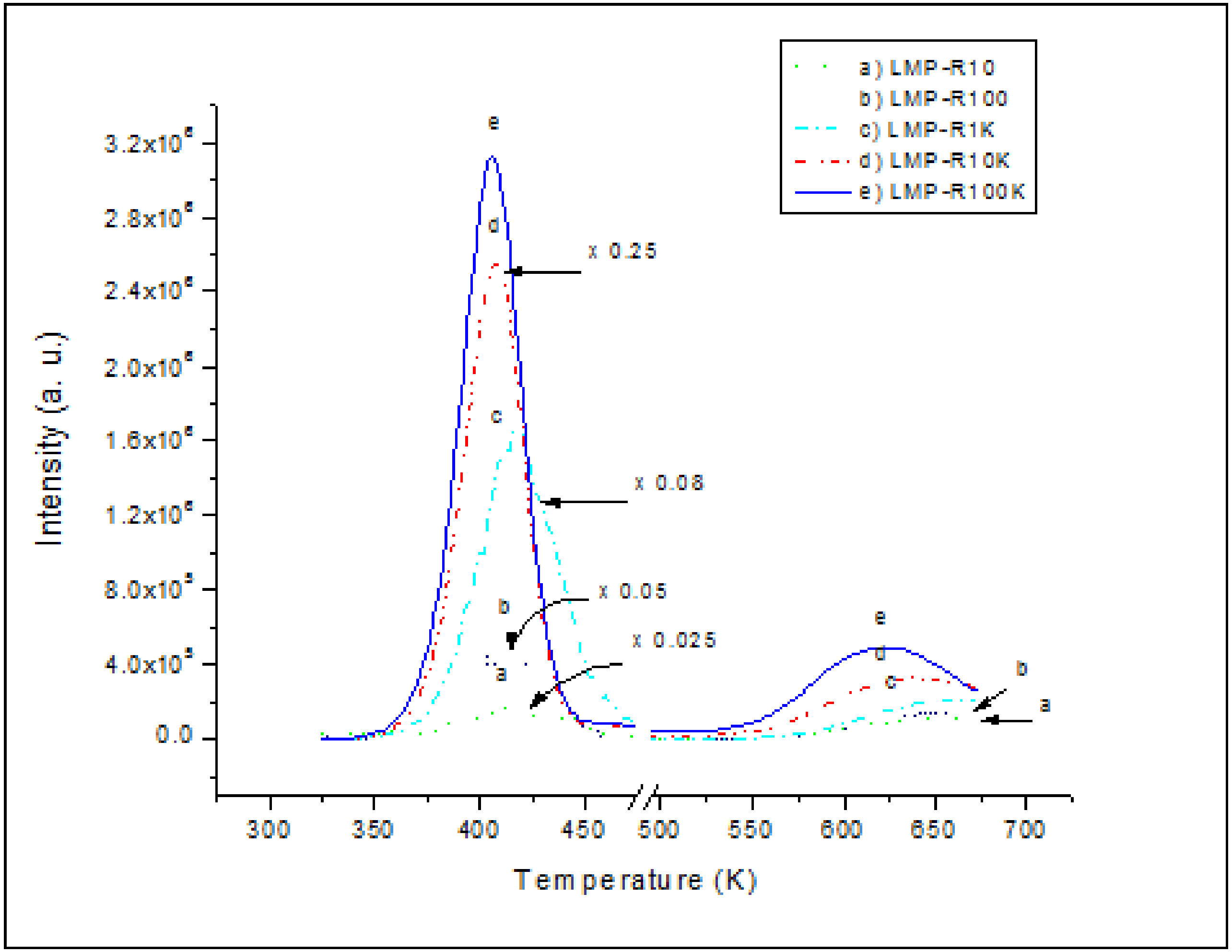
1. Changes in TL glow curve/sensitivity of a TLD Phosphor due to shape and size (morphology) of the TLD Phosphor:

A case of the LiF:Mg,Cu,P nanophosphor

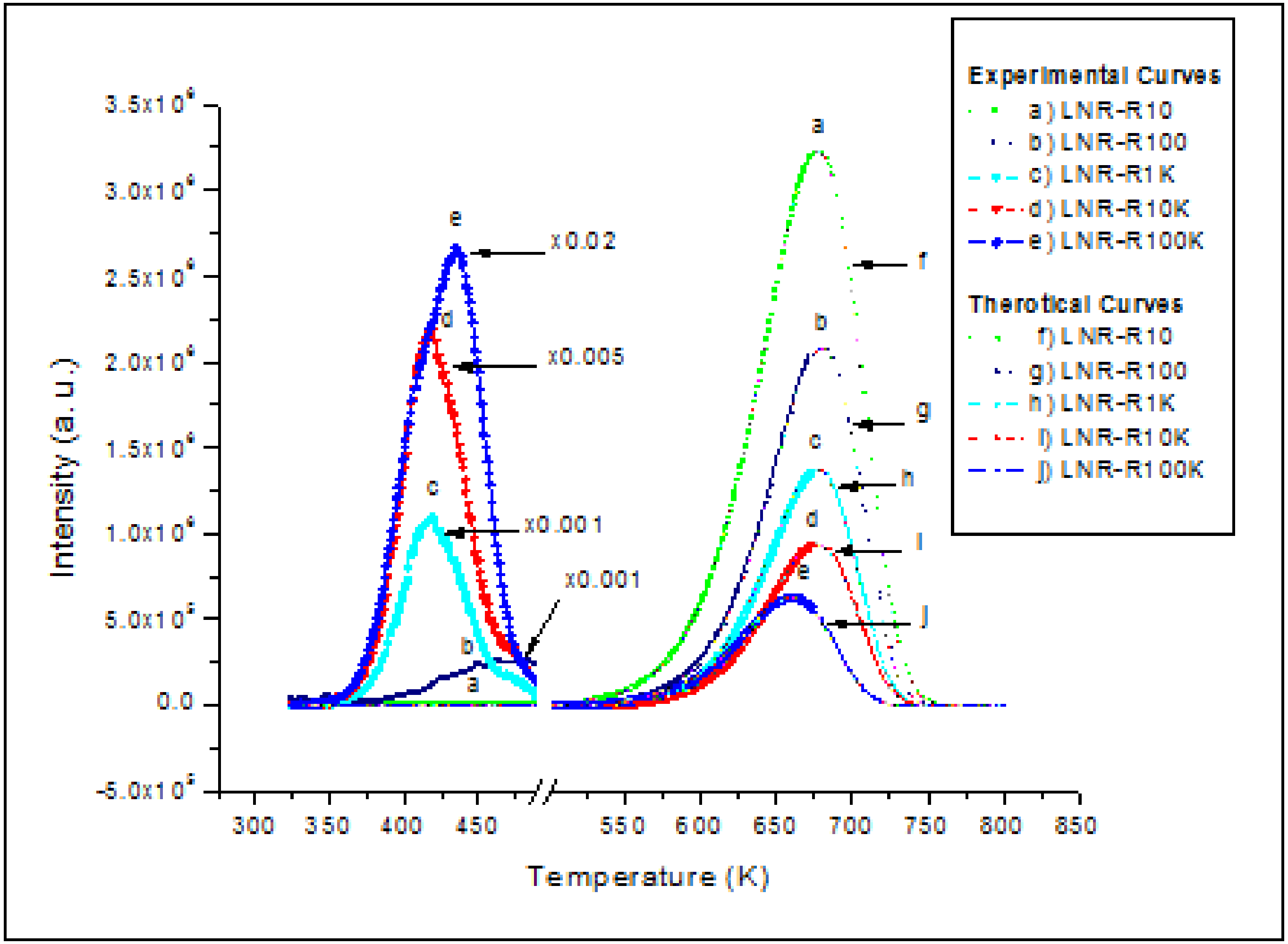
P. D. Sahare, et al., J. Lum. 130 (2010) 258.



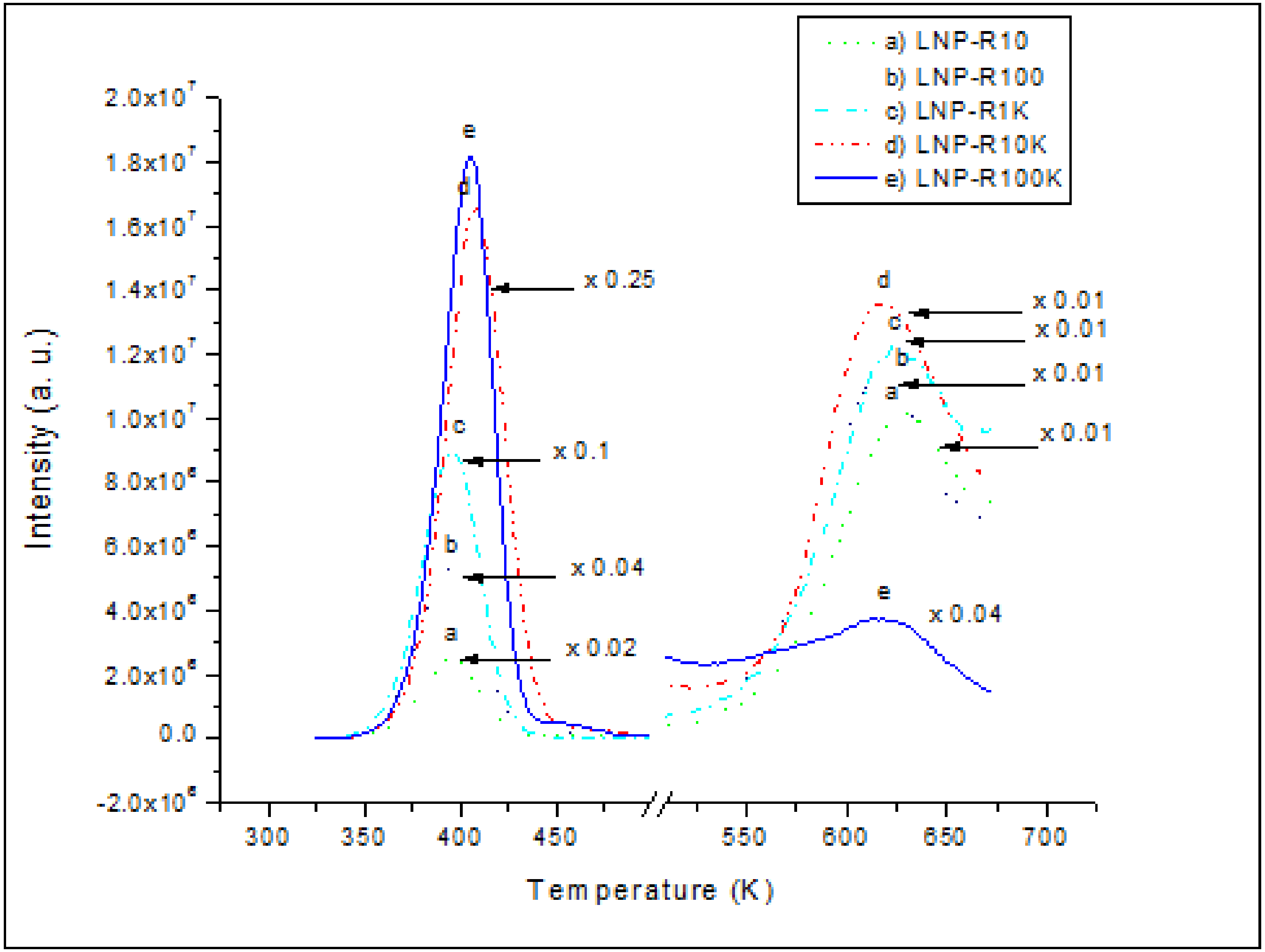
SEM PHOTOGRAPHS OF LiFM:Mg,Cu,P PHOSPHOR



TL Glow Curves of LiF:Mg,Cu,P Phosphor Microcrystalline



TL Glow Curves of LiF:Mg,Cu,P Phosphor Nanorods



TL Glow Curves of LiF:Mg,Cu,P Phosphor Nanoparticles

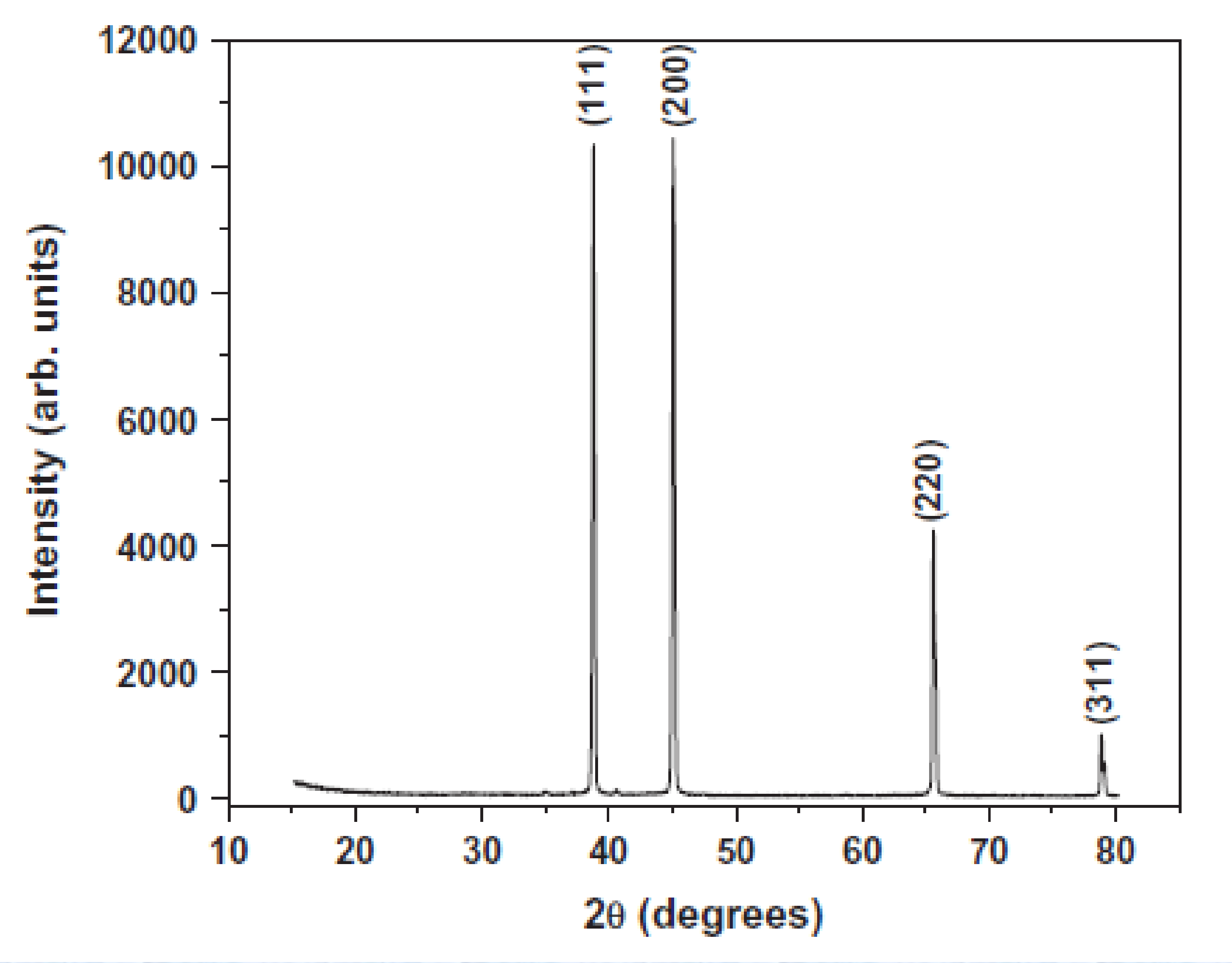
Bulk LiF: Mg, Cu, P (TLD 700 H)

- It is a tissue equivalent, very sensitive, commercially available and widely used TLD phosphor.
- But the problem with the phosphor is its sensitivity changes on heating during taking readouts beyond 523 K.
- If not heated beyond this temperature some deep traps still persists and there is a possibility of inaccuries in measurements.

