PREPARATION OF Nd – FLUORIDE LASER GLASS AND INVESTIGATION OF ITS CHARACTERISTICS

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ABSTRACT

Fluorophosphate neodymium laser glass has been prepared by discontinuous melting technique. Special melting and casting conditions were followed to prevent devitrification of glass samples. Furnace melting followed by slow cooling resulted formation of non vitreous glass. Problems of high viscosity melt and incomplete solubility and immiscibility of glass components were encountered by adjusting composition of glass components. X-ray diffraction analysis of the prepared glass samples proved the formation of amorphous phase. The prepared Nd – fluoride glass has low refractive index which is an important parameter for high power laser application. Optical properties of Nd – fluoride glass samples were investigated. UV – visible spectra showed almost total absorbance of light at wave length below 400 nm, while in the visible range a typical spectrum of Nd^{3+} ions covers the entire range. Infra – red spectral properties of these samples were studied. Transmission of the glass was found to be dependent on neodymium concentration.

KEYWORDS

Nd- laser Glass, Refractive Index, Optical Absorption, Infra- Red Measurement, Glass Density, X-ray Diffraction, Glass Casting and Phosphate Glass.

الخلاصة

زجاج ليزر النيودميوم الفلوروفوسفاتي تم تحضيره بطريقة الصهر الغير مستمر. وقد اتبعت ظروف خاصة لعمليتي الصهر و الصب (القولبة) لمنع حدوث ظاهرة التبلور في نماذج الزجاج. عند إجراء عملية الصهر في الفرن يتبع ذلك التبريد البطئ لوحظ حدوث ظاهرة التبلور(اللازجاجية) في نماذج الزجاج. تم معالجة مشكلتي اللزوجة العالية للمنصهر وعدم الذوبانية الكاملة والامتزاج التام لمكونات الخليط الزجاجي بالسيطرة على مكونات الخليط الزجاجي. أظهرت نتيجة الفحص بطريقة حيود الأشعة السينية إن النماذج الزجاجية المحضرة عشوائية التركيب والتكوين. إن نماذج زجاج النيودميوم- الفلوريدي المحضرة كانت تتميز بانخفاض معامل الانكسار الضوئي وهو شرط مهم في تطبيقات زجاج القدرة العالية. الخواص الضوئية لزجاج النيودميوم- الفلوريدي جرت دراستها حيث تبين إن الضوء يمتص كليا في منطقة الطول ألموجي الأقل من 400 نانومتر من الطيف المرئي – فوق البنفسجي بينما في منطقة الضوء المرئي فان طيف ايون النيودميوم يغطي غالبية المدى من الطول ألموجي. أما الخواص الضوئية للزجاج في منطقة تحت الحمراء فقد تمت دراستها حيث وجد إن نفوذية الضوء تعتمد على تركيز النيودميوم وبدرجات مختلفة وحسب الطول ألموجي.

INTRODUCTION

The glass laser currently provides pulse of high power, energy, and radiance, and shorter duration **(Young 1967)**. There are several characteristics of the glass host which are important.

Glass host is isotropic, durable, can accept large dipping concentration uniformly, and can be fabricated inexpensively in various shapes and large sizes with diffraction limited optical quality **(Snitzer and Young 1968)**. The index of refraction of host glass can be varied from 1.4 to almost 2.0 and the thermal properties can be selected to minimize the optical aberrations caused by temperature variation in the laser rod **(Loh 1966)**. One of the most useful laser systems is that which results when the Nd^{3+} ion present as an impurity atom in glass **(Snitzer and Young 1968)** and **(Johnson and Nassau 1961)**. The first report of laser action using a glass host material was by Snitzer in 1961 using a potassium barium silicate glass containing 2-wt% neodymium oxide **(Snitzer 1966)**. Since then much research has been carried out to determine the effects of glass composition on the parameters which affect the laser performance of glasses doped with rare earth ions **(Patek and Edwards 1970)**. The Nd^{3+} doped glasses have been studied in most detail but the behavior of other fluorescents rare earth ions has also been examined, e.g. Yb^{3+}, Ho^{3+}, and Er^{3+} **(Young 1984)**.

In addition to oxide host glasses (including tellurite and germanate as well as the more familiar silicate, borate and phosphate systems) the work has included a number of halide and oxyhalide systems **(Weber 1983)**

The small refractive index of some fluoride glasses makes them a prime material for high powered lasers, such as those used for nuclear fusion research. A good fluoride glasses may be defined as one that has a low refractive index, resistant to moisture attack, and can be made into a large block without devitrification. Pure BeF_2 glasses would be ideal if it where not for the fact that BeF_2 is hygroscopic. Other less soluble fluorides such as CaF_2, MgF_2, etc. must be incorporated to raise the resistance to moisture attack, even though their presence increases the probability of devitrification.

In the binary systems of fluoride glasses containing BeF_2 and alkali fluoride or alkaline earth fluoride, a large mole fraction of BeF_2 has to be present in order to form a glass **(Rawson 1967)**. This requirement is also the case in the ternary systems; alkali / alkaline earth / Be fluorides found by Vogel **(Vogel 1971)**. The resulting glasses are sensitive towards moisture attack. To over come this problem is by reducing BeF_2 fraction but this may lead to devitrification of glass and loss of its optical properties. Sun found that this problem can be solved by substitution of AlF_3 for BeF_2 **(Sun 1949), (Sun 1949) and (Sun and Huggins 1951)**.

One glass made by Imoka has the mol % composition 12 BeF_2, 32 AlF_3, 29 CdF_2, and 27 PbF_2 **(Imaoka 1954)**. These results indicate that AlF_3 is a good intermediate in a glass formation; it yields glasses with superior optical quality, stable with respect to moisture attack and devitrification.

The refractive index of fluoride glasses varies with their composition. Goldstein and Sun reviewed refractive index values and composition of 114 fluoride glasses **(Poulin et al. 1977) and (Vogel 1966)**.

Sun developed a composition of vitreous fluorophosphate systems on the base metaphosphate aluminum and fluorides of metal from the first and second group of the periodic table of the chemical elements **(Goldschmidt 1972), (Heyne and Anorg 1933), (Mackenzie and Baldwin 1976) and (Sun 1950)**. Several authors have studied domains of glass forming and some physicochemical and optical properties in fluorophosphate glasses. IR spectroscopic investigations of the glasses show that structural lattices of these glasses have phosphate, fluoride and fluorophosphates groups **(Golubtsov et al. 1969), (Golubtsov et al. 1971)**, **(Golubtsov et al. 1970) and (Golubtsov et al. 1971)**. The presence of different rare earth ions at different mole percentages were investigated **(Kolobkov et al. 1971), (Chalilev et al. 1979) and (Chlilev et al. 1978)**.

