Development of CaF_2 based Glass Ceramic.

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

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By

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NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

2010

CERTIFICATE

This is to certify that the thesis entitled, **“**Development of CaF_2 based Glass Ceramic**”** submitted by Ms. Priya Darshini Jani, (Roll no:10608007) in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date: 07.05.2010

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1. ABSTRACT

In the present work the glass of composition 40 % SiO_2, 5 % Al_2O_3, 15 % Na_2O, 5 % CaO , 12,5 % NaF , 21 % CaF_2 and 1.5 % Sb_2O_3 (mol%) was prepared to investigate the crystallization of CaF_2 in the parent glass matrix. To accelerate the crystallization and to develop the up conversion fluorescence property Er_2O_3 was doped in 0.5% , 1 % and 1.5 % (mol%). The casted glass was subjected to thermal treatment between 600 – 750°C. To observe the effect of rare earth on crystallization glass samples were examined in DSC. Spectroscopic property of the base glasses were studied using UV-Visible spectrophotometer. Phase authentication was carried out using X-Ray diffraction analysis.

2. Introduction

The rare-earth doped solid-state upconverter can find applications in numerous photonic devices including color displays, upconversion lasers, sensors, infrared laser viewers, and optical data storage etc. For these applications rare earth doped oxyfluoride transparent nano glass ceramics, are more appropriate for practical applications due to their low phonon energies compared to oxide glasses as well as excellent chemical durability and mechanical strength compared to fluoride glasses. Since long highly efficient upconversion luminescence of rare earth ions are obtained in PbF_2 and CdF_2 nano-crystals. Today, the demand for alternative materials of Pb and Cd is growing, since they have been designated as toxic substances. CaF_2 can be considered as alternative material for PbF_2 and CdF_2. Therefore, the effect of rare earth doping into CaF_2 nano-crystals in oxide glass matrix are of scientific and technical interest.

The present work aims to develop the CaF_2 nano crystals in silicate glassy matrix and study of the effect of Er^{3+} doping upon crystallization behavior and spectroscopic properties.

3. Literature review

Rare-earth doped low phonon optical glasses are important materials for infrared solid lasers, optical broadband amplifiers, upconversion laser, and visible display devices etc. For this purpose the glassy host is required to possess a minimal absorption coefficient within the wavelength region of interest, plus the capability of incorporating large rare earth concentrations, low vibrational energies, transparency and a high refractive index**.**

Advantages of conventional glass and glass ceramic processing are as follows:

1. Glasses can be synthesized in various shapes and without the same size limitation by melt quenching method. No costly instrument is required for fabrication of glassy materials
2. For practical applications, oxide glasses have an advantage superior to fluoride glasses due to their chemical durability, thermal stability, and mechanical strength.
3. It is well recognized that crystallization of glass is one of the effective methods for fabrication of nanostructures

But Limitation of oxide glasses are

1. the maximum doping level is limited due to rare-earth (RE) clustering tendency
2. large phonon energy of these oxide glasses increases the non radiative decay rate that reduces the luminescence efficiency

One the other hand fluorides materials have the following advantages.

1. Fluoride material can offer a low phonon environment favorable to enhance the radiative rate and quantum efficiency.
2. Fluoride single crystals can produce narrow fluorescence line widths and enhanced emission cross sections relative to glasses.
3. Fluoride nano crystal is preferred over the oxide one mainly to avoid non-radiative transitions [1].
4. The solubility of the rare earth is also larger in the fluoride medium than in the oxide [2].

But poor chemical and mechanical properties and low laser damage threshold make fluorides unsuitable for practical use and also are costly to produce. Fluoride crystals also have maximum size limitation.

The invention of rare earth ions-doped transparent oxyfluoride glass ceramics containing fluoride nanocrystals have attracted great interest due to their excellent optical properties like fluoride crystals and good mechanical, chemical properties like oxide glasses. The advantages of these materials are that the rare earth ions are incorporated selectively in the fluoride crystal phase with lower phonon energy after heat-treatment and the material remains transparent due to much smaller size (which is essentially in nanometer range) of precipitated crystals than the wavelength of visible light.

The portioning of rare-earth ions into fluoride crystalline environment with large band gap and low phonon energy is necessary for the enhancement of up-conversion fluorescence properties of oxyfluoride glass ceramics. It is well known that, besides the rare earth ions concentration, the thermal treatment conditions, and the microstructure of glass ceramics, also affect the up-conversion fluorescence of the material.

