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Final Report NEW LASER MATERIALS

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Introduction

In the Interim Report No. 1, it was reported⁽¹⁾ that the fluorescence lifetime (≥ 750 μ s) in Nd doped $\text{Y}(\text{PO}_3)_3$ was longer by a factor of three as compared to YAG. This means potentially three times as much energy storage and consequently more efficient for flashlamp pumping. It also makes diode pumping easier. In addition, since the Y site is octahedrally coordinated, there is a possibility of energy transfer using Cr as the sensitizing element. As suggested by W. Krupke, we decided to explore the trivalent cation metaphosphates systematically. The compounds investigated can be represented by the general formula $\text{A}(\text{PO}_3)_3$ where $\text{A} = \text{Y, Lu, In, Sc, Ga and Al}$. The active dopants are either Nd or Cr, or both, depending on the host compound. The object is to study the fluorescence characteristics of Nd and Cr as well as the effectiveness of energy transfer from Cr to Nd. In addition, we also investigated other possible laser host crystals, notably $\text{CaMgSi}_2\text{O}_6$ (diopside), LaBO_3 and $\text{La}(\text{BO}_2)_3$. Results on these materials will also be discussed.

Trivalent Cation Metaphosphates

The trivalent cation metaphosphate has the chemical formula $\text{A}(\text{PO}_3)_3$ where $\text{A} =$ Group IIIA and IIIB elements. It covers a wide range of cation sizes from La (1.18 Å) to Al (0.53 Å). The crystal structure of each compound depends on the coordination number of the cation as well as the linkage of the PO_4 network. Four major type of structures have been determined thus far^(2,3,4,5,6):

1. Type 1: Orthorhombic ($\text{C}222_1$), e.g. $\text{Nd}(\text{PO}_3)_3$ where
Nd is 8-fold coordinated,
2. Type 2: Monoclinic ($\text{P}2_1/\text{a}$), e.g. $\text{Bi}(\text{PO}_3)_3$ where
Bi is 7-fold coordinated,
3. Type C: Monoclinic ($\text{P}2_1/\text{c}$), e.g. $\text{Yb}(\text{PO}_3)_3$ where
Yb is 6-fold coordinated, and
4. Type A: Cubic ($\text{I}43\text{d}$), e.g. $\text{Al}_4(\text{F}_4\text{O}_{12})_3$ where
Al is 6-fold coordinated.

There are at least 3 or 4 known but not determined structural forms where cations are

trivalent transition metals.

Our primary interest is the Type C and Type A structures where the trivalent cation is 6-fold coordinated. This limits the maximum cation size to about 0.9Å and Y is the largest host cation. In these two structures we have an interesting situation in that both the Nd and the Cr are substituting the same Y site unlike the codoping situation in garnets or perovskites where Nd and Cr are substituting two different cation sites. For the Type C structure $Y(PO_3)_3$ there are three inequivalent Y sites. The distribution coefficients for both Nd and Cr are different for each specific site. As we will discuss in more detail, these distribution coefficients are not mutually independent to one another. And in the case of $Y(PO_3)_3$, the spectroscopic performance improves when it is codoped.

Synthesis of Trivalent Cation Metaphosphates

An early study⁽⁷⁾ showed that $Y(PO_3)_3$ melts congruently at 1460°C. In our Interim Report No. 1 we indicated that it was not possible to produce the melt in an open crucible because of the excessive evaporation and loss of P_2O_5 . Instead the melt always produced the compound $Y_2P_4O_{11}$ regardless how the melt was prepared.

Facing this problem, we decided first just to synthesize these compounds with the desired structure, composition and doping by solid state reactions and then evaluate them spectroscopically in the crystalline powder form. Details of the synthesis procedure were reported in the Interim Report No. 1. A brief description is given here: First mix the oxides including dopants with $(NH_4)_2HPO_4$ and $(COOH)_2 \cdot 2H_2O$. Then heat the mixture in an oven overnight at 120°C and subsequently react in the oven at 350-400°C for one day before finally sintering at 800°C for another day. The product was well crystallized and the structure was confirmed by powder x-ray diffraction pattern.

So far we have synthesized 6 metaphosphate compounds with cations including Y, Lu, In, Sc, Ga and Al. The first four compounds were doped with Nd, Cr or both. The Ga and Al metaphosphates were doped with Cr only since Nd is too large for the cation sites.

Melting Experiments on Metaphosphates

As stated previously, it has been reported⁽⁷⁾ that both $\text{Y}(\text{PO}_3)_3$ and $\text{Gd}(\text{PO}_3)_3$ melted congruently at 1460°C and 1280°C, respectively. Those experiments were done using sealed Pt capsules. Since the preliminary spectroscopic study of the solid state synthesized powders showed that the metaphosphates are promising crystal hosts for both Nd and Cr, it is necessary to develop a process to grow large crystals of these compounds. The congruent melting nature of the compounds makes them ideal for melt growth since the growth rates of other known growth techniques are significantly slower.

Unfortunately, there is no report on the melting point nor the nature of melting on other metaphosphate compounds with one possible exception. $\text{Al}(\text{PO}_3)_3$ was inferred to melt congruently at 1490°C⁽⁸⁾. In addition to the evaporation problem, melts of these compounds are most likely viscous and glass-forming due to the polymerization nature of the phosphate framework. Nevertheless, because all these compounds have the same structural framework and the melting mechanism is dominated by the bond breaking process of the phosphate framework, we believe that all these compounds will have similar melting behavior. In other words, we believe that all these compounds will likely melt congruently and that the melting temperatures will also be very similar, around 1500°C. Because of the evaporation problem, we also decided to conduct the melting experiment using the sealed Pt capsules.

Pre-synthesized metaphosphate powders were filled in the Pt capsules (0.5" dia. x 2" long x 0.010" wall thickness) and sealed by arc welding. Three or four of these capsules were then placed in an alumina crucible inside an Ir crucible and subjected to RF induction heating to a predetermined temperature for a few hours and then cooled slowly to room temperature over a period of 20 to 60 hours. The capsules were cut open to check any evidence of melting as well as crystallization from the melt.

Even before cutting the capsules, we noticed a few serious problems associated with this technique. First, some of the capsules were badly bulged due to the internal pressure generated during heating. Second, many of the capsules cracked and leaked after the run. There was little correlation between the bulging and cracking. Examining the cracked capsules under a microscope, we noticed that the Pt grains of the capsule wall were extensively recrystallized. The fractures occurred always nicely along a grain boundary. We speculated that fracture may be associated with the grain

growth during recrystallization. The movement of the grain boundary causes the weakness and fracture. Based on the Ostwald ripening theory, the grain growth rate or the grain boundary movement reduces in proportion to the cubic of average grain radius. By preannealing the Pt capsules to large grain size, both the total grain boundary area and the grain boundary movement will be drastically reduced. Indeed, the idea worked and the capsule fracture was significantly reduced in the subsequent experiments. Still in the temperature range of 1500 to 1600°C where these compounds melt, we are working at the physical limits of Pt metal (m.p. = 1773.5°C).