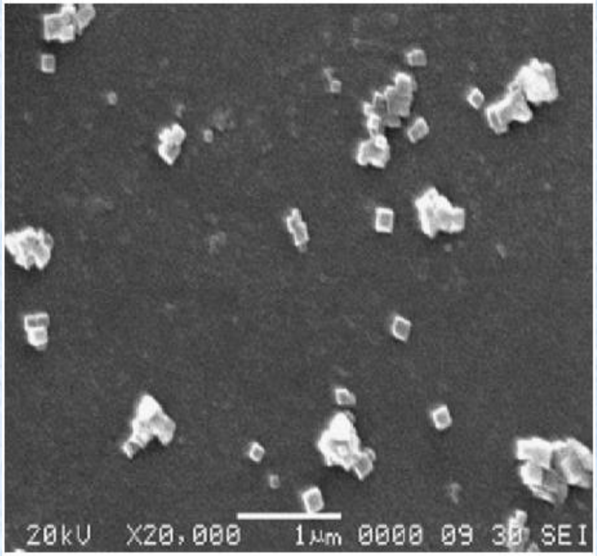
1. LiF:Cu Phosphor

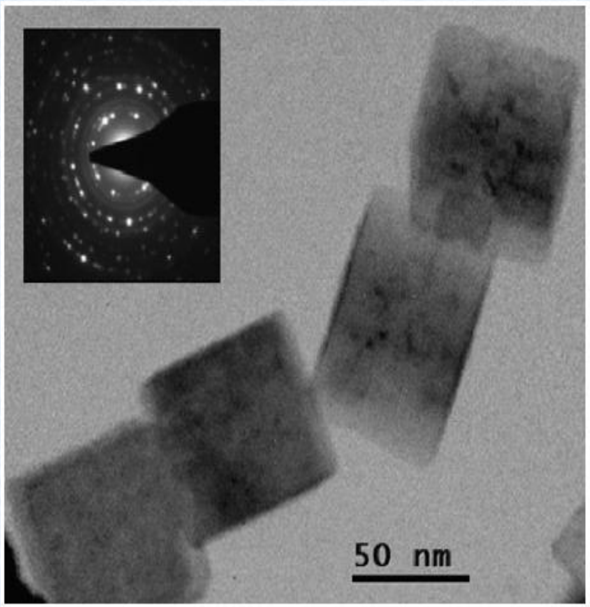
An example, how the changes in the ionic states of the impurity change the glow curve structure and sensitivity of a TLD Phosphor

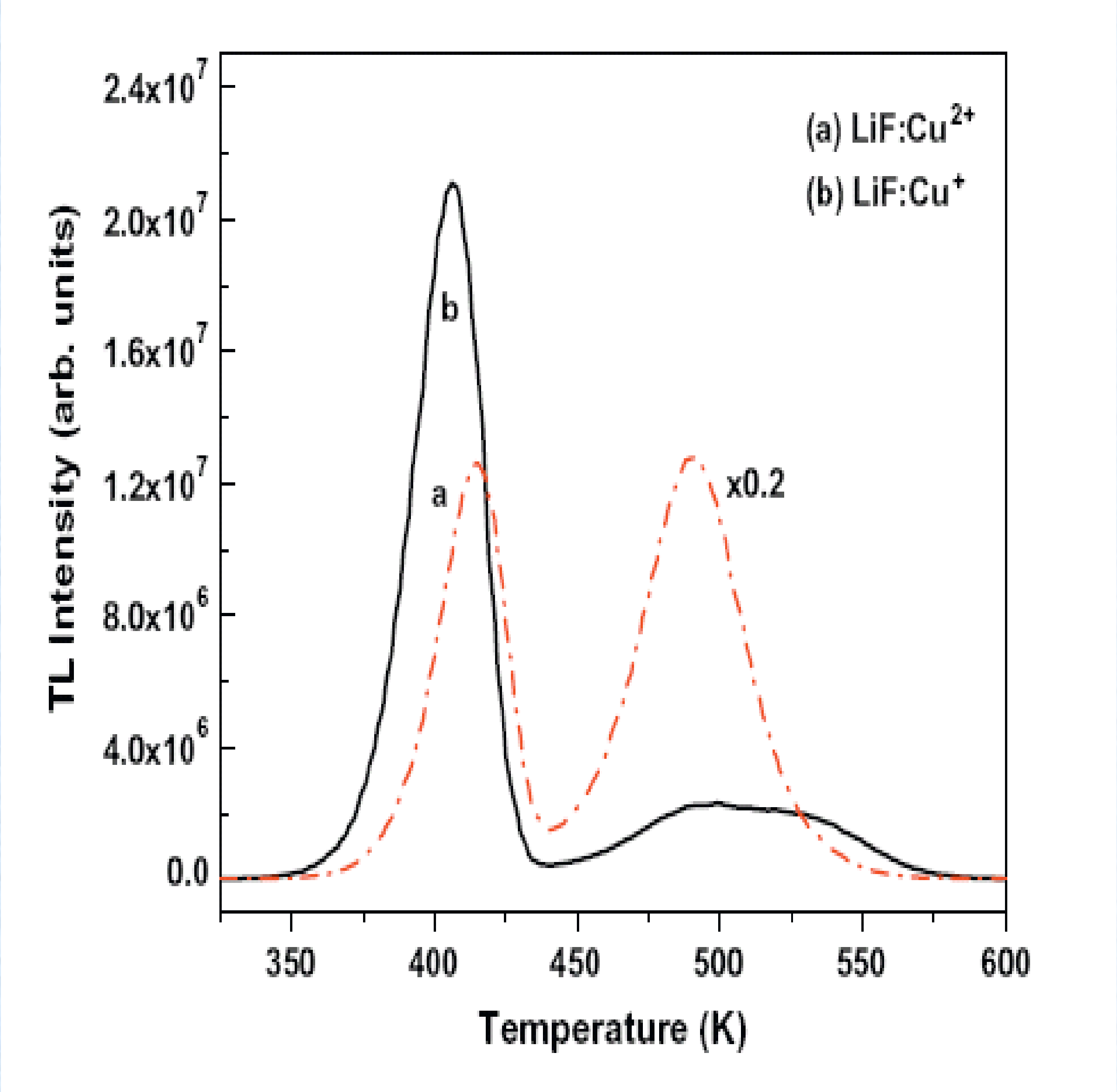
Manveer Singh and P. D. Sahare, Radiat. Measur. 47 (2012) 1083

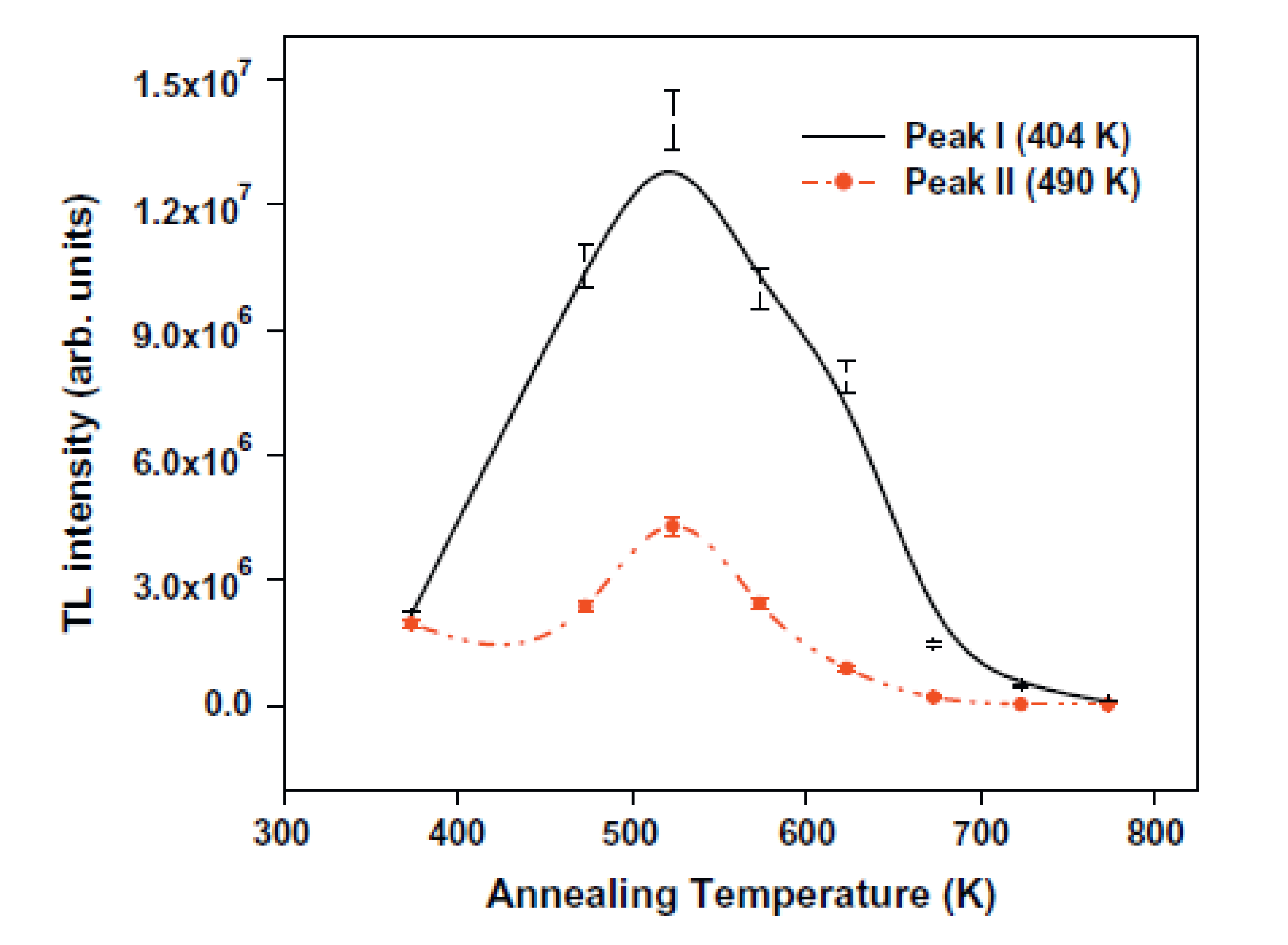


12000
10000
8000
6000
4000
2000
0
Intensity (arb. units)
(111)
(200)
(220)
(311)
10
20
30
40
50
60
70
80
2θ (degrees)

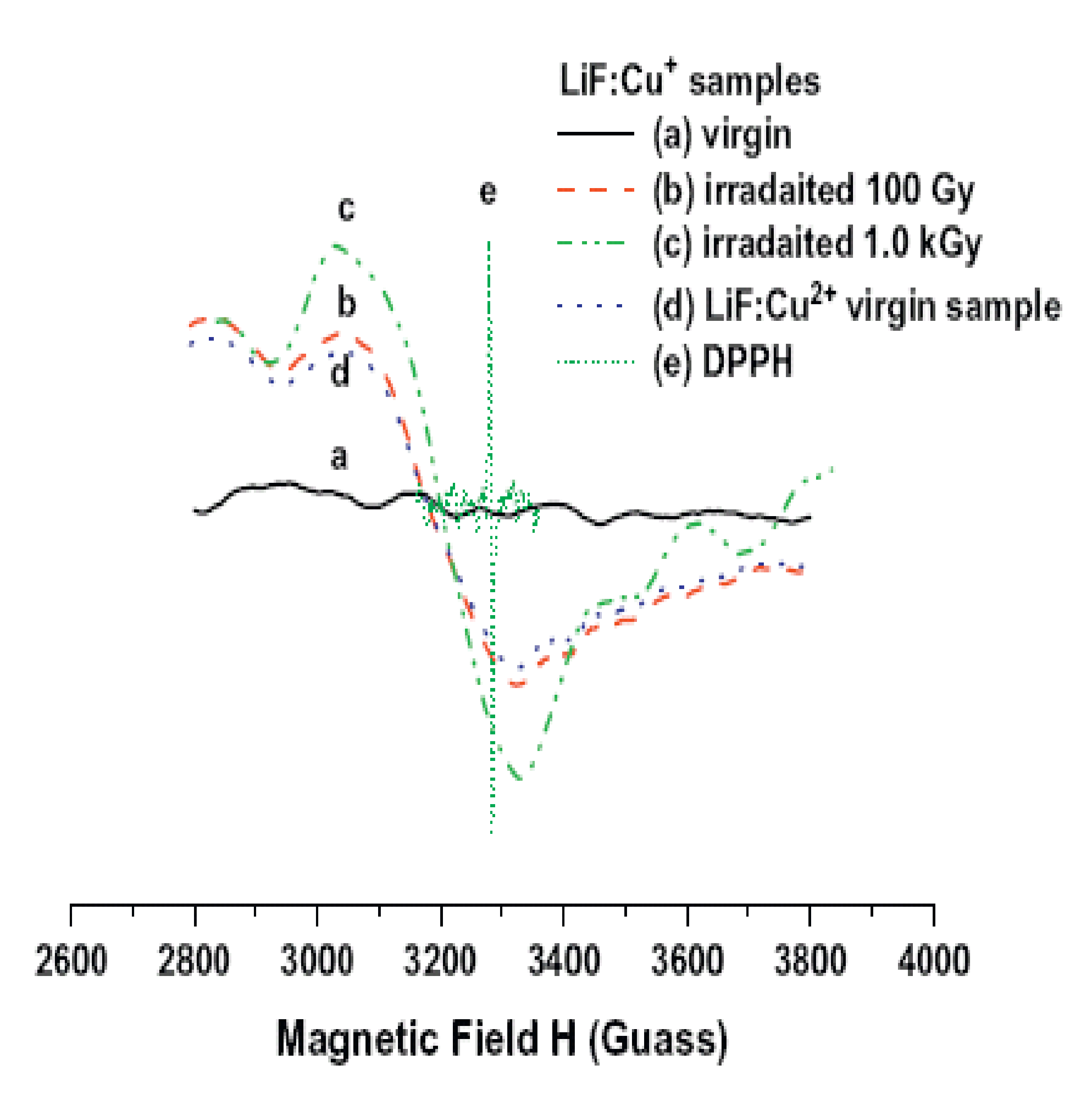

20kV X20,000 1μm 0000 09 30 SEI


50 nm

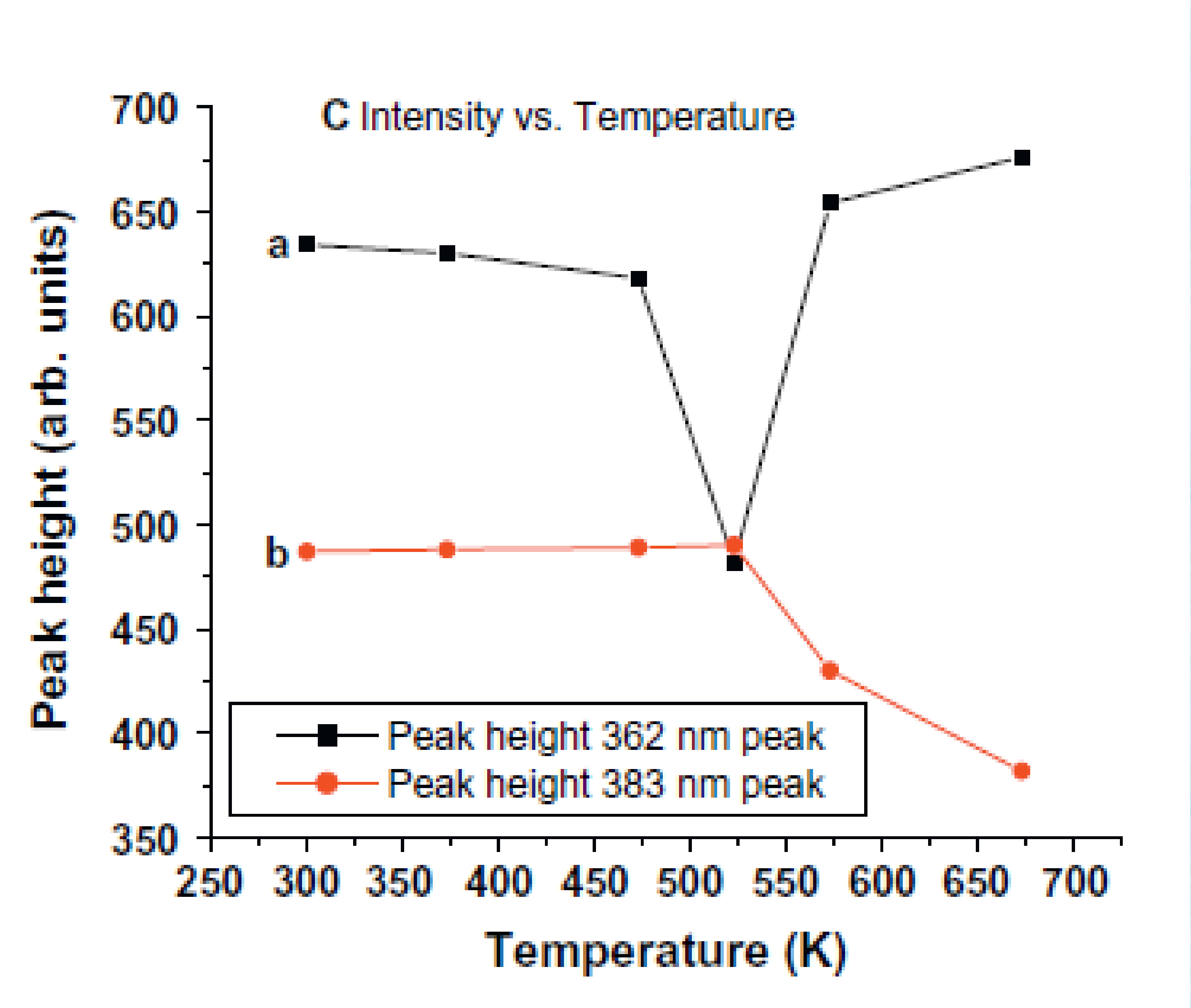

(a) LiF:Cu2+
(b) LiF:Cu+
b
a
x0.2
TL Intensity (arb. units)
Temperature (K)
2.4x10^7
2.0x10^7
1.6x10^7
1.2x10^7
8.0x10^6
4.0x10^6
0.0
350
400
450
500
550
600