In this work phosphate – borate based Nd doped fluoride glasses were prepared. Formations of vitreous phase were examined together with some optical properties.

EXPERIMENTAL WORK

Materials, Equipments and Instruments

Chemical compounds: the following compounds were used: B_2O_3 (as H_3BO_3), P_2O_5, MgF_2, NaF and Nd_2O_3. Their purity is the highest available, but not less than 99%.
Crucibles: made from platinum, nickel, porcelain, silica, alumina, graphite and Pyrex.
Melting equipments: electrical furnace type (Nabertherm FRG) and high temperature torch (Butane – oxygen) were used.
Analytical balance: type: Sartorious (FRG) sensitivity 0.1 mg was used for weighing process of the raw materials. It was used for density measurement.
Refractive Index Measurements: a traveling microscope was used. Method described else were **(Krylova and Poluehktov 1995)**.
X-Ray Diffraction: measurements were carried out using Phillips XRD machine type PW-1840 with copper target.
Optical Measurements: SHIMADZU spectrophotometer type (UV – 1650 PC) (Japan) was used for ultra- violet to visible range spectra absorption measurements in the wave length range 200 – 1100 nm.
SHIMADZU spectrophotometer type (FTIR -8000) (Japan) was used for recording transmission of the glass samples in the frequency range 500 – 4000 cm^{-1}.

Preparation of glass samples

The aim of the experimental work is to find a successful combination of different working parameters that ultimately yield a glass sample suitable for examination and presentation as a laser glass medium. These parameters involve:

1. The selection of chemical formulation which contain adverse materials or compounds that differ in;
   - Thermal stability, during heating and melting.
   - Solubility and miscibility with other compounds.
   - Do not suffer segregation or phase separation upon cooling.
   - Resistance to devitrification, which usually results a non-glass medium.
2. Suitable heating, melting and cooling steps.
3. Inertness towards atmospheric attack, so it is easier practically to carry out the work under normal atmosphere and no further complication for need of inert atmosphere or special containment.
4. Due to the presence of fluoride ions in the glass melt, only platinum crucibles are suitable for melting and graphite mould for casting.
5. Only melting furnace or gas torch is suitable to carry out melting steps which is followed by pouring out the melt into the graphite mould.

As mentioned above there is a need for a compromise to yield a proper glass sample suitable for optical examination.

RESULTS AND DISCUSSION

Glasses can be made from many substances oxide and non oxide. Traditionally, glass must contain a major percentage of silica which is the glass forming oxide. Attempts to find a new glass forming oxide have led to the discovery of phosphate and borate glasses. Recently, new types of glasses are prepared to meet specific requirements and applications, these are germinate, arsenate, tellurite, tungestate, titanate, molybdate, vanadate and plumbate glasses **(Snitzer and Young 1968)**. The non oxide glasses systems mainly chlorides and fluorides. These glasses transmit to longer wave length in the infra – red than do the silicate glass, and may eventually replace silica – based fibers in optical communication systems **(Drexhage 1985) and (Trans et al. 1984)**.

Upon addition of aluminum oxide or fluoride to silica, the cation Al^{3+} substitutes for Si^{4+} in the lattice thereby leads to the stability of the network, and thus is referred as network intermediate. Neodymium oxide or fluoride which is an intermediate acts as active medium in the lasing process.

The previously mentioned compositional facts have found to affect the properties of the prepared glass. Many experiments were carried out aimed to prepare neodymium containing glass of fluorophosphate base by discontinuous melting technique. The glass mixture is heated rapidly to a temperature higher than the melting point of its components, stirred and mixed well to assure complete mixing and miscibility of mixture, and then cast rapidly in a graphite mould i.e. quenched.

Only platinum crucible was found suitable for this work. Porcelain, quartz and silica crucibles were cracked while nickel and stainless steel crucibles were attacked vigorously due to reaction of the melt (fluoride ions) with nickel and iron at high temperature **(Trans et al. 1984)**.

Many experiments were carried out to achieve the proper composition of the glass components. A new formula containing nearly 50 wt % of both glasses formers (B_2O_3, P_2O_5) and glass intermediate (AlF_3, MgF_2, NaF, Nd_2O_3) gave successfully glass samples suitable for laser work. The chemical composition is given in **table (1)**. Nd_2O_3 varies as in the following (LG9: 4wt %, LG10: 2wt %, LG11: 1wt% and LG12: 0wt %). Glass samples LG9 has intense violet color, the color intensity decreases as the concentration of the Nd_2O_3 is decreased, as shown in **Fig. (1)**.

In laser glass research, the aim is to manufacture a low refractive index glass. This target was found to be possible with fluoride glasses but the refractive index varies with their composition. In the prepared glass, the average value of index of refraction Nd = 1.392 ± 0.053 and thus, the refraction loss R = 2.7 %, and the transmitted light is 94.6 %.

Since fluoride glass is a mixture of many compounds; therefore, it is expected that the glass density is an average figure of fractional densities of its components. The measured densities of the prepared fluoride glass samples have an average value in the range 2.5±0.07. Glass density is an important technological factor; it is a critical factor in melting as in casting processes. It affects the refractive index and other optical properties.

To prove the formation of glass material from non – oxide or non – silicate compounds mixture, a blend of known composition was taken, sodium and magnesium fluoride added to it boron oxide (as boric acid) and phosphorous pentoxide. The compounds of this blend were mixed thoroughly and examined using x-ray diffraction technique which revealed clear pattern of these compounds. This is shown in **Fig. (2)**. When the mixture was melted, cast and cooled, then examined by x-ray diffraction technique. The spectrum showed no pattern, only amorphous phase which is an evidence for glass formation; this is shown in **Fig. (3) (ASTM Cards)**. Thus fluoride glass can be formed when alkali and alkaline earth fluorides are melted together with boron oxide and phosphorous pentoxide (glass formers) in the presence of aluminum oxide or better aluminum fluoride, the glass intermediate which plays the role of glass modifier. Furthermore, rapid cooling of the melt prevents devitrification process and thus only glass phase is formed **table (2)**.