Since the melting was not observable in situ and therefore difficult to determine, we decided to resolve the problems in two steps, the strip heating experiment and the induction heating experiment.

(A) Strip Heating Experiment:

The advance of strip heating is that it is fast and that it uses significantly less material. Because of the large temperature gradient that exists from the center hot zone to either side of the electrode, completely melting of the charge will not occur. It is easier to estimate the melting temperature based on the extent of melting and also on the power level. In addition, by bringing down the power level slowly, we have a situation of miniaturized Bridgman growth. It is a true test of the tendency of glass formation of the melt, since seeds are provided from the unmelted crystalline powder particles.

Preannealed small Pt tubes (0.150" diam. x 1.5" long x 0.005" wall thickness) were used in these experiments. The tubes were crimped on both sides and welded. Sample charges were located at the center section which was the hottest region during heating. The total charge of each sample was very small, typically 0.5 gram. The hottest point of the Pt tube was monitored continuously with a pyrometer. Temperatures were recorded with the emissivity set at 0.2. For the compounds we studied, the estimated melting points were:

$\text{Y}(\text{PO}_3)_3$	-- 1480°C
$\text{In}(\text{PO}_3)_3$	-- 1530°C
$\text{Sc}(\text{PO}_3)_3$	-- 1550°C

By slow cooling the charge, we successfully crystallized the entire melt. Powder x-ray diffraction study confirmed the crystallinity of the molten charge. Moreover, we demonstrated that both $\text{Y}(\text{PO}_3)_3$ and $\text{In}(\text{PO}_3)_3$ crystallized in the Type C structure which is the same as the solid state reaction material. However, $\text{Sc}(\text{PO}_3)_3$ crystallized in cubic Type A structure. This result is consistent with the literature⁽⁵⁾ that $\text{Sc}(\text{PO}_3)_3$ will convert from the monoclinic Type C structure to the cubic Type A structure above 1200°C. This phase transition seems to occur only in the direction to higher temperatures and in the reverse direction it is very sluggish.

There is a systematic increasing melting temperature with decreasing size of the cations. The result is not surprising, since the charge density is higher with smaller cations. Therefore higher energy is needed to break the bonds. The melting experiment also indicates higher glass forming tendency with decreasing cation sizes. This is more evident in the induction heating experiments which will be discussed later on.

We have stated before that in many cases heating caused the bulging of the Pt capsules, but the result is not consistent. We have assumed all along that the bulging is caused by the decomposition of the phosphate melt and the generation of P_2O_5 vapor. Since the Pt tubes used in the strip heating experiments are only half the thickness of regular size tubes, we noticed that in many cases the tubes started to bulge around 600°C, far below the decomposition temperature of the metaphosphate compounds. The only logical cause for the bulging is the moisture content of the sample charge. Metaphosphate compounds tend to absorb moisture even though there is no apparent solubility nor chemical reactions. Indeed, we noticed several milligrams weight loss if the Pt tube loaded with charge (avg. 0.5 gram) was dried in the oven at 120°C for a few hours before welding. Also, the oven dried tubes did not have the bulging problem until they were above 1500°C consistent with our speculation. Therefore in the later melting experiments all the capsules were first dried in the oven before sealing. There was a great improvement of reproducibility of the experimental results and the loss due to tube fracture was also reduced.

(B) Induction Heating Experiment:

Knowing the congruent nature of the metaphosphate melt, the next step was to produce large grains of the crystal by slow cooling of the melt. We used the 1/2"

diameter Pt tube to load the charge. Since the induction heating set up is intended for crucibles 2" or bigger, the RF coupling to such a small tube was not effective. We decided to use a 3" Ir crucible as the susceptor. An alumina cup placed inside the Ir crucible was used to contain the Pt tubes to avoid the contact, since Pt and Ir alloy to each other at very low temperatures.

Despite knowing the melting temperatures, a few tries were still needed to locate the power level for the melting since the emissivity in this geometry was different from the strip heating experiment and the pyrometer readings could not be compared. So far we have studied the Y, In, Sc and Al metaphosphate systems with most effort spent on the Y system. As mentioned before the tendency of glass forming increases with decreasing size of the cation. Thus far $\text{Y}(\text{PO}_3)_3$ is the only compound crystallized from the melt directly without the need for seeding. In the induction heating experiments of the other three compounds, we have not yet been able to crystallize the melt with the present setup and seeding is not possible with the arrangement. Therefore, in the subsequent discussion we will only concentrated on the Y system.

The difficulty with the In, Sc and Al metaphosphate systems is further increased due to higher melting temperatures. The chances of Pt tube rupture are also increased. Glasses produced from these compounds doped with 5 to 10% Cr were transparent but significantly darker and greener than the corresponding crystalline compounds. Both the absorption and the fluorescence spectra were blue-shifted and they look similar regardless of the host cation. The results indicate that in the glasses the positions of the Cr ions are no longer substituting the sites of the host cations but have their own independent sites. The fluorescence lifetimes are also short ($< 30 \mu\text{s}$) and non-radiative, indicating multiple and highly irregular sites. These glasses do not appear to have any potential as laser host for either Cr or Nd.

$\text{Y}(\text{PO}_3)_3$ is the only compound crystallized readily from a melt at a reasonable cooling rate (≈ 10 to 15°C per hour). Since a seed is not provided, the crystal size depends on the number of nuclei formed in the melt. In most cases, the nuclei appeared formed on the wall of the Pt tube and grew inward. The compounds were doped with Nd alone (5 at%) or codoped with both Nd and Cr (either 5 at% and 5 at%, or 5 at% and 2at%, respectively). The dopants apparently had little effect on both the melting behavior and the easiness of crystallization. With the amount of melt ($\approx 1.5 \text{ cm}^3$) studied, we were able to produce crystals several mm in size.

Even though $Y(PO_3)_3$ is the only system that has crystallized reproducibly in our study, we also demonstrated the feasibility of crystallizing melts of the other three compositions in the strip heating experiments where seeding was automatically provided. We believe that single crystal growth from these metaphosphate melts is possible by the Bridgman method in a sealed container if a seed is provided. We are proceeding in that direction now.