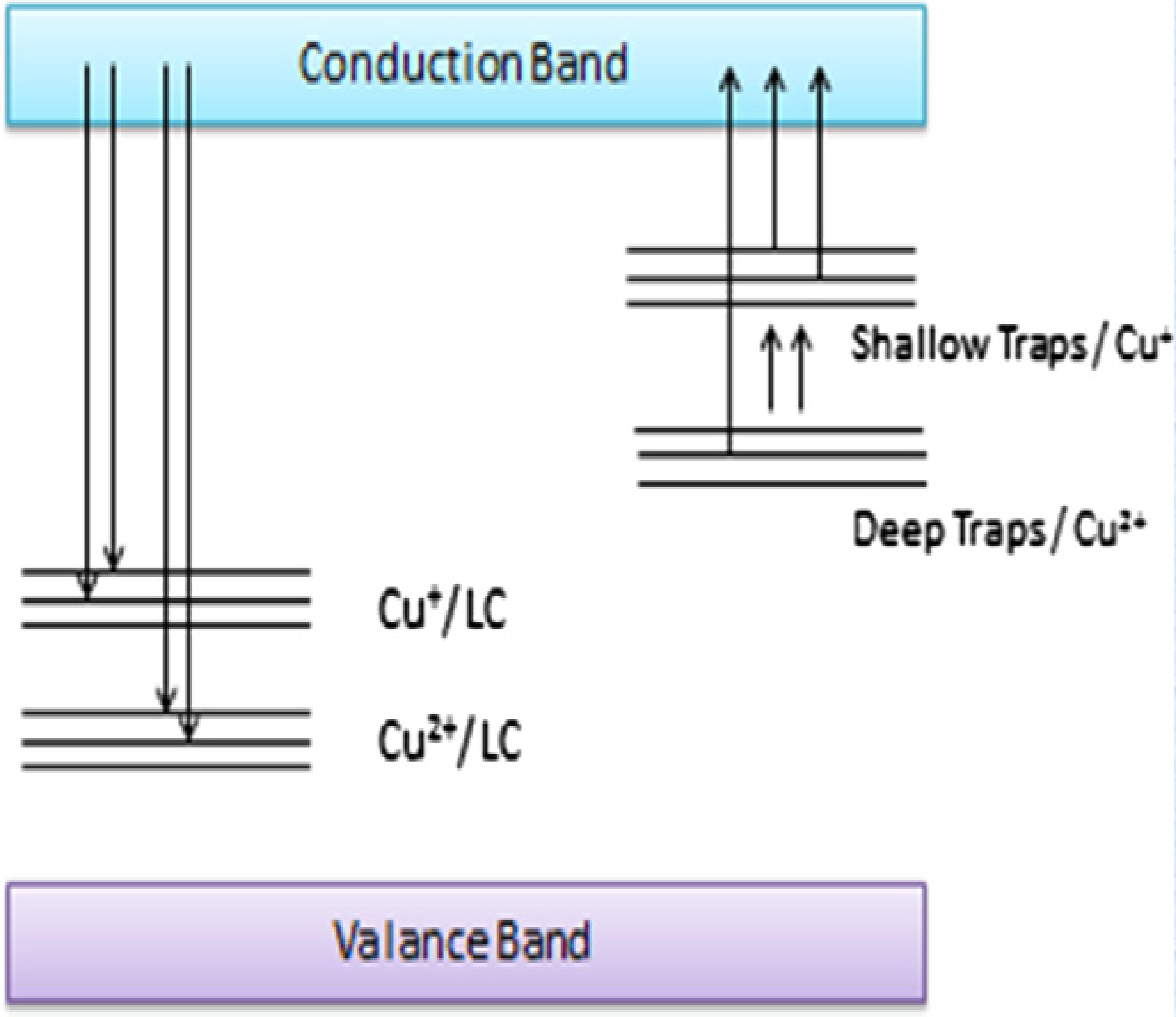
Change in the intensity of the glow peaks of LiF with the annealing temperature



ESR of irradiated samples



Changes in PL intensity with the annealing temperatures

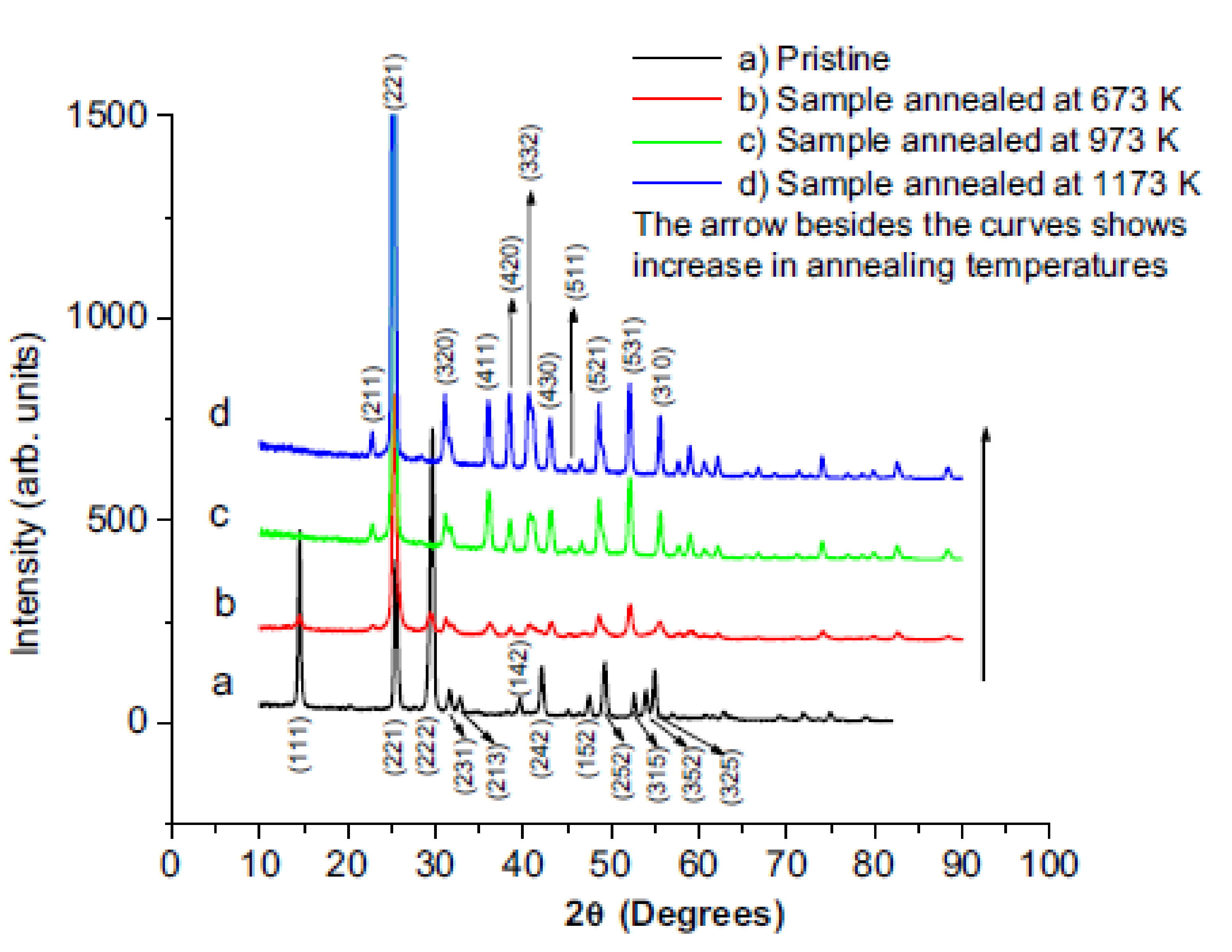


TL Mechanism in LiF:Cu^+

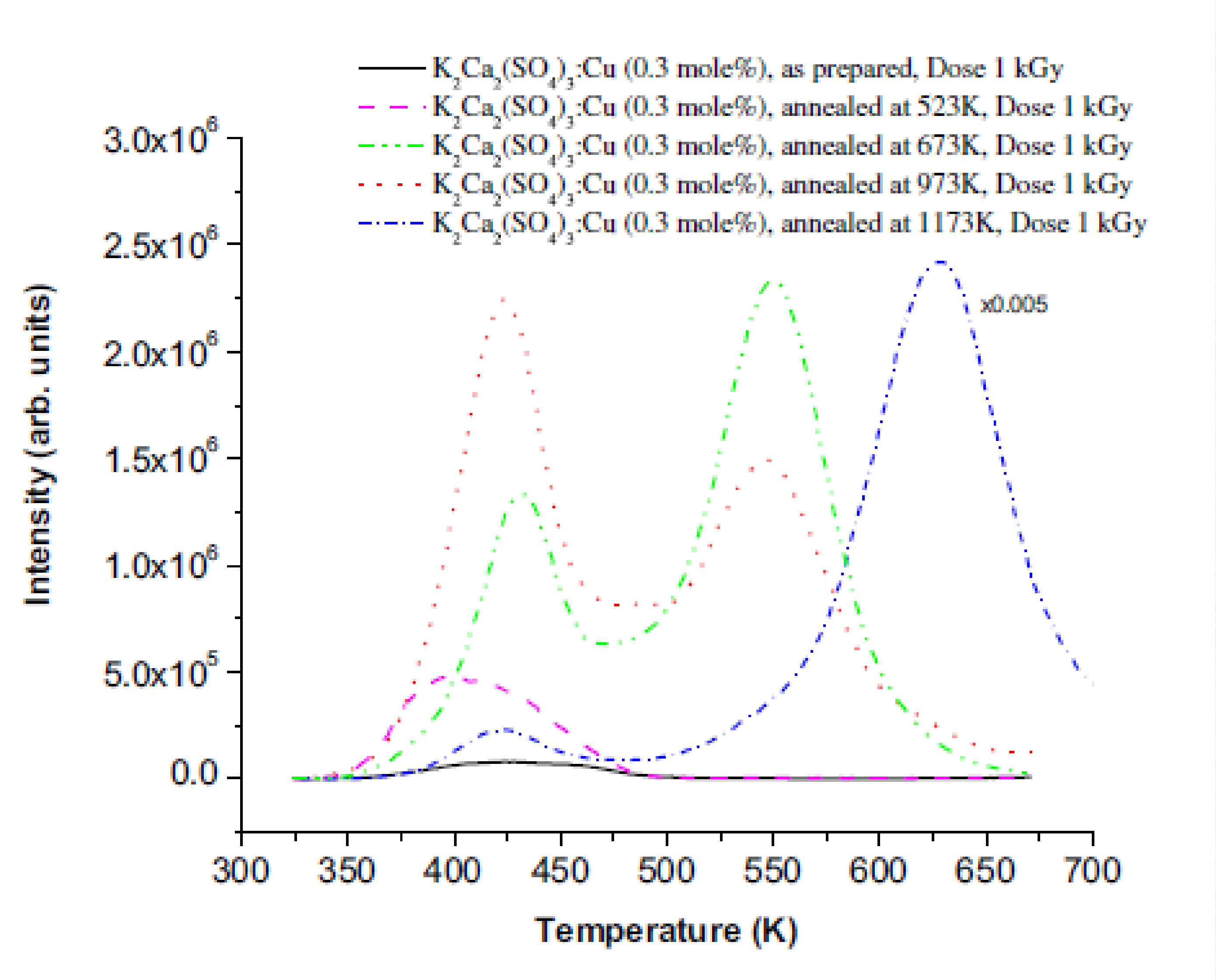
2. Changes in TL glow curve/sensitivity due to phase change of the TLD Phosphor:

A case of the $K_2Ca_2(SO_4)_3$:Cu nanophosphor

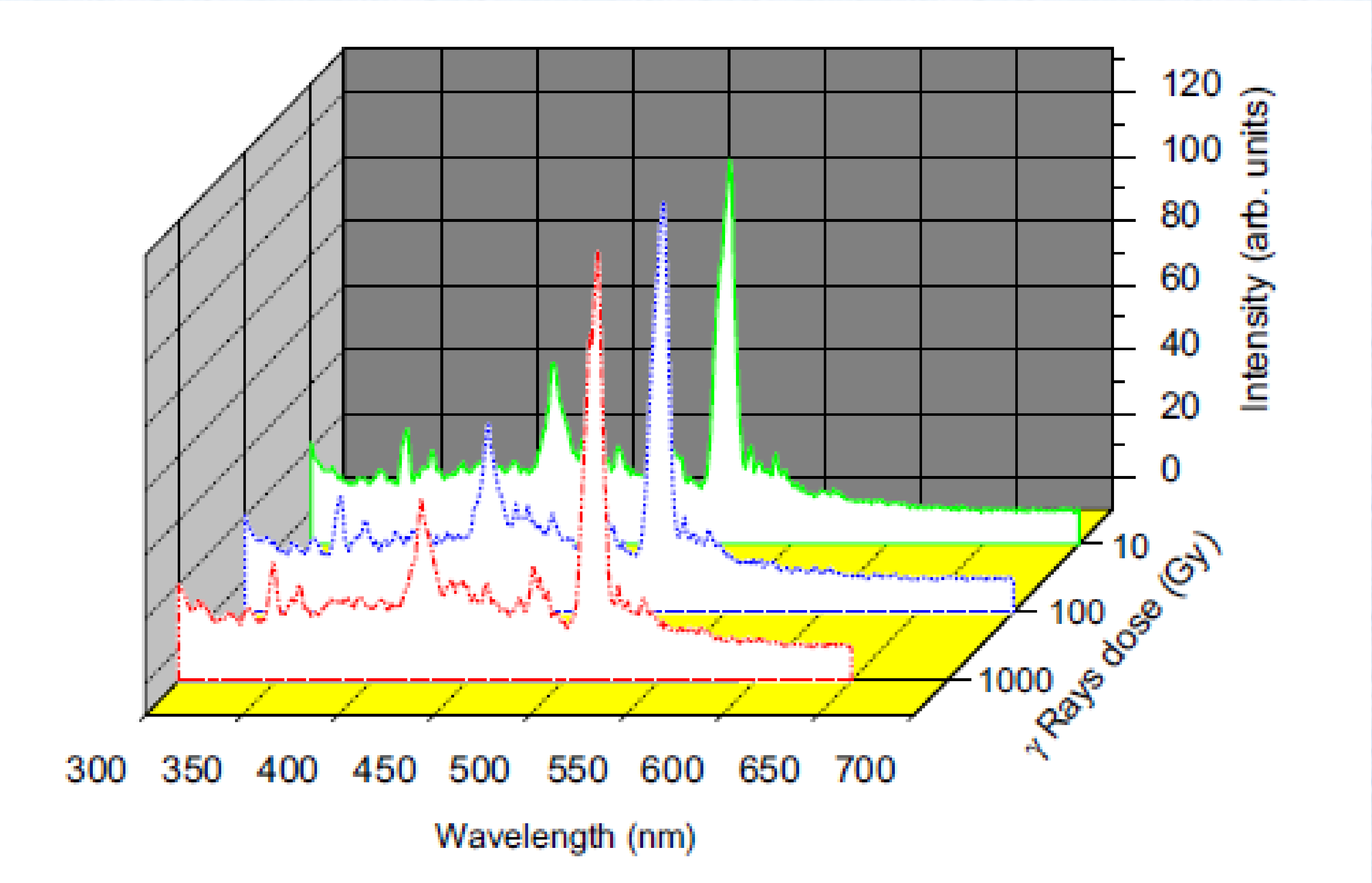
P. D. Sahare, et al. Radiat. Measur. 47 (2012) 1083