According to Judd-Ofelt theory, the enhancement of up conversion is attributed to the decrease in parameter Ω_2 [3,4] Ω_2 is sensitive to the environmental configuration symmetry of rare-earth ions, and it decreases with the changing of the host from a covalent bond with the oxide ligand to a predominantly ionic bond with the fluorides [5]. With the increasing of thermal treatment temperature, the volume fraction of crystals as well as the crystallinity of fluoride nano-crystals containing rare earth ions increases, thereby causing more rare earth ions to be located at a more symmetrical site, which results in the decrease of Ω_2. With an increase in the heating temperature, the emission lifetime, the quantum efficiency and the intensities of near-infrared and up-conversion emissions increases significantly, due to the fact that more fraction of rare earth ions incorporated into the precipitated fluoride nano-crystals of lower phonon energy. It is well known that the upconversion luminescence of rare earth ions is usually baffled by the multiphonon relaxation. The multiphonon relaxation probability depends primarily upon the energy gap between two successive levels and the phonon energy of the host [6] The smaller is the phonon energy of the host, the lower is the multiphonon relaxation probability.

Thus it can be concluded that the luminescence properties of rare earth ions in transparent glass ceramic systems strongly depend on the chemical composition of the host and the thermal treatment conditions. Even a slight component modification of the host matrix or a change of annealing time and temperature influence glass devitrification and the degree of rare earth incorporation into the crystalline phase. The local environment and its modification, as well as the concentration and distribution of the optically active ions in the crystalline and noncrystalline part of the host matrix affect the emission parameters like intensity, efficiency, cross section, line width, and lifetime. These parameters play an important role for selection of the rare earth doped luminescent materials.

Er^{3+} ion is one of the most useful rare earth dopants because it can be utilized as fiber amplifiers of 1.5 μm telecommunication range and for the upconversion lasers of visible green emission. Thus it is interesting to investigate the evolution of spectroscopic properties of CaF_2 containing oxyfluoride glass ceramic doped with Er^{3+} ions in this materials. A schematic energy diagram of different energy level of Er^{3+} ion is presented in Fig.1.

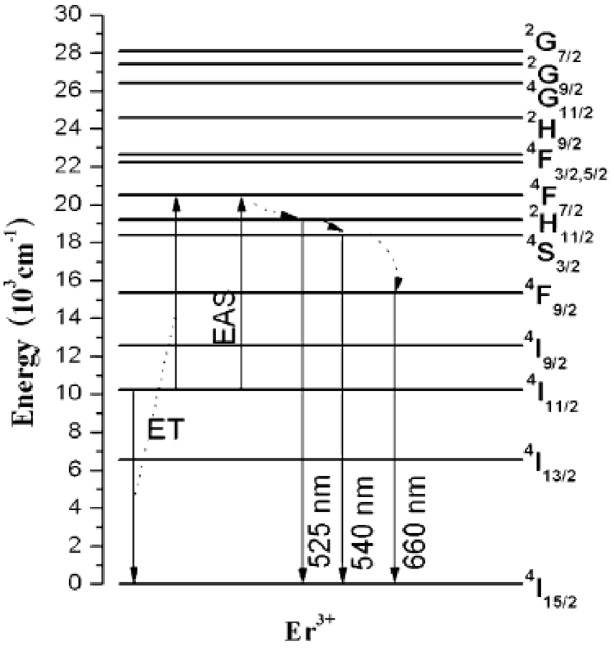

Fig 1: Simplified energy-level diagram of Er^{3+} ions and the possible up conversion mechanisms

Till now various researchers has already worked on different aspects of CaF_2 based transparent Glass ceramics which are listed below

