

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**AN INVESTIGATION ON THE LUMINESCENCE AND STRUCTURAL
PROPERTIES OF ERBIUM DOPED CADMIUMNİOBATE PHOSPHORS**

M.Sc. THESIS

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Department of Sceince and Letters

Physics Engineering Programme

Anabilim Dalı : Herhangi Mühendislik, Bilim

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SEPTEMBER 2013

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**AN INVESTIGATION ON THE LUMINESCENCE AND STRUCTURAL
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FOREWORD

This master thesis was written during the time-period from summer 2012 to spring 2013, under the supervision of Professor **Gönul ÖZEN**, University of Istanbul technical university. The intent of the thesis was to examine how to best implement existing new phosphors for diode lazer. I want to thank my supervisor, Prof.Dr. **Gönul ÖZEN**, Dr.Murat Erdem, Dr.Mete Kaan Ekmekçi, University of Marmara and Prof. Dr.Ayhan Mergen,University of Marmara for their being great help during the development of this thesis, Prof.Dr.Adnan Tekin Research Laboratory ,being so supportive with the necessary equipmenst and mesurments and of course my sister Elnaz of being so patient with me the last 2 years!

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ABBREVIATIONS

CdNb	: Cadmium Niobate
Er	: Erbium
XRD	: X-ray Diffraction
SEM	: Scanning Electron Microscopy
EDS	: Energy Dispersive X-ray Spectroscopy
PL	: photoluminescence
PLE	: Photoluminescence excitation
MSS	: Molten Salt Synthesis

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AN INVESTIGATION ON THE LUMINESCENCE AND STRUCTURAL PROPERTIES OF ERBIUM DOPED CADMIUM NIOBATE PHOSPHORS

SUMMARY

The successful combination of various physical properties with chemical inertness, high resistance to heat and moisture, and mechanical strength puts the niobates the most important materials of the new technology. A luminescent material or phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above thermal radiation. Even though the electromagnetic radiation emitted by a phosphor is usually in the visible range, it can also be in other spectral regions such as the UV or infrared.

Columbite-type niobates with MNb_2O_6 general formula having interesting optical, dielectric and microwave dielectric properties have been intensively studied recently. There is a lack of study on the luminescent properties of columbite metal niobates. In the present study, rare earth doped CdNb_2O_6 compounds with columbite structure, were produced by molten salt method and synthesized by using starting materials of metal nitrates and niobium oxide and salt systems such as, Li_2SO_4 - Na_2SO_4 by 1:1 molar ratios.

The Morphological properties of the powders as determined from X-ray diffraction and Scanning Electron Microscopy. The mechanism of this behavior has been studied by measuring the spectral characteristics of the photoluminescence and photoluminescence excitation spectra on the crystalline CdNb_2O_6 doped with 0.5, 1, 3, 6% Er^{+3} compounds indicated CdNb_2O_6 phase (JCPDS file No., 38-1428). The samples exhibited a single phase and all of the peaks were found to be CdNb_2O_6 phase at high temperature of over 900°C . The SEM pictures and The EDS of the material are the rod-like particles that seem to be distributed homogeneously. Therefore, the particle size increased along with the sintering temperature. However, the big particles were condensed by assembled micrograins, as found in the SEM results.

The luminescence properties of columbite compounds were investigated at low (200-800 nm) and high (900-1100 nm) wavelengths. However $\text{Er}^{+3}:\text{CdNb}_2\text{O}_6$ compound increased the luminescence intensity. The emission intensity of CdNb_2O_6 with increasing rare earth dopant Er_2O_3 concentration due to transfer of excitation energy absorbed by rare earth dopants to the NbO_6 groups. Photoluminescence analysis performed between (900-1100nm) showed that, luminescence intensity of CdNb increased by increasing the dopant ratio but, concentration quenching was observed for CdNb_2O_6 above 1%mol dopant concentration.

Er₂O₃ KATKILI CdNb₂O₆ FOSFOR TOZLARIN SENTEZİ ,MICROYAPI KARAKTERİZASYONU VE LÜMINESANS VERİMLERİ

ÖZET

Fotolüminesans malzemeler, doğal veya yapay bir ışığa maruz kaldıklarında karanlıkta parlayan malzemelerdir. Fotolüminesans özellik malzemenin belirli dalga boyunda bir ışığı absorblaması sonucu malzemenin yapısına, kompozisyonuna ve kalitesine de bağlı olarak belirli bir dalga boyunda ışık yayması sonucu oluşmaktadır. Fotolüminesans malzemelerin çok farklı kullanım alanları mevcuttur. Üstün özelliklere sahip fotolüminesans malzemeler karanlıkta yüksek şiddette ışık yayarlar ve ışıldama özellikleri 12-24 saate kadar çıkabilir.

Fotolüminesans malzemelerin ticari olarak kullanımı gün geçtikçe artmakta olup, bu alanlardan en önemlilerinden bazıları; optik elektronik, telekomünikasyon, optik olarak aktif ticari malzemelerdir. Yakın bir geçmişe kadar bilinen tek fosforesans malzeme Cu⁺ ve Co²⁺ katkılı çinko sülfür (ZnS) bileşiğiydi. Bu bileşik iki floresans özeliğe sahip olmasına rağmen, iki önemli dezavantaja sahiptir:1) Parıldama ömrünün kısa olması sadece 1 saat kadar parlaklığını koruyabilecek özellik göstermekteydi.2) Neme hassasiyet: yüksek oranda nem çekme özelliğine sahip olması yaygın bir şekilde kullanımını ve büyük ölçüde kullanım alanlarını sınırlamaktaydı.

Sayılan bu dezavantajlara rağmen çinko sülfür, kol ve duvar saatinde karanlıkta görülebilmeyi sağlamak için kullanılmıştır. 10-15 yıl kadar önce fosforesans özelliğin hızlı kaybını engelleyebilmek için ZnS yapısı içerisine promethium, mesothorium ve tritium gibi radioaktif malzemeler katkılanmıştır. Display ve aydınlatma teknolojilerindeki ilerlemeler, daha düşük maliyetli, daha yüksek performanslı ve farklı dalga boylarında emisyon gösteren lüminesans malzemelerin geliştirilmesi ihtiyacını doğurmuştur.

Örneğin, son zamanlarda, fotolüminesans kullanan likit kristal göstergeler (LCD) ve plazma gösterge panelleri (PDP) CRT'lerin yerini almaktadır. Ayrıca, son yıllarda düz elektrolüminesans, plazma veya alan emisyon display'lerin endüstriyel uygulamalarının yüksek oranda artması stabilite, parlaklık, ve endüstriyel olarak işleme kabiliyeti gibi özellikler bakımından daha üstün özelliklere sahip fotolüminesans malzemelerin geliştirilmesini zorunlu kılmıştır.

Elektronik cihazlar, bilgi iletişiminin hızını belirgin şekilde arttırmışlardır. Elektronik cihazlardaki teyplere ve çiplere depolanan bilgi, insan gözüyle görülebilir haldedir. Display cihazlar, insan gözü ile elektronik cihazlar içindeki görülemeyen bilginin görselliği için, bir ara yüz olarak geliştirilmişlerdir. Display cihazlardaki ekranlarda çizilen görüntüler, fosfor ekranlardan kathodolüminesans (CL) yada fotolüminesans (PL) sayesinde gerçekleştirilir. Bu alanlarda kullanılma potansiyeli

bulunan ve yoğun arařtırmalar yapılan bir ok farklı seramik malzeme bulunmakta olup, bu malzeme grubundan bir tanesinde metal niyobatlarđır.

Nadir toprak iyonu katkılı malzemelerde lüminesans, son zamanlarda geniş bir yankı uyandırmıřtır. Nadir toprak (RE) iyonlarının bir grubu $4f^n$ konfigürasyonunun enerji seviyeleri arasında elektronik geiřlerden kaynaklanan bir ıřıma gösterir. Bu $4f$ elektronları, komřu iyonların $5s^2$ ve $5p^6$ elektronları tarafından olduka iyi perdelenir. Bundan dolayı host (katkılamanın yapıldığı) malzeme RE enerji seviyelerinin üzerinde olduka zayıf bir etkiye sahiptir. Tb^{3+} , Pr^{3+} , Tm^{3+} ve Eu^{3+} gibi RE iyonları olduka düşük salınım řiddetine (10^{-5} – 10^{-8}), host kristali içinde uzun uyarılmış halli ömrüyle (ms) dar spektral genişliğe (5 – 20 cm^{-1}) sahip özellikler gösterir. Diğerk nadir toprak iyonları (Ce^{+3} , Eu^{+3}) $4f^n$ – $15d^1$ uyarılmış hali ile $4f^n$ arasında geiřlerin sonuçlanmasıyla lüminesans olabilir. izgisel ıřımalardan farklı $5d$ uyarılmış hali $5s^2$ ve $5p^6$ elektronları tarafından, kristal alanındanb keskin bir řekilde perdelenemez. Bundan dolayı spektral özellikler, host malzemenin örgüsü tarafından kuvvetlice etkilenir.

Örneğın, nadir toprak element katkılı niyobatlar x-ıřınları luminesans malzemelerinde host malzeme olarak yoğun bir kullanım alanına sahiptir. MNb_2O_6 ($M= Co^{2+}$, Sr^{2+} , Ni^{2+} , Cd^{2+}) kolombit yapılı bileřiklerin, farklı tuz/tuz ve tuz/oksit karıřım molar oranları ile ergimiř tuz sentezi ile üretilmiş.

İlk önce kullanılacak metal oksitlerinin/tuzlarının ve ergitilecek alkali metal klorür, florür ve sülfat tuzlarının molar oranlarına göre stokiyometrik miktarlarının hesabı yapılmıřtır.Daha sonra hesaplanan miktarlarda geiř metali oksiti veya stokiyometrik karıřılığı olarak geiř metali tuzu ve niyobyum oksit,sonra da ergitici tuzlar tartılmıřtır.Oksit karıřımları bir agat havanda,tuz karıřımları ise bir porselen havanda karıřtırılarak iyice öğütölmüřtür.Son olarak,oksit ve tuz karıřımları agat havanda karıřtırılarak ve tekrar öğütölerek kalsinasyon iřlemi için hazır hale getirilmişlerdir.

Daha sonra bu karıřımdan bir miktar alınarak, bir potaya aktarılmıř ve istenilen sıcaklıklarda 4 saat bir gradient fırında, ilgili sıcaklıklarda kalsinasyona tabi tutulmuřtur.Soğuyan örnek, sıcak destile su ile birkaç seferde yıkanarak bir behere aktarılmıřtır.Daha sonra oluřan bileřiği tuzlardan kurtarmak amacıyla beher , $200\text{ }^\circ\text{C}$ 'ye ve 300 rpm 'ye ayarlanmış bir manyetik karıřtırıcılı ısıtıcı üzerine konarak içindeki madde sıcak destile su ile yıkanarak süzülmüřtür.Süzüntöde kalitatif reaksiyonlar ile Cl^- , F^- ve SO_4^{2-} iyonlarının varlığı arařtırılmıştır.

Daha sonra,son yıkama suyu ilave edilen örnek,ayrıca 2 defa da vakumdan süzülmüş ve yine son yıkama suyunda iyonların varlığı arařtırılmıştır.Tuzlardan kurtarılan örnekler $110\text{ }^\circ\text{C}$ 'ye ayarlı bir etövde kurutularak XRD analizine gönderilmişlerdir.alıřma kapsamında kolombit yapılı $CdNb_2O_6$ bileřikleri öncelikle ergimiř tuz yöntemiyle sentezlenecek ve sentezlenen bileřikler farklı yöntemler kullanılarak karakterize edildikten sonra üretilen metal niyobatların lüminesans özellikleri ölçölecektir.

Yapılacak alıřma kapsamında tuzların, oksit/tuz oranlarının, niyobatların oluřum sıcaklıklarına, tane řekillerine ve morfolojilerine ve lüminesans özelliklerine etkileri sistematik bir řekilde alıřılacaktır. Buna ilaveten farklı katkılarla Er_2O_3 , üretilecek metal niyobatlar yine ergimiř tuz yöntemiyle sentezlenerek herbir katkının metal niyobatların fotolüminesans özelliklerine etkileri saptanacaktır. alıřma kapsamında uygulanack yöntem ve karakterizasyon teknikleriyle ilgili detaylı bilgi verilmiřtir.

Nb_2O_5 , CdO , oksitler ve inorganik tuz karışımları $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ kullanılarak ergimiş tuz yöntemiyle niyobatlar üretilecektir. Üretilen niyobatlara farklı oranlarda Er_2O_3 oksitler katkılacaktır. Laboratuvarımızda bulunan Makine Teçhizat ve Olanaklar:1)Yüksek Sıcaklık Fırını .2) XRD (X Işınları Difraktometresi).3) SEM (Taramalı Elektron Mikroskobu).4) Luminesans Spektrofotometresi.5) FT-IR Spektrofotometresi.Metal niyobat bileşiklerinin sentezi, ergimiş tuz yöntemi ile gerçekleştirilecektir.