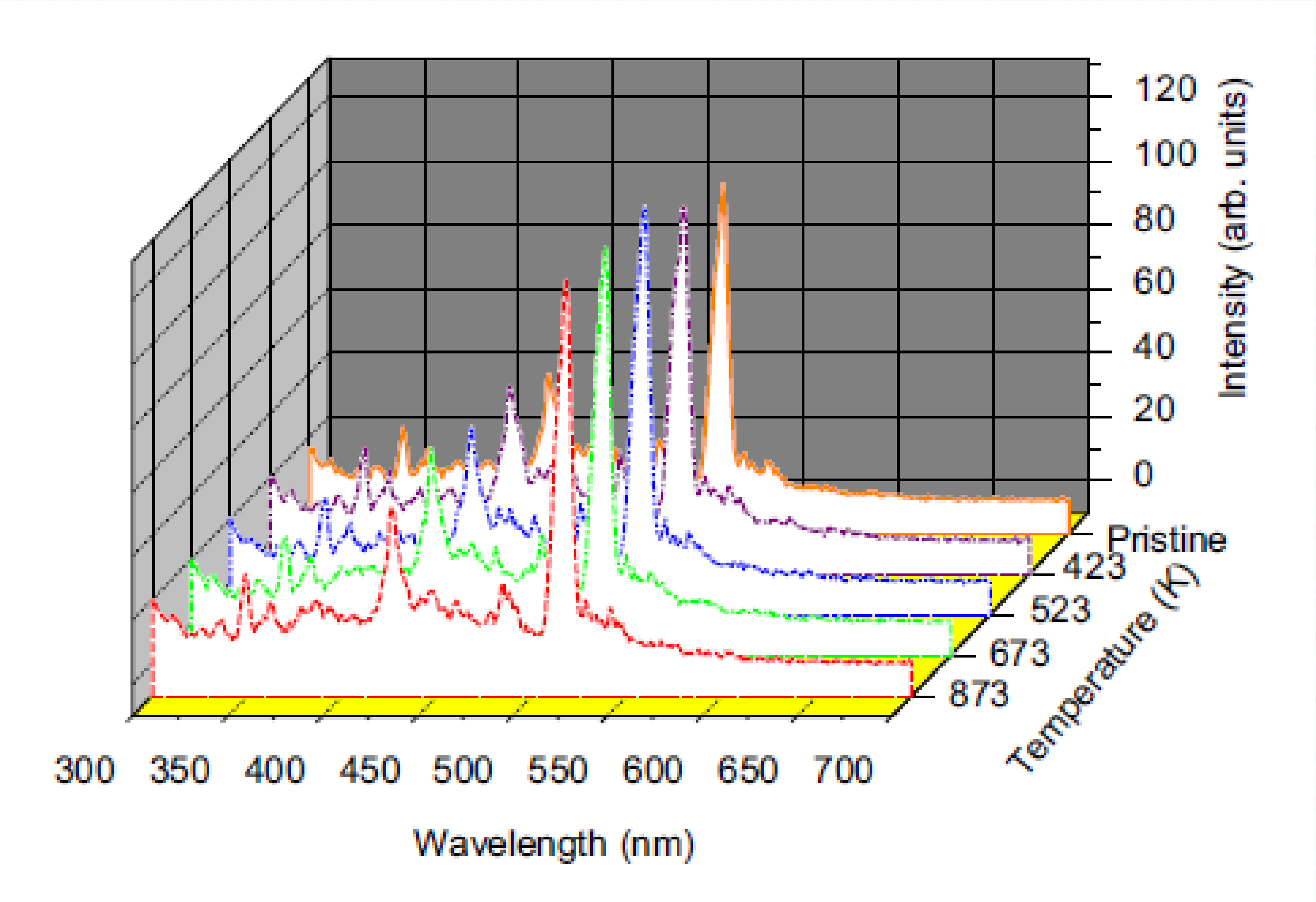
XRD of $K_2Ca_2(SO_4)_3$:Cu samples annealed at different temperatures



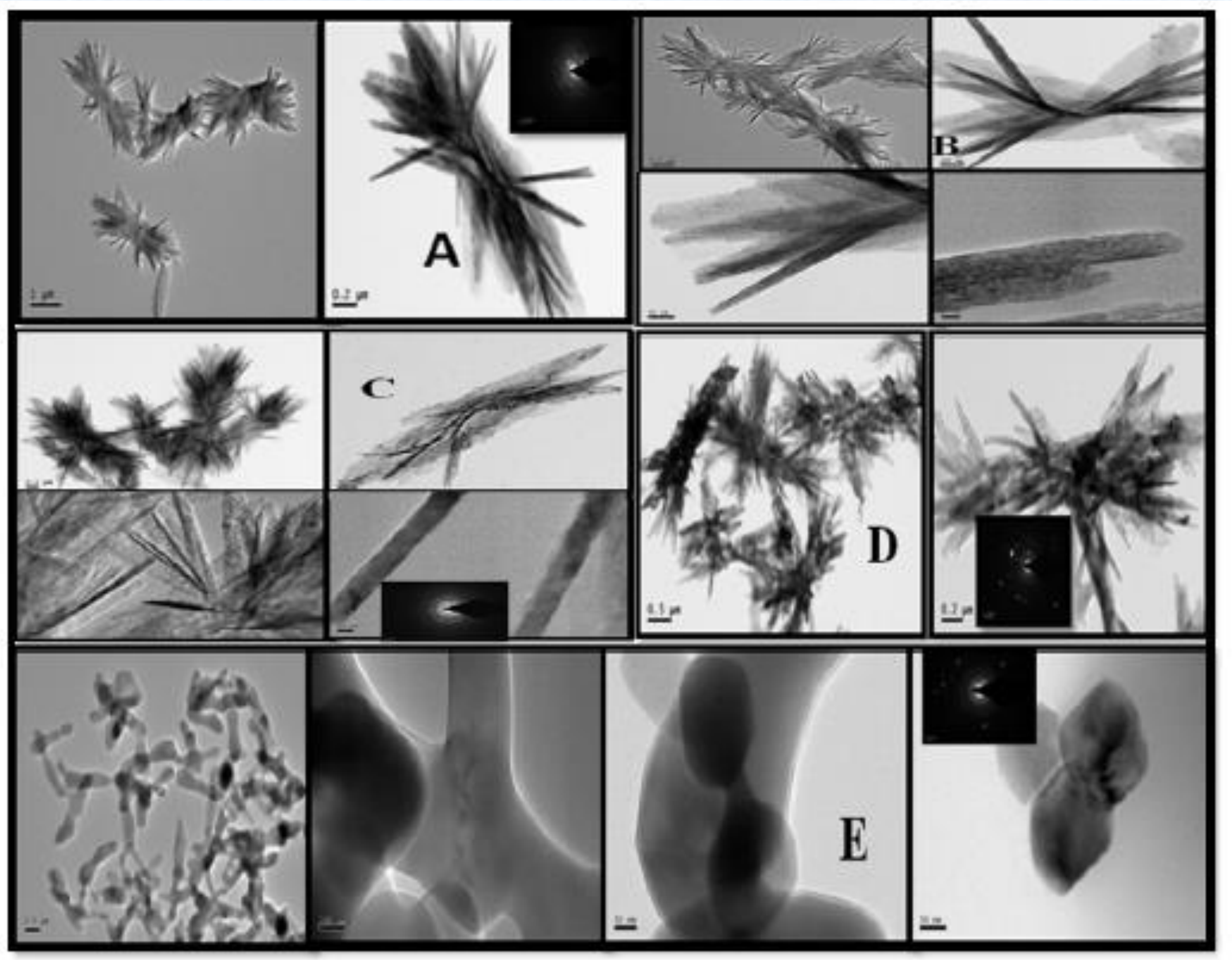
TL glow curves of $K_2Ca_2(SO_4)_3$:Cu samples annealed at different temperatures



PL spectra of the samples irradiated for different doses of γ rays



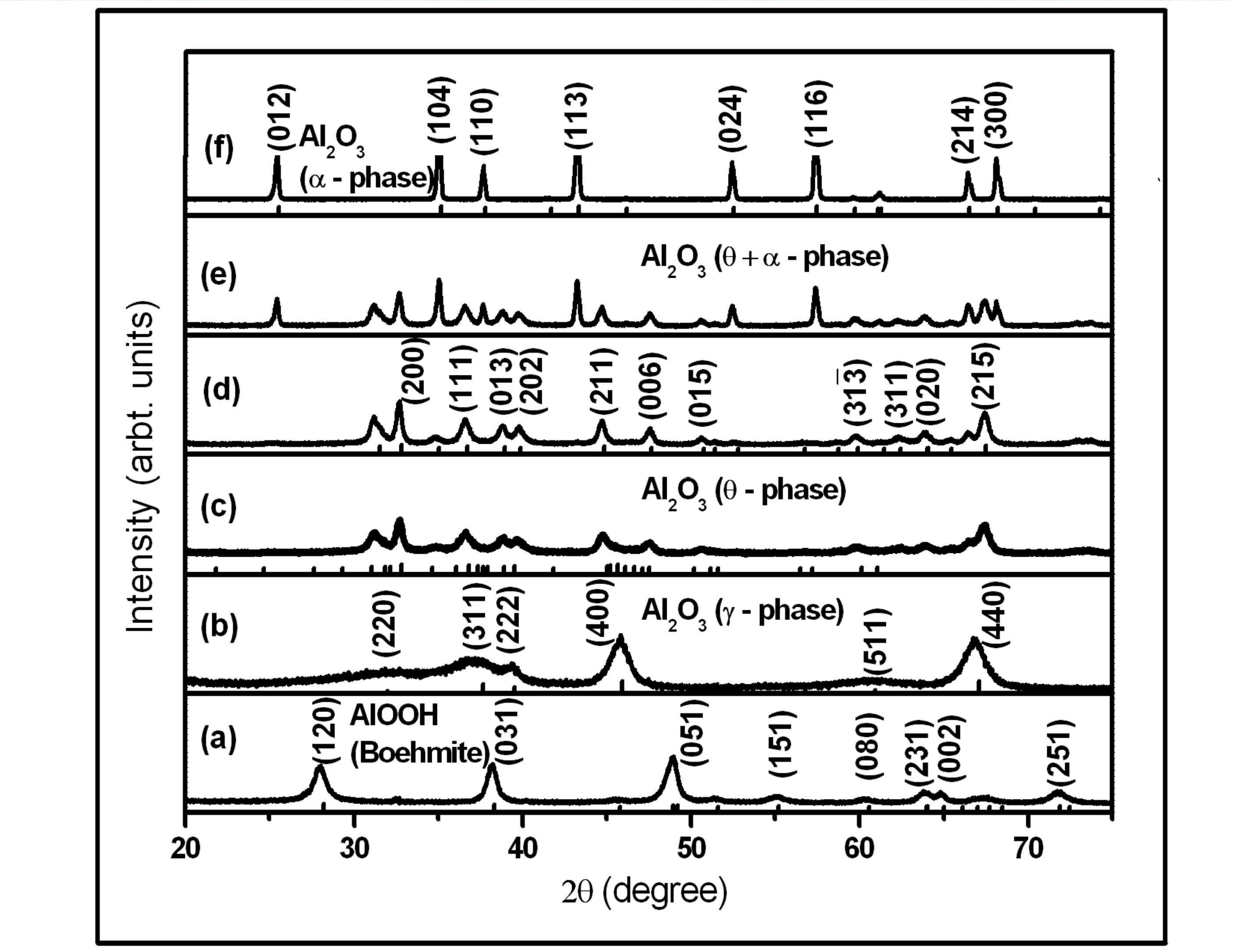
PL spectra of the samples annealed for different temperatures



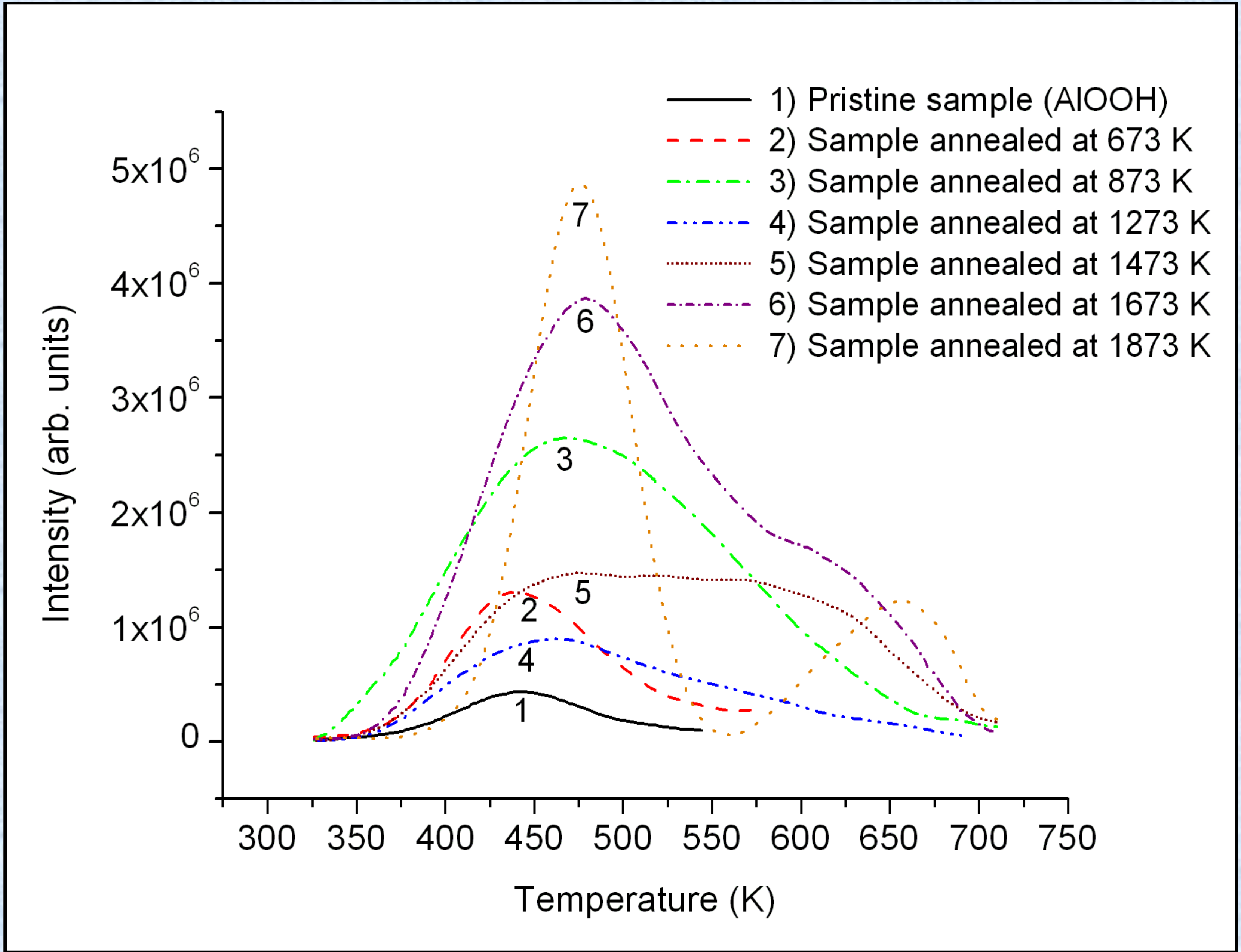
TEM photograph

Al_2O_3

P. D. Sahare and Geeta Rani, J. Lum. (in Press)



XRD of different phases of Al_2O_3



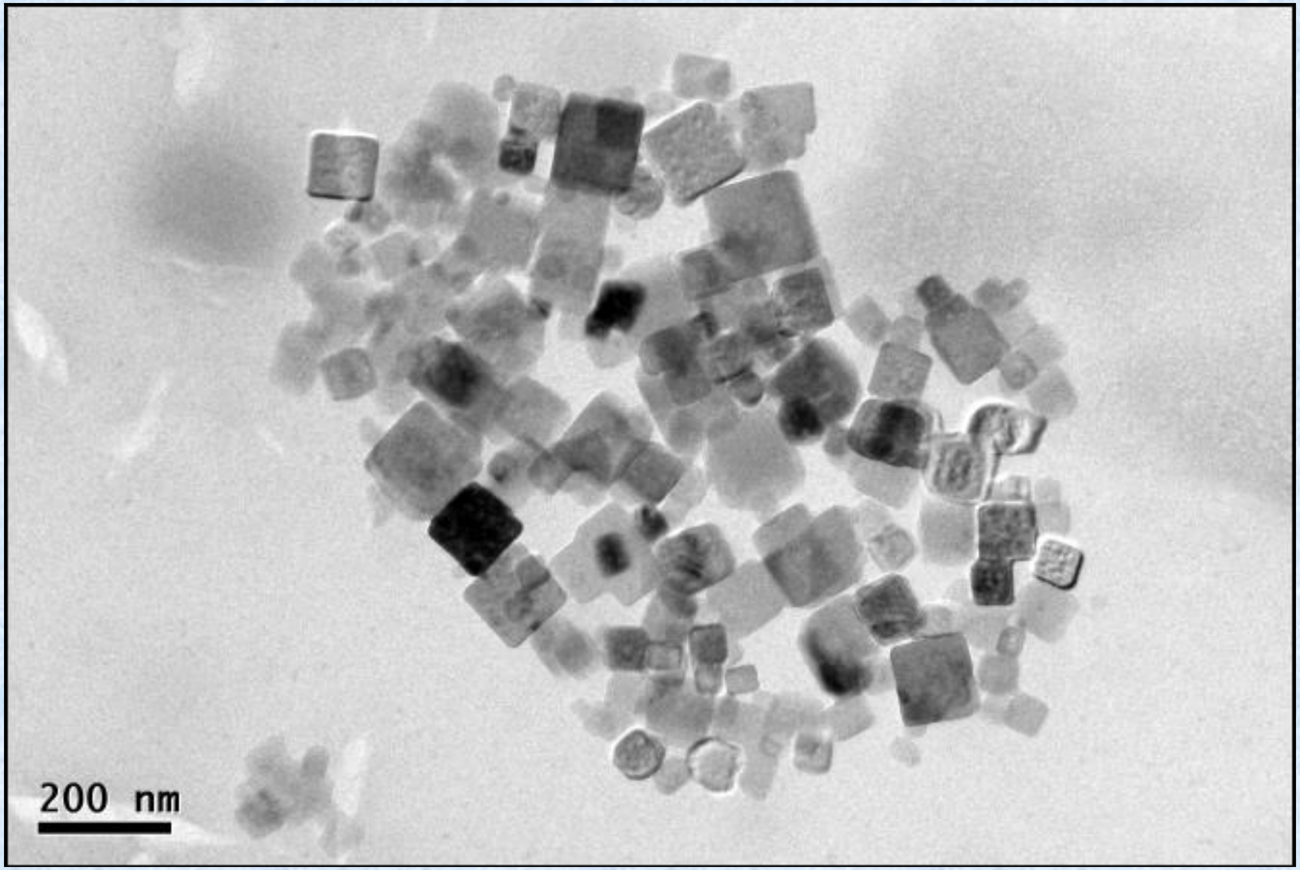
1) Pristine sample (AlOOH)
2) Sample annealed at 673 K
3) Sample annealed at 873 K
4) Sample annealed at 1273 K
5) Sample annealed at 1473 K
6) Sample annealed at 1673 K
7) Sample annealed at 1873 K
Intensity (arb. units)
Temperature (K)