Authors	Titles	Year	Journals
Sun, X.-y., Huang, S.-m.	Tb^{3}+-activated SiO_2-Al_2O_3-CaO-CaF_2 oxyfluoride scintillating glass ceramics	2010	Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment
Wang, R., Zhou, J., Li, B., Li, L.	CaF_2-AlF_3-SiO_2 glass-ceramic with low dielectric constant for LTCC application	2010	Journal of Alloys and Compounds 490 (1-2), pp. 204-207
Lakshminarayana, G., Yang, R., Mao, M., Qiu, J., Kityk, I.V.	Photoluminescence of Sm^{3}+, Dy^{3}+, and Tm^{3}+-doped transparent glass ceramics containing CaF_2 nanocrystals	2009	Journal of Non-Crystalline Solids 355 (52-54), pp. 2668-2673
Secu, M., Secu, C.E., Polosan, S., Aldica, G., Ghica, C.	Crystallization and spectroscopic properties of Eu-doped CaF_2 nanocrystals in transparent oxyfluoride glass-ceramics	2009	Journal of Non-Crystalline Solids 355 (37-42), pp. 1869-1872
Sun, X.-y., Gu, M., Huang, S.-m., Jin, X.-j, Liu, X.-l., Liu, B., Ni, C.	Luminescence behavior of Tb^{3}+ ions in transparent glass and glass-ceramics containing CaF_2 nanocrystals	2009	Journal of Luminescence 129 (8), pp. 773-777
Păcurariu, C., Lazău, R.I., Lazău, I., Ianoş, R., Tița, B.	Non-isothermal crystallization kinetics of some basaltic glass-ceramics containing CaF_2 as nucleation agent	2009	Journal of Thermal Analysis and Calorimetry 97 (2), pp. 507-513
Chen, Y.-Y., Lu, A.-X.	Crystallization kinetics and microstructures of NaF-CaF_2-Al_2O_3-SiO_2 glass-ceramics	2009	Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals 19 (5), pp. 887-893
Babu, P., Jang, K.H., Kim, E.S., Shi, L., Seo, H.J.	Optical properties and White-light emission in Dy^{3}+-doped transparent oxyfluoride glass and glass ceramics containing CaF_2 nanocrystals	2009	Journal of the Korean Physical Society 54 (4), pp. 1488-1491
Kanno, M., Honma, T., Komatsu, T.	Two-Dimensional mapping of Er^{3}+ photoluminescence in CaF_2 crystal lines patterned by lasers in oxyfluoride glass	2009	Journal of the American Ceramic Society 92 (4), pp. 825-829

3.1 Reference:

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6. R. Reisfeld, L. Boehm, Y. Eckstein, N. Lieblich, J. Lumin. 10 (1975) 193

4. OBJECTIVES OF THE THESIS

1. Development of rare earth doped CaF_2 based glass and glass ceramic.
2. Effect of Rare earth on crystallization behavior of glass ceramics
3. Study of spectroscopic properties.

5. EXPERIMENTAL WORK

5.1 BATCH COMPOSITION PROVIDED

Compositions of various glass-ceramic were studied in order to choose appropriate composition for our purpose. While going through different journals, following observations were made which reflects the effects of various chemicals on bioactivity of glass and glass ceramics.

Some of standard composition glass-ceramics are in Table1.

PARENT BATCH COMPOSITION

ELEMENT	MOLE%
SiO_2	40
Al_2O_3	5
Na_2O	15
CaO	5
NaF	12.5
CaF_2	21
Sb_2O_3	1.5

BATCH 1 : 20gm (0.5Er_2O3)

ELEMENT	MOLE%
SiO_2	40
Al_2O_3	5
Na_2O	15
CaO	5
NaF	12
CaF_2	21
Sb_2O_3	1.5
Er_2O_3	0.5

Now, Er_2O_3 is being doped with varying in amount

BATCH 2 : 20gm ($1Er_2O_3$)

ELEMENT	MOLE%
SiO_2	40
Al_2O_3	5
Na_2O	15
CaO	5
NaF	11.5
CaF_2	21
Sb_2O_3	1.5
Er_2O_3	1

BATCH 3 : 20gm ($1.5Er_2O_3$)

ELEMENT	MOLE%
SiO_2	40
Al_2O_3	5
Na_2O	15
CaO	5
NaF	11
CaF_2	21
Sb_2O_3	1.5
Er_2O_3	1.5

5.2 GLASS MELTING

Raw Materials as provided were taken in different compositions and were approximately weighed and batch calculations were done. After getting appropiate samples each sample was mixed thoroughly in the specified mixing method. Each samples were taken in the Pt crucible, before using these crucibles they were properly washed out using NaOH and Na_2CO_3, heating it at 1600°C and then dipping in the HCl after bubbling is over , again kept in furnace at 1000°C-1200°C.It is done in order to make sure that we are using proper cleaned off crucibles. Sample system with the Pt crucibles are kept in old furnace at 1450°C/2hrs.Molten glass is taken out by melt quenching method. Annealing is done at 300°C.