Optical properties of Nd fluoride glasses

Developments of new optical materials become necessary when measurement and discrimination of electromagnetic radiation reached beyond the visible spectrum into ultraviolet and infra–red.

The spectral range of transmission is limited on the short wavelength side by electronic resonances and on the long wavelength side by atomic resonances. Light intensity is reduced by reflection which depends on the refractive index of the material, angle of incidence of the light, and in the absorption region on the absorption coefficient **(McCarthy 1963)** .

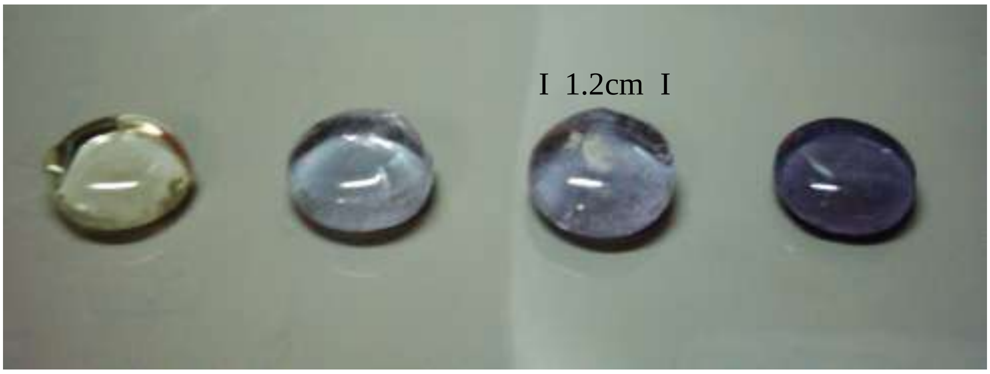
Further intensity losses are caused by light scattering resulting from irregularities on the surface or inclusions inside the material. For laser applications, absorption coefficient measurements can insure that the specific wavelength absorption of the laser beam is below required level.

Spectral absorbencies for glass samples LG9, LG10, LG11, and LG12 were measured in the uv-visible range between 200 and 1100 nm. The results of all samples are shown in **Fig. (4)- (7)**, the following observation can be made:

- Light is completely absorbed in the wavelength below 300 nm and partially absorbed between 300 –400 nm. This case is similar to that found in window glass (soda lime glass) which has a composition Na_2O – CaO – SiO_2.
- In relatively pure quartz the absorption edge is placed approximately at the wavelength λ=190 nm in the ultra – violet region of the spectrum **(Sigel 1973)**, Pure sodium fluoride and magnesium fluoride do not absorb uv-light, their absorption edge are 140 nm and 110 nm for single crystal respectively. Vitreous boron trioxide with an absorption edge at 170 nm transmits well in the ultra-violet region of the spectrum **(Vaughen 1944)**. Boron oxide and aluminum fluoride, both of them are trivalent, thus furnish the glass matrix with pairs of free electrons which enhanced resonances of the radiation with frequencies of electrons of various level of bonding. Therefore, the location of the absorption edge in the ultra-violet region of the spectrum depends upon the composition of the glass as well as the chemical nature of its components **(Nc Swain 1963)**.
- Glass LG12 does not contain absorbing component, thus it is transmitive for radiation in the visible region of the spectrum, see **Fig. (7)**.
- Nd doping of fluoride glass is necessary factor in laser application, thus glasses LG9, LG10 and LG11 are doped with 4, 2 and 1 % Nd as Nd_2O_3 respectively. The violet fluoride glasses revealed complex absorption spectra in the visible region which is a characteristic spectrum of rare-earth ion **(Stewart and Kato 1958)**; this complex spectrum is due to strong absorption due to transitions between different electronic configurations. In rare-earth ions in solid matrix, the 4f levels are strongly shielded from the crystal field by filled 5s and 5p shells and as a result, the emission lines are well defined sharp and narrow and the level structure varies slightly from one host to another **(Dieke 1958)**.
- A plot of absorption maxima of Nd^{3+} ion in the glass of different wavelength against neodymium concentration is shown in **Fig. (8)**. The absorption increases as the concentration is increased, but the rate of increased is lowered at 4% Nd concentration which means that higher Nd concentration is not useful, but trouble may be faced regarding solubility of glass components and its transparency. The figure implies that all spectra lines are due to neodymium since the absorbencies increase with the Nd concentration.

The energy of most molecular vibrations corresponds to that of the infrared region of the electromagnetic spectrum. Quanta of infrared radiation can excite atoms to vibrate directly, thus, the absorption of infrared radiation gives rise to the infrared spectrum. The largest vibrations are exhibited by the charges of the so called dipoles in resonance **(Banwell 1972)**.

The IR spectra of the glasses contain characteristic bands related to alkaline metaphosphate which are observed in the spectral range 1425 – 1350 cm^{-1} **(Corbridge and Lowe 1954)**. Wassilac et al investigated properties, structure and spectroscopy of fluorophosphate glasses doped with Nd. They established correlation between shift in spectral lines and concentration of fluorides in the glass **(Kolobkav et al. 1977)**. The presence of bands in 760 – 730 cm^{-1} is due to P-O-P vibration or P-F bands in monofluorophosphate anion **(Margaryan and Arutunyan 1973)**. **Fig. (9)** to **(12)** show the infrared spectra of fluoride glasses of the system B_2O_3 – P_2O_5 – AlF_3 – MgF_2 – NaF prepared in our laboratory. Glasses LG9, LG10 and LG11 are shown in **Fig. (9)**, **(10)** and **(11)** respectively. The spectra are identical but differ in percentage of transmission. They are characterized by the appearance of the spectral bands at 3450, 2450, 1750, 1650, 1550, 1300, 1100, 650 and 500 cm^{-1}. The transmission of these bands increase as the neodymium concentration is increased. Glass LG12 which is free from Nd shows different IR spectrum especially in the range 800 -1600 cm^{-1}.