Sample/Phase	Annealing temp. (K)	$T_{max.}$ (K)	E (eV)	S (s^{-1})	b	FOM
AlOOH	373					0.02%
	Peak 1	403	0.35	$2.6x10^{3}$	1.8	
	Peak 2	441	0.69	$1.3x10^{7}$	1.8	
	Peak 3	515	0.67	$5.1x10^{5}$	1.7	
AlOOH	673					0.46%
	Peak 1	436	0.61	$1.7x10^{6}$	1.7	
	Peak 2	491	0.9	$3.8x10^{8}$	1.7	
	Peak 3	565	0.74	$4.4x10^{5}$	1.7	
γ-Al_2O_3	873					0.04%
	Peak 1	398	0.54	$1.1x10^{6}$	1.7	
	Peak 2	459	0.48	$2.4x10^{4}$	1.8	
	Peak 3	534	0.81	$6.1x10^{6}$	1.8	
	Peak 4	597	0.87	$2.6x10^{6}$	1.8	
	Peak 5	700	2.93	$4.1x10^{20}$	1.7	
δ-Al_2O_3	1273					0.03%
	Peak 1	405	0.75	$5x10^{8}$	1.8	
	Peak 2	453	0.6	$6.9x10^{5}$	1.8	
	Peak 3	536	0.46	$1.7x10^{3}$	1.7	
	Peak 4	658	1.85	$3.4x10^{13}$	1.5	
(δ+θ)-Al_2O_3	1473					0.01%
	Peak 1	485	0.67	$1.3x10^{6}$	1.7	
	Peak 2	533	1.49	$3.4x10^{13}$	1.8	
	Peak 3	568	2.21	$1.6x10^{19}$	1.7	
	Peak 4	602	0.75	$2.0x10^{5}$	1.7	
θ-Al_2O_3	1673					0.05%
	Peak 1	421	0.67	$2.5x10^{7}$	1.7	
	Peak 2	473	0.69	$3.8x10^{6}$	1.8	
	Peak 3	543	0.58	$2.4x10^{4}$	1.7	
	Peak 4	635	1.34	$8.5x10^{9}$	1.8	
α-Al_2O_3	1873					0.57%
	Peak 1	476	0.86	$2.5x10^{8}$	1.5	
	Peak 2	616	1.93	$1.6x10^{15}$	1.8	
	Peak 3	663	2.15	$6.5x10^{15}$	1.8	

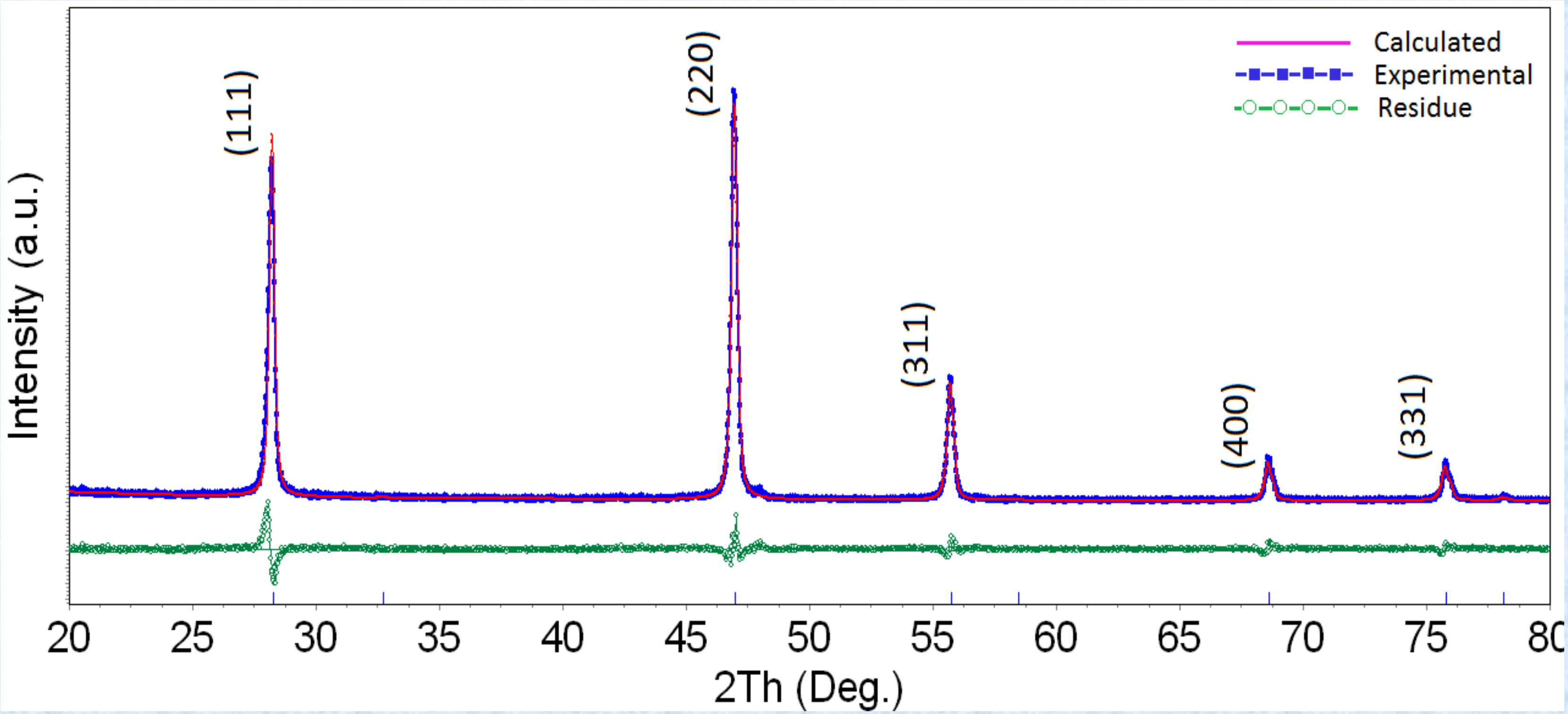
CaF_2: Mn,

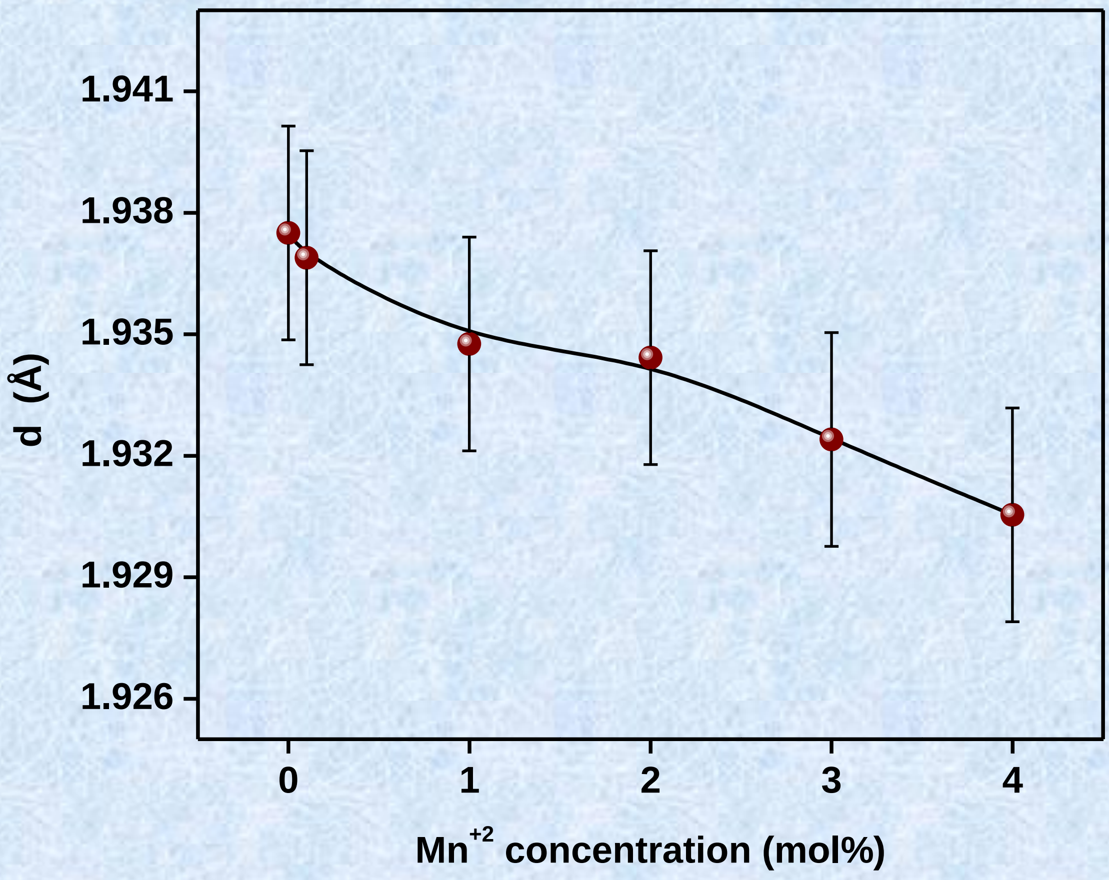
An example of changes in glow curve due to phase changes of the heavily doped impurity in the material

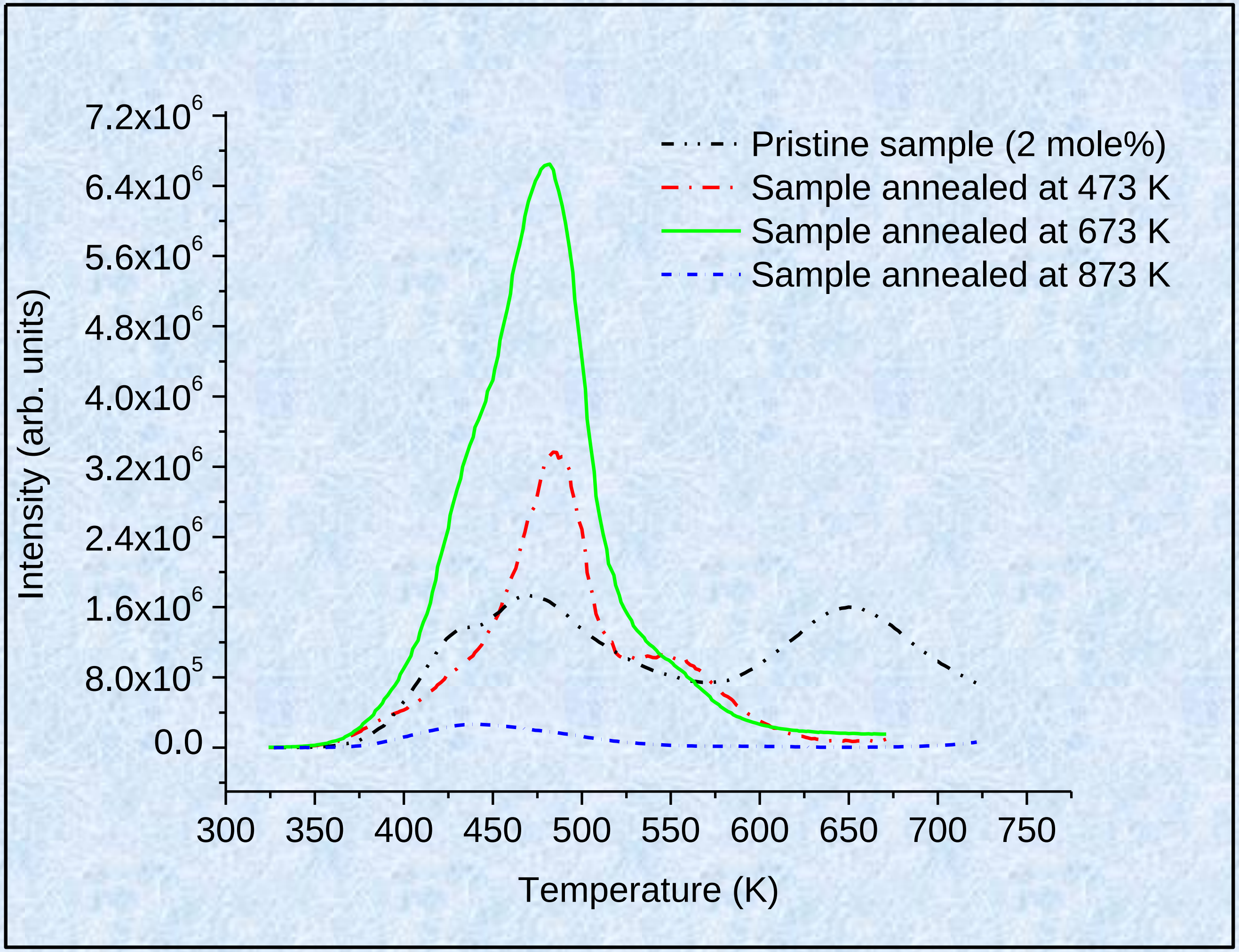
P. D. Sahare and Manveer Singh, J. Appl. Phys. (in Press)



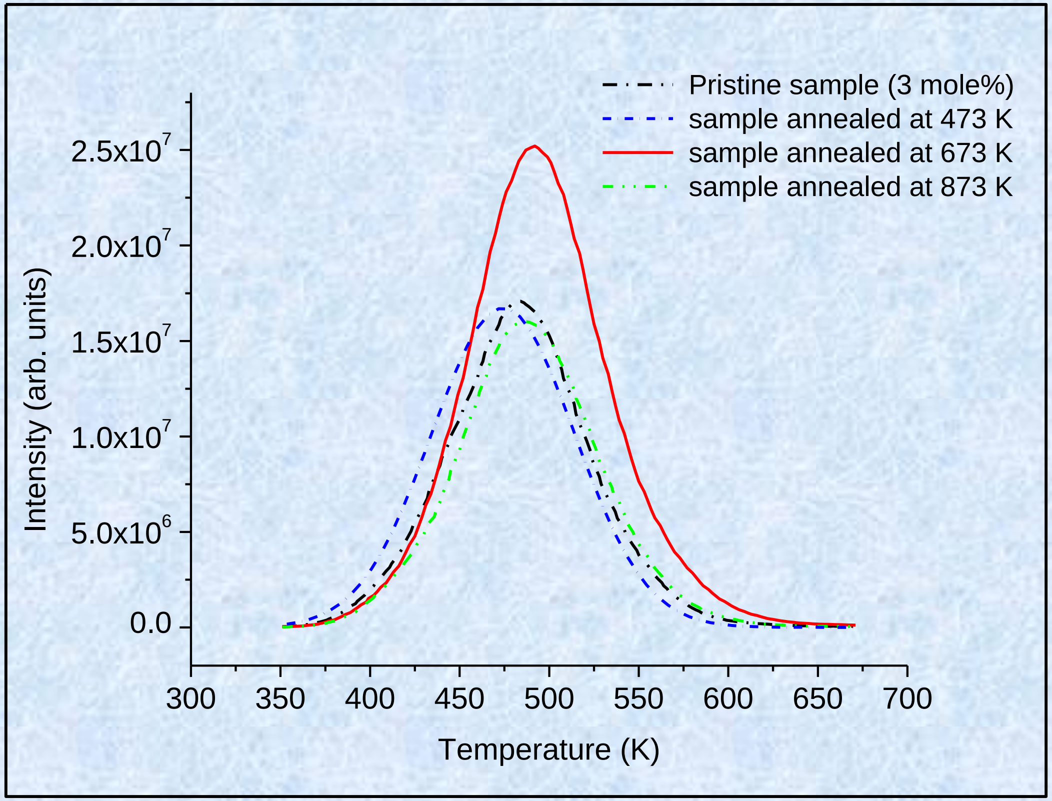
TEM Photograph


Calculated
Experimental
Residue
(111)
(220)
(311)
(400)
(331)
Intensity (a.u.)
20
25
30
35
40
45
50
55
60
65
70
75
80
2Th (Deg.)