Ergimiş tuz sentezi düşük sıcaklıklarda uygulanan kimyasal bir yöntemdir. Ergimiş tuz sentezi sadece kompleks oksit mikro kristallerinin ve nano kristallerin boyut ve şekillerinin kontrollü üretimini mümkün kılan bir yöntem değil, aynı zamanda, bileşenlerin yüksek difüze edilebilirliklerinden dolayı, düşük sentez sıcaklıklarına ve daha düşük reaksiyon sürelerine imkan sağlayan bir yöntemdir. Bunun yanında, ergimiş tuz yöntemi ile üretilen bileşiklerin tanecik morfolojisi de kontrol edilebilmektedir.

Yapılması önerilen bu çalışmada, CdO oksitler Nb_2O_5 ile stokiometrik miktarlarda olmak üzere ve belirlenecek farklı oranlardaki ergimiş inorganik tuz karışımları eşliğinde polipropilen bir kap içerisinde bilyalar ve etil alkol kullanılarak karıştırıldıktan sonra bir alüminyum oksit kroze yüklenerek ayarlanabilir bir yüksek sıcaklık fırınında yüksek sıcaklıkta 900°C sürede 4 saat reaksiyona sokulacaktır.

Elde edilen ürünler klorsuz sıcak destile su ile birkaç kez yıkanarak tuzlar uzaklaştırılacaktır. Elde edilen tozların özellikleri karakterize edilecek.Sentez işleminde farklı parametrelerin toz tane boyutuna, şekline, aglomerasyon derecesine ve istenilen fazların oluşum sıcaklığına etkileri incelenecektir.Farklı teknikler kullanılarak üretilen metal niyobat tozlar ve metal niyobat bileşikleri detaylı olarak incelenecektir.

Karakterizasyon yöntemlerinden bazıları aşağıda verilmiştir.Sentezlenen metal niyobatların tuz oranlarına, tuz karışımlarına ve kalsinasyon sıcaklıklarına göre metal niyobatların oluşum sıcaklıkları, metal niyobatların oluşumu esnasında faz gelişimleri ve üretilen tek fazlı yapıda varsa ikincil fazların varlığı XRD kullanılarak saptanacaktır. Sentezlenen metal niyobatların şekilleri ve morfolojileri taramalı elektron mikroskobu (SEM) kullanılarak incelenecektir.Sentezlenen metal niyobatların luminesans özellikleri fotospektrometre kullanılarak belirlenecektir.

Karakterizasyon işlemlerinden sonra, Erbiyum oksiti ile sentezlenen CdNb_2O_6 colombit malzemesi katkılanarak XRD analizleri ile fazların yapıları karakterize edilecektir. Morfolojiler ve mikro yapılar SEM analizleri ile belirlenecektir. Daha sonra Uyarılma ve emisyon spektrumları ise bir spektrofotometre cihazı ile ölçülerek belirlenecektir. Bütün ölçümler oda sıcaklığında gerçekleştirilecektir.

CdNb_2O_6 uyarıldığında, çok güçlü mavi luminesans sergilemektedir.bu maddenin lazer ve lazer host (katkılamanın yapıldığı) malzemesi olarak kullanıldığını rapor etmişlerdir. Ayrıca bu maddenin, Er^{3+} ile dope edildiğinde, düşük maliyetli fosfor lambası olarak kullanılabileceği ortaya konmuştur.

1.INTRODUCTION

The rare-earth (RE) doped laser crystals, glasses and ceramics, which possess trivalent RE ions, are popular solid-state gain media. The RE ions are also used as codopants for quenching the population in certain energy levels by the energy transfer processes, or for realizing saturable absorbers, or as optically passive constituents of laser crystals. Rare-earth ions doped materials have received significant attention for optical temperature sensors because their absorption and emission properties relative to operating temperature could cause changes in the fluorescence intensity. In the past decades, a number of optical temperature sensors have been presented and the most outstanding approach is based on the fluorescence intensity ratio (FIR) technique which can help to reduce the influence of measurement condition and therefore, improve the measurement sensitivity. The electro-optical properties of metal niobates have attracted a great amount of interest for applications. [10]

The Niobates of various metals are widely used in contemporary technology. They are usually used as the pure compounds or as components of solid solutions, which exhibit ferro, piezo, and pyro-electric, electro optical, and other properties. Materials based on them are employed in the production of ceramic generators of ultrasound, sound pickups, piezoelectric microphones and telephones, strain gauges, hydro acoustic collectors (receivers) of energy, laser crystals, etc. The development of the newest technology and the consequent requirement for new materials has aroused exceptional interest in the niobates. The successful combination of various physical properties with chemical inertness, high resistance to heat and moisture, and mechanical strength puts the niobates the most important materials of the new technology.

A luminescent material or phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above thermal radiation. Even though the electromagnetic radiation emitted by a phosphor is usually in the visible range, it can also be in other spectral regions such as the UV or infrared. [19]

The binary niobate ceramics, with the formula $M^{2+}Nb_2O_6$ where $M^{2+}=Ca, Mg$, or a transition metal (TM), have the orthorhombic columbite structure.

The best known members of this group are zinc niobate ($ZnNb_2O_6$) and magnesium niobate ($MgNb_2O_6$), but Ca, Co, Ni, Mn, Cu, Cd , and Fe^{2+} cations can also be included in the columbite structure, which is formed due to distortions on octahedral NbO units and in consequence the formation of short $Nb-O$ bonds takes place. Metal niobates are known as interesting photoactive host materials and the luminescent properties of $LiNbO_3, KNbO_3$ and $LaNbO_4$ have been studied extensively. $CdNb_2O_6$ is also suitable reference material for dielectric ceramic. $CdNb_2O_6$ is an important intermediate phase for the preparation of $Cd_2Nb_2O_7$ ferroelectric ceramics, the orthorhombic $CdNb_2O_6$ single crystalline phase was observed by The molten-salt synthesis. Ceramic powders are prepared from solid, liquid, and gas phases by various methods (Rahaman, 2003). One of the methods of preparing ceramic powders is the Molten salt synthesis. Typical examples of salts used in molten salt synthesis are chlorides and sulfates. The amount of salt is small, typically a few percent of the total weight.

In fact, 1) The identity as well as the size of the anion associated with the salt,
2) The solubilities/dissolution rates of the constituent components within the molten salt itself,
3) The precise melting point of either the salt or complex salt mixture used,
4) The heating temperature and duration, as well as
5) the unique morphological and chemical composition of the precursors involved are all important, readily controllable factors that influence the growth rate as well as the resultant structural characteristics (size, shape, and crystallinity) of the as-prepared particles.[14]

2. BACKGROUND

2.1 Columbite Niobates

MnNb_2O_6 may suffer from variations in oxidation state of the component metal ions, as undoubtedly happens in FeNb_2O_6 and CuNb_2O_6 tends to form as two polymorphs, the orthorhombic columbite phase and a monoclinic phase. Despite all these issues, it is simple to make high quality microwave ceramics of many columbites from a standard solid-state synthesis process. Other processing techniques can be utilized to produce single-phase columbites at lower temperatures and as nanopowders and reaction sintering can form highly dense ceramic samples. Columbites are also highly suitable for growth as single crystals and monocrystalline fibers. The biggest obstacle to many applications of columbites as microwave ceramics is their relatively large negative τ_f values and the phenomena behind τ_f in columbites is not well understood. However progress has been made on making temperature compensated columbite-based ceramics, combined with a highly positive τ_f ceramic to make a composite ceramic material with near zero τ_f . They have only a superficial degree of ordering and do not require complex processing furthermore, MgNb_2O_6 is in wide use as a precursor to synthesis single phase PMN ($\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$) in the “columbite” process and NiNb_2O_6 is being investigated as a catalyst for splitting water and organic compounds. CaNb_2O_6 and CdNb_2O_6 also have interesting optical properties. This review will concentrate on the optical and dielectric properties and applications, as this is the greatest area of interest of these ceramics.[20]

2.2 The Structure of the Columbites

The mineral columbite, which is the ore from which niobium metal is extracted, is also known as ferrocolumbite, manganocolumbite, niobite, and niobite-tantalite, with the nominal formula $[(\text{Fe}/\text{Mn}/\text{Mg})(\text{Nb}/\text{Ta})_2\text{O}_6]$. The tantalum-rich form is the ore tantalite. It is a black mineral (Fig.1) with an orthorhombic crystal structure. The

columbites discussed in this review are binary niobate ceramics, with the formula $M\text{Nb}_2\text{O}_6$ where $M=2+$ cation, and are one of the end members of the perovskite $\text{BaM}_{0.33}\text{Nb}_{0.67}\text{O}_3$ group (the other being BaO). They are isostructural with the orthorhombic columbite space group= Pnca and form stable single phase compounds with the exception of CuNb_2O_6 , as discussed below.[20]



Figure 2.1 : The mineral ferrocolumbite (photo from the Grenier Collection).

As long as the ionic radius of M^{2+} is $\leq 1.0\text{\AA}$, the structure seems to be columbite, with Ba^{2+} , Sr^{2+} and mixed Ba/Sr compounds the crystal structure is not columbite. The ionic radii of M^{2+} for all the reported columbite compounds, and those of Ba^{2+} and Sr^{2+} , are shown in Table I. In the AB_2O_6 columbite structure, the A and B cations are at the center of octahedral surrounded by six oxygen atoms. The AO_6 and BO_6 octahedra form independent zig-zag chains by sharing edges, and the chains are connected by sharing corners in the order AO_6 chain- BO_6 chain- BO_6 chain (Fig2.2)

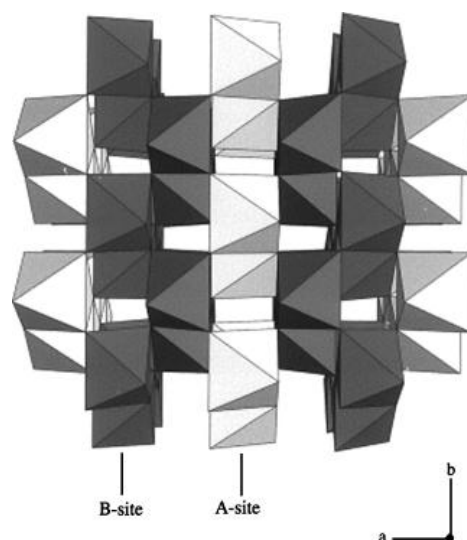


Figure 2.2 : Columbite octahedral structure ($A=M^{+2}$, $B=\text{Nb}^{+5}$).

In the fully ordered state, this forms repeating ABBABB octahedral layers, with an orthorhombic α -PbO₂-type structure, first solved by Sturdivant. The unit cell is orthorhombic, space group no. 60 (either Pbcn or Pcan), with lattice parameter ratios of approximately 1:1.14:2.5 (Fig. 3). Lattice parameters, densities and cell volumes for columbite niobates are given in Table 2. CuNb₂O₆ has two polymorphs, the black orthorhombic columbite form, normally forming above 900°C, and a yellowishgreen monoclinic form present between 700° and 900°C. Between these temperatures the two forms can coexist, although annealing at 800°–900°C can complete conversion into the orthorhombic CuNb₂O₆.

Table 2.1 : Ionic Radii of M⁺² Ions (Six Coordinate, from Shannon).

M ⁺² Cation	Ionic radius/A °
Ba ⁺²	1.35
Sr ⁺²	1.18
Ca ⁺²	1.00
Cd ⁺²	0.95
Zn ⁺²	0.74
Mg ⁺²	0.72
Ni ⁺²	0.69
Mn ⁺²	0.67
Co ⁺²	0.65
Fe ⁺²	0.61

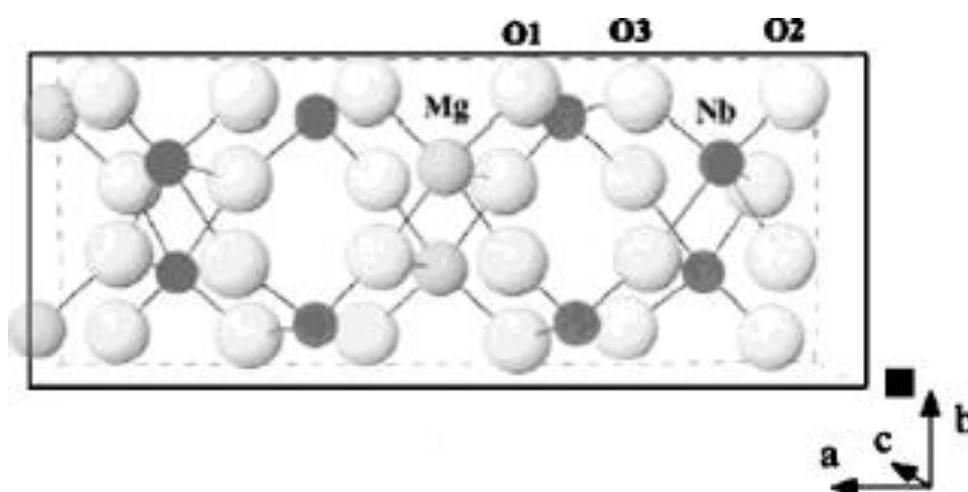


Figure 2.3 : Unit cell of columbite MgNb₂O₆.