LG12 LG11 LG10 LG9

Fig. (1) Samples LG9-LG12

Table (1)

Composition of fluorophosphate laser glass LG9

Compound	Weight %		Mole fraction %	
AlF_3	30		27.8	
NaF	10	50	18.6	58.9
MgF_2	10		12.5	
Nd_2O_3	4		0.9	
B_2O_3	26	46	29.1	40.1
P_2O_5	20		11.0	
Element	**Weight %**		**Mole fraction %**	
Al	9.6		6.7	
Na	5.5		4.4	
Mg	3.9		3.0	
Nd	3.6		0.48	
B	8.2		14.1	
P	8.7	16.9	5.3	19.4
F	31.0		31.0	
O	29.5		35.0	
F/P	3.56		5.85	
F/B	3.78		2.20	
B/P	0.94		2.66	

Table (2)

X-ray diffraction lines of infused glass
LG9 components **Fig. (2)**

Angle 2θ	Spacing d	compound
14.7	5.984	AlF_3
14.7	5.980	B_2O_3
16.0	5.515	AlF_3
27.3	3.261	B_2O_3
27.7	3.210	B_2O_3
28.8	3.091	AlF_3
35.1	2.545	MgF_2
40.4	2.227	MgF_2
43.8	2.062	MgF_2
49.9	1.823	B_2O_3
53.4	1.712	MgF_2
56.8	1.617	MgF_2

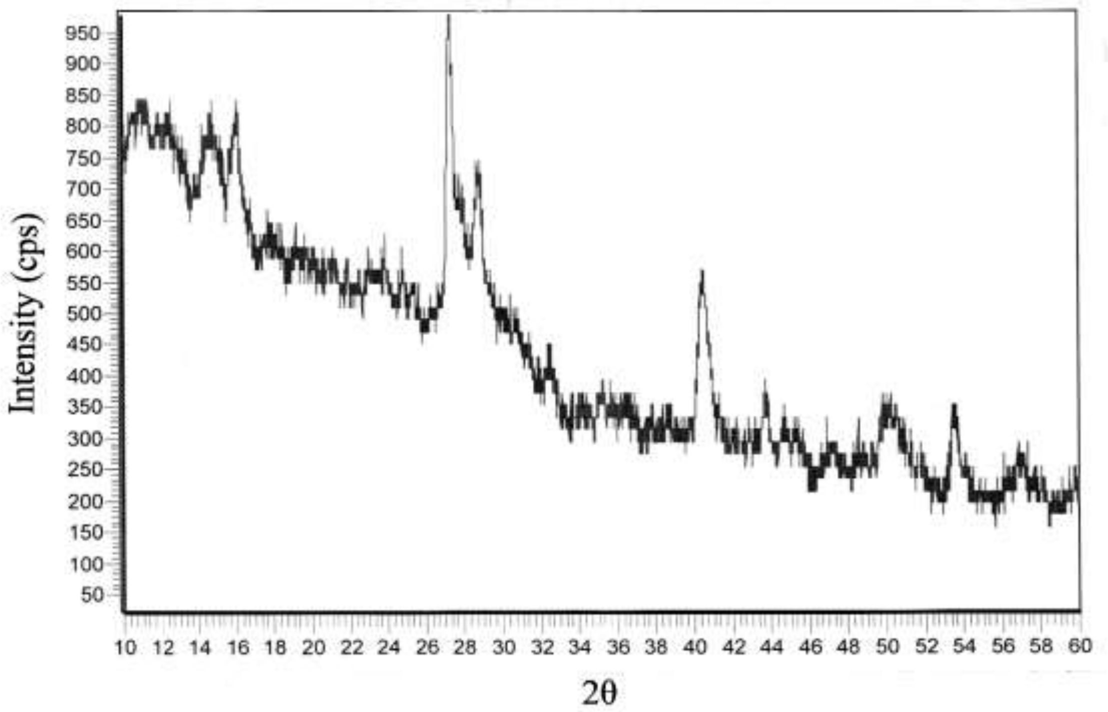


Fig. (2). X-ray diffraction for the sample LG9 (before melting)

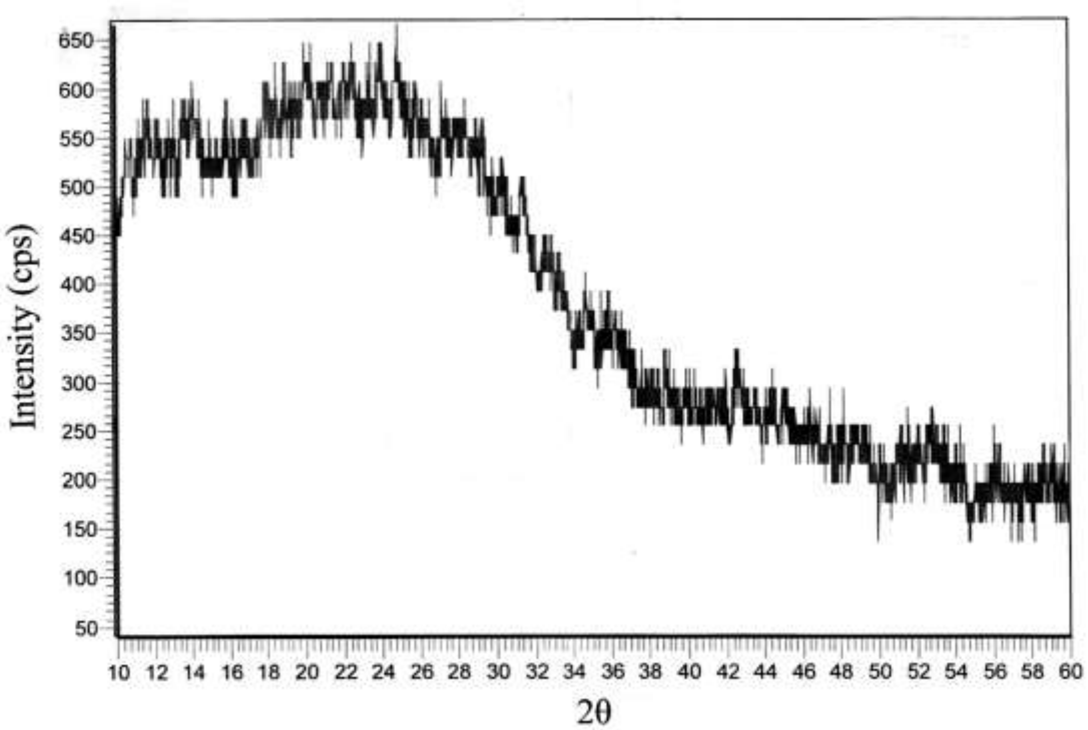


Fig. (3). X-ray diffraction for the sample LG9 (after melting)