5.3 CHARECTERIZATION

5.3.1 Thermal

Thermal decomposition of preferred Glass samples were studied using differential scanning calorimetric and thermo gravimetric (DSC-TG) by heating the sample at 10/min in argon in a thermal analyzer (Nietzsche, Germany).

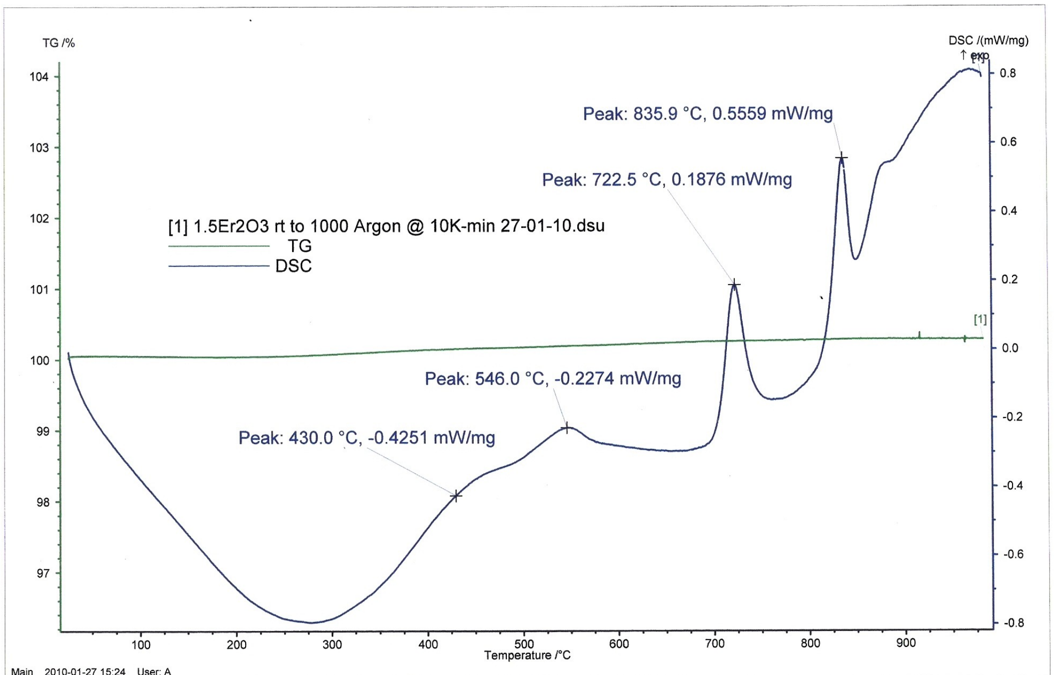
5.3.2 UV SPECTROSCOPY

The three glass ceramic samples were analyzed by the UVSpectroscope It uses light in the visible and ultra violet ranges.

5.3.3 X-ray diffraction

The phase identification of the glass ceramic samples were characterized by Philips X-Ray Diffractometer PW 1730 with nickel filtered Cu Kα radiation (1.5406 A°) at 40 kV and 30mA. X-ray diffraction was done at an angle of 10-80 continuous at 0.004 speed.