The lattice parameters for monoclinic CuNb_2O_6 (P21/c (14)) are $a=5.0064 \text{ \AA}$, $b=14.1732 \text{ \AA}$, $c=5.7615 \text{ \AA}$, $d=5.61 \text{ g cm}^{-3}$, cell volume= $408.65 \times 10^6 \text{ pm}^3$ (ISCD no =00-045-0561). It has been shown that substitution of just 10% of the Cu^{2+} ions in CuNb_2O_6 with Zn^{2+} leads to a monoclinic compound being formed, even after heating over 900°C , and monoclinic $\text{Cu}_{0.85}\text{Zn}_{0.15}\text{Nb}_2\text{O}_6$ has the lattice parameters $a=5.005 \text{ \AA}$, $b=14.17 \text{ \AA}$ and $c=5.751 \text{ \AA}$, very similar those of monoclinic CuNb_2O_6 . [20]

3. OPTICAL SPECTROSCOPY

3.1 Absorption

Luminescent materials only emit radiation when the excitation energy is absorbed. Excitation spectra and absorption spectra typically show a strong correlation and both indicate that excitation energy can be absorbed either by the host lattice or by the activator itself. When high energy excitation such as fast electrons, gamma rays or X-rays and vacuum ultraviolet radiation are used, this always results in host lattice excitation. On the other hand, direct excitation of the activator is only possible with near-ultraviolet or visible radiation. The excitation spectra can tell us whether the host lattice or the activator absorbs the incident radiation.

The optical properties of a particular luminescent center in different host lattices are usually different because the immediate surroundings of such a center have been changed. Two main factors can be said to be responsible for the influence of the host lattice on the optical properties of a given activator in different host lattices. The first factor is covalency and the other is the crystal field. For higher covalency, the host lattice interactions between the electrons are reduced because they spread out over wider orbitals. Hence electronic transitions between different energy levels, which are determined by electron interaction shift to lower energy. A higher covalency also means that the constituent ions have a lower electronegativity difference between them so that the charge transfer transitions between these ions also shift to lower energy. For example, because YF_3 is more ionic than Y_2O_3 , the charge transfer absorption band of Eu^{3+} shifts to a lower energy in the more covalent Y_2O_3 . Based on this, we can assume that Sr substitution for Ca would yield a more covalent compound and cause the excitation band to move to a lower energy or higher wavelength. Conversely, alloying with Zn would move the excitation band to higher energies, which would be consistent with our goal of shifting to lower excitation wavelengths. Ta has approximately the same electronegativity as Nb and so it is difficult to judge this effect in the metaniobate alloy system.[7]

The effect of the crystal field of the host lattice on the optical properties of a luminescent ion is the second factor that influences the properties of an activator. The crystal field is the electric field imposed on the ion due to its surroundings. The strength of the crystal field then determines the spectral position of certain optical transitions. Different host lattices yield different crystal fields, which in turn yield different splittings such that the luminescent center can serve as a probe of the surroundings. Thus, the crystal field is responsible for the splitting of certain optical transitions and these observed splittings yield site symmetry. One visible effect of the host lattice is the inhomogeneous broadening of the spectra. In powders, for example, the external surface may be large and activator ions, such as Eu^{3+} , near the surface may experience a covalency and a crystal field that is different from the bulk. These ions therefore have their optical transitions at slightly different energies from those in the bulk, which causes the spectra to broaden. Point defects in the crystal structure also contribute to this broadening. This effect helps to explain why even though calcium metaniobate is highly crystalline, we see a broad host absorption band. This broad band is also due to the vibrational overlap that occurs as a result of the interaction between the optical center and the vibrations of its surroundings.[7]

3.2 Emission and Luminescence

Emission can be defined as a radiative return to the ground state. Such a radiative return can occur when the absorption and emission processes occur in the same luminescent ion or center, or it can occur as a result of the influence of the host lattice on the emission transitions. Typically, there is little or no emission during the relaxation process. The system can then return to the ground state upon the emission of radiation. This emission occurs spontaneously in the absence of a radiation field, while absorption can only occur in the presence of a radiation field. Emission in the presence of a radiation field is known as stimulated emission, but this process is not within the scope of this thesis. The energy difference between the maximum of the excitation band and that of the emission band is known as the Stokes' shift (Figure 3.1).

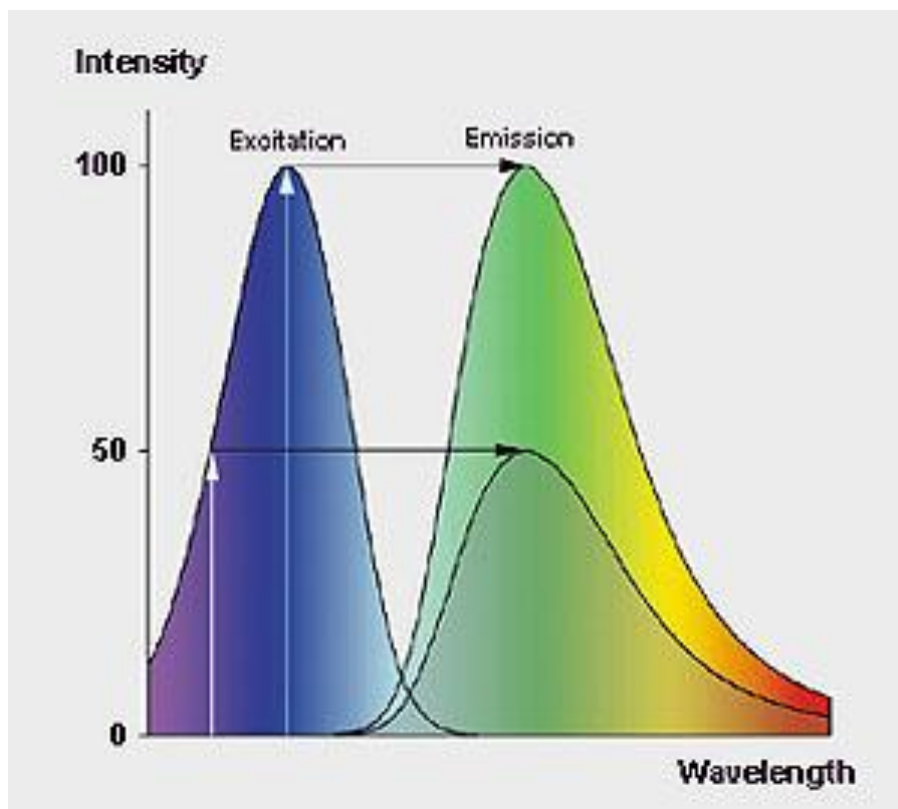
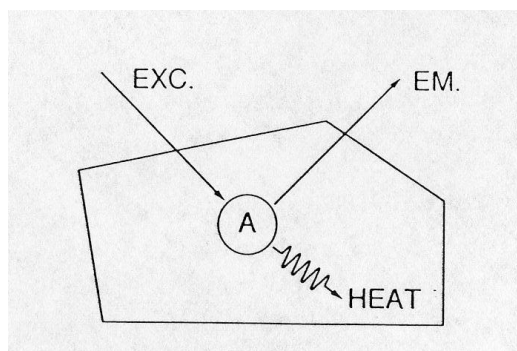


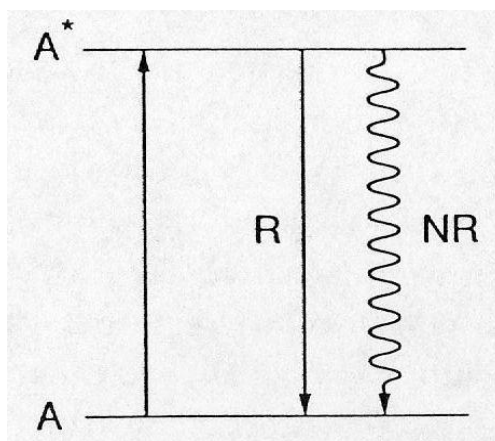
Figure 3.1 : The energy difference between the maximum of the excitation band and that of the emission band is known as the Stokes' shift.

A typical case of stronger coupling is well-known in groups like tungstates and vanadates, which are oxidic anions with a central metal ion which has no d electrons, e.g. WO_4^{2-} , WO_6^{6-} , VO_4^{3-} and MoO_4^{2-} . Because the Stokes' shift of their emission is usually very large ($\sim 16000 \text{ cm}^{-1}$), energy migration is completely hampered, even at room temperature, e.g. in CaWO_4 . In other cases such as YVO_4 , thermally activated energy migration occurs and the Stokes' shift is much smaller ($\sim 10,000 \text{ cm}^{-1}$). The luminescent groups in WO_4^{2-} and NbO^{3-} have been proven to be isolated luminescent centers in spite of the short distance to their nearest neighbors. The nature of the luminescent species determines the strength of the electron lattice coupling, for example, in the weak coupling case, the zero phonon line dominates and we see narrow peaks as in an Eu^{3+} emission. The coupling can be intermediate, in which case there is a gradual progression in the symmetrical stretching mode and where there is a broad band, this is an indication of strong coupling such as in CaNb_2O_6 . Transition metal ion complexes with a formally empty d shell typically show intense broad-band emission with a large Stokes shift on the order of $10\,000 \text{ cm}^{-1}$ - $20\,000 \text{ cm}^{-1}$. Examples are VO_4^{3-} , NbO_6^{7-} , WO_4^{2-} and WO_6^{6-} . In the excited

state, the electronic charge has moved from the oxygen ligands to the central metal ion and this is considered to be a charge transfer state. After emission, A luminescent material or phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above thermal radiation. Even though the electromagnetic radiation emitted by a phosphor is usually in the visible range, it can also be in other spectral regions such as the UV or infrared. Luminescence can be classified according to the different types of energy used to excite the phosphor namely: 1.) Photoluminescence, which involves excitation by an electromagnetic radiation that is usually UV radiation. 2.) Cathodoluminescence, which is excitation by a beam of energetic electrons. 3.) Electroluminescence occurs when the source of excitation is an electric voltage. 4.) Triboluminescence, which is produced by mechanical energy such as grinding. 5.) X-ray Luminescence, when excitation is by x-rays. 6.) Chemiluminescence, when the material is excited by the energy of a chemical reaction. The luminescent center reaches a high vibrational level of the ground state, from which it relaxes to the lowest vibrational level of the ground state. Energy transfer can occur between a pair of dissimilar luminescent centers or between identical luminescent centers. The case of dissimilar luminescent centers involves two centers, a sensitizer S and an activator A separated in a solid by a distance R, where R is assumed to be so short that S and A have a non-vanishing interaction with one another. This means that if S is in an excited state while A is in the ground state, then the relaxed excited state of S may transfer its energy to A. Actually, the amount of charge transfer is normally small but a significant amount of electronic reorganization occurs whereby electrons are promoted from bonding orbitals in the ground state to anti bonding orbitals in the excited state. [7]



(a)



(b)

Figure 3.2 : (a) Physical model of luminescence, where Exc : Excitation, EM:Emission or radiative return to the ground state,HEAT: Non-radiative return to the ground. (b) Energy Level Diagram of processes in (a), where A*:Excited State of Aactivator, A: Ground State ofActivator, R: Radiative return to the ground state or emission, NR: Non-radiative return to the ground state.

In the simple mechanism described above and shown in figures 3.2a and 3.2b, the host lattice does not participate in optical processes, but simply “holds” the activator ion tightly while the activator absorbs the energy and emits the radiation. A well-known example is ruby, $\text{Al}_2\text{O}_3:\text{Cr}^{2+}$, and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. However, if another ion is added to the host lattice, this ion may absorb the excitation energy and then transfer it to the activator.composed partly of the blue Sb^{3+} emission and partly of the Mn^{2+} emission.[7]

Generally, the concentration of the activator or luminescent center is of the order of 1 mol % and the centers are approximated as being randomly distributed throughout the host lattice. However, the activator concentration can sometimes be 100 % in which case, the activator ion or group is both a luminescent center and a building unit of the host lattice. A well-known example is CaWO_4 where the tungstate group (WO_4^{2-}) is the luminescent center and CaNb_2O_6 where the niobate octahedron ($\text{Nb}_2\text{O}_6^{2-}$) is the luminescent center. This class of phosphors is known as “self-activated” because the host lattice both absorbs and emits the radiation. Another mechanism of luminescence is one in which the host lattice is excited and then transfers its excitation energy to the activator. In this case, the host lattice acts as a sensitizer and this mechanism is typical of high-energy excitation, such as by x-rays or cathodoluminescence.