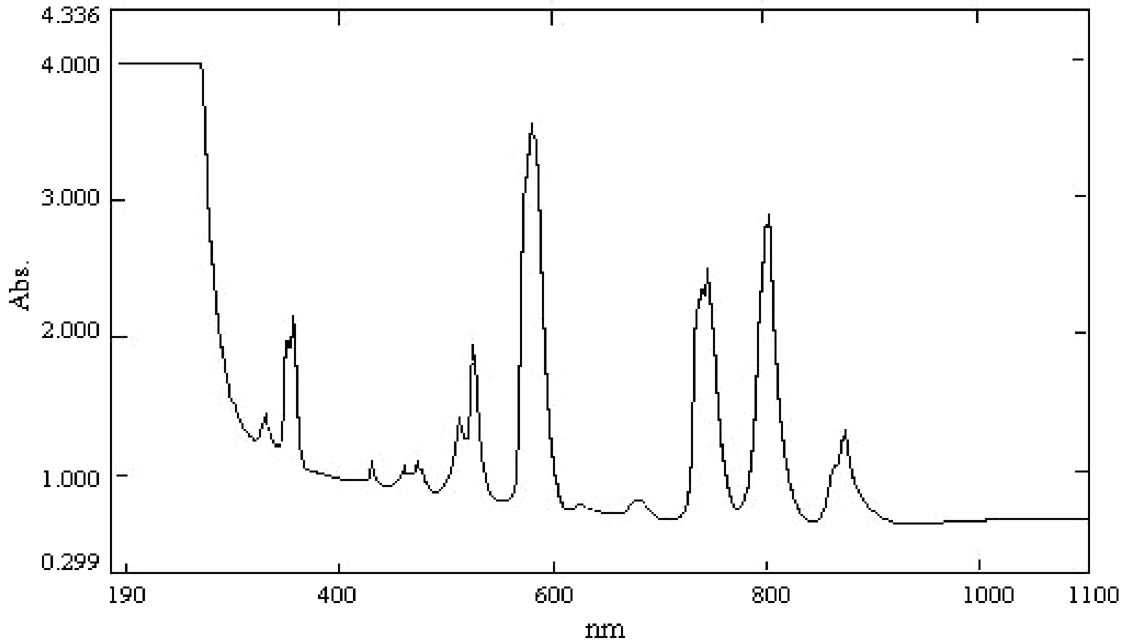


Fig. (4) uv-visible spectrum of Nd- glass sample LG9

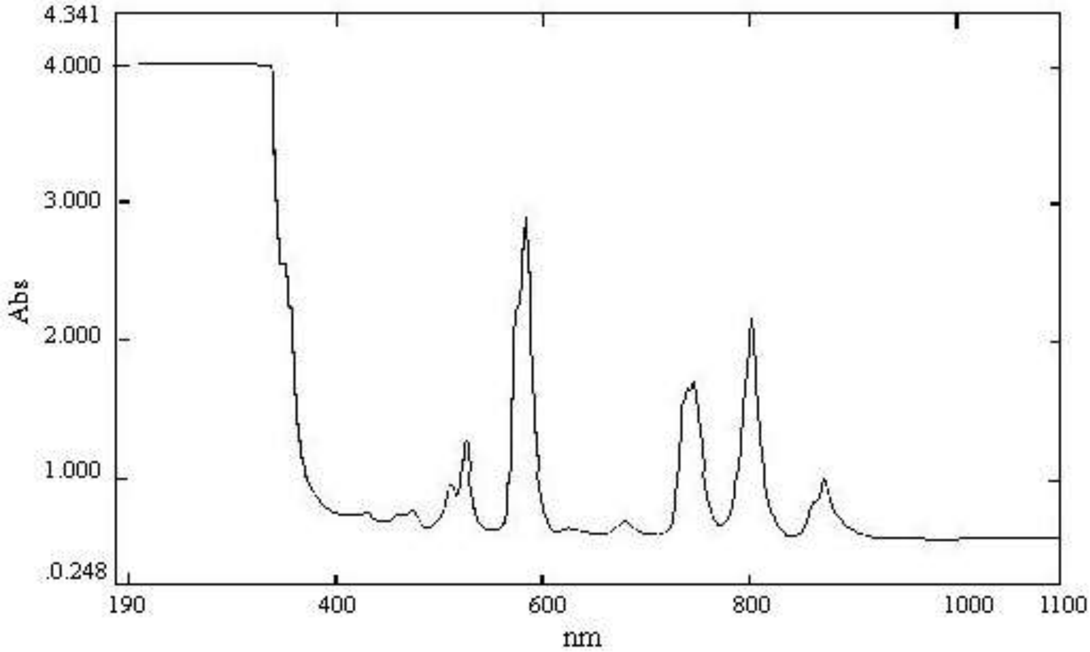


Fig. (5) uv-visible spectrum of Nd glass sample LG10