6. RESULTS AND DISCUSSIONS



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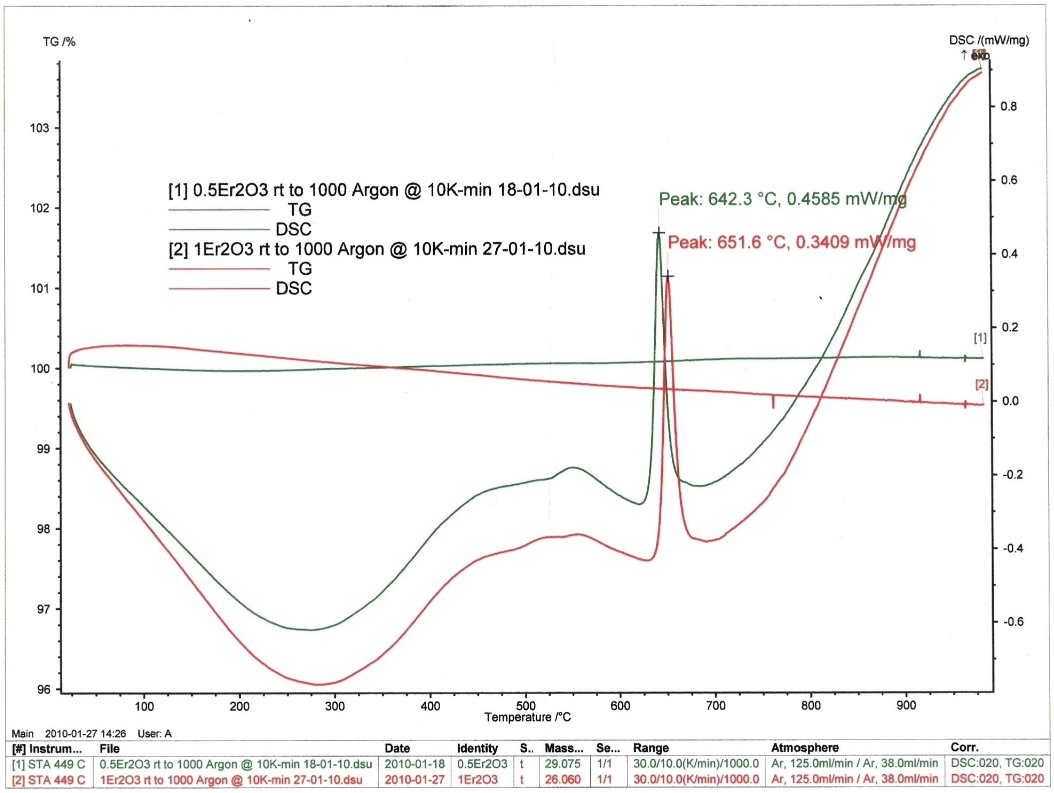
Instrument : NETZSCH STA 449 C **File :** C:\ngbwin\ta\user\1.5Er2O3 rt to 1000 Argon @ 10K-min 27-01-10.dsu

Project :	t	**Material :**	Empty	**Segments :**	1/1
Identity :	1.5Er2O3	**Correction file :**	Baseline rt to 1500 Argon @ 10K-min 12-11-09.bsu	**Crucible :**	DSC/TG pan Al2O3
Date/time :	1/27/2010 1:37:56 PM	**Temp.Cal./Sens. Files :**	temp cal 8-4-08.tsu / Sens cal 8-4-08.esu	**Atmosphere :**	Ar / Ar
Laboratory :	TMC Lab	**Range :**	30.0/10.0(K/min)/1000.0	**TG corr./m. range :**	020/5000 mg
Operator :	Rana	**Sample car./TC :**	DSC(/TG) HIGH RG 4 / S	**DSC corr./m. range :**	020/5000 µV
Sample :	t, 25.666 mg	**Mode/type of meas. :**	DSC-TG / Sample + Correction		

Fig 2: DSC graph of glass containing doped with 1.5 mol % Er_2O_3

Fig 2 shows DSC graph of glass containing doped with 1.5 mol % Er_2O_3. It has been observe that two different sharp crystallization peaks appear at around 722^{o}C and 835^{o}C.



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[#] Instrum...	File	Date	Identity	S..	Mass...	Se...	Range	Atmosphere	Corr.
[1] STA 449 C	0.5Er2O3 rt to 1000 Argon @ 10K-min 18-01-10.dsu	2010-01-18	0.5Er2O3	t	29.075	1/1	30.0/10.0(K/min)/1000.0	Ar, 125.0ml/min / Ar, 38.0ml/min	DSC:020, TG:020
[2] STA 449 C	1Er2O3 rt to 1000 Argon @ 10K-min 27-01-10.dsu	2010-01-27	1Er2O3	t	26.060	1/1	30.0/10.0(K/min)/1000.0	Ar, 125.0ml/min / Ar, 38.0ml/min	DSC:020, TG:020

Fig 3: DSC graph of glass containing doped with 0.5 mol %and 1 mol % Er_2O_3

Fig 3 shows DSC graph of glass containing doped with 0.5 mol %and 1 mol % Er_2O_3. It has been observe that two different sharp crystallization peaks appear at around 642°C and 651°C for 0.5 mol %and 1 mol % Er_2O_3 doped glass respectively. It has been observed with increasing Er_2O_3 content crystallization peaks shift towards higher temperature.