3.3 Photoluminescence (Fluorescence, Phosphorescence and excited molecular deactivation process)

Fluorescence is a spectrochemical method of analysis where the molecules of the analyte are excited by radiation at a certain wavelength and emit radiation of a different wavelength. The emission spectrum provides information for both qualitative and quantitative analysis. As shown in Figure 3.3 when light of an appropriate wavelength is absorbed by a molecule (i.e., excitation), the electronic state of the molecule changes from the ground state to one of many vibrational levels in one of the excited electronic states. The excited electronic state is usually the first excited singlet state, S_1 (Figure 3.3). Once the molecule is in this excited state, relaxation can occur via several processes. Fluorescence is one of these processes and results in the emission of light (Refer to Figure 3.3 during the following discussion).[9]

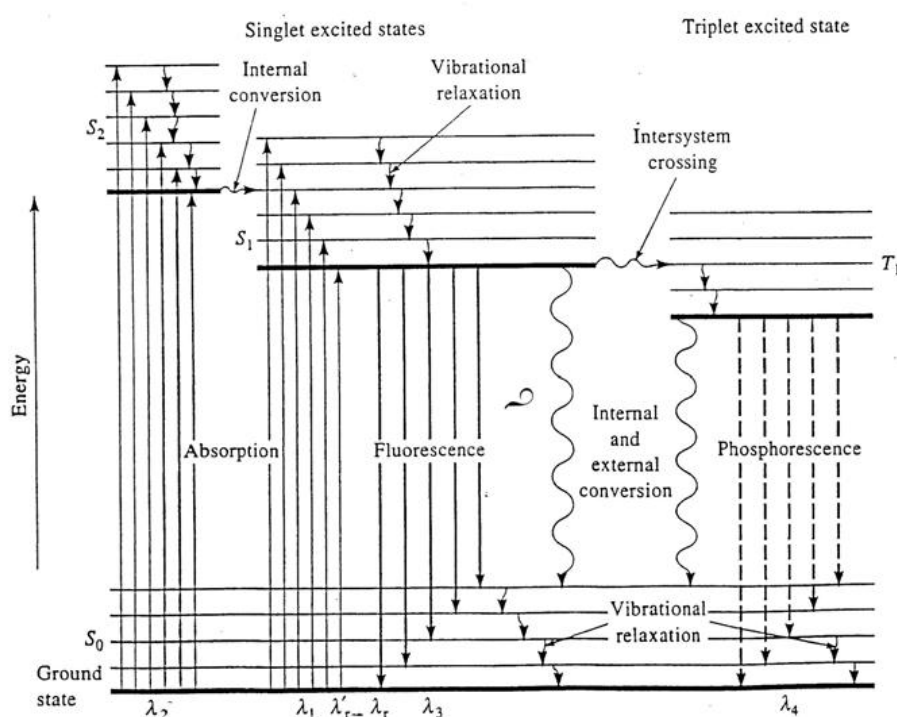


Figure 3.3 : Electronic transition energy level diagram.

Following absorption, a number of vibrational levels of the excited state are populated. Molecules in these higher vibrational levels then relax to the lowest vibrational level of the excited state (vibrational relaxation). From the lowest vibrational level, several processes can cause the molecule to relax to its ground state. The most important pathways are:

1. Collisional deactivation (external conversion) : Leading to nonradiative relaxation.

2. Intersystem Crossing (10^{-9} s): In this process, if the energy states of the singlet state overlaps those of the triplet state, as illustrated in Figure 2.2, vibrational coupling can occur between the two states. Molecules in the single excited state can cross over to the triplet excited state.

3. Phosphorescence : This is the relaxation of the molecule from the triplet excited state to the singlet ground state with emission of light. Because this is a classically forbidden transition, the triplet state has a long lifetime and the rate of phosphorescence is slow (10^{-2} to 100 sec).

4. Fluorescence : Corresponds to the relaxation of the molecule from the singlet excited state to the singlet ground state with emission of light. Fluorescence has short lifetime ($\sim 10^{-8}$ sec) so that in many molecules it can compete favorably with collisional deactivation, intersystem crossing and phosphorescence. The wavelength (and thus the energy) of the light emitted is dependent on the energy gap between the ground state and the singlet excited state. An overall energy balance for the fluorescence process could be written as:

$$E_{\text{fluor}} = E_{\text{abs}} - E_{\text{vib}} - E_{\text{solv.relax}} \quad (3.1)$$

where E_{fluor} is the energy of the emitted light, E_{abs} is the energy of the light absorbed by the molecule during excitation, and E_{vib} is the energy lost by the molecule from vibrational relaxation. The $E_{\text{solv.relax}}$ term arises from the need for the solvent cage of the molecule to reorient itself in the excited state and then again when the molecule relaxes to the ground state. As it can be seen from Equation.1 and from Table3.1. fluorescence energy is always less than the absorption energy for a given molecule. Thus the emitted light is observed at longer wavelengths than the excitation.

5. Internal Conversion : Direct vibrational coupling between the ground and excited electronic states (vibronic level overlap) and quantum mechanical tunneling (no direct vibronic overlap but small energy gap) are internal conversion processes. This is a rapid process (10^{-12} sec) relative to the average lifetime of the lowest excited singlet state (10^{-8} sec) and therefore competes effectively with fluorescence in most

molecules. Other processes, which may compete with fluorescence, are excited state isomerization, photoionization, photodissociation and acid-base equilibria. Fluorescence intensity may also be reduced or eliminated if the luminescing molecule forms ground or excited state complexes (quenching) , Figure 3.4 shows completely.[16]

Transition	Process	Rate Constant	Timescale (Seconds)
$S(0) \Rightarrow S(1)$ or $S(n)$	Absorption (Excitation)	Instantaneous	10^{-15}
$S(n) \Rightarrow S(1)$	Internal Conversion	$k(ic)$	10^{-14} to 10^{-10}
$S(1) \Rightarrow S(1)$	Vibrational Relaxation	$k(vr)$	10^{-12} to 10^{-10}
$S(1) \Rightarrow S(0)$	Fluorescence	$k(f)$ or Γ	10^{-9} to 10^{-7}
$S(1) \Rightarrow T(1)$	Intersystem Crossing	$k(pT)$	10^{-10} to 10^{-8}
$S(1) \Rightarrow S(0)$	Non-Radiative Relaxation Quenching	$k(nr), k(q)$	10^{-7} to 10^{-5}
$T(1) \Rightarrow S(0)$	Phosphorescence	$k(p)$	10^{-3} to 100
$T(1) \Rightarrow S(0)$	Non-Radiative Relaxation Quenching	$k(nr), k(qT)$	10^{-3} to 100

Figure 3.4 : Timescale range for Fluorescence Processes.

4. EXPERIMENTAL PROCEDURE

4.1. Molten Salt Synthesis of Ceramic Powders

Molten salt synthesis, one of the methods of preparing ceramic powders involves the use of a molten salt as the medium for preparing complex oxides from their constituent materials (oxides and carbonates). Ceramic powders are prepared from solid, liquid, and gas phases by various methods (Rahaman, 2003). For large scale commercial production, ceramic powders are fabricated mainly from the solid phase by a conventional powder metallurgical method. Molten salt synthesis is a modification of the powder metallurgical method. Salt with a low melting point is added to the reactants and heated above the melting point of the salt. The molten salt acts as the solvent. Molten salts have been used as additives to enhance the rates of solid state reactions for a long time. The amount of salt is small, typically a few percent of the total weight. In contrast, in molten salt synthesis, a large amount of salt is used as the solvent to control powder characteristics (size, shape, etc.). In this sense, molten salt synthesis is different from the flux method, which uses the salt as an additive to enhance the reaction rate. Typical examples of salts used in molten salt synthesis are chlorides and sulfates. In many cases, eutectic mixtures of salts are used to lower the liquid formation temperature. The melting points of NaCl and KCl are 801°C and 770°C, respectively, and that of 0.5NaCl– 0.5KCl (eutectic composition) is 650°C. For example, 0.635Li₂SO₄–0.365Na₂SO₄ is the most commonly used salt among sulfates because of its low melting temperature, which is 594°C, whereas that of Na₂SO₄–K₂SO₄ is 823°C. Generally, a complex oxide powder is prepared from reactants by the following procedure. A mixture of the reactants and salt is heated above the melting temperature of the salt. At the heating temperature, the salt melts and the product particles form. The characteristics of the product powder are controlled by selecting the temperature and duration of the heating. Then, the reacted mass is cooled to room temperature and washed with an appropriate solvent (typically, water) to remove the salt. The complex oxide powder is obtained after

drying. The procedure is the same as that of a conventional powder metallurgical method and is easily scaled up for the fabrication of large quantities of materials.

The role of the molten salts is : (1) to increase the reaction rate and lower the reaction temperature, (2) to increase the degree of homogeneity (the distribution of constituent elements in the solid solution),(3) to control particle size, (4) to control particle shape and (5) to control the agglomeration state.

The major purpose of employing molten salt synthesis is : (1) to prepare powders for sintering and (2) to prepare anisometric particles. In sintering of powders, a good sintered compact is obtained from a powder with grains of submicrometer size and a low degree of agglomeration (Rahaman, 2003). Recently, textured ceramics are prepared by the templated grain growth method, in which anisometric particles with sizes from several to a few tens micrometers are required .[15]

4.2. Fundamentals Of Molten Salt Synthesis

4.2.1 Preparation procedure

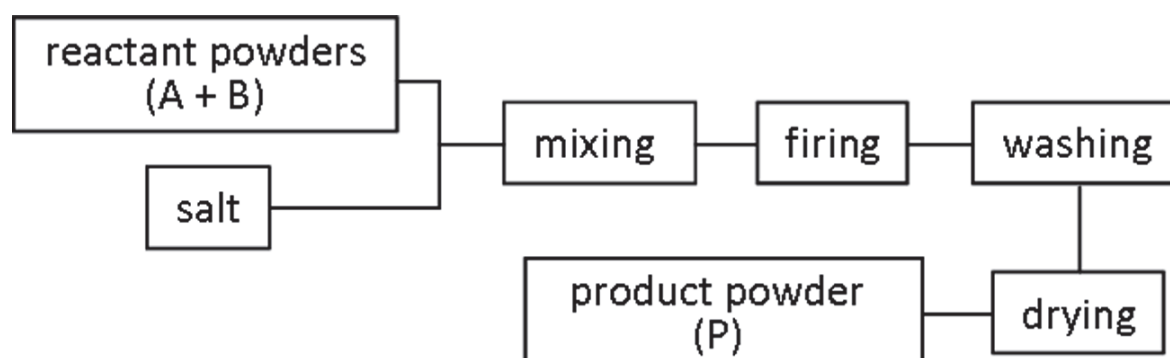
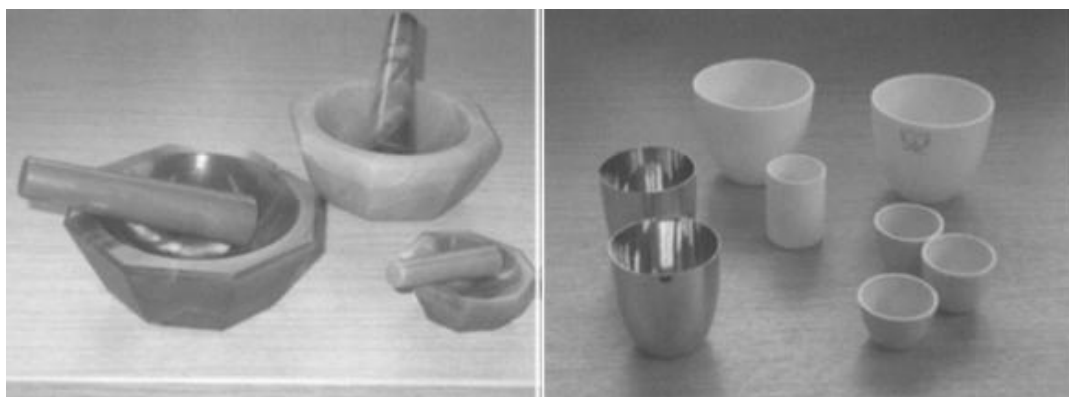
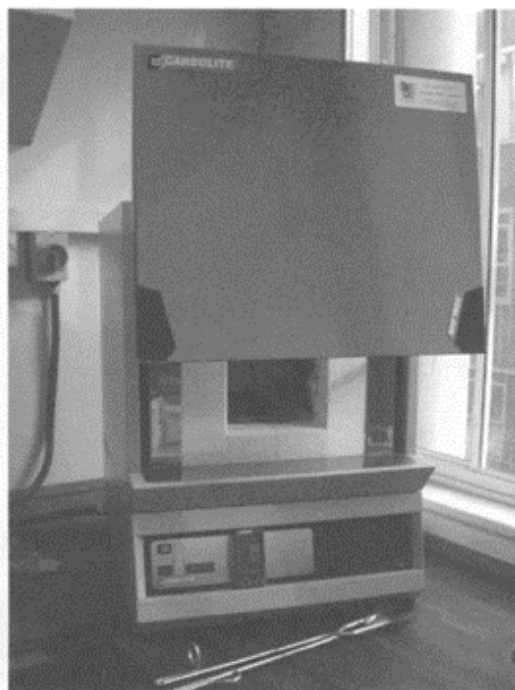


Figure 4.1 : Preparation procedure in molten salt synthesis.