Synthesis of Diopside

Diopside ($CaMgSi_2O_6$) is one of the common rock forming minerals. Structurally, it belongs to the chain silicate pyroxene group where the linkage of SiO_4 tetrahedra shares two of the four corners to form continuous chains of composition $(SiO_3)_n$ along the c-axis⁽⁹⁾. The chains are linked laterally by Ca and Mg ions. The Mg ions (M_1 sites) are octahedrally coordinated whereas the Ca ions (M_2 sites) are 8-fold coordinated. Since both the sizes and the coordinations of the two host ions match well with Cr and Nd, we are considering it as a possible codoping laser host. However, there is a problem due to the very fact that both Cr and Nd are 3+ charged whereas both Mg and Ca are 2+ charged. To substitute any Cr or Nd in diopside structure will require proper charge compensation.

The phase relationship of diopside in the CaO - MgO - SiO_2 system was extensively studied by Kushiro⁽¹⁰⁾. Stoichiometric diopside melted incongruently at 1391.5°C. But he suggested that a diopside solid solution (Di_{ss}) with a composition near $Di_{90}En_{10}$ and between the joins of Diopside-Enstatite and Diopside-Fosterite would melt congruently, although the precise composition of the congruently melting Di_{ss} was not known. Attempts to pull single crystals of diopside from melt were also reported⁽¹¹⁾. There were serious problems of cracking and containing akermanite ($Ca_2MgSi_2O_7$) inclusions which were suggested as being due to the evaporation of SiO_2 . The as grown boule had the composition $Ca_{0.92}Mg_{1.08}Si_2O_6$.

In our experiment, 1 at% Nd and/or 0.5 at% Cr were added to the melt as dopants, excess amount of Na was also added for the charge compensation as well as to account for the evaporation loss. We melted the charge in an Pt crucible and froze it slowly. There was little loss of SiO_2 . $Mg/Ca \approx 1.1$ was used and also needed to prevent the formation of akermanite. Even with this ratio, the frozen charge was still incongruent with diopside as the major phase mixed with a small amount of

cristobalite. The true congruent composition was about 3% deficient of silica consistent with Kushiro's data. Most of our studies were done by the melt freeze technique. We tried twice to pull a crystal from the melt but in both cases the pulled crystal was badly fractured. Moreover, the center of the pulled crystal was more bluish green than the periphery when doped with Cr. At present we have no explanation for the observation.

Because of the similar sizes between Nd and Ca as well as between Cr and Mg, doping with high concentrations is not a problem. Na works well as charge compensator for both Nd and Cr, even though it does evaporate from the melt. Since both Nd and Cr are 3+ charged, it is expected that they will stay as far from each other as possible in the structure. Indeed the observed poor energy transfer from Cr to Nd supports the idea. We tried Al^{3+} as charge compensator substituting Si^{4+} without improvement. Be^{2+} can also be used as charge compensator. We have not tried it yet.

The diopside melt is rather viscous and the pulling rate is likely to be slow (< 1 mm/hr). We have not devoted enough effort to perfect the growth. However, it is fair to say that there exists a congruent melt composition and that crystal growth from the melt is possible, but probably difficult. Spectroscopic data described later on indicate that it is an interesting material for either Nd or Cr doping.

Lanthanum Borate and Metaborate

In the search for light new laser host crystals for both Nd and Cr, we decided also to look into the borate system. Borates are known to quench the Nd fluorescence in glass system. It is not clear how the crystalline systems behave. We have synthesized both the lanthanum borate, LaBO_3 , and the lanthanum metaborate, $\text{La}(\text{BO}_2)_3$, doped with 1 at% Nd. The $\text{La}_2\text{O}_3\text{-B}_2\text{O}_3$ system is well known⁽¹²⁾. Both compounds melt congruently at 1660°C and 1150°C, respectively. However, there is a phase transition for LaBO_3 at 1490°C and we were unable to obtain large clear crystals frozen from the melt. Large clear crystals of $\text{La}(\text{BO}_2)_3$ were easily obtained by slow freezing. La is 9-fold coordinated in LaBO_3 and 10-fold coordinated in $\text{La}(\text{BO}_2)_3$. Both sites are somewhat distorted, especially the latter one. Preliminary study showed that both compounds had good Nd fluorescence intensity. The lifetimes appeared radiative but very short, 100 and 50 μsec , respectively. We have not determined whether the short

lifetime was due to quenching or site distortion. We will continue to explore and synthesize other borates for further study.

Spectroscopic Studies of Metaphosphates

The Nd fluorescence decay from all our powder samples (Interim report No. 1, July 1986) showed an initial fast decay of about $60\mu\text{s}$ followed by a slow decay of about $800\mu\text{s}$. In this reporting period, we have continued our effort to determine the origin of the short-lived site and to eliminate it by varying the growth conditions.

Two possible causes for the short-lived site are considered: (1) The short lifetime is nonradiative in nature, and is induced by defects such as vacancies, impurities, or O-H bonds. (2) The Nd sites are so distorted that the oscillator strength of the fluorescence transition is enhanced by the lowering of the local site symmetry. Spectroscopic measurements were made in a series of $\text{Y}(\text{PO}_3)_3$ samples which were melted and crystallized under controlled conditions. Results are analyzed in two categories.

Yttrium Metaphosphate Doped With Nd

There are three nonequivalent sites⁽⁴⁾ for Nd to substitute in the monoclinic form of Y metaphosphate. It is conceivable that these sites may have different degrees of site distortion. From the fluorescence decay measurements in powder samples, which were reacted and annealed at 800°C , the population ratio of Nd between the short-lived and the long-lived sites is close to 1 (Interim Report No. 1). The ratio was only slightly reduced in samples which were either sintered or melted at a significantly higher temperatures (1400 - 1600°C). These results indicated that if the difference in lifetimes was indeed due to the Nd in different Y sites, the site preference must not be very strong and the melt crystallized equilibrium distribution of Nd in different sites was not far from a totally random distribution of the low temperature synthesized powder samples. However, we did observe slight changes in the fast decay time constant in samples crystallized from the melt. Figure 1 shows three fluorescence decay curves. Curves (a) and (b) were measured from samples crystallized in sealed Pt tubes. Curve (c) was the starting powder sample with an annealing temperature of 800°C . The melting temperature of the curve (b) sample was not measured, but was believed to be around 1500°C . The sample of curve (a) was also crystallized from the melt with

slightly faster cooling rate. The lifetime of the initial fast fluorescence decay increased from about 60 μ s in the powder sample to 95 μ s and 110 μ s for samples (a) and (b), respectively. These slight increases in lifetime were probably due to the release of strain at the more distorted Nd sites resulting from the melting and slow crystallization of the sample charge.

The linewidth of the Nd fluorescence of the melt frozen samples was just as broad as that of the powder samples. This broad linewidth was attributed to the nonequivalent sites for Nd (Interim Report No. 1). From the large difference of the two decay constants, the short-lived site has to be significantly distorted. It is therefore reasonable to expect some energy shift in the electronic levels between the two types of sites.