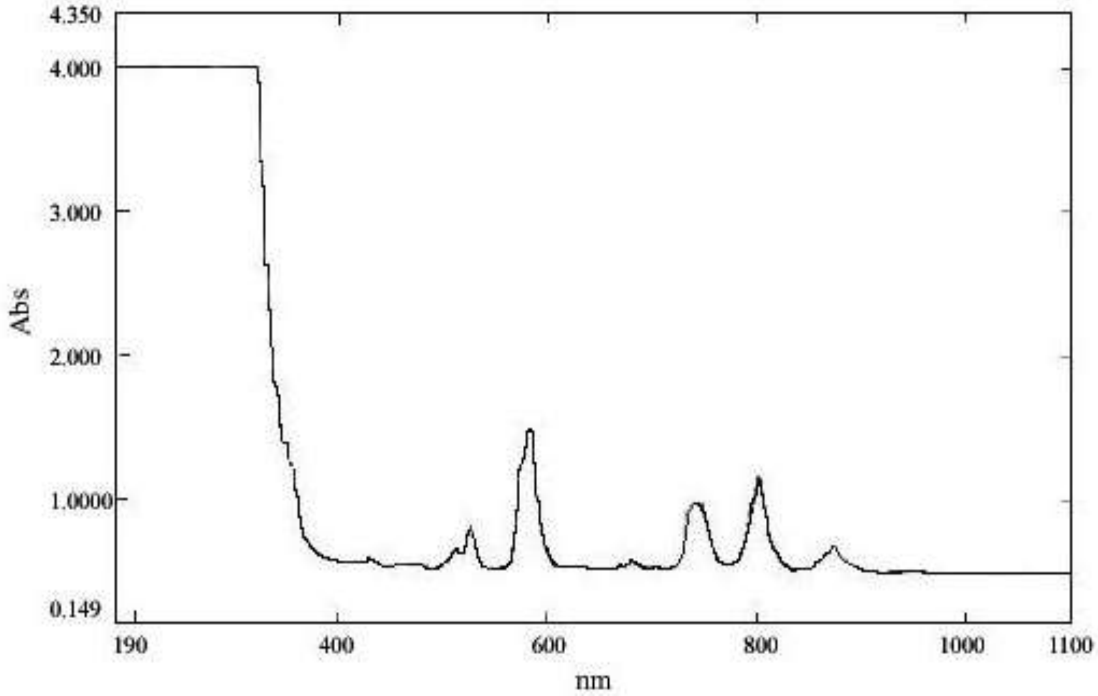


Fig. (6) uv-visible spectrum of Nd glass sample LG11

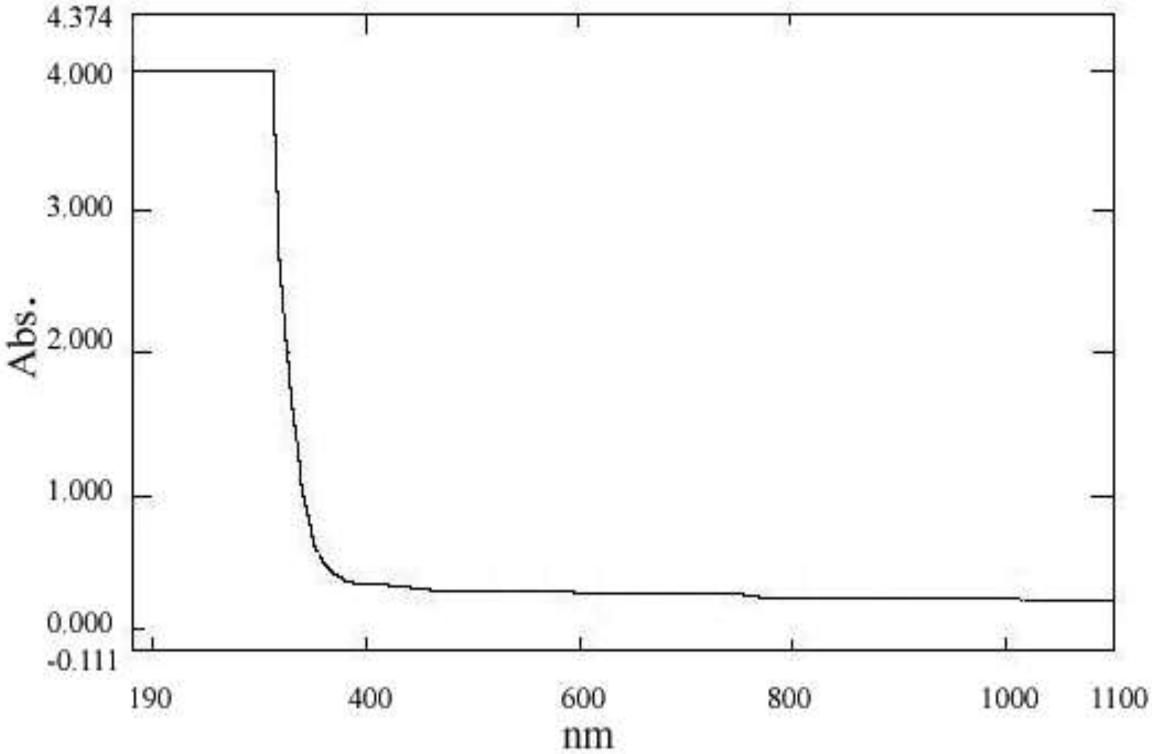
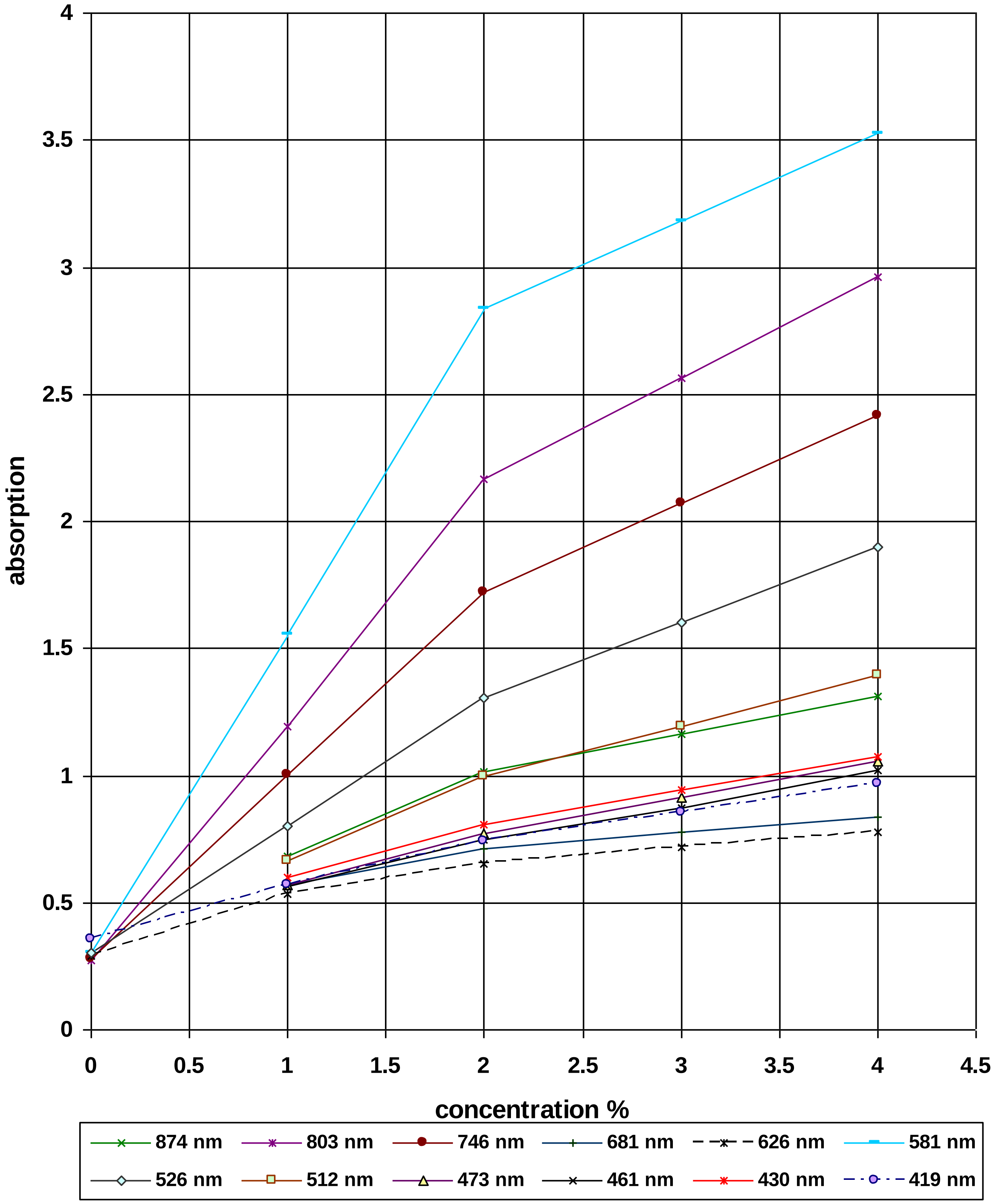