(a),(b)



(c)

Figure 4.2 : The basic apparatus for the ceramic method: (a) pestles and mortars for fine grinding; (b) a selection of porcelain, alumina, and platinum crucibles; (c), furnace.

often not homogeneous in composition, this is because as the reaction proceeds a layer of the ternary oxide is produced at the interface of the two crystals, and so ions now need to diffuse through this before they react. It is usual to take the initial product, grind it again, and reheat several times before a phase-pure product is obtained. Trial and error usually has to be used to find out the best reaction conditions, with samples tested by powder X-ray diffraction to determine the phase purity. Solid state reactions up to 2300 K are usually carried out in furnaces which use resistance heating: the resistance of a metal element results in electrical energy being converted to heat, as in an electric fire.[1]

This is a common method to 2300K, but above this, other methods have to be employed. Higher temperatures in samples can be achieved by directing an electric arc at the reaction mixture (to 3300 K), and for very high temperatures, a carbon dioxide laser (with output in the infrared) can give temperatures up to 4300 K. Containers must be used for the reactions which can both withstand high temperatures and are also sufficiently inert not to react themselves; suitable crucibles are commonly made of silica (to 1430 K), alumina (to 2200 K), zirconia (to 2300 K) or magnesia (to 2700 K), but metals such as platinum and tantalum, and graphite linings are used for some reactions. If any of the reactants are volatile or air sensitive,

then this simple method of heating in the open atmosphere is no longer appropriate, and a sealed tube method will be needed.[1]

4.2.2. Heat treatment

The mixture of reactants and salt is put in a covered or sealed crucible and heated in a furnace. A platinum crucible is used in the laboratory experiment. Alternatively, alumina and zirconia crucibles may be used if the chemical interaction between the crucible and the reactants and product is negligible. The heating conditions such as temperature and duration are determined by the desired powder characteristics. In general, the rate of material transport is increased with an increase in the heating temperature. At the same time, the salt evaporation increases as well. The heating duration is determined by the reaction rate and the size and shape of the product particles. Typical conditions are temperatures between 800°C and 1100°C with durations between 30 and 60 min. In a particular system, the heating rate influences the size of the product particles (Yoon et al., 1998). After heating, the product mass is washed with an appropriate solvent to remove the salt. Ordinarily, this is water, which means that water-soluble salts are typically used in molten salt synthesis. The solubilities of chlorides and sulfates are generally high and washing with water three or four times seems sufficient to remove all the salt. Nevertheless, the ions from the dissolved salt may adsorb on the surfaces of the product particles, and then, repeated washing is necessary. The chloride ions are sometimes detected by an Ag⁺ solution even after ten times of washing. To desorb ions efficiently, the use of hot, instead of cold, water is recommended. After washing, the supernatant water is decanted and the remaining powder is dried.[15]

5 . MATERIALS AND METHODES

5.1 The Synthesis of CdNb_2O_6

CdNb_2O_6 ceramic powder has been prepared by a molten salt method using rare earth doped compounds with columbite structure were synthesized using starting materials of metal nitrates , niobium oxide and salt. The mechanism of this behavior has been studied by measuring the spectral characteristics of the photoluminescence and photoluminescence excitation spectra on the crystalline and morphological properties of the powders as determined from investigations indicated that while single phase CdNb_2O_6 compound was produced using $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ salt systems, CdNb_2O_6 columbite niobates were produced by using the optimum parameters which were determined from XRD (Rigaku Dmax-33), SEM (JSM 5910LV) and the surface morphology and microstructure were examined by The excitation and emission spectra were recorded on a fluorescence spectrofluorometer systems (FLUOROMATE FS/2 SCINCO). In the present study , CdNb_2O_6 compounds with columbite structure were synthesized using starting materials of metal nitrates and niobium oxide and salt systems such as , $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ at salt/oxide molar ratios and at heat treatment temperatures .All chemical materials are given inTable5.1.

Table 5.1 : Chemical materials in use of synthesis Columbite compounds.

Chemical material	Factory	Purity	CAS
Cadmium nitrate	AlfaAesar	98.5%	10022-68-01
Niobium(v) Oxide	AlfaAesar	99.9%	1313-96-8
Sodium Sulfate	Merck	99.0%	536092

The CdNb_2O_6 was prepared by the following route. The starting materials were weighed and mixed and grind very fine in an agate mortar and pestle. Using MSS method, the dry mixture of the precursors in the stoichiometric composition was

mixed with an equal weight of salt. Salts used in this experiment were eutectic mixture of $0.635\text{Li}_2\text{SO}_4$ - $0.365\text{Na}_2\text{SO}_4$ 1:1 molar ratio.

then mixture placed in a crucible and heated in a porselen crucible (to prevent salt evaporation) at 900°C temperature .After thermal treatment the sulfate were removed from the products by washing with hot deionized water several times until the filtrates gave no reaction with silver nitrate solution. The calcination temperature of the samples annealed with heating rate $250^\circ\text{C}/\text{h}$ and after calcination process at this temperature, again cooled over $250^\circ\text{C}/\text{h}$ cooling rate to room temperature .The calcination temperature was 900°C .The cooled sample was washed with warm distilled water and transferred to beaker , by trying to remove salts from the mixture ,so placed on magnetic mixer heating and set out 300d/d at 200°C for 15min .This work repeated for 5 or 6 times by washing with warm distilled. Finally the wet powders were dried in a drying oven at 82°C for 10 hours.

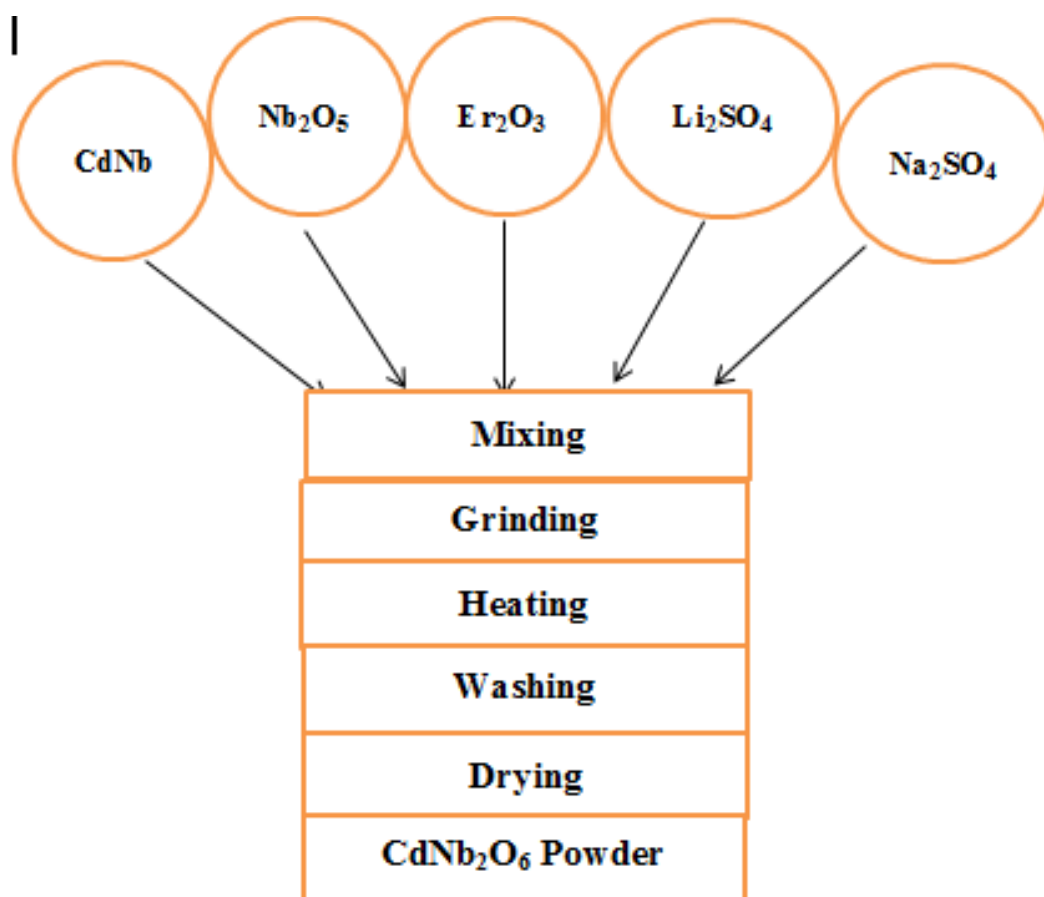


Figure 5.1 : Schematic of synthesized process of undoped CdNb_2O_6 .

5.1.1 Er₂O₃ doped cadmium niobate (CdNb₂O₆)

CdNb₂O₆ columbite components doped with 0.5,1.0, 3.0,6.0 % mole Er₂O₃ .After adding Er⁺³ in mixture of starting materials, all steps of MSS should be done again. There are ratio of doping and salt systems in Table 5.2.

Table 5.2 : Ratio of doping and salt systems.

Columbite component	Doped types	Doped amount %	Salt systems
CdNb ₂ O ₆	Er ₂ O ₃	0.5,1,3,6	Li ₂ SO ₄ /NaSO ₄



(a),(b),(c)



(d)

Figure 5.2 : (a),(b),(c),(d) shows all steps of molten salt methods.

5.2. Structural Characterization

5.2.1 Basics of Diffraction and X-Ray Diffraction (XRD) analysis

Crystalline materials are characterized by the orderly periodic arrangements of atoms. The unit cell is the basic repeating unit that defines a crystal. Parallel **planes of atoms** intersecting the unit cell are used to define **directions** and **distances** in the crystal. These crystallographic planes are identified by **Miller indices**.

The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract light. Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles. The electrons in an atom coherently scatter light. The electrons interact with the oscillating electric field of the light wave. Atoms in a crystal form a periodic array of coherent scatterers. The wavelength of X rays are similar to the distance between atoms. Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal. X Rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.

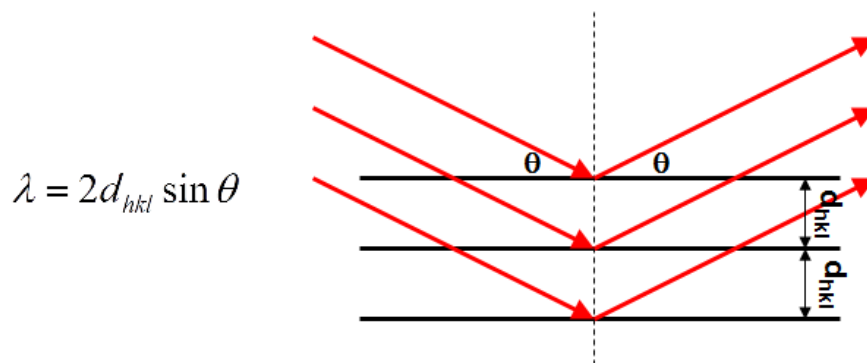


Figure 5.3 : Bragg's Law.

Bragg's law is a simplistic model to understand what conditions are required for diffraction.

for parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied. In our diffractometers, the X-ray wavelength λ is fixed. Consequently, a family of planes produces a diffraction peak only at a specific angle θ . Additionally, the plane normal must be parallel to the diffraction vector. Plane normal: the direction perpendicular to a plane of atoms. Diffraction vector: the vector that bisects the angle between the incident and

diffracted beam .The space between diffracting planes of atoms determines peak positions. The peak intensity is determined by what atoms are in the diffracting plane

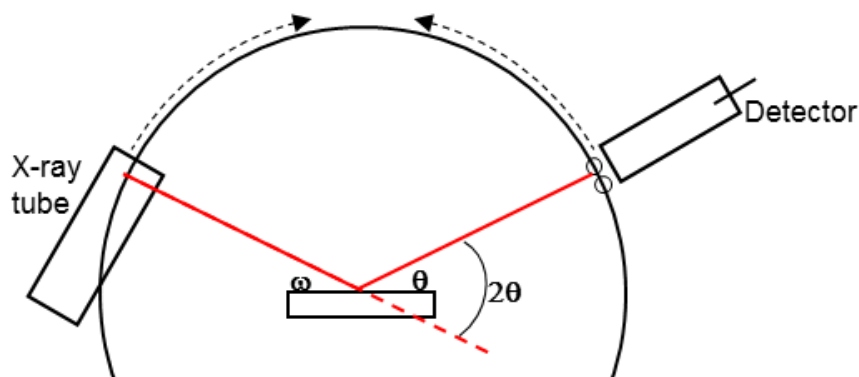


Figure 5.4 : Powder diffractometer.

powder diffractometers typically use the Bragg-Brentano geometry. The incident angle, ω , is defined between the X-ray source and the sample. The diffracted angle, 2θ , is defined between the incident beam and the detector angle. The incident angle ω is always $\frac{1}{2}$ of the detector angle 2θ . In a $\theta:2\theta$ instrument (e.g. Rigaku), the tube is fixed, the sample rotates at θ°/min and the detector rotates at $2\theta^\circ/\text{min}$. In a $\theta:\theta$ instrument (e.g. PANalytical X'Pert Pro), the sample is fixed and the tube rotates at a rate $-\theta^\circ/\text{min}$ and the detector rotates at a rate of θ°/min .