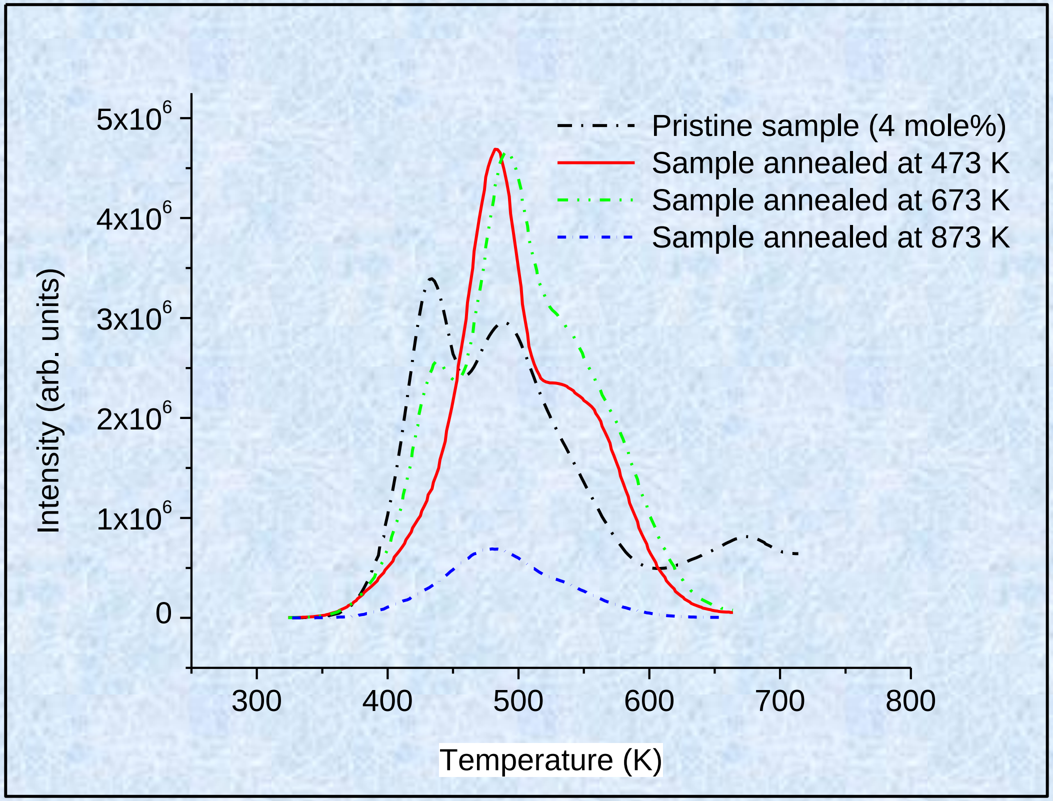

1.941
1.938
1.935
1.932
1.929
1.926
d (Å)
0
1
2
3
4
Mn+2 concentration (mol%)

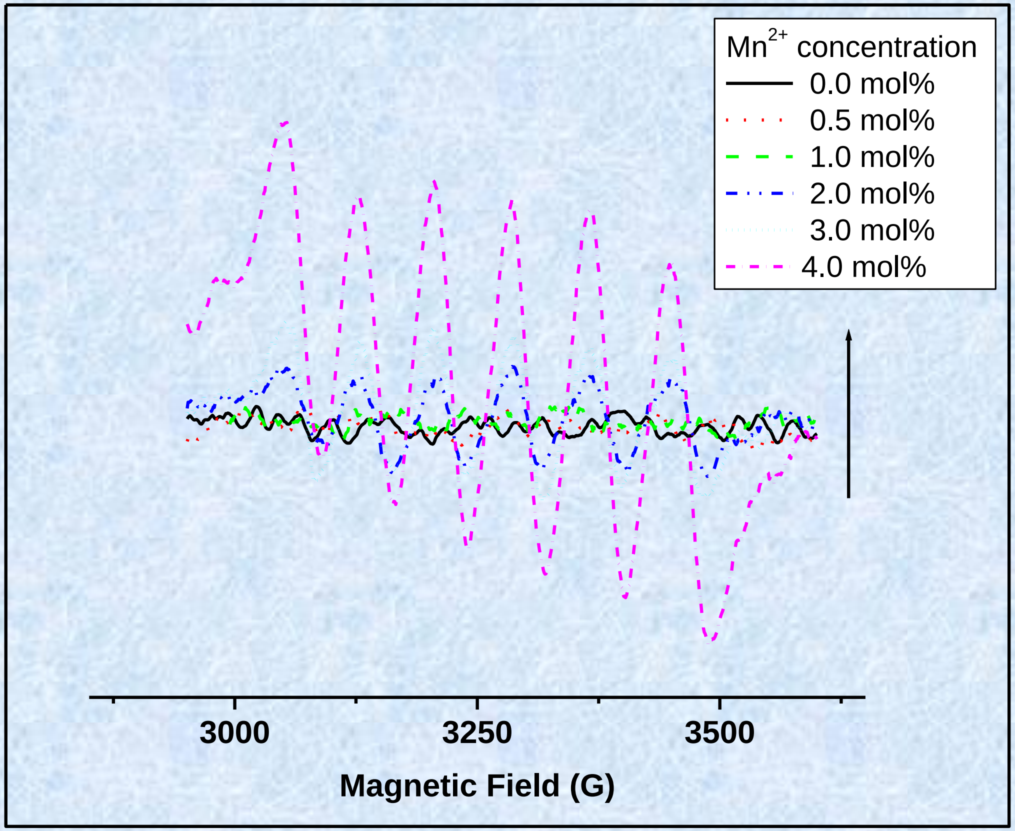


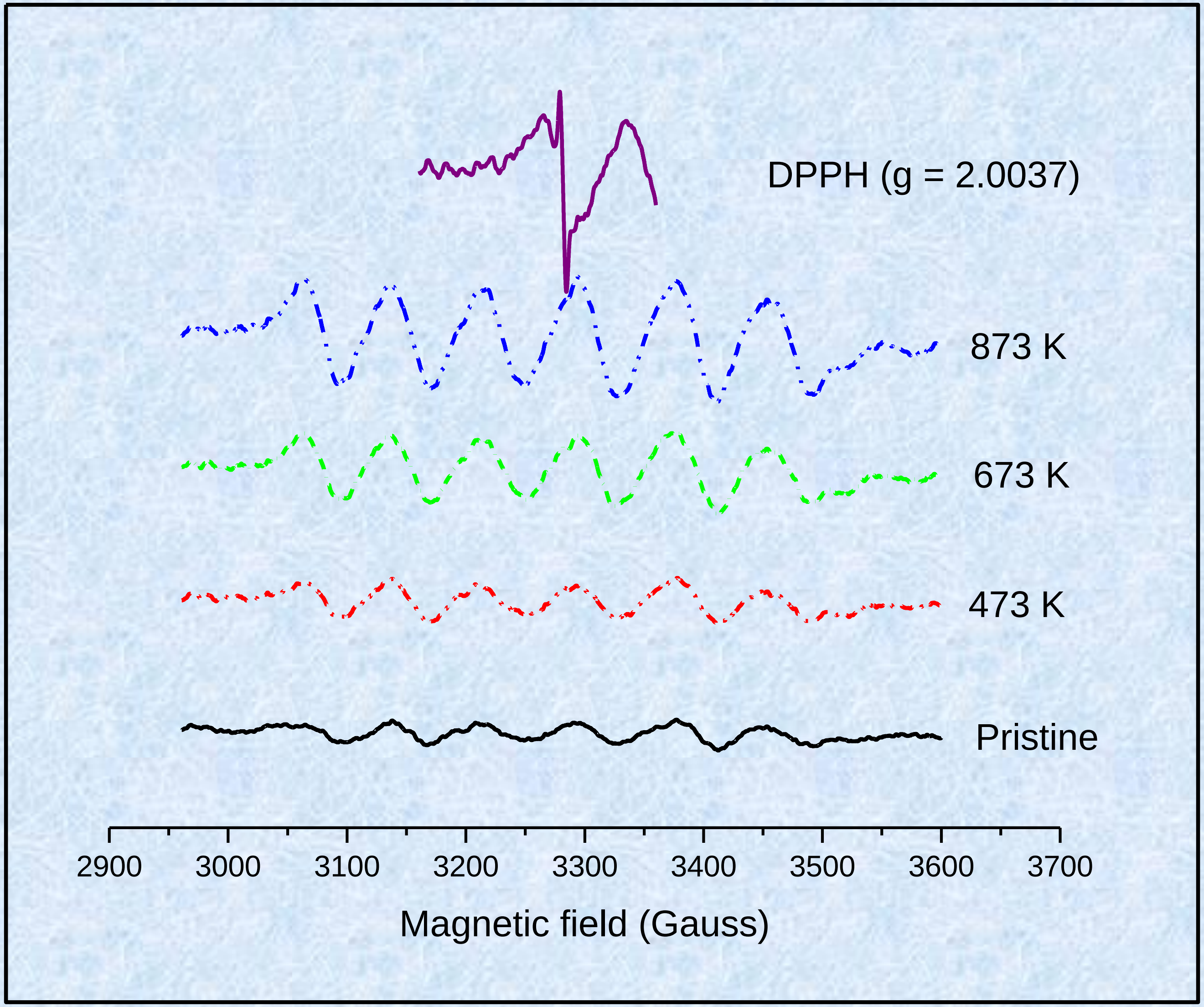
7.2x10^6
6.4x10^6
5.6x10^6
4.8x10^6
4.0x10^6
3.2x10^6
2.4x10^6
1.6x10^6
8.0x10^5
0.0
Intensity (arb. units)
300
350
400
450
500
550
600
650
700
750
Temperature (K)
Pristine sample (2 mole%)
Sample annealed at 473 K
Sample annealed at 673 K
Sample annealed at 873 K

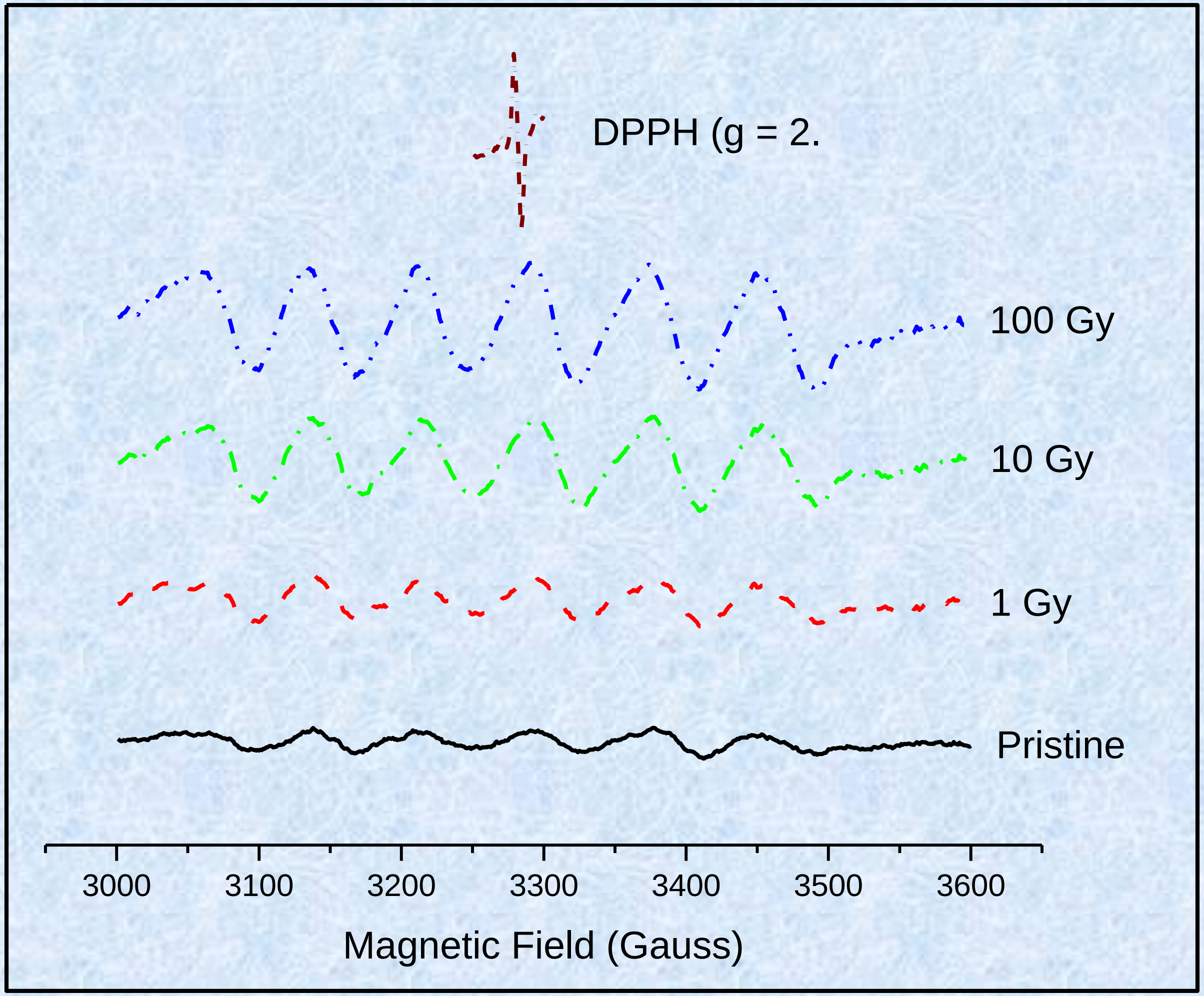


Pristine sample (3 mole%)
sample annealed at 473 K
sample annealed at 673 K
sample annealed at 873 K
2.5x10^7
2.0x10^7
1.5x10^7
1.0x10^7
5.0x10^6
0.0
Intensity (arb. units)
300
350
400
450
500
550
600
650
700
Temperature (K)

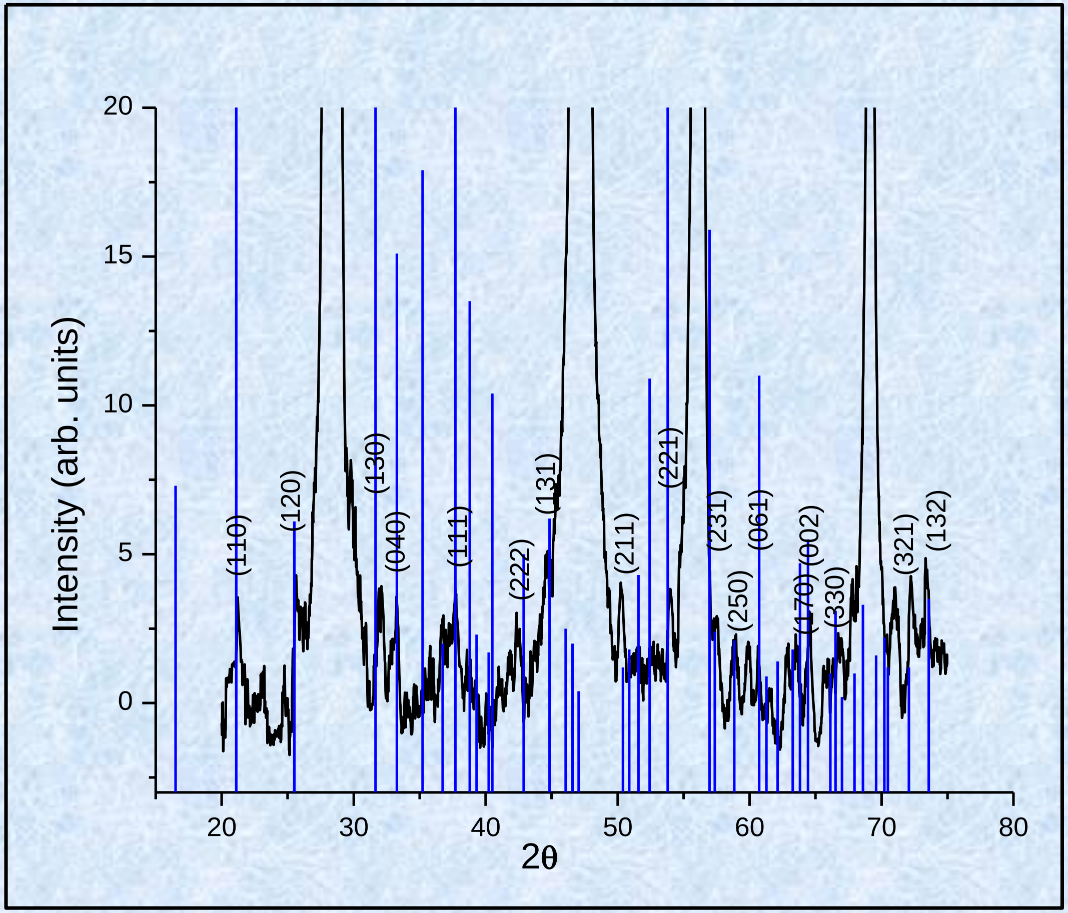

5x10^6
4x10^6
3x10^6
2x10^6
1x10^6
0
Intensity (arb. units)
300
400
500
600
700
800
Temperature (K)
Pristine sample (4 mole%)
Sample annealed at 473 K
Sample annealed at 673 K
Sample annealed at 873 K