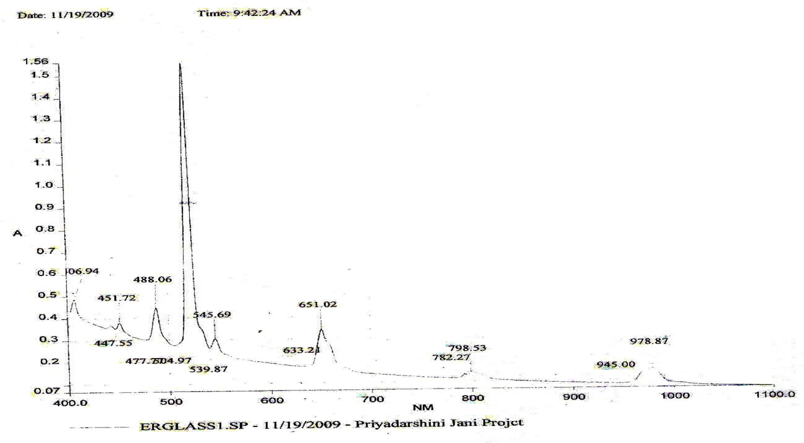

Fig 4: UV visible absorption spectra for 0.5 mol% Er_2O_3 glass

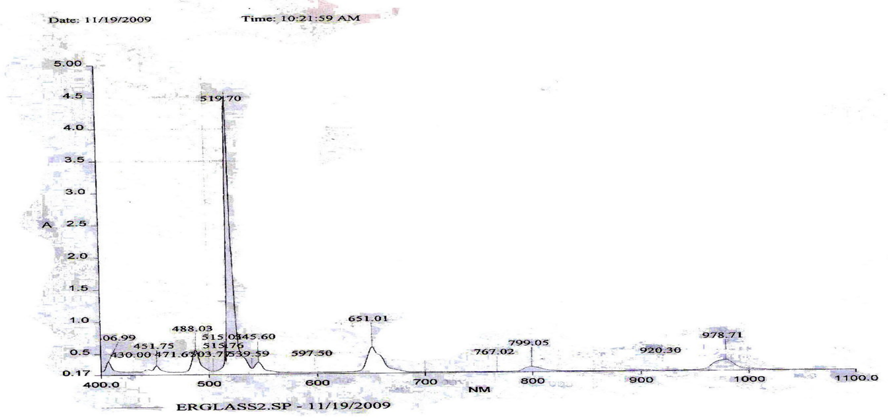

Fig 5: UV visible absorption spectra for 1 mol% Er_2O_3 glass

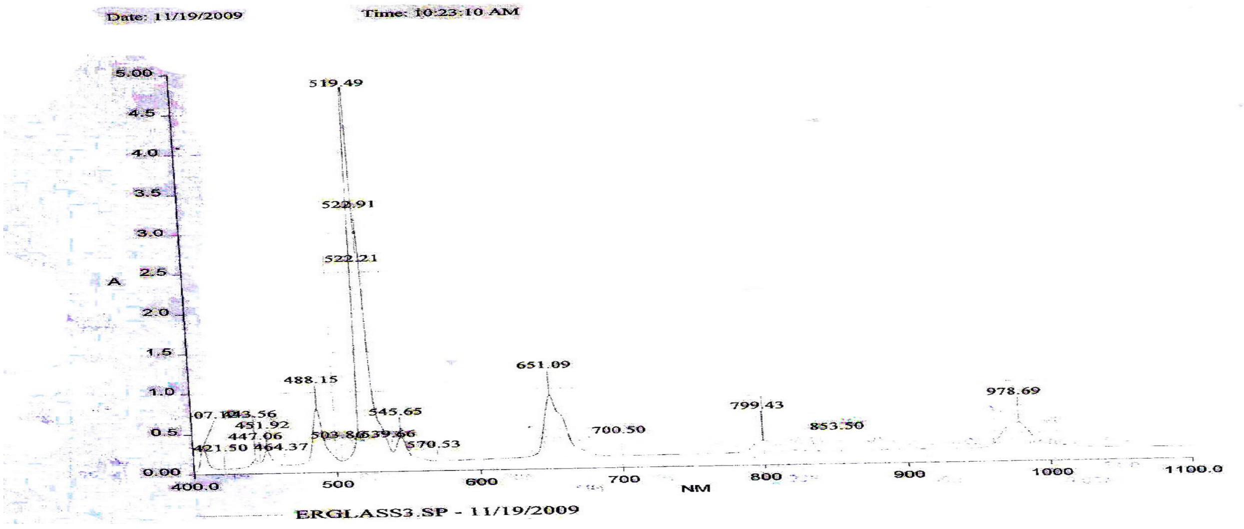

Fig 6: UV visible absorption spectra for 1.5 mol% Er_2O_3 glass

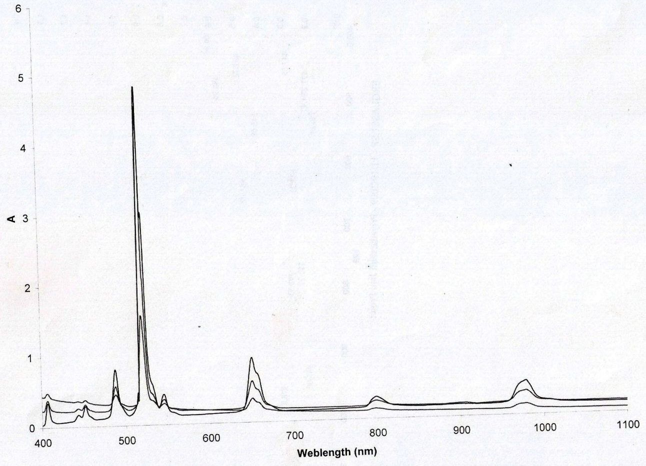

Fig 7: UV visible absorption spectra for without Er_2O_3 glass

From Fig 4 to 7 show different absorption spectra for Er_2O_3 glass

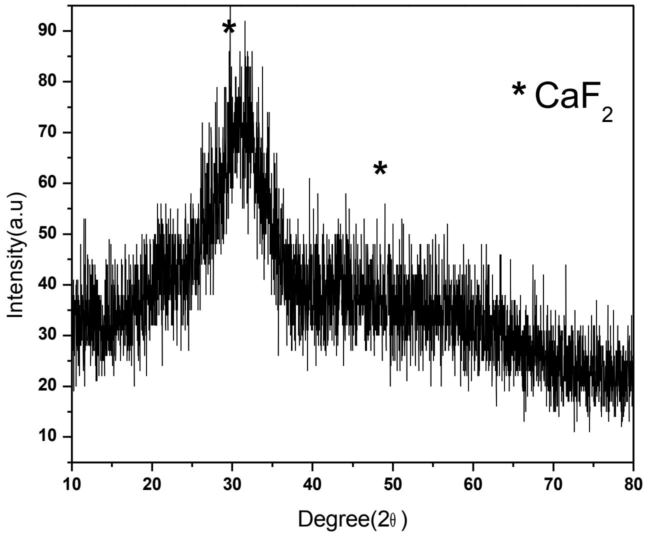

Fig 8 : XRD pattern for 1 % Er_2O_3 doped glass heat treated at 650°C for 0.5 hours