X-ray Diffraction (XRD) is a powerful technique used to uniquely identify the crystalline phases present in materials and to measure the structural properties (strain state, grain size, phase composition, preferred orientation, and defect structure) of these phases. The diffractometer was used a Rigaku D-MAX 2200 model, equipped with a cooper X-ray tube. X-Ray Diffractometer have been done by grinding powders in agate mortar and placing at aluminum sample. The measurements were taken at a generator tension of 40 KV and a current of 20mA. All traces were recorded using CuK α and the diffractometer setting in the 2θ range from 20° to 60° with a stepsize of 0.02° . $10-70^\circ$, $1^\circ/\text{min}$ of scanning speed. The X-ray diffraction spectra show the intensities of the diffraction peaks as a function of the detecting angle 2θ . The inter planar spacings d , corresponding to the peaks are calculated from Bragg's diffraction law. These specific directions appear as spots on the diffraction pattern called reflections.[2]

5.2.2 Scanning Electron Microscopy(SEM)

Any physical process that can be induced by the presence of an electron beam and that can generate a measurable signal can be used to produce an image in the SEM. The SEM can also be used to provide crystallographic information. Surfaces that to exhibit grain structure (fracture surfaces, etched, or decorated surfaces) can obviously be characterized as to grain size and shape. Electrons also can be channeled through a crystal lattice and when channeling occurs, fewer back scattered electrons can exit the surface. The channeling patterns so generated can be used to determine lattice parameters and strain. Detector sensitivity drops off at the high-energy and greater than 20keV. The particle morphology of the starting materials and synthesized powders was taken by this SEM (JEOL JSM 5910LV) perovskite phase was observed in all the prepared samples. The collection of SEM images taken from the surface of Au-Pd solder sample contaminated with a low concentration of Au, (Polaron Range SC7620 Sputter Coater). The X-ray energy dispersive spectra (EDS) were measured by using a (EDS, OXFORD Industries INCAx-sight 7274, 133-eV Resolution) and investigated.[18]

5.2.3 Fluorescence spectrometer system

The established fluorescence spectrometer system (SCINCO, FluoroMate FS-2, Korea) in this study is shown in Figure 5.4. Table 5.4 shows the specifications of the fluorescence spectrometer system. Information about devices are used for Characterization process are in table 5.3.



Figure 5.5 : FluoroMate FS-2 fluorescence spectrometer system.

The sample was put on a solid sample holder. The sample used in the experiment comprised of 150 intact seeds and 150 aged seeds and these were grouped into 15 seeds per holder. The excitation was set to 5 nm increments between 200~700 nm and emission wavelength was scanned with 1 nm intervals between 100~900 nm.[4]

Table 5.3 : Information about devices for Characterization process.

Instrument	Mark and model	Factory
X-RAY DIFFRACTOMETRE(XRD)	D-MAX 2200	RIGAKU
(SEM) SCANNING ELECTRON MICROSCOPY	JSM 5910LV	JEOL
FLOURESCENCE SPECTROFLUOROMETER	FLUOROMATE	SCINCO
LASER SUPPLY PHOTOLUMINESCENCE SPECTROSCOPY	ACTON SP255I	APOLLO INSTRUMENTS
DIODE LASER SYSTEM	350mw 1064	APOLLO INSTRUMENTS
ELECTRONIC BALANCE	N810.3FT.18	KNFLAB
MAGNETIC MIXER OVEN	MR3001KFORTE MEDCENTER	HEIDOLPH MMM-GROUP

Table 5.4 : Specification of the FS-2 fluorescence spectrometer system.

Component	Type
Xenon-arc lamp	150W
Wavelength Range	190~900 nm
Monochromator	1200 groove/mm
Minimum Resolution	0.5nm

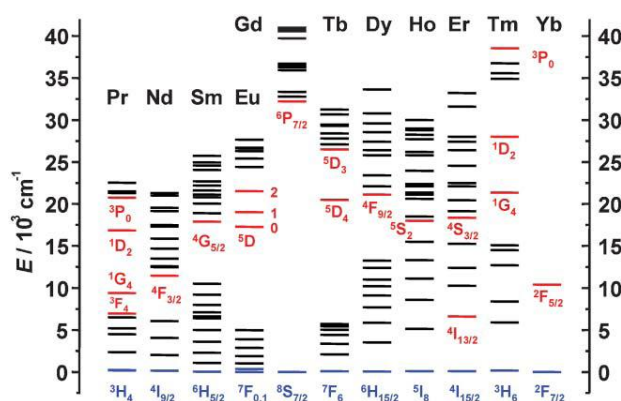


Figure 5.6 : Partial energy diagrams for the lanthanide aquo ions.

5.2.4 Photoluminescence instrumentation

Photoluminescence spectroscopy has been accomplished through vacuum Ultra violet (VUV) excitation followed by a photon emission measurement. Excitation photons were produced with a Deuterium Lamp – Hamamatsu Model L1835, which is capable of efficient emission in the range from 115 nm to 400 nm. The light produced is then directed to a spherical mirror, which focuses the photon stream to the entrance slit of the vacuum monochromator – ARC Model VM-502. The selection of the excitation wavelength was achieved with a 1200 G/mm grating that is coated with Iridium, allowing it to be used in the far UV regime of the electromagnetic spectrum. The light coming from the entrance slit of the vacuum monochromator as a point source falls on the grating so that the full spectrum is achieved. The grating is rotated so that the wavelength is selected using an ARC Spectra Drive Model 748 which is computer controlled with LabView drivers. Photons with a specific wavelength are then focused to the entrance slit of the sample chamber. A Turbo dyne pump was used to keep the spherical mirror housing, sample chamber and monochromator/grating under vacuum. The samples are irradiated in a sample chamber with a four-specimen holder, each specimen having a 10 mm diameter by 1 mm thick cavity with MgF2 cover plates.

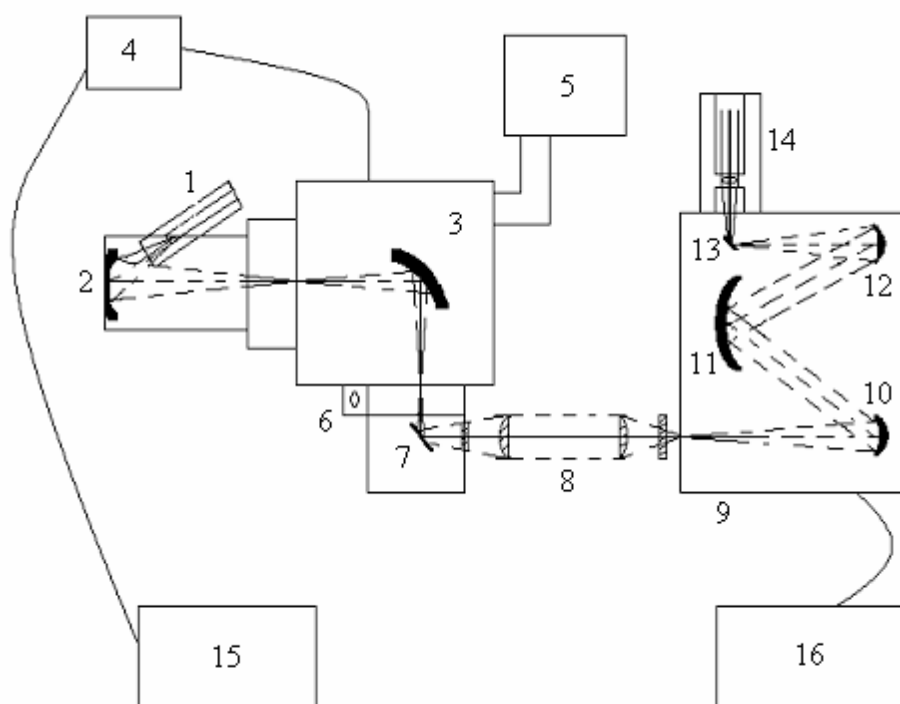


Figure 5.7 : Arrangement of photoluminescence spectroscopy system.

1. Deuterium Lamp – Hamamatsu Model L1835 (150W)
2. Spherical Mirror
3. VUV Monochromator with Iridium Coated Grating (1200 G/mm) ARC Model VM-502
4. Monochromator Control-ARC SpectraDrive Model 748
5. TurboDyne Pump
6. Beam Monitor
7. Sample Chamber with (4) Specimen Holder
8. Collimating and Focusing Lenses followed by 335 nm Optical Filter
9. Spectrometer – ISA Model 270M (0.27 m focal length)
10. Collimating Mirror
11. Grating (1200 G/mm)
12. Focusing Mirror
13. Side Exit Mirror
14. Photomultiplier Tube Housing with Focusing Lens
15. Computer No.1 – controlling excitation wavelength
16. Computer No.2 – controlling spectrometer and PMT.

5.2.5 Photoluminescence analysis (PL) and Photoluminescence Excitation measurements (PLE)

For measurements that require very high excitation source power, monochromatic exciting radiation, the ability to illuminate a very small sample volume, excitation with short light pulses, or propagation of the exciting light over large distances, it may be necessary to use a laser source. Photoluminescence (PL) tends to exhibit somewhat better limits of detection than lamp-excited fluorescence. However, the detection-limit advantage of PL tends to be much less dramatic than one might expect, because of the blank-limited nature of fluorometry. Because the wavelength of the exciting light must correspond to an absorption band of the analyte, fixed-wavelength lasers are not generally suitable for fluorescence spectrometry. A laser source for fluorometry should exhibit wavelength tunability over a fairly wide range in the UV or visible ranges. Thus, many applications of PL use a dye laser as the excitation source. The pump laser may consume a great deal of electrical power. Eventually, dye lasers may largely be replaced in fluorometry by compact solid state lasers with low electricity requirements. Small solid-state lasers have been used in

fluorometric analyses of compounds that absorb in the visible or near infrared. However, these devices cannot presently produce tunable UV (250 to 380 nm) output—needed for many applications of fluorometry—at high enough power to exploit the fluorescence advantage. Laser sources (usually argon ion lasers) are used in fluorescence flow cytometers, which are commercial instruments used to count and sort biological cells and other particles.[6]

The photoluminescence spectrum (PL) is obtained by the selection of a single excitation wavelength followed by the spectroscopic scanning of multiple emission wavelengths. A scan rate of 0.5 nm per step with an integration time of one second is used. Due to differences in the experimental conditions before the measurements, such as changes in the intensity of the reflected beam of the standard sample, PL patterns samples recorded at different times are corrected for the 1200 G/mm grating used in the spectrometer and factored with respect to the PL curve of the standard sample. Photoluminescence excitation (PLE) measurements involve excitation by a range of wavelengths, while the wavelength of the emitted photons is fixed. Thus, the monitoring wavelength is selected as the peak position determined in the PL measurement, unless one is interested in collecting an excitation spectrum at another emission wavelength. As the spectrometer / PMT is commanded to count photons for a specified length of time while the excitation wavelengths are scanned, a time versus intensity plot is produced. The time must then be converted to wavelengths based on the excitation scan rate of 12 nm per minute that is typically used. However, because the Deuterium Lamp (Hamamatsu L1835) has an extremely high peak corresponding to significant photon production of 162 nm wavelength, the spectrum of the sample taken must also be adjusted relative to the intrinsic spectrum of the lamp.

6. RESULTS AND DISCUSSION

6.1 Structural Characterization of undoped CdNb_2O_6

In order to affect the crystal structure and hence tune the chromaticity and emission intensity of CdNb_2O_6 , the XRD spectrum and SEM pictures of pure cadmium niobate is shown in Figure 6.1 and Figure 6.2 below. The X-ray spectrum of cadmium niobate shows a good crystallinity with an intense and narrow primary peak.

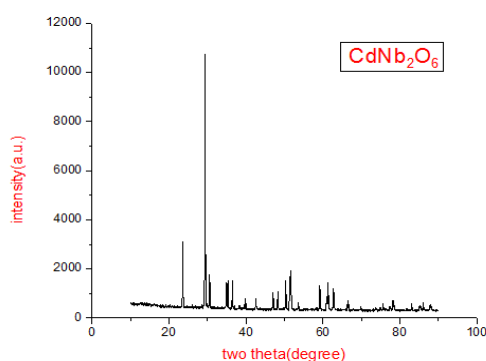


Figure 6.1 : XRD pattern Cadmium Niobate fired at 900 °C .

It can be observed from Figure 6.2 that the powder pattern undoped components has the columbite crystal structure.

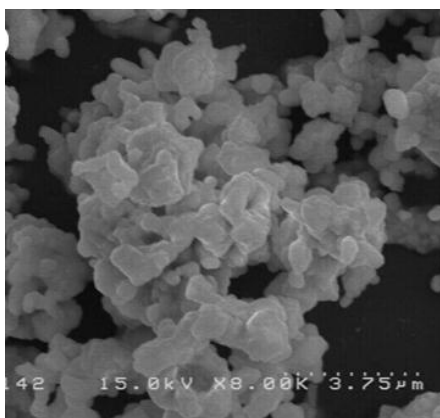


Figure 6.2 : Scanning electron micrographs of CdNb_2O_6 precursor powders annealed at 900 °C for 3 h.

6.2 X-Ray Diffraction and SEM images of CdNb_2O_6 doped with 0.5, 1, 3, 6 %mole Er^{+3}

In the present study ,rare earth doped CdNb_2O_6 compounds with columbite structure were synthesized by using starting materials of metal nitrates and niobium oxide and salt systems such as $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ salt/oxide with 1:1 molar ratio and at 900°C 4 hours heat treatment temperatures.