We attempted to resolve the fluorescence lines by lowering the sample temperature in order to reduce thermal broadening. However, the linewidth remained broad even at 60°K. It is safe to assume that the broad linewidth was not thermally induced (Fig. 2). To investigate the nonequivalent Nd sites, we searched for the energy shift by monitoring the change in fluorescence decay at various excitation wavelengths. The excitation wavelength was set between 590 and 574nm in 4nm decrements. Measurements were made at 60°K in a relatively clear melt crystallized Nd doped Y(PO₃)₃ sample and the results are shown in Fig. 3. The intensity of all curves has been normalized so that they have the same value at the start of the pump pulse. We note that the initial decay constant is identical for all excitation wavelengths. The difference among the traces in Fig. 3 is the relative amount of admixture of the long lifetime decay at the late time. The results show a decrease in the admixture of the long-lived sites as the excitation wavelength decreases from 590nm to 574nm, indicating that the long-lived sites are at a lower energy.

Nd,Cr codoped Y(PO₃)₃

Although the Nd doped Y(PO₃)₃ samples crystallized from their congruent melt have shown significantly better in crystal quality and an improvement in lengthening the initial fluorescence decay time, the gap between the longest observed initial lifetime of 110 μ s and the subsequent 800 μ s lifetime does not appear likely to be eliminated by optimizing the growth parameters. In contrast, the similarly prepared Nd, Cr codoped Y(PO₃)₃ samples intended for the study of energy transfer showed a

dramatic increase of the initial fluorescence decay constant. Fluorescence decay was measured in a series of samples prepared at slightly different temperatures near the melting point. The results are shown in Fig. 4. For the purpose of clarity, the traces are vertically displaced and are arranged in the order of decreasing sample heating temperatures. Because of the melting experiment set up, the temperatures recorded by the pyrometer were the uncalibrated apparent black body radiation temperatures of the Ir crucible containing the alumina cup and the sample capsules. Therefore the temperatures referred to here are only as references for comparison and not the absolute temperature of the sample. The samples (codoped with 2 at% Cr and 5 at% Nd) treated at 1550°C (Curve e) and 1625°C (Curve d) were well sintered and recrystallized but not truly melted. The fluorescence decays already showed a dramatic change of the initial lifetime indicating a sharp reduction of Nd in the short-lived sites. As the heating temperatures further increased to 1665°C true melting occurred. Fluorescence decay curves (b and c) showed that samples crystallized from the melt had practically no Nd in the short-lived sites. Further increasing the temperature showed little improvement (Curve a). The Nd fluorescence lineshape also showed a significant narrowing in the codoped samples (Fig. 5). As to the energy transfer, there was little evidence of improvement as compared with low temperature synthesized powder samples.

The elimination of Nd in the short-lived site by codoping with Cr comes as a pleasant surprise. At present the result is very preliminary. The exact mechanism by which Cr eliminates the short-lived Nd sites will be the subject of study in the coming months. We can only speculate on the role of Cr at this point. All five samples used in Fig. 4 have 5% Nd and 2% Cr. Assuming Cr ions have strong preference for the short-lived sites, it is still a surprise that the 2% Cr in the codoped samples can have nearly 100% effectiveness in blocking Nd ions from entering the short-lived sites. We will start to test the effect of other smaller trivalent cations on the site distribution ratio of Nd. The two particularly interesting cations are Al and Sc.

Spectroscopic Studies of Diopside

Fluorescence properties of diopside doped with Nd and/or Cr were also studied. The fluorescence spectrum and decay curve of diopside doped with 1 at% Nd are shown in Figs. 6a and 6b. As we can see, the peaks are very sharp and the lifetime

(375 μ s) is also reasonably long as compared to YAG (250 μ s) or any other garnets. We also measured the diopside samples doped with 0.5 at% Cr which are shown in Figs. 7a and 7b. The Cr fluorescence spectrum is very similar to that of GSAG or GSGG. However, the lifetime (48 μ s) is significantly shorter due to the more distorted octahedral site. This combined with lower refractive indices will give quite high emission cross section ($\approx 3 \times 10^{-20}$ cm²) as compared to most known Cr doped compounds. As mentioned in the diopside synthesis section, the charge repulsion between Nd and Cr ions makes the energy transfer ineffective.

Nevertheless, we strongly feel that based on the spectroscopic results diopside can be a useful crystal host for singly doped either Nd or Cr.

Spectroscopic Studies of Lanthanum Borates

Borate is known to quench Nd fluorescence in glass systems. We decided to look into this effect in crystalline system. Both LaBO₃ and La(BO₂)₃ were doped with 1 at% Nd. The fluorescence spectra of both compounds were practically the same and sharp, and both the fluorescence lifetimes were short with the lifetime of LaBO₃ (100 μ s) twice that of La(BO₂)₃ (50 μ s). The fluorescence spectrum and decay of La(BO₂)₃ are shown in Figs. 8a and 8b. In both cases, the fluorescences were strong. We have not yet determined whether the short lifetime is due to quenching or site distortion. Nd is 9-fold coordinated in LaBO₃ and 10-fold in La(BO₂)₃ and both sites are quite distorted.

Summary

We have devoted most of the effort on melt crystallization of metaphosphates in the second part of the contract work. Combining with the Interim Report No. 1 (Appendix A), we can summarize the highlights of this contract work as follows:

- (1) We have successfully synthesized A(PO₃)₃ compounds where A = Y, Lu, In, Sc, Ga and Al doped with Nd and/or Cr.
- (2) Spectroscopic evaluations were made of most of the synthesized compounds.
- (3) We found that both In(PO₃)₃ and Sc(PO₃)₃ doped with Cr are potential tunable laser candidates due to their fluorescence wavelength ranges (peak at 920 nm), reasonable lifetimes (≈ 120 μ s) and rather high emission cross-sections (≈ 1.5 -

$2.0 \times 10^{-20} \text{ cm}^2$).

(4) We found that by codoping $\text{Y}(\text{PO}_3)_3$ with Nd and Cr, the Nd fluorescence lifetime improved dramatically. It is a significant step towards the usefulness of this material as laser host.

(5) We have demonstrated that all the metaphosphates melt congruently and that despite the strong tendency of glass forming, it is possible to grow crystals from the melt provided that proper seedings are made.

(6) Diopsides doped with either Nd or Cr were synthesized and evaluated. It is also an interesting laser host material for both dopants.

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Appendix

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Fig. 1. Fluorescence decay of Nd in Nd doped Y(PO₃)₃. Measurements were made in samples grown from melt, (a) and (b), and in a powder sample (c).

Fig. 2 Fluorescence spectrum of Nd in a Nd doped $\text{Y}(\text{PO}_3)_3$ at 60K. The Nd concentration is 5 at.% in melt. Spectral resolution is 0.45nm.