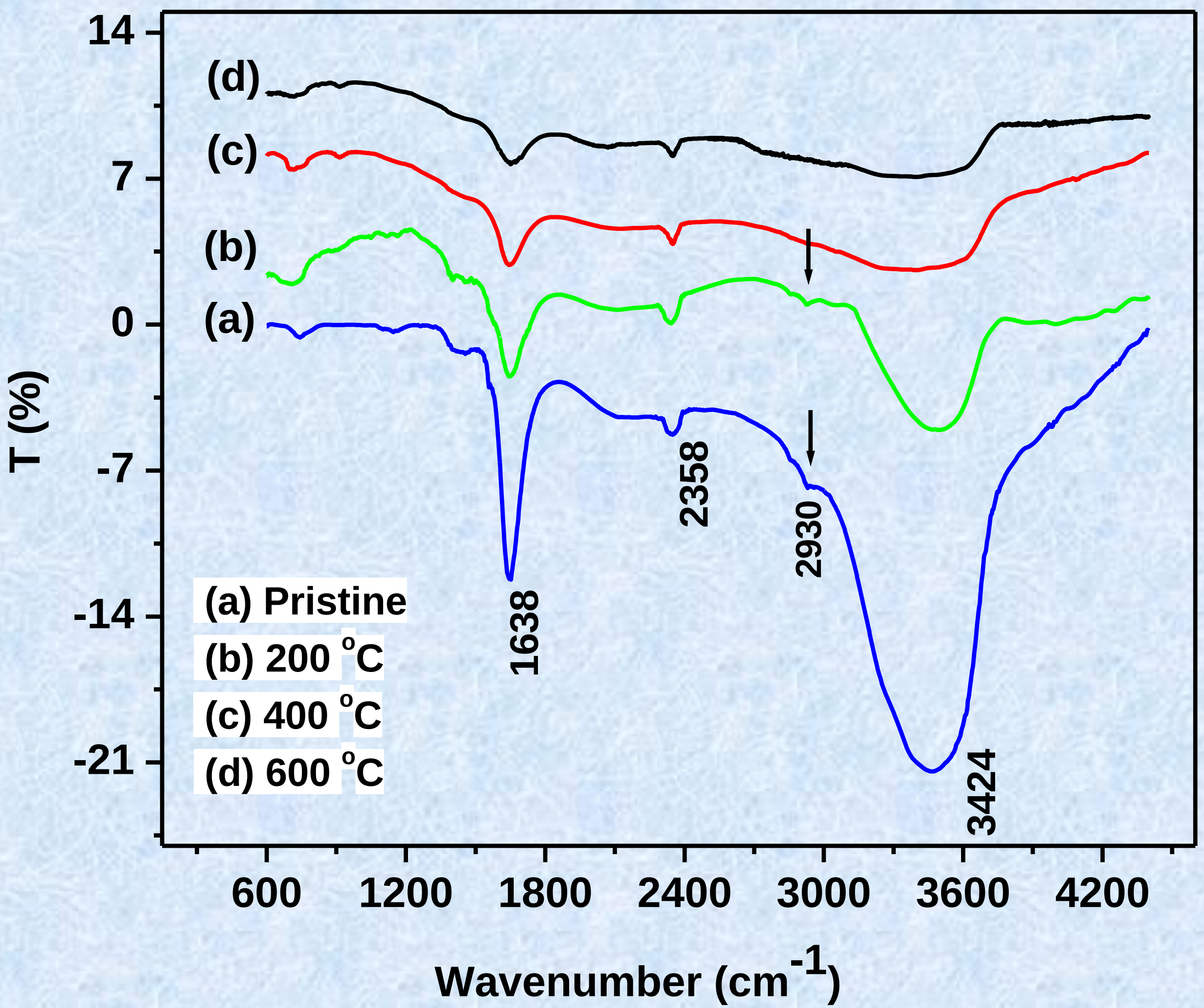

Mn2+ concentration
0.0 mol%
0.5 mol%
1.0 mol%
2.0 mol%
3.0 mol%
4.0 mol%
3000
3250
3500
Magnetic Field (G)


DPPH (g = 2.0037)
873 K
673 K
473 K
Pristine
2900
3000
3100
3200
3300
3400
3500
3600
3700
Magnetic field (Gauss)

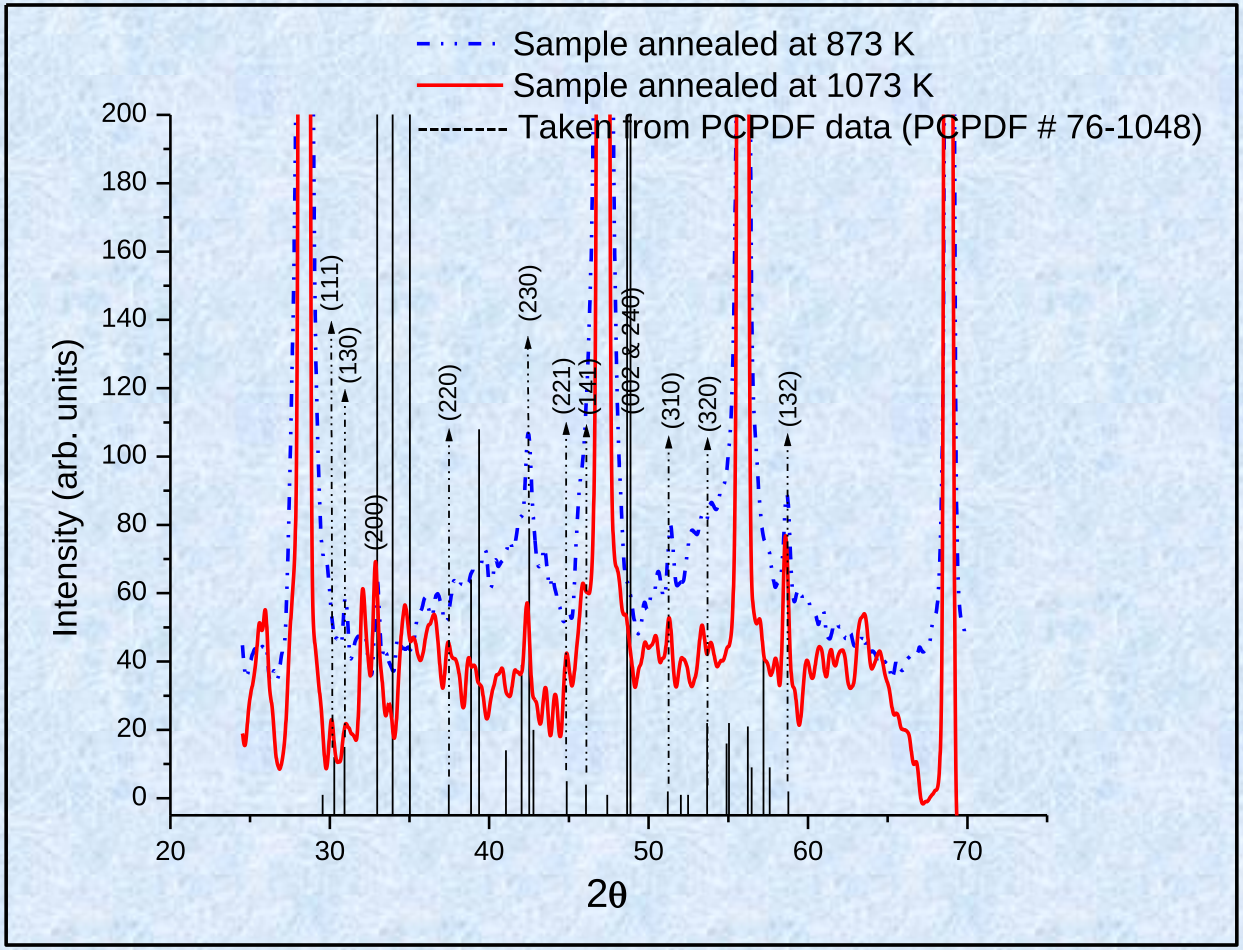

DPPH (g = 2.
100 Gy
10 Gy
1 Gy
Pristine
3000
3100
3200
3300
3400
3500
3600
Magnetic Field (Gauss)

MnOOH impurity phase 4 mole%

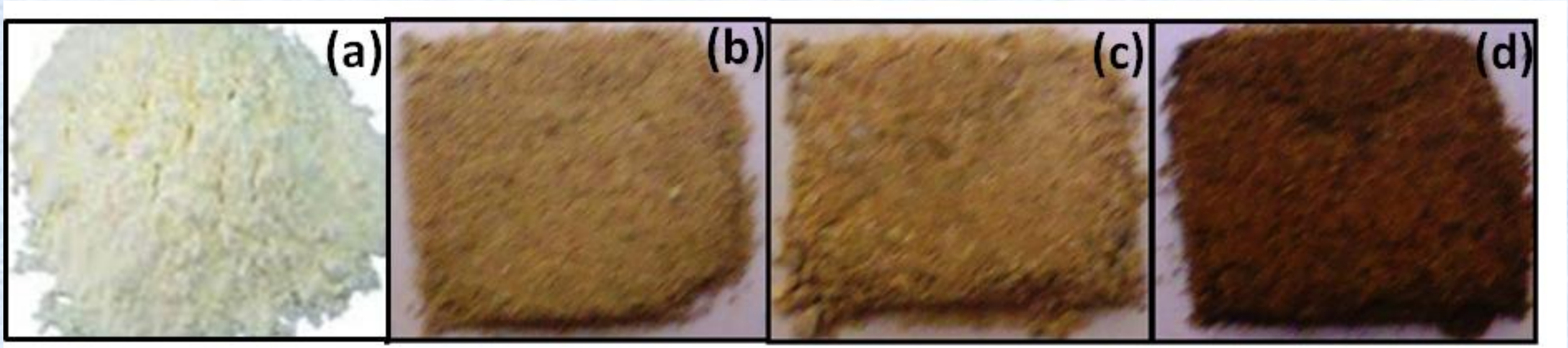



14
7
0
-7
-14
-21
T (%)
(d)
(c)
(b)
(a)
1638
2358
2930
3424
(a) Pristine
(b) 200 ^{o}C
(c) 400 ^{o}C
(d) 600 ^{o}C
600
1200
1800
2400
3000
3600
4200
Wavenumber (cm^{-1})

Formation of the Mn_3O_4 Phase in CaF_2



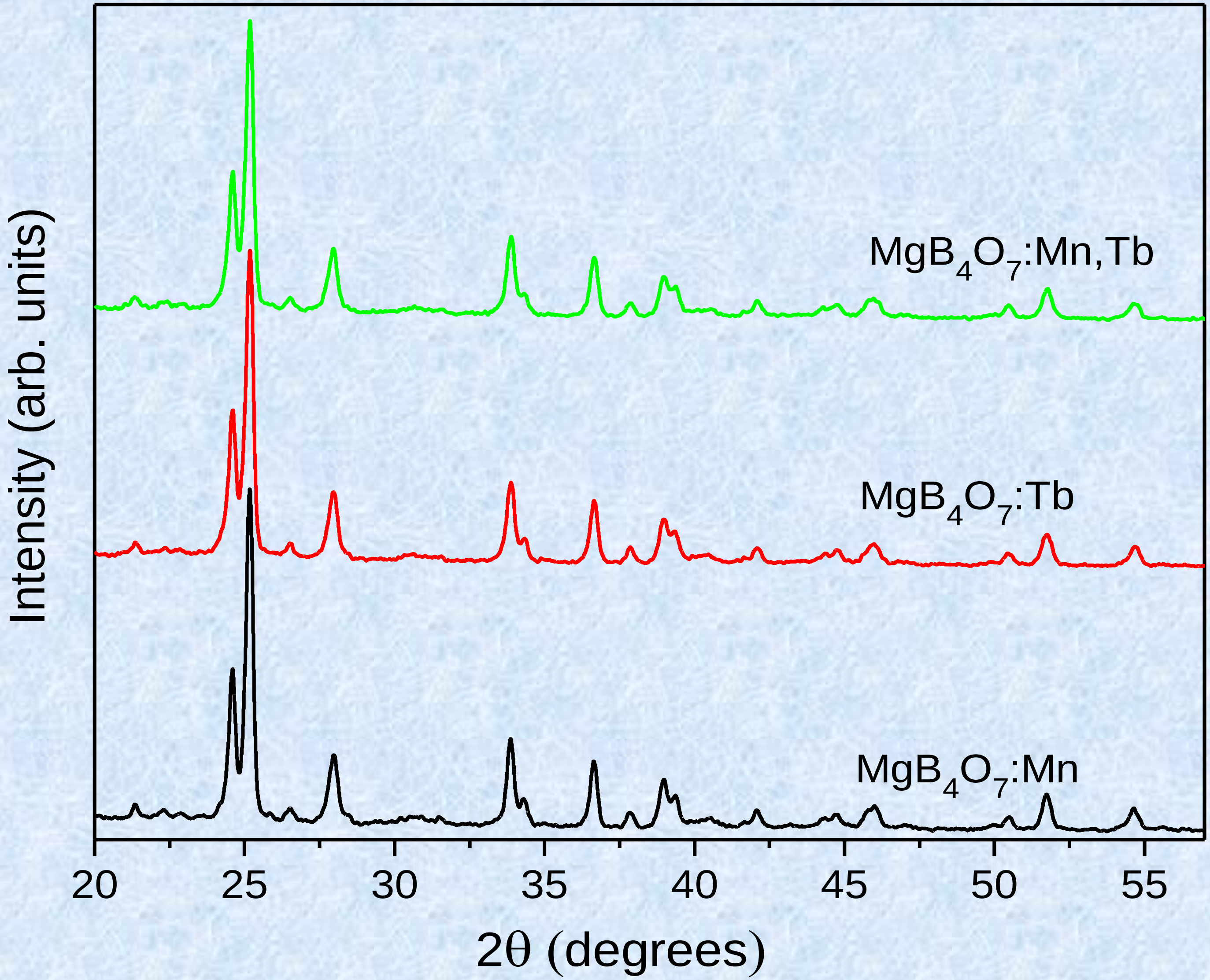
Change in colour on annealing at different temperatures:

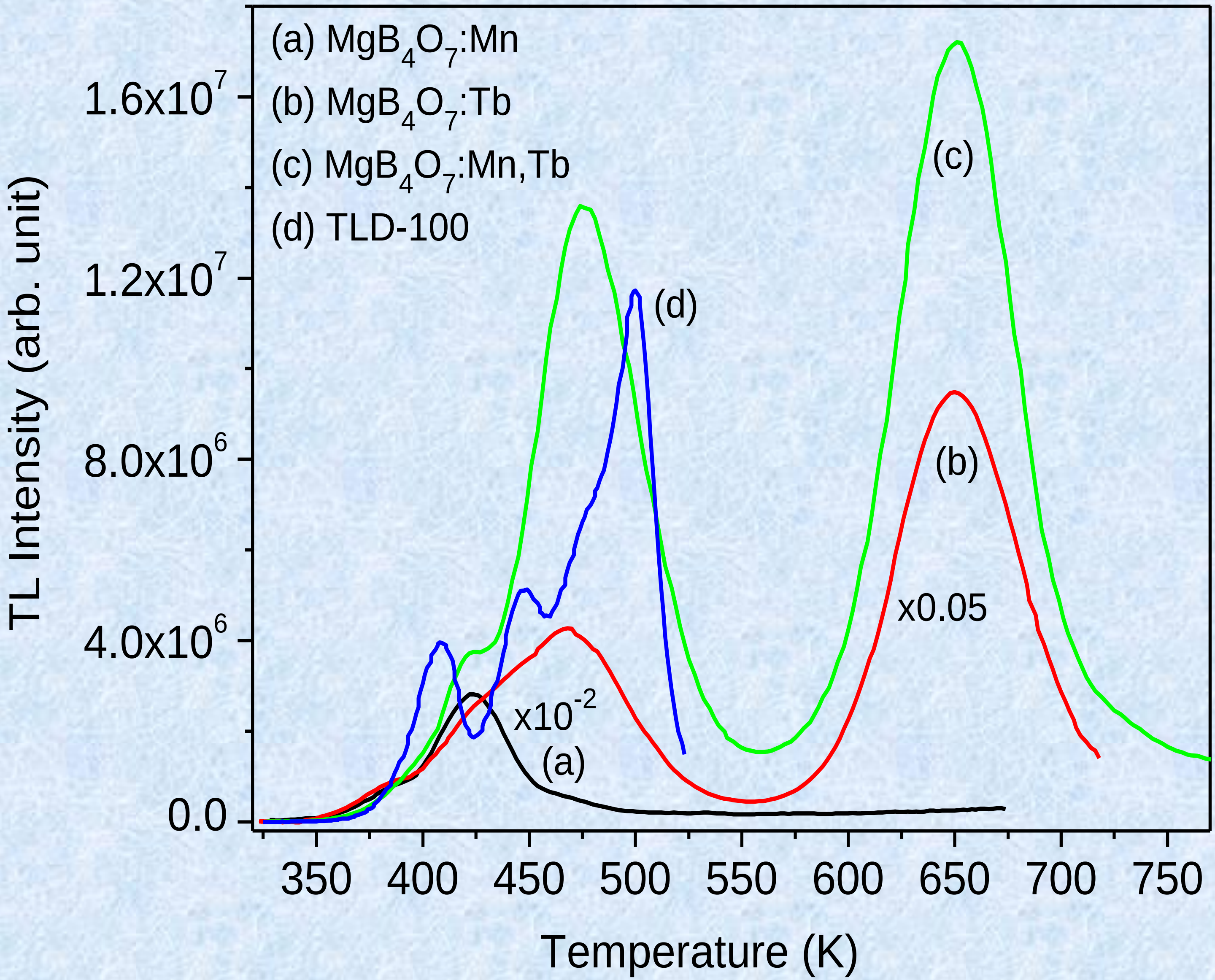


As prepared | Annealed 673 K | Annealed 873 K | Annealed 1073 K

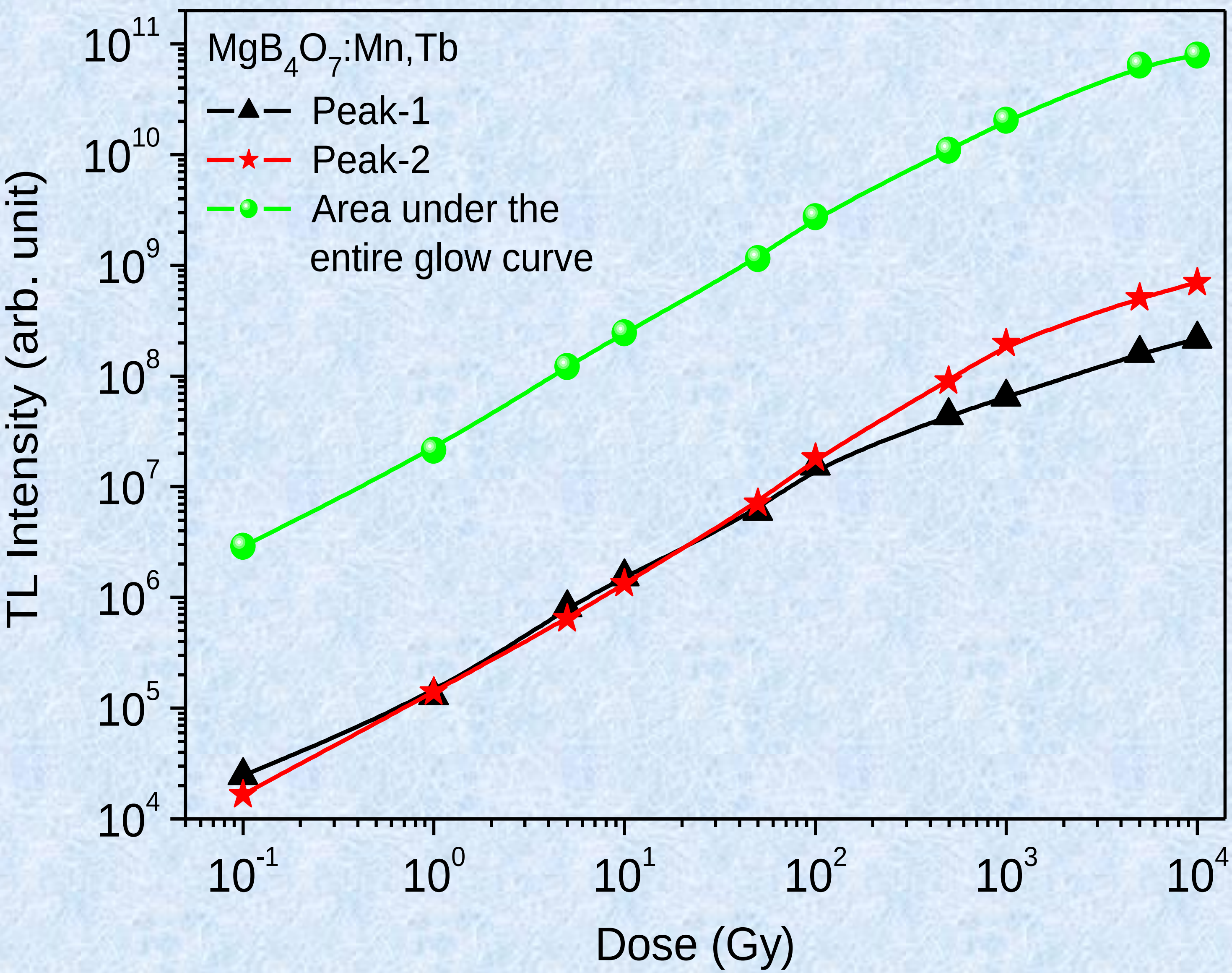
Problem of High fading in Borates

MgB_4O_7:Mn in microcrystalline form could be prepared by simple diffusion method. It has a simple glow curve structure (two well separated TL peaks centered at around 475 and 650 K). They are sufficiently above the room temperature (RT) to show low fading (~10% in a month after storing in dark at RT). However, the fading is much faster, if exposed to sunlight/room light/UV radiation. This has been a serious problem with many borate based phosphors. A detailed study on bleaching to UV-visible light of different wavelengths (energies) has been carried out and a new mechanism based on redox reactions is proposed.

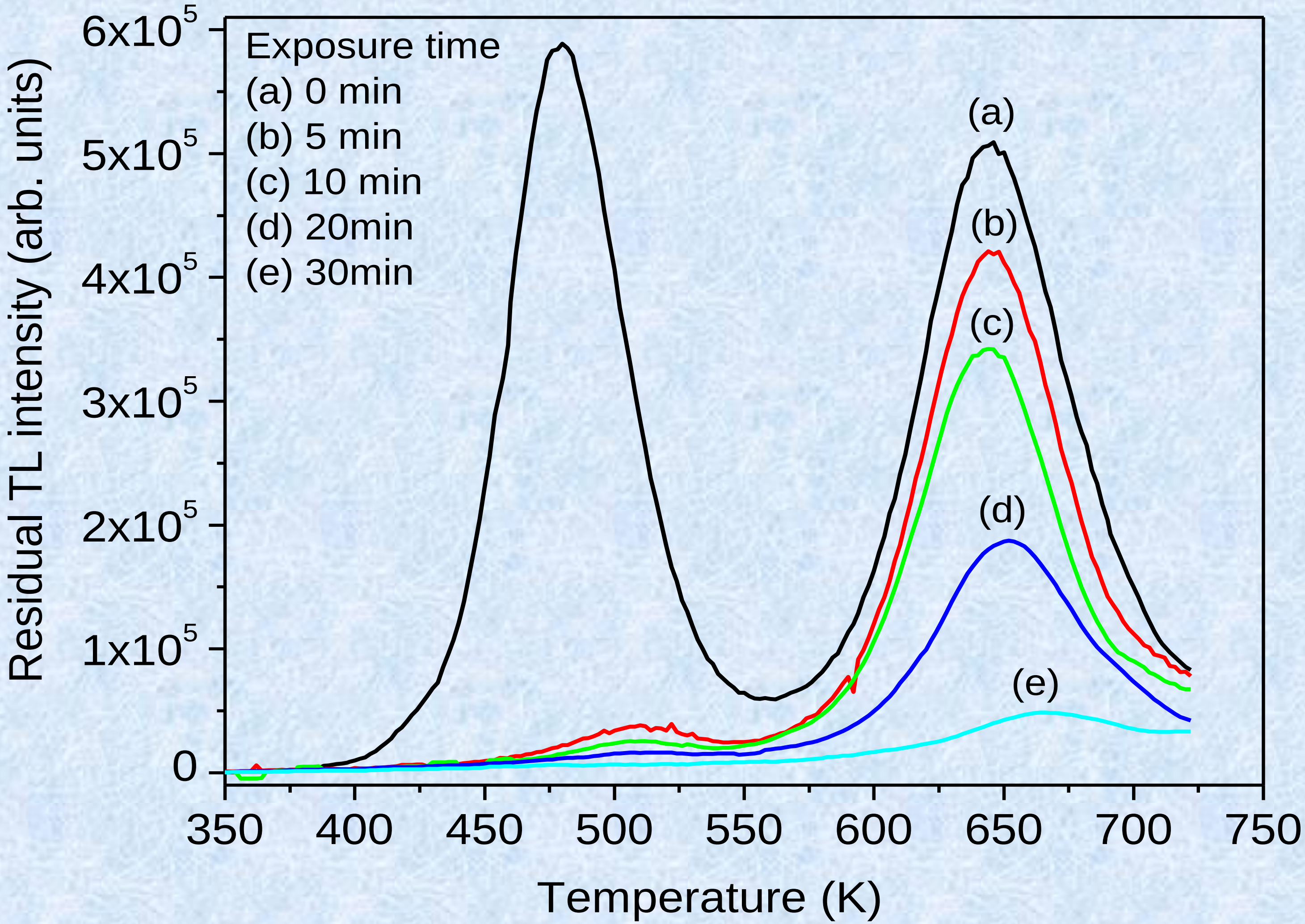

MgB4O7:Mn,Tb
MgB4O7:Tb
MgB4O7:Mn
Intensity (arb. units)
20
25
30
35
40
45
50
55
2θ (degrees)



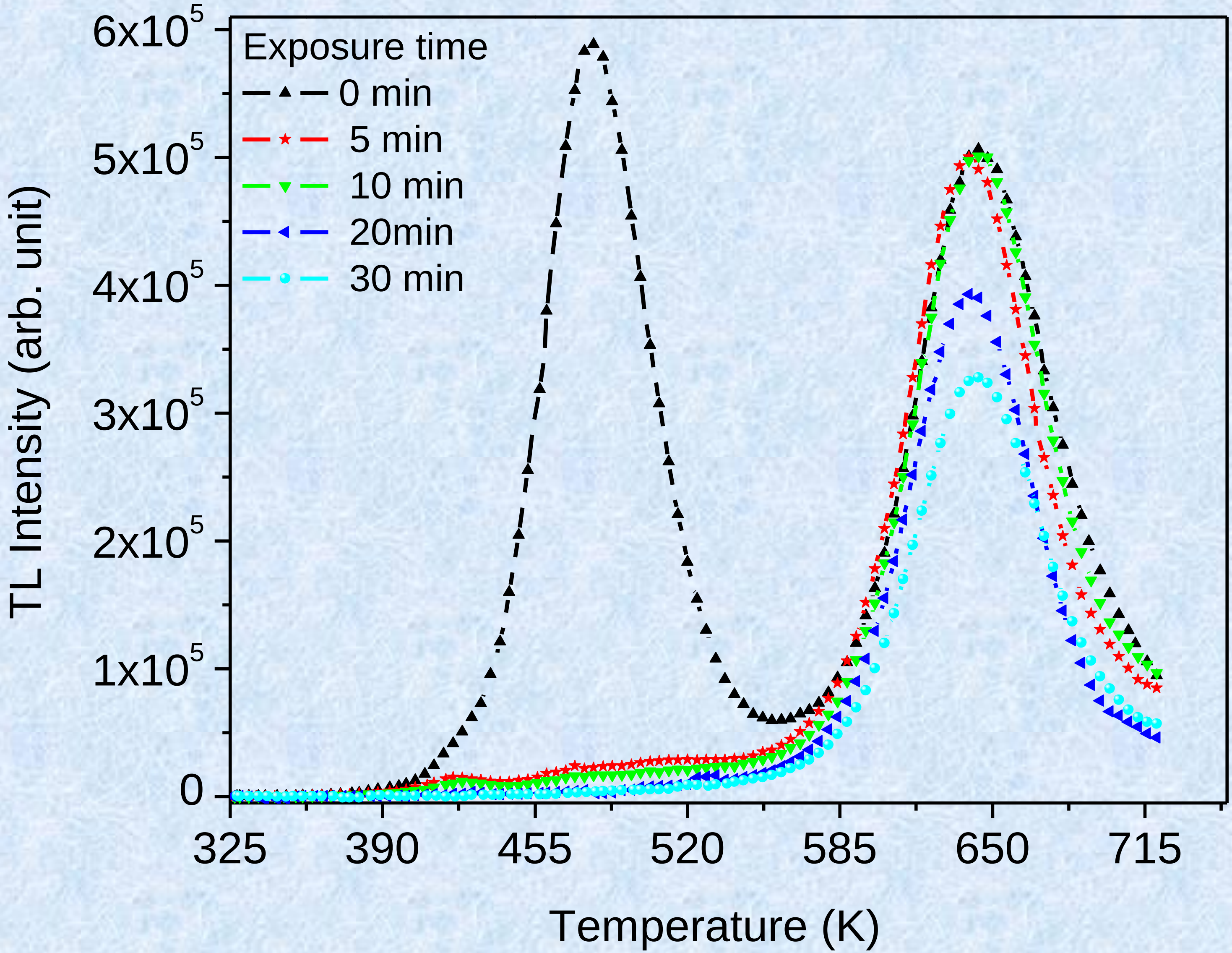
(a) MgB4O7:Mn
(b) MgB4O7:Tb
(c) MgB4O7:Mn,Tb
(d) TLD-100
TL Intensity (arb. unit)
Temperature (K)
1.6x10^7
1.2x10^7
8.0x10^6
4.0x10^6
0.0
350
400
450
500
550
600
650
700
750
(a)
(b)
(c)
(d)
x10^-2
x0.05



10^{11}
10^{10}
10^9
10^8
10^7
10^6
10^5
10^4
TL Intensity (arb. unit)
MgB_4O_7:Mn,Tb
Peak-1
Peak-2
Area under the entire glow curve
10^{-1}
10^0
10^1
10^2
10^3
10^4
Dose (Gy)



Residual TL intensity (arb. units)
6x10^5
5x10^5
4x10^5
3x10^5
2x10^5
1x10^5
0
350
400
450
500
550
600
650
700
750
Temperature (K)
Exposure time
(a) 0 min
(b) 5 min
(c) 10 min
(d) 20min
(e) 30min
(a)
(b)
(c)
(d)
(e)



Exposure time
0 min
5 min
10 min
20min
30 min
TL Intensity (arb. unit)
0
1x10^5
2x10^5
3x10^5
4x10^5
5x10^5
6x10^5
325
390
455
520
585
650
715
Temperature (K)

Reasons for high fading in borates:

Stimulation of traps by UV exposure and even generation some radicals such, BO_2^{2-}, O^-, O_2^-, O_3^-, O_2^+ and $[O_V]^-$ by UV radiation in borate materials could also be the reasons responsible for fast fading as observed in the present case and in other several cases. The borate TLD phosphor materials, therefore, should in general be protected from room/sun light to avoid fast fading.

- **Concluding Remarks**

  Nanocrystalline phosphors are a bit less sensitive to ionizing radiation at low doses but it is also an advantage as they do not saturate for high doses,

They also have other good characteristics:

- ► Their studies are useful using TL technique for more information about the phenomenon of TL.
- ► They have a good sensitivity and linear response over a large span of exposures and Less fading.
- ► Easy method of preparation.
- ► They could be used to estimate doses from very low to very high values.
- ► All the above characteristics make them good TLD.

Thank you