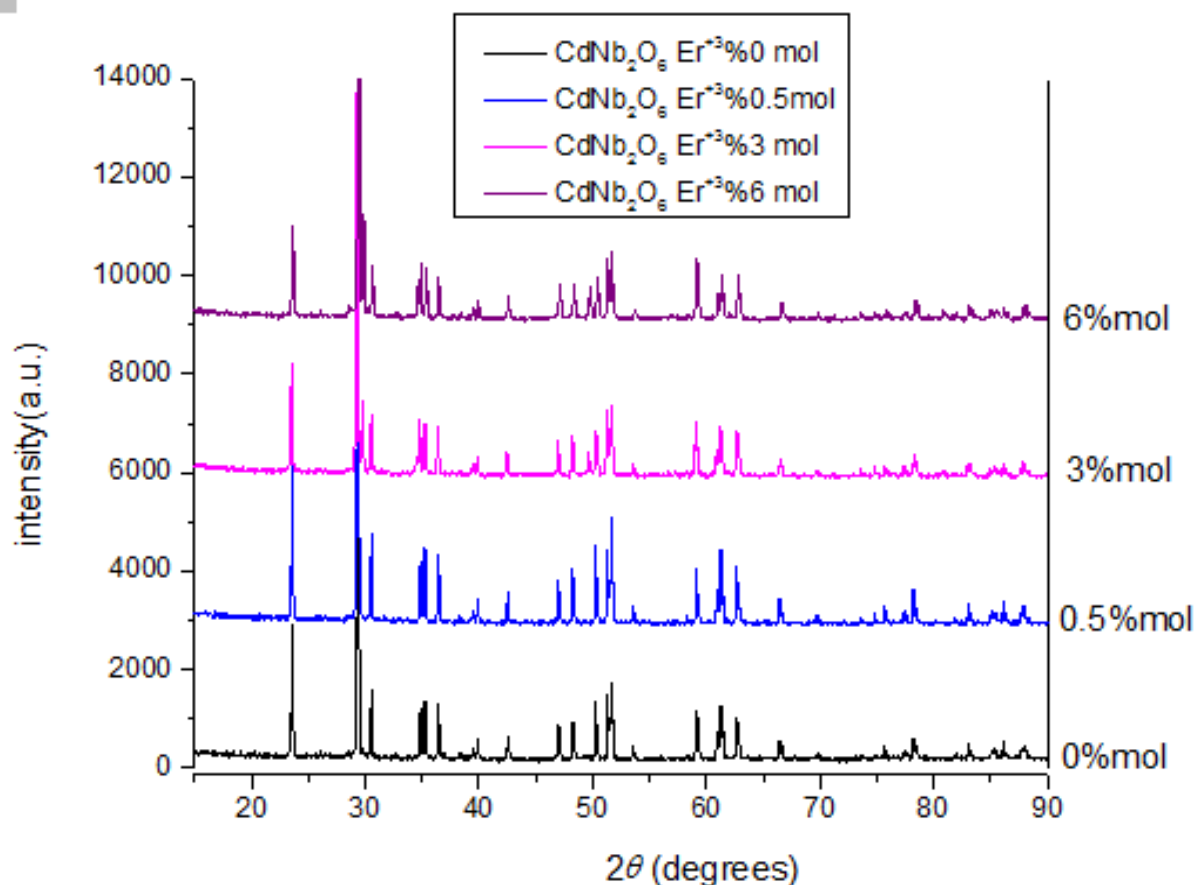
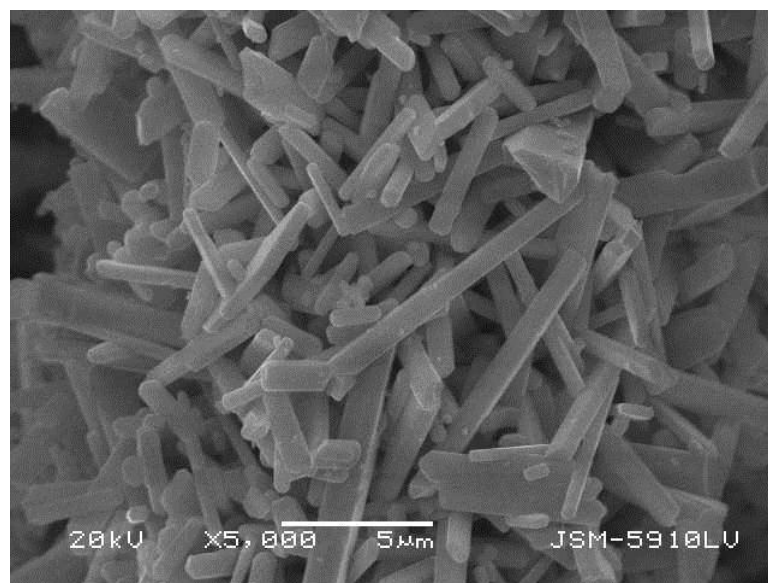
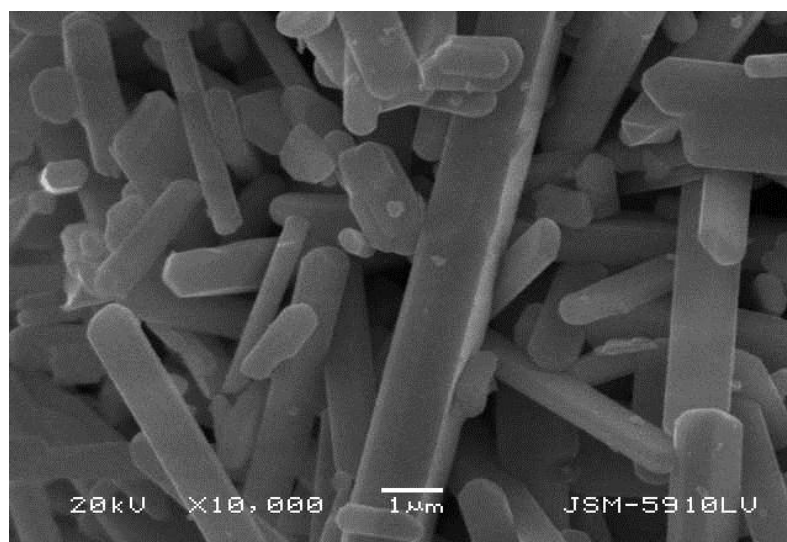


Figure 6.3: XRD graphs of $\text{CdNb}_2\text{O}_6\text{:Er}^{+3}$ powders.

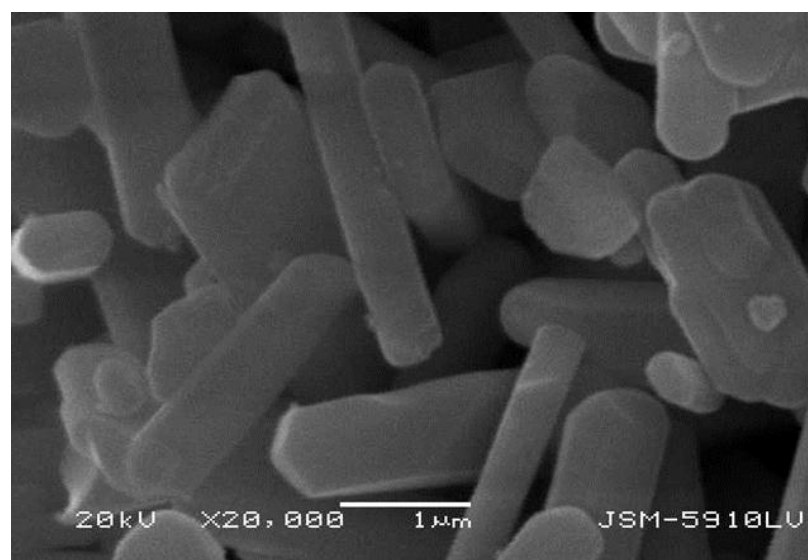
The XRD patterns of CdNb_2O_6 powders annealed at temperature of 900°C for 4 h is at Fig 6.3. It can be found CdNb_2O_6 phase (JCPDS file No., 38-1428) .The samples exhibited a single phase and all of the peaks were found to be CdNb_2O_6 phase at high temperature of over 900°C . The SEM pictures and The EDS of the material sintered at 900°C are shown in Fig 6.4.a–d and Fig 6.5.The rod-like particles seem to be distributed homogeneously.It is believed that a higher temperature and doping enhanced higher atomic mobility and caused faster grain growth.Therefore, the particle size increased along with the sintering temperature.However, the big particles were condensed by assembled micrograins, as found in the SEM results.



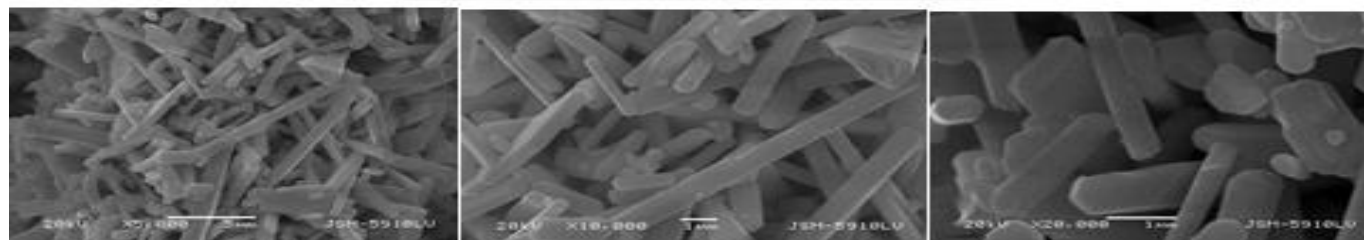
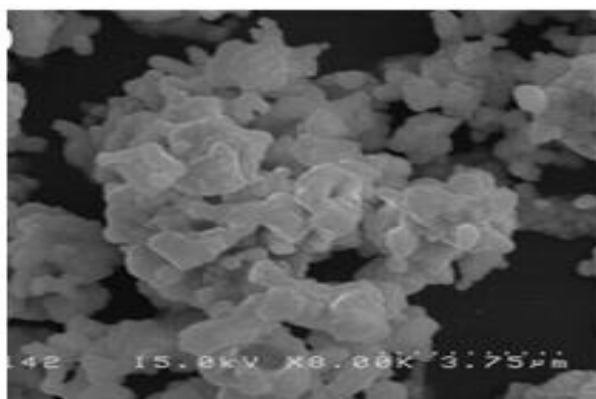
(a)



(b)



(c)



(d)

Figure 6.4 : (a),(b),(c) and (d) SEM of $\text{CdNb}_2\text{O}_6:\text{Er}^{+3}$ 1% mole doped powders

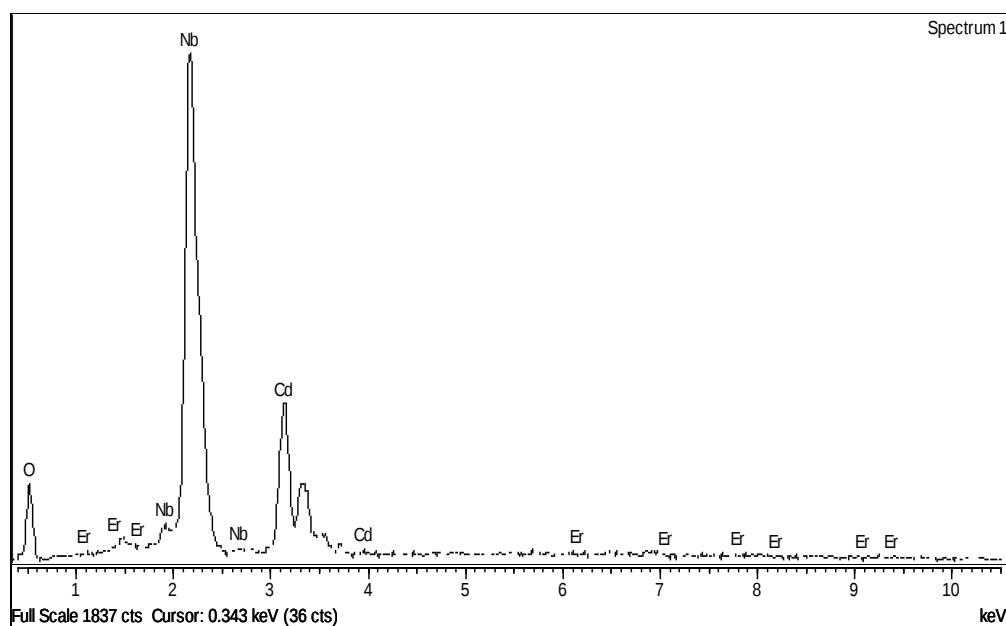


Figure 6.5 : The EDS graph of $\text{CdNb}_2\text{O}_6:\text{Er}^{+3}$

6.3 Optical Characterization

The optical characterization of the doped of CdNb_2O_6 was done by photoluminescence and photoluminescence excitation measurements. These measurements show a change in the emission intensity and the excitation maxima as

a function of alloying in order to allow us to correlate this data with the structural and chemical data from XRD.