Fig. (7) uv-visible spectrum of Nd glass sample LG12



absorption
concentration %
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
874 nm
803 nm
746 nm
681 nm
626 nm
581 nm
526 nm
512 nm
473 nm
461 nm
430 nm
419 nm

Fig. (8) Dependence of uv-visible absorption maxima on neodymium concentration

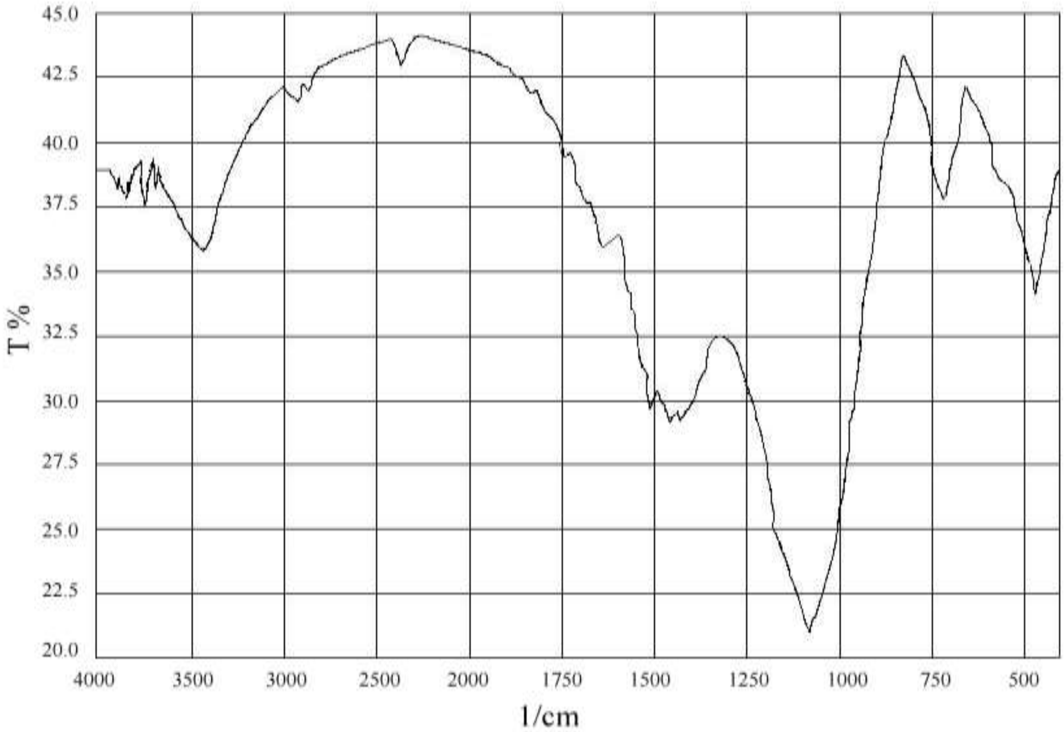