Fig. 3 Fluorescence decay of Nd in a Nd doped $Y(PO_3)_3$ at various excitation wavelengths. The fluorescence at 876nm was monitored while the excitation wavelengths were set between 590 and 574nm in 4nm decrements for the curves (a) through (e) respectively.

Fig. 4 Fluorescence decay of Nd in Cr and Nd codoped $\text{Y(PO}_3)_3$. The melt temperatures of the samples for the curves (a) through (e) are 1700°C, 1665°C, 1665°C, 1625°C, and 1550°C respectively.

Fig. 5 Fluorescence spectrum of Nd in a Cr and Nd codoped Y(PO₃)₃ at room temperature. Spectral resolution is 0.6nm.

Figure: 6.

(A) FLUORESCENCE SPECTRUM OF DIOPSIDE $\text{CaMgSi}_2\text{O}_6$: 1 at% Nd

PUMP SOURCE = 583 nm

(B) FLUORESCENCE DECAY OF DIOPSIDE $\text{CaMgSi}_2\text{O}_6$: 1 at% Nd

LIFETIME = 375 μsec

Figure: 7.

(A) FLUORESCENCE SPECTRUM OF DIOPSIDE $\text{CaMgSi}_2\text{O}_6$: 0.5 at% Cr

PUMP SOURCE = 650 nm

(B) FLUORESCENCE DECAY OF DIOPSIDE $\text{CaMgSi}_2\text{O}_6$: 0.5 at% Cr

LIFETIME = 48 usec

Figure: 8.

(A) FLUORESCENCE SPECTRUM OF $\text{La}(\text{BO}_2)_3$: 1 at% Nd

PUMP SOURCE = 581 nm

(B) FLUORESCENCE DECAY OF $\text{La}(\text{BO}_2)_3$: 1 at% Nd

LIFETIME = 50 usec

Interim Report No. 1

New Laser Materials

Prepared by

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Covering the period April 1, through July 15, 1986

For

The Lawrence Livermore National Laboratory

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Participants in this work:

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Introduction

The monoclinic crystal system metaphosphates $A(PO_3)_3$ where $A = Y, Lu, Sc, In, Ga$, and Al , were suggested by W. Krupke as candidates for Nd laser hosts. In previous work, Nd in $Y(PO_3)_3$ was reported to have fluorescence lifetime significantly longer than in $^{*}AG(1)$. The long fluorescence lifetime in general provides a larger energy storage capacity, the option of diode pumping, and a prolonged flashlamp lifetime by operating farther from the explosion limit. Several attempts were made to grow the metaphosphates by Czochralski technique but the structure was not stable at its melting temperature. All metaphosphate samples used in the spectroscopy were prepared by solid state reaction method. The scope of the spectroscopy was to evaluate systematically the characteristics of the Nd and Cr fluorescence and the energy transfer process between Cr and Nd in the codoped samples.

Spectroscopy

A series of $A(PO_3)_3$ metaphosphates were investigated. The object was to study how Nd behaves in such phosphates and the effectiveness of the Cr sensitization in the Cr,Nd codoped phosphates. Three inequivalent Nd sites have been reported in the metaphosphates.⁽²⁾ Hence, some degree of inhomogeneous broadening is expected in the Nd fluorescence linewidth. Figures (1) through (4) are the Nd fluorescence spectra from $Lu(PO_3)_3$, $Y(PO_3)_3$, $In(PO_3)_3$, and $Sc(PO_3)_3$ respectively. The emission lines from the $^4F_{3/2}$ to $^4I_{9/2}$ and $^4F_{3/2}$ to $^4I_{11/2}$ multiplets are so overlapping that two broad bands are observed at about 880 nm and 1055 nm. Part of the broadening may be attributed to the phonon coupling at room temperature. Multiplets associated with different Nd sites may become narrow at low temperatures. Different Nd sites could then be studied by selective excitation process.

The fluorescence decay of Nd in the metaphosphate hosts are shown in Figures (5) and (6). They all have an initial fast decay followed by a slow tail. Earlier work (1) indicated only a long fluorescence lifetime. There is a possibility that the different growth procedures may cause the Nd to partition differently among the three possible sites. Due to the relatively fast cooling in the preparation of our samples in the solid state reaction process, the Nd is expected to distribute fairly even among all sites. In a slow cooling process, the most preferred site would more likely be occupied. There is no theoretical ground on which we may assign the long-lived and the short-lived sites by the type of Nd sites in metaphosphates.

From the extrapolation of the long lifetime component in the Nd decay curve, it is possible to estimate the excited state density ratio of the long-lived sites to the short-lived sites. Table I shows the decay time constants of the fast component at its first e-fold time, and the long decay lifetime at the late time of Nd in different metaphosphates.

Table I. The Nd fluorescence decay times τ and population ratios

	τ at early time (μ s)	τ at late time (μ s)	long-lived/short-lived population ratio
Lu(PO ₃) ₃	35	860	2.6
Y(PO ₃) ₃	59	820	0.8
In(PO ₃) ₃	20	510	1.5
Sc(PO ₃) ₃	16	540	1.7

The population ratio ranges from ≈ 1 to ≈ 2.5 in favor of the long-lived sites. With the limited spectroscopic measurements made so far, we can only speculate as to the origin of the short-lived sites. In the case of $\text{Sc}(\text{PO}_3)_3$, the degree of distortion relative to a perfect octahedron is comparable for the three Nd sites(2). It is therefore unlikely that the Nd lifetime would be an order of magnitude different among these sites. However, intrinsic or extrinsic vacancies or point defects could have a preference for association with one of three sites. The short lifetime is therefore speculated to be a result of nonradiative processes.

The effect of Cr codoping was also investigated. We looked for evidence of Cr to Nd energy transfer and evaluated its merit by comparing it to the same process in the GSAG and LaScO_3 systems. In the presence of the Nd, the Cr fluorescence lifetime is expected to decrease due to energy transfer to the Nd ions. The Cr fluorescence decay curves for the singly doped Cr samples versus those for the Cr and Nd codoped sample are shown in Figures (7) through (10). The lifetime shortening is in general very small for up to 2% Cr 2% Nd codoped metaphosphates. Only a small amount of transfer was indicated in $\text{Lu}(\text{PO}_3)_3$ and $\text{Y}(\text{PO}_3)_3$, and hardly any in $\text{In}(\text{PO}_3)_3$ and $\text{Sc}(\text{PO}_3)_3$ hosts. We also studied energy transfer through the Nd fluorescence while the Cr ions were excited. Two modes of optical pumping were used: a short pulse mode of ≈ 5 ns in duration and a quasi-cw mode of about 2 ms in duration. Fluorescence spectra with a short pulse excitation at 640 nm are shown in Figures (11) and (12) for a 2% Cr 2% Nd and a 5% Cr 5% Nd codoped $\text{Sc}(\text{PO}_3)_3$ respectively. The Nd fluorescence bands at 900 nm and 1050 nm are not present in the 2% Cr 2% Nd spectrum, and are only barely discernable in the 5% Cr 5% Nd spectrum. Slight improvement is noted in a 5% Cr 5% Nd doped $\text{In}(\text{PO}_3)_3$ spectrum