6.3.1 PL and PLE of $\text{CdNb}_2\text{O}_6:\text{Er}^{+3}$

The contaminated system CdNb_2O_6 for 0.5, 1, 3, 6% mole was investigated. There were the increases in compare to the emission intensity of pure CdNb_2O_6 . However, as the sample approaches a non-luminescent CdNb_2O_6 phase and this is consistent with the PLE results shown in figure 6.6. This is also consistent with a discontinuity in the solid solution as shown. The positions of the emission peaks increase with additions of Er^{+3} .

1

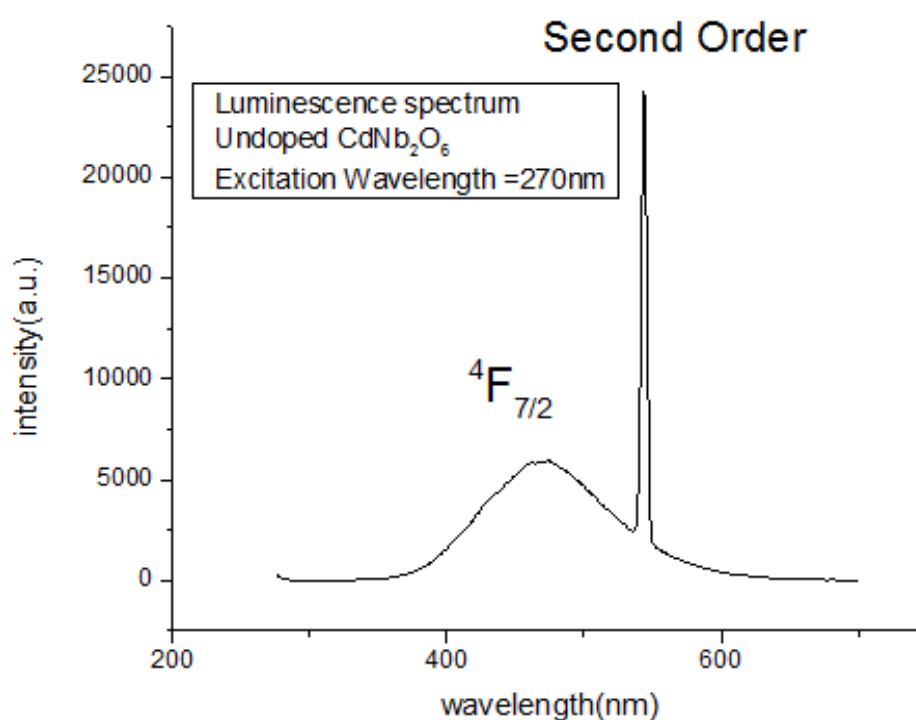


Figure 6.6 : The PLE results non-luminescent CdNb_2O_6 phase.

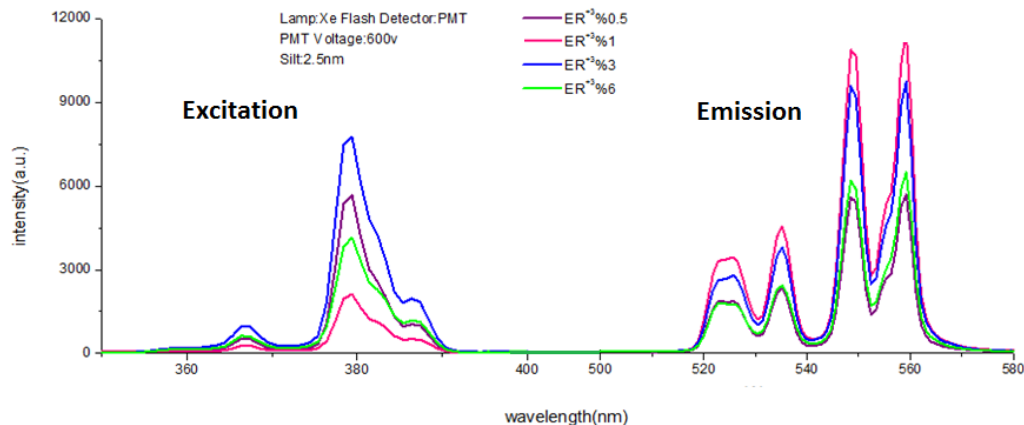


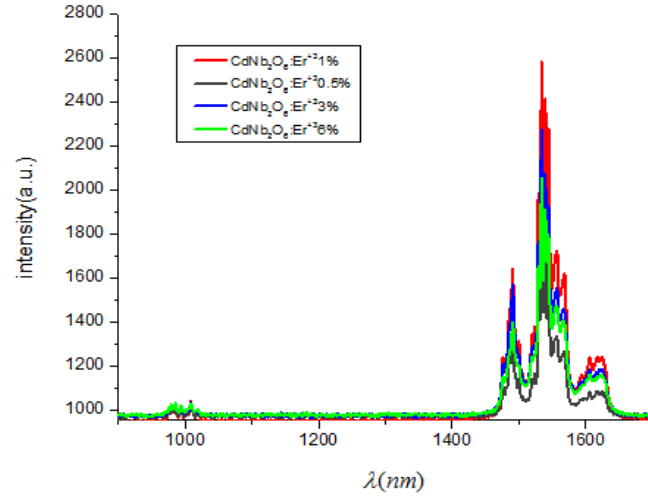
Figure 6.7 : Excitation spectra of the emission centered at 549nm due to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition in $CdNb_2O_6:Er^{3+}$ powders. Emission spectra of $CdNb_2O_6:Er^{3+}$ powders between 500 and 600nm when the Er^{3+} ions are excited at 379nm wavelength due to $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition.

The emission spectra showed the strongest band of the luminescence corresponded to the $^2H_{11/2} \rightarrow ^4S_{3/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at 379 nm, the excitation spectra showed clear with small bandwidth and high intensity. $CdNb_2O_6$ showed strong red luminescence during grinding, but when doped with Er^{3+} ions exhibited intensive red and green luminescence. It has been reported that rare-earth activated emission from Er^{3+} doped $CdNb_2O_6$ at 300 K is better than that of $CdNb_2O_6$. whereas the incorporation of Er^{3+} showed only the characteristic green emission. The cadmium-rich members were found to be superior in the study also investigated luminescence in the Er^{3+} doped $CdNb_2O_6$ system, with samples excited by an Ar ion laser at 805 nm and 9 K.

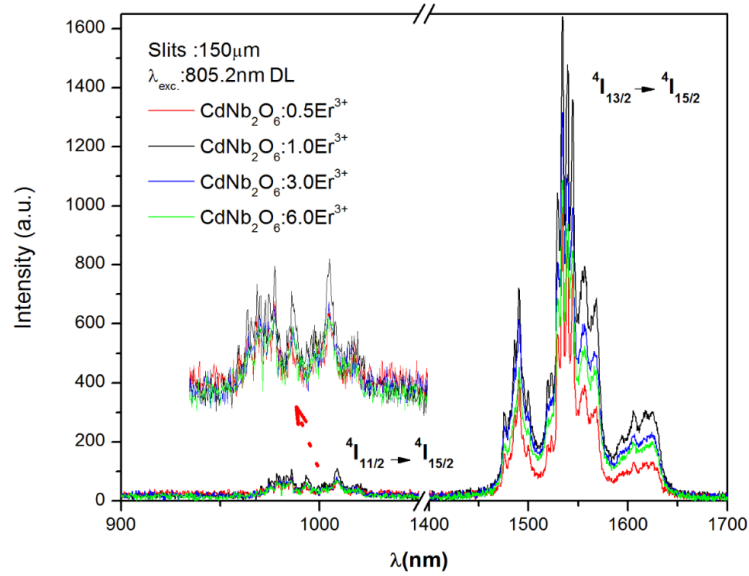
By contrast, the mixed $CdNb_2O_6:Er^{3+}$ system exhibited a dependence on Er^{3+} concentration, with broadening of spectral peaks, and a new peak appearing at ?% Er^{3+} . This indicated a second type of Er^{3+} emitting site at defect sites, and this new peak became stronger with ?% Er^{3+} and with increasing Er^{3+} content to a Pure $CdNb_2O_6$ with ?% Er^{3+} showed even more peaks as evidence of multiple Er^{3+} emitting sites.

The PL properties of pure prepared by a molten salt method, were studied in detail by a emission band centered at 379 nm was observed. Intensity of the host $CdNb_2O_6$ increased until the doping concentration reached 6 % mole, and was attributed to the energy transfer from Er^{3+} to NbO_6 groups. The luminescence of all peaks increased

due to a concentration quenching activated effect. Luminescence spectra of the samples doped with Er^{3+} ion were conducted in the wavelength-range of 900-1700 nm at 300K. Figure 6.8 shows that the concentration quenching occurred in high Er^{3+} ions doped sample.



(a)



(b)

Figure 6.8 : (a) Photoluminescence spectra of $\text{CdNb}_2\text{O}_6:\text{Er}^{3+}$ powders between 900nm and 1700 nm when the Er^{3+} ions are excited at 805nm wavelength. (b) Photoluminescence spectra of $\text{CdNb}_2\text{O}_6:\text{Er}^{3+}$ powders between 900nm and 1700 nm when the Er^{3+} ions are excited at 805nm wavelength.

6.4 Shape of Particles during Particle-Growth Stage

The free energy associated with the particle/molten-salt interfaces decreases during the particle-growth process via two routes. The first is the reduction of the surface area, resulting in particle growth. The second is the disappearance of surfaces with high energy, resulting in a shape change towards the equilibrium form. The particle growth at this stage is caused by Ostwald ripening, and the growth rate is determined by the solubility and diffusion coefficient of the product oxide (Rahaman, 2003).

Therefore, the heating temperature is a decisive factor in determining the particle size. The size can be controlled by selecting the heating temperature and its duration (Kimura & Yamaguchi, 1983). The exceptions are observed in highly faceted particles. The highly faceted surfaces have a high degree of smoothness at the atomic scale and high step energy, and their growth is sluggish (Kang et al., 2009). Advances in Ceramics - Synthesis and Characterization, Processing and Specific Applications grow in the particle-growth stage (Kimura & Yoshida, 2006). The top and side faces of the particles are highly faceted.

A typical example is obtained in $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$. The shape of the particles in the reaction stage is rectangular and changes to oblate in the particle-growth stage has a layered structure and platelike particles form in $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ the reaction and particle-growth stages. The (001) cusp is sharp in NaCl-KCl and shallow in $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$, as expected from their shapes in the particle-growth stage. A change in the particle shape as a function of the heating temperature is reported for heating at 900°C results in the formation of platelike particles and that at 900°C produces near-rectangular particles. The origin of this shape change is the change in the surface structure from smooth to rough at the atomic scale. The smooth surfaces have high step energy and develop the facets, leading to the platelike shape. The various crystallographic faces on the rough surfaces have almost the same growth rate, resulting in the near-rectangular shape. The rate-determining step is also changed from reaction-controlled to diffusion-controlled.

7. CONCLUSIONS

The goal of the research presented in this thesis was to investigate the microstructure and the photoluminescence properties of CdNb_2O_6 doped with various amounts of Er^{3+} ions and it was also necessary to find ways to increase its photoluminescence intensity. Thus, the only method of improving its intrinsic luminescence was to modify the crystalline size of the host lattice. The mechanism of this behavior has been characterized by XRD, SEM, EDS, PL and PLE analysis. The XRD patterns of samples exhibited a single phase and all of the peaks were found to be CdNb_2O_6 phase (JCPDS file No., 38-1428) at high temperature of over 900°C . The Morphology and particle size were also analyzed by SEM and the samples indicated that the rod-like particles seem to be distributed homogeneously. Therefore, the particle size increased along with the doping and sintering temperature. It is believed that a higher temperature and doping enhanced higher atomic mobility and caused faster grain growth. However, the effect of doping and annealing temperature on the particle is the unique morphological of the precursors involved are all important, readily controllable factors that influence the growth rate as well as the resultant structural characteristics (size, shape, and crystallinity) of the as-prepared particles. It was observed that while the particles are smooth and reasonably well crystallized, the particle sizes are not uniform and the shapes are uneven. Therefore, an improved synthesis procedure could help to make the particles more even or rectangular and make the sizes more uniform within the powder, which would lead to additional gains in the photoluminescence efficiency and intensity. By measuring the spectral characteristics of the photoluminescence and photoluminescence excitation spectra on the crystalline and morphological properties of the powders. However, The luminescence properties of columbite compounds investigated at low (200-800 nm) and high (900-1100 nm) wavelengths depending on dopant type addition into various amount of $\text{Er}^{+3}:\text{CdNb}_2\text{O}_6$ compound increased the luminescence intensity. The emission intensity of CdNb_2O_6 with increasing rare earth dopant concentration due to transfer of excitation energy absorbed by rare earth dopants to the NbO_6 groups. The

Laser induced spectroscopic analysis performed between (900-1100nm) showed that luminescence intensity of cadmium niobate increased by increasing dopant ratio but concentration quenching was observed for CdNb_2O_6 above 1%mol dopant concentration. Thus, it has the possibility of being used in other applications such as in high energy lamps for lighting.

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