Fig 8 shows onset of CaF_2 formation at 650°C.

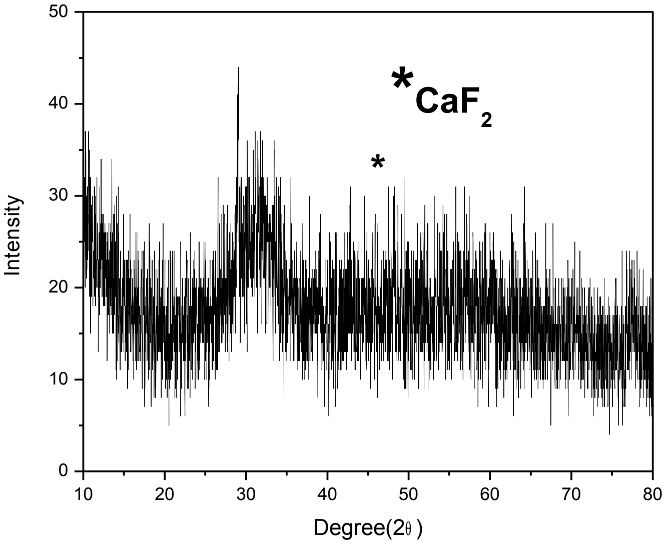

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Fig 9 : XRD pattern for 0.5 % Er_2O_3 doped glass heat treated at 650°C for 0.5 hours

Two different glasses are heat treated at 650°C which shows that with 1 mol% Er_2O_3 doping crystallization was better and glass ceramics also maintained it transparency.

7. CONCLUSIONS

It could be concluded that :
(1) with increasing Er_2O_3 content crystallization shifts towards higher temperature and 650°C is the temperature at which 1mol% Er_2O_3 glass shows good crystallization.