as shown in Figure (13). Under quasi-cw excitation at 647 nm, the spectrum from a 2% Cr 2% Nd doped $\text{In}(\text{PO}_3)_3$ (Figure (14)) had a Nd fluorescence intensity comparable to that in the 5% Cr 5% Nd spectrum (Figure (13)). This result indicates that the density of the excited Nd ions is higher in the steady state than at the time window of the pulsed excitation. The time delay used in the measurement is about 20 μs from the excitation pulse since the energy transfer time or the rise time of the Nd fluorescence is likely to be longer than 50 μs . A direct measurement of the rise time was not attempted due to the weak Nd intensity, evident in figures (13) and (14), and the interference by the Cr fluorescence background even at 1050 nm.

The most encouraging energy transfer results were observed in a 5% Cr 5% Nd doped $\text{Y}(\text{PO}_3)_3$. The fluorescence spectrum under quasi-cw pumping is shown in Figure (15). To evaluate the merit of the Cr-Nd transfer in the metaphosphates, we compare it to the fluorescence spectra of a 1% Cr 1% Nd doped LaScO_3 , which is included here in Figure (16) for comparison. The Nd ion density in a 1% Nd doped LaScO_3 is $7.5 \times 10^{19} \text{ cm}^{-3}$. The lattice constants of $\text{Sc}(\text{PO}_3)_3$ and $\text{Yb}(\text{PO}_3)_3$ are reported in the literature (1),(3). The ionic radius of Y is larger than that of Yb or Sc. We use the $\text{Yb}(\text{PO}_3)_3$ lattice constants with the understanding that the value represents an upper bound estimate for the Nd density in $\text{Y}(\text{PO}_3)_3$. In 5% Nd doped $\text{Yb}(\text{PO}_3)_3$, the Nd density is $2.7 \times 10^{20} \text{ cm}^{-3}$ which is 3.5 times the density of the 1% Nd doped LaScO_3 . Yet the Nd fluorescence intensity relative to the Cr fluorescence is higher in LaScO_3 . Allowing for the

uncertainty of the Cr segregation in LaScO_3 , the result still tends to suggest the Cr-Nd energy transfer is significantly more efficient in LaScO_3 than in $\text{Y(PO}_3)_3$ host.

As indicated by the peak position of its fluorescence band, Cr ions in metaphosphates can be categorized to be in low crystal field sites. Even in $\text{Al(PO}_3)_3$, in which the Cr ion is to replace the smaller Al ion, the $^4\text{T}_2$ fluorescence band peaks at 770 nm (Fig. 17), indicating that the Cr crystal field in $\text{Al(PO}_3)_3$ is lower than that in GSGG . The Cr fluorescence peak shifts in succession towards longer wavelengths in $\text{Ga(PO}_3)_3$, $\text{Sc(PO}_3)_3$ and $\text{In(PO}_3)_3$ as shown in Figures (18) and (19) respectively. The Cr lifetimes and the fluorescence peak positions in metaphosphates are listed in Table II.

Table II. The Cr Fluorescence Characteristics in Metaphosphates

	Fluorescence peak (nm)	Lifetime (μs) (comment)
$\text{Al(PO}_3)_3$	770	44
$\text{Ga(PO}_3)_3$	880	8 (nonexponential)
$\text{Sc(PO}_3)_3$	890	126
$\text{In(PO}_3)_3$	890	146
$\text{Y(PO}_3)_3$	900	27 (nonexponential)
$\text{Lu(PO}_3)_3$	910	38 (nonexponential)

The lifetimes of the nonexponential decays are the time constant at the first e-fold of the decay. The relatively long lifetime of the Cr in $\text{Sc(PO}_3)_3$ and $\text{In(PO}_3)_3$ and their single exponential decays indicate promise for these two hosts as tunable lasers centering at $\lambda \approx 920$ nm. Emission cross sections were calculated for $\text{Sc(PO}_3)_3$ and

$\text{In}(\text{PO}_3)_3$ using the measured lifetimes and the estimated indexes of refraction of ^{1.54}~~1.52~~ and ^{1.55}~~1.57~~ respectively(4). As is shown in Figure (20), the peak emission cross sections are 1.85 and $1.47 \times 10^{-20} \text{ cm}^2$ for $\text{Sc}(\text{PO}_3)_3$ and $\text{In}(\text{PO}_3)_3$ respectively. The emission cross sections may be higher if the fluorescence spectra are not isotropically polarized as one would expect for monoclinic crystals.

Synthesis of Rare Earth and Transition Metal Metaphosphates

Trivalent cation metaphosphates with a general formula of $\text{A}(\text{PO}_3)_3$, where A can be rare earths, transition metals or other Group IIIA elements, are of interest because they are potential laser hosts for Nd^{3+} , Cr^{3+} or both. We have engaged a systematic study of the metaphosphate compounds with $\text{A} = \text{Y}, \text{Lu}, \text{In}, \text{Sc}, \text{Ga}$ and Al . The scope of the work is to synthesize these compounds doped with either Nd or Cr to provide samples for preliminary spectroscopic studies. In the process, we evaluate various techniques of growing these crystals.

The literature contains extensive work on trivalent cation metaphosphates. Most is focused on crystal structure and phase transitions. It has been shown that $\text{A}(\text{PO}_3)_3$ exists in at least four major structural modifications: I, C, A, and the type $\text{Bi}(\text{PO}_3)_3$ plus several other metastable modifications. Type I has orthorhombic structure ($\text{C}222_1$) and can be represented by $\text{Nd}(\text{PO}_3)_3$, where Nd is 8-fold coordinated. Type C has monoclinic structure ($\text{P}2_1/\text{C}$) and can best be represented by $\text{Yb}(\text{PO}_3)_3$ where Yb is 6-fold coordinated. Type A is cubic structure ($\bar{1}43\text{d}$) can be represented by $\text{Al}_4(\text{P}_4\text{O}_{12})_3$ where Al is 6-fold coordinated. $\text{Bi}(\text{PO}_3)_3$ is also monoclinic in structure ($\text{P}2_1/\text{a}$)

and the coordination of Bi is seven. For our purpose, we are primarily interested in the Type C monoclinic structure where the 6-fold coordinated cation site can be doped with both Cr and Nd.