Fig. (9) IR- spectral of Nd glass sample LG9

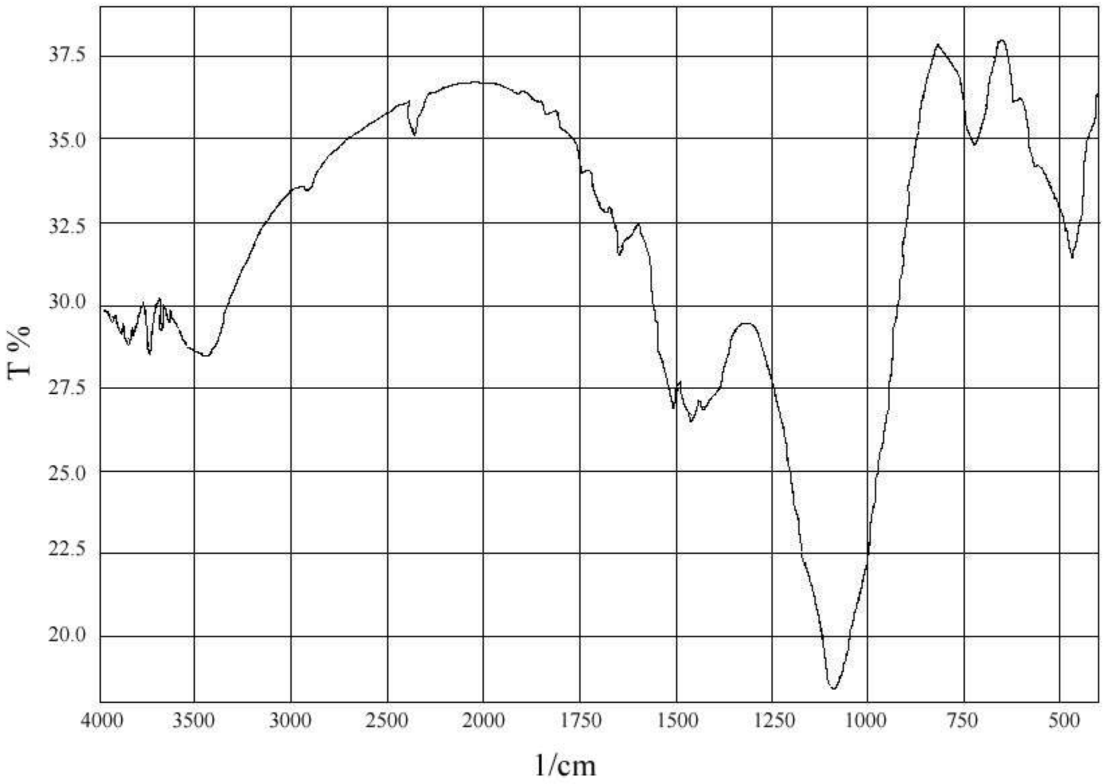


Fig. (10) IR- spectral of Nd glass sample LG10

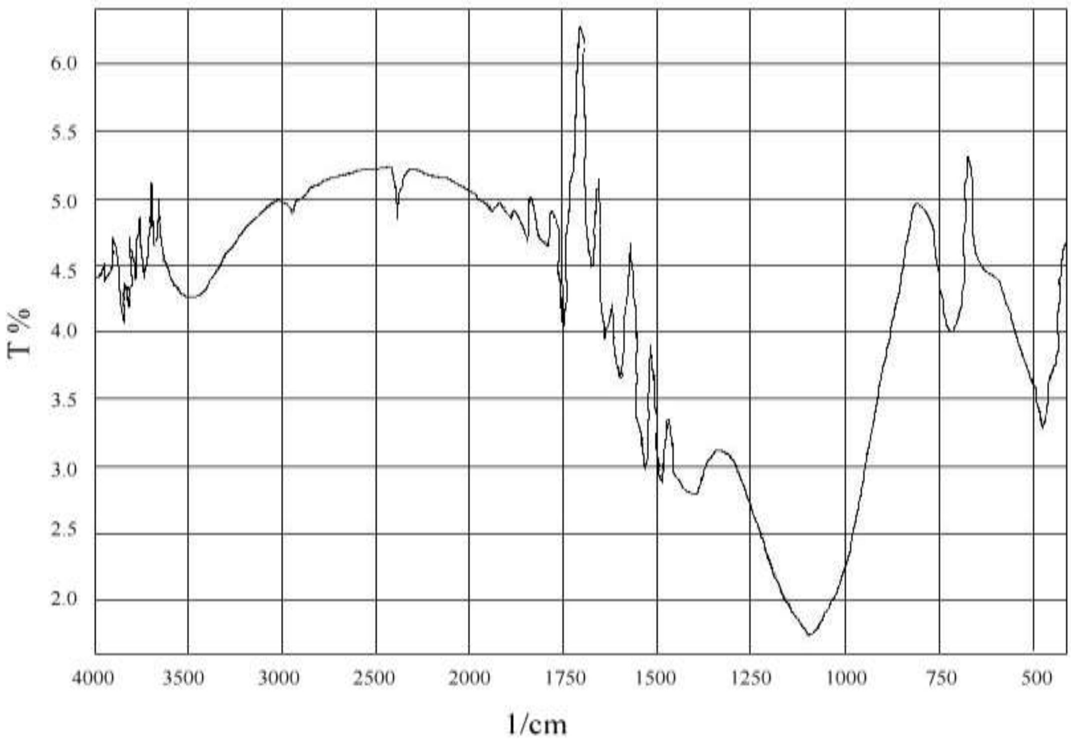


Fig. (11) IR- spectral of Nd glass sample LG11

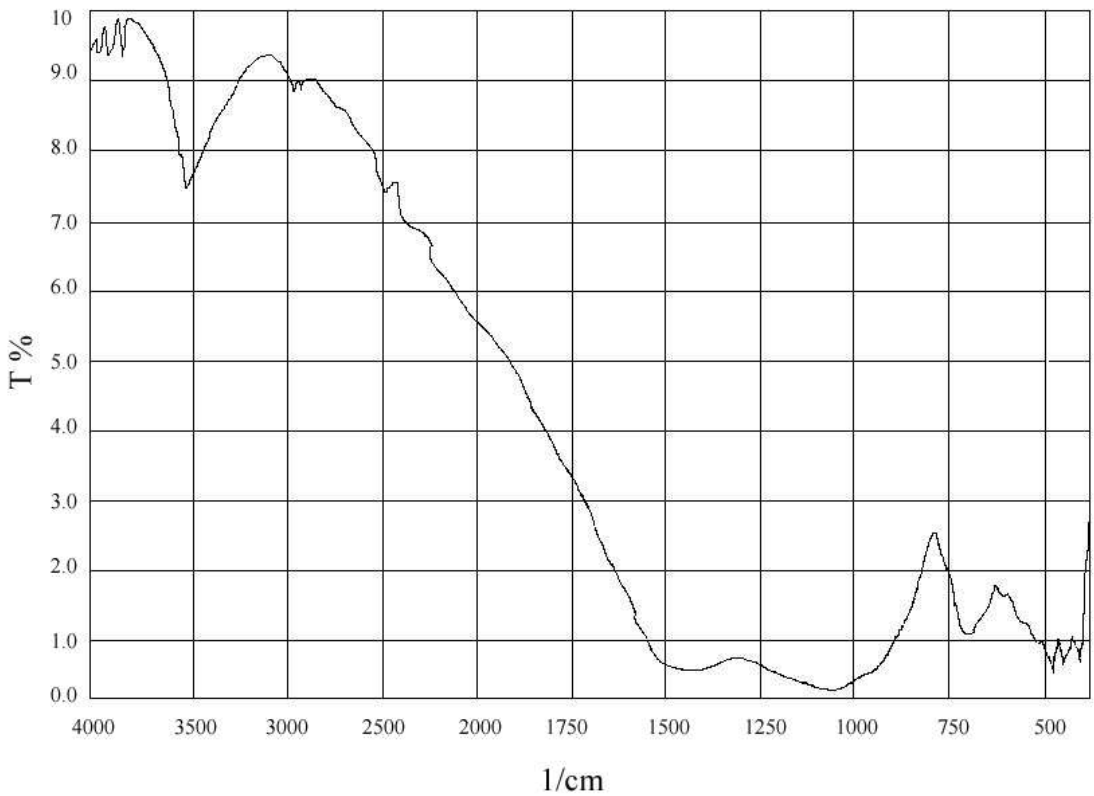


Fig. (12) IR-spectral of Nd glass sample LG12

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