Crystal Synthesis:

Early work done at Penn state by Agrawal and Hummel⁽⁴⁾ suggested that both $\text{Y}(\text{PO}_3)_3$ and $\text{Gd}(\text{PO}_3)_3$ melted congruently at 1460°C and 1280°C respectively. This work was done using sealed Pt. capsules. Our first attempt was to synthesize $\text{Y}(\text{PO}_3)_3$ doped with Nd and Cr by slow cooling from the melt in open Pt. crucibles. We have tried three different ways to prepare the melt.

(1) Reacting Y_2O_3 with $(\text{NH}_4)\text{H}_2\text{PO}_4$ in stoichiometric proportion at low temperatures (~ 600°C) and then heating to melting temperature.

(2) Reacting Y_2O_3 with 85 wt% H_3PO_4 at low temperatures (~ 300°C) and then heating to melting temperature.

(3) Presynthesizing the compound $\text{Y}(\text{PO}_3)_3$ using the method described later and then heating the compound to melting temperature.

In all situations, we have experienced excessive smoking (white smoke) during the heating up period. The smoking was significantly reduced when the charge was fully melted. By slow cooling, the melts crystallized without forming glass. However, the powder x-ray diffraction pattern showed that in all three cases the compound formed was not $\text{Y}(\text{PO}_3)_3$ but $\text{Y}_2\text{P}_4\text{O}_{13}$ (or $\text{Y}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$). This we attribute to evaporation loss in our open system.

Because of the difficulty in synthesis of these compounds from open melts, we decided to attempt synthesis of the crystalline powders with the desired structure, composition and doping. The synthesizing

method was based on a report by Khodzhamberdiev, et. al.⁽⁵⁾ Using $Y(PO_3)_3$ compound as an example, the starting materials were Y_2O_3 , $(NH_4)H_2PO_4$, with Nd_2O_3 and $Cr(OH)_3$ as dopant. The $(NH_4)H_2PO_4$ is 10% in excess to accomodating any possible evaporation loss. Oxalic acid $((COOH)_2 \cdot 2H_2O)$ was used as a flux or mineralizer, which accelerates the solid state synthesis rate. We used a 1:3 molar charge to flux ratio. Powders were well mixed in a mortar and transferred to a fused silica tube which was heated overnight in an oven at $120^\circ C$ and then transferred to a hot plate and heated at $235^\circ C$ overnight. The tube was finally placed in a tube furnace and annealed at $800^\circ C$ for 1 day. Oxalic acid was completely decomposed and evaporated as H_2O and CO_2 .

The product appeared to be well crystallized. Portions of the powder was used for x-ray powder diffraction to check the phase composition. Small pellets were also made with the powder using boric acid as binding agent. These were used for spectroscopic studies. Table III lists the 24 samples which we prepared. X-ray powder diffraction patterns were made on each sample and results were compared with published data. We found that, regardless of the dopant and the doping level, $Y(PO_3)_3$, $Lu(PO_3)_3$, $In(PO_3)_3$ and $Sc(PO_3)_3$ exhibited the same x-ray powder diffraction pattern which matches the published data for Type C monoclinic structure ($P2_1/c$). $Al(PO_3)_3$ synthesized was neither the monoclinic Type C nor the cubic Type A structure. Instead it matched with the x-ray pattern of a metastable unknown form Type B (x-ray powder file 13-226). We have synthesized the Al compound twice and the results were identical indicating that the structure is in fact quite stable. The complexity of the x-ray

powder pattern suggests a structure of rather low symmetry, possibly triclinic system. Among the synthesized materials charges, $\text{Ga}(\text{PO}_3)_3$ produced the coarsest grain size with crystals ~ 1 mm in size. While the x-ray powder diffraction pattern was not complex, we cannot match it to any of the known $\text{Al}(\text{PO}_3)_3$ x-ray powder diffraction patterns. Neither can match it to any known compound in the gallium-phosphate system.

Table 111. List of $\text{Al}(\text{PO}_3)_3$ compounds synthesized by solid state reactions.

Sample No.	Compound Composition	Dopant Concentration (at.%)		Remarks
		Cr	Nd	
1	$\text{Y}(\text{PO}_3)_3$ -1	5		Type C ($\text{P}2_1/\text{c}$)
2	$\text{Y}(\text{PO}_3)_3$ -2		5	Type C ($\text{P}2_1/\text{c}$)
3	$\text{Y}(\text{PO}_3)_3$ -2A		5	Type C ($\text{P}2_1/\text{c}$)
4	$\text{Y}(\text{PO}_3)_3$ -3	5	5	Type C ($\text{P}2_1/\text{c}$)
5	$\text{Lu}(\text{PO}_3)_3$		2	Type C ($\text{P}2_1/\text{c}$)
6	$\text{Lu}(\text{PO}_3)_3$ -2	2		Type C ($\text{P}2_1/\text{c}$)
7	$\text{Lu}(\text{PO}_3)_3$ -3	2	2	Type C ($\text{P}2_1/\text{c}$)
8	$\text{In}(\text{PO}_3)_3$	2		Type C ($\text{P}2_1/\text{c}$)
9	$\text{In}(\text{PO}_3)_3$		2	Type C ($\text{P}2_1/\text{c}$)
10	$\text{In}(\text{PO}_3)_3$	2	2	Type C ($\text{P}2_1/\text{c}$)
11	$\text{In}(\text{PO}_3)_3$	2		Type C ($\text{P}2_1/\text{c}$)
12	$\text{In}(\text{PO}_3)_3$	5		Type C ($\text{P}2_1/\text{c}$)
13	$\text{In}(\text{PO}_3)_3$	10		Type C ($\text{P}2_1/\text{c}$)
14	$\text{In}(\text{PO}_3)_3$	5	5	Type C ($\text{P}2_1/\text{c}$)
15	$\text{Sc}(\text{PO}_3)_3$		2	Type C ($\text{P}2_1/\text{c}$)
16	$\text{Sc}(\text{PO}_3)_3$ -2	2		Type C ($\text{P}2_1/\text{c}$)
17	$\text{Sc}(\text{PO}_3)_3$ -3	2	2	Type C ($\text{P}2_1/\text{c}$)
18	$\text{Sc}(\text{PO}_3)_3$	2		Type C ($\text{P}2_1/\text{c}$)
19	$\text{Sc}(\text{PO}_3)_3$	5		Type C ($\text{P}2_1/\text{c}$)
20	$\text{Sc}(\text{PO}_3)_3$	10		Type C ($\text{P}2_1/\text{c}$)
21	$\text{Sc}(\text{PO}_3)_3$	5	5	Type C ($\text{P}2_1/\text{c}$)
22	$\text{Ga}(\text{PO}_3)_3$	2		Coarse crystals (mm size) structure unknown.
23	$\text{Al}(\text{PO}_3)_3$ -1	2		Type B. X-ray powder file 13-266.
24	$\text{Al}(\text{PO}_3)_3$ -2	2		

Summary

The population ratio of the Nd long-lived sites vs. the short-lived sites are in excess of 1 in most metaphosphates we studied. The short-lived sites are likely to be due to crystal defects which may be reduced or eliminated in better quality single crystals. The long Nd lifetimes are in excess of 500 μ s in all metaphosphates studied, providing higher energy storage capability and prolonged flashlamp operation in comparison to Nd:YAG. The Nd linewidths are broad at room temperature. Tunability across the fluorescence bands is likely. In Cr:Nd codoped $A(PO_3)_3$, where $A = Sc, In, Lu, Y$, $Y(PO_3)_3$ shows the most promise for the Cr sensitization. The transfer efficiency in $Y(PO_3)_3$ is less than that in $LaScO_3$, but is probably comparable to that in GSAG or GSGG. More accurate determination will be made when better quality single crystal metaphosphates are available.

Several attempts were made to grow metaphosphates by the Czochralski technique. However the resulting materials were of the form $(A_2O_3)_2(P_2O_5)$ where $A = Y, Sc$, etc. We concluded that metaphosphates will have to be grown by an alternative approach. All samples used in the spectroscopy measurements were prepared by solid state reaction. X-ray powder diffraction spectra were measured for all of our powder samples. Except for the $Ga(PO_3)_3$ all spectra showed sharp lines which could be identified with the reported x-ray line pattern. However, there is no assurance that the reported measurement was made from completely single phase material.

Preparations are underway to grow metaphosphate single crystals in sealed platinum tubes. A high quality single phase crystal will help to confirm the structure and the phase composition of our powder samples. It may be used to sort out the spectroscopic characteristics which may only pertain to the powder samples such as the broad Nd linewidth and possibly the short lifetime Nd sites.

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Fig. 1. Fluorescence spectrum of Nd in $\text{Lu}(\text{PO}_3)_3$. Spectral resolution is 0.3 nm. Concentration of Nd is 2at. %.

Fig. 2. Fluorescence spectrum of Nd in Y(PO₃)₃. Spectral resolution is 0.3 nm. Concentration of Nd is 5at.%.

YPo_F5 DISC#: 06

YPo_F6 DISC#: 06

52 14

Fig. 3. Fluorescence spectrum of Nd in $\text{In}(\text{PO}_3)_3$. Spectral resolution is 0.3 nm. Concentration of Nd is 2at.%.

InPo_F5 DISC#: 86

InPo_F6 DISC#: 86

2% Nd

Fig. 4. Fluorescence spectrum of Nd in Sc(PO₃)₃. Spectral resolution is 0.3 nm. Concentration of Nd is 2at.%.

ScPo_F2 DISC#: 86

ScPo_F3 DISC#: 86

22 N₁

Fig. 5. Fluorescence decay of Nd in Lu(PO₃)₃. The Nd concentration is 2at.%.

Fig. 6. Fluorescence decay of Nd in (a) $\text{Y}(\text{PO}_3)_3$, (b) $\text{In}(\text{PO}_3)_3$ and (c) $\text{Sc}(\text{PO}_3)_3$. The Nd concentrations are 5at.%, 2at.% and 2at.% respectively.

YPo_L6 DISC#: 86

5% Nd

InPo_L1 DISC#: 87

2% Nd

ScPo_L1 DISC#: 87

2% Nd

Fig. 7. Fluorescence decay of Cr in 2at.% Cr singly doped $\text{Lu}(\text{PO}_3)_3$ (a), and in 2at.% Cr 2at.% Nd codoped $\text{Lu}(\text{PO}_3)_3$ (b).

Fig. 8. Fluorescence decay of Cr in 5at.% Cr singly doped $\text{Y}(\text{PO}_3)_3$ (a), and in 5at.% Cr, 5at.% Nd codoped $\text{Y}(\text{PO}_3)_3$ (b).

YPo_L1 DISC#: 05

5% Cr

YPo_L7 DISC#: 07

5% Cr 5% Nd

Fig. 9. Fluorescence decay of Cr in 2at.% singly doped $\text{In}(\text{PO}_3)_3$ and 2at.% Cr, 2at.% Nd codoped $\text{In}(\text{PO}_3)_3$.

InPo_L1 DISC#: 85

2% Cr

InPo_L2 DISC#: 87

2% Cr, 2% Nd

Fig. 10. Fluorescence decay of Cr in 2at.% Cr singly doped $\text{Sc}(\text{PO}_3)_3$ (a), and 2at.% Cr, 2at.% Nd codoped $\text{Sc}(\text{PO}_3)_3$ (b).

ScPo_L2 DISC#: 87

2% Cr

ScPo_L4 DISC#: 87

2% Cr 2% Nd

Fig. 11. Fluorescence spectrum of $\text{Sc}(\text{PO}_3)_3$ doped with 2at.% Cr and 2at.% Nd. The Cr ion was selectively pumped at 640 nm by a pulse dye laser. Spectral resolution was 0.6 nm.

ScPo_F03 DISC#: 07

2% Cr 2% Nd

Fig. 12. Fluorescence spectrum of Sc(PO₃)₃ doped with 5at.% Cr and 5at.% Nd. The Cr ion was selectively pumped at 640 nm by a pulse dye laser. Spectral resolution was 0.6 nm.

Fig. 13. Fluorescence spectrum of $\text{In(PO}_3)_3$ doped with 5at.% Cr and 5at.% Nd. The Cr ion was selectively pumped at 640 nm by a pulse dye laser. Spectral resolution was 0.6 nm.

Fig. 14. Fluorescence spectrum of $\text{In}(\text{PO}_3)_3$ doped with 2at.% Cr and 2at.% Nd. The Cr ion was selectively pumped at 647 nm by a chopped krypton laser. Spectral resolution was 0.6 nm.

Fig. 15. Fluorescence spectrum of Y(PO₃)₃ doped with 5at.% Cr and 5at.% Nd. The Cr ion was selectively pumped at 647 nm by a chopped krypton laser.

YPO_F3 DISC#: 85

5% Cr 5% Nd

Fig. 16. Fluorescence spectrum of LaScO_3 doped with 1at.% Cr and 1at.% Nd (in melt). The Cr ion was selectively pumped at 640 nm by a pulse dye laser.

Fig. 17. Fluorescence spectrum of Cr doped $\text{Al}(\text{PO}_3)_3$.

Fig. 18. Fluorescence spectrum of Cr doped Ga(PO₃)₃.

Fig. 19. Fluorescence spectra of Cr doped $\text{In}(\text{PO}_3)_3$ and $\text{Sc}(\text{PO}_3)_3$.

Emission X-Sect.(1E-20cm)

Fig. 20. Calculated emission cross sections of Cr doped $\text{In}(\text{PO}_3)_3$ and $\text{Sc}(\text{PO}_3)_3$.