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DEVELOPMENT OF HOST CRYSTALS FOR CE(+3) BLUE AND BLUE-GREEN SOL--ETC(U)

JUL 82 R D RAUH, A N SCOVILLE

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DEVELOPMENT OF HOST CRYSTALS FOR  $Ce^{+3}$   
BLUE AND BLUE-GREEN SOLID-STATE LASERS

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July 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Blue-green lasers operating at ~480 nm, a region of sea water trans- parency, could become an integral part of undersea and air-to-sea commu- nication and imaging systems. During Phase I of this program, wide band gap oxides were examined which could support Ce <sup>+3</sup> luminescence in this region. A basic requirement for observing Ce <sup>+3</sup> luminescence in this region is a cubic site symmetry as is found in the Th <sup>+4</sup> or Ce <sup>+4</sup> position		

*Equivalent  
material  
(7.3) (H4)*

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20. Abstract (Cont.)

of  $\text{ThO}_2$  and  $\text{CeO}_2$ , or the  $\text{La}^{+3}$  position of  $\text{LaAlO}_3$  and  $\text{LaAl}_{1-x}\text{Sc}_x\text{O}_3$  (perovskites). These oxides were synthesized, doped with  $\text{Ce}^{+3}$ , using either oxidation of mixed oxalates for  $\text{ThO}_2\cdot\text{Ce}$ , or a combination of component oxides in a molten  $\text{BaCO}_3/\text{BaF}_2$  flux for the perovskites. Total luminescence spectra of the oxides revealed a two component fluorescence between 400 and 500 nm in all cases, with two excitation maxima between 320 and 380 nm. Some contribution to the spectra from  $\text{Ce}^{+4}$ , or from an impurity or defect center could not be ruled out. A concerted effort on production of optical quality specimens of the promising materials, either as clear ceramics or single crystals, is recommended for Phase II of this investigation so that they may be evaluated as lasers.

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## INTRODUCTION

The transparency of sea water to a narrow range of frequencies centered at 480 nm is the basis for intense interest by the Navy in developing high power blue-green lasers.<sup>1</sup> Such lasers would have applications as pulsed depth finders and in underwater imaging. In addition, various air-to-ground applications are perceived, including airborne submarine detection, submarine-to-airplane communication, and communications between satellites and submarines. To date, most research and development of blue-green lasers has focused on gas phase devices, particularly such as the HgBr<sub>2</sub>/HgBr dissociation laser (502 nm). At present, the gas phase lasers have serious lifetime limitations, which may ultimately compromise their use.

Solid-state blue-green lasers are a potential alternative to the gas phase devices. Their life is expected to be limited by the flash lamp used for optical pumping. Otherwise, solid-state lasers would have the advantages of stability, compactness and capability for high power operation which are crucial in satellite mounted sources, sought under the Navy's OPSATCOM program.

The search for ultraviolet and high energy visible solid-state lasers has focused on rare earth ions which show 4f → 5d luminescent transitions.<sup>2-6</sup> These transitions are in the appropriate energy range for several di- and trivalent rare earth ions, e.g., Nd<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Pr<sup>3+</sup>, Eu<sup>2+</sup> and Ce<sup>3+</sup>.<sup>2,3</sup> In contrast with the more frequently employed f → f laser transitions, these high energy bands can be symmetry allowed and hence broad. Therefore, d → f lasers can be pumped with broad band sources and are potentially tunable.

In this program we have been investigating Ce<sup>3+</sup> for blue-green laser operation, since it is a simple 4f<sup>1</sup> ion and shows no intermediate f → f transitions in the visible spectrum. The f → d absorption and d → f fluorescence is highly host dependent. As shown in Figure 1, in

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<sup>1</sup>Laser Focus, June, 1981.

<sup>2</sup>A. A. Kaminskii, Laser Crystals, Springer Series in Optical Sciences, Vol. 14 (New York: Springer-Verlag, 1981).

<sup>3</sup>K. H. Yang and J. A. DeLuca, Appl. Phys. Lett., 29, 499 (1976).

<sup>4</sup>R. R. Jacobs, W. F. Krupke and M. J. Weber, Appl. Phys. Lett., 33, 410 (1978).

<sup>5</sup>J. F. Owen, P. B. Dorain and T. Kobayasi, J. Appl. Phys., 52, 1216 (1981).

<sup>6</sup>D. J. Ehrlich, P. F. Moulton and R. M. Osgood, Jr., Optics Lett., 4, 184 (1979).

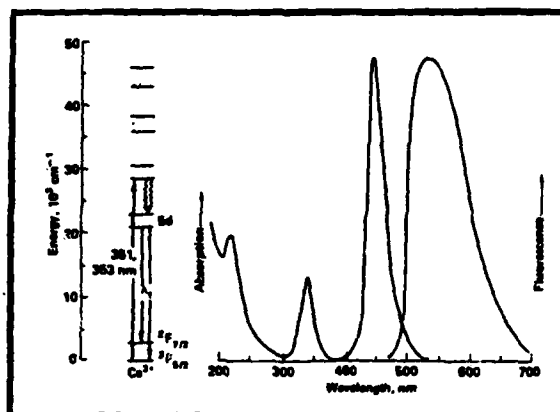


Figure 1. Absorption and luminescence spectra of  $\text{Ce}^{+3}$  in  $\text{Y}_3\text{Al}_5\text{O}_{12}$  cubic host lattice.<sup>6</sup>

yttrium aluminum garnet (YAG), where  $\text{Ce}^{+3}$  is surrounded by an 8-fold cubic array of  $\text{O}^-$  ions, the luminescence is centered at  $\sim 550$  nm. However, extensive surveys by Blasse and co-workers<sup>7-9</sup> of  $\text{Ce}^{+3}$  luminescence in various oxide hosts reveals luminescence in the 300-400 nm region to be most common. Blasse and Brill<sup>7</sup> associated the ultraviolet emission with octahedral or trigonal prismatic symmetry. The energy level diagrams in Figure 2 show that the splitting of the d-levels is reversed for octahedral and cubic coordination. The lowest excited state should be closer to the ground state in the cubic case where it is associated with d orbitals of  $e_{2g}$  symmetry, displaced from the center of gravity by  $(3/5)\Delta$  by the crystal field. Due to a further tetragonal distortion in YAG, additional splitting pushes the lowest d orbital even closer to the ground state. Since the luminescence in YAG is at too low an energy for blue-green operation, we seek other cubic but more highly symmetrical oxide hosts.

A further complication in designing an appropriate host material relates to the failure to observe laser action in  $\text{Ce}^{+3}$ -doped YAG. Several investigators have recorded transient absorption in optically excited  $\text{Ce}^{+3}$  YAG.<sup>4, 5</sup> This may be due to a transition from the  $\text{Ce}^{+3}$

<sup>4</sup>Jacobs et al., loc. cit.

<sup>5</sup>Owen et al., loc. cit.

<sup>6</sup>Ehrlich et al., loc. cit.

<sup>7</sup>G. Blasse and A. Brill, J. Chem. Phys., 47, 5139 (1967).

<sup>8</sup>G. Blasse and A. Brill, Appl. Phys. Lett., 11, 53 (1967).

<sup>9</sup>A. Brill, G. Blasse and J. A. de Poorter, J. Electrochem. Soc., 117, 346 (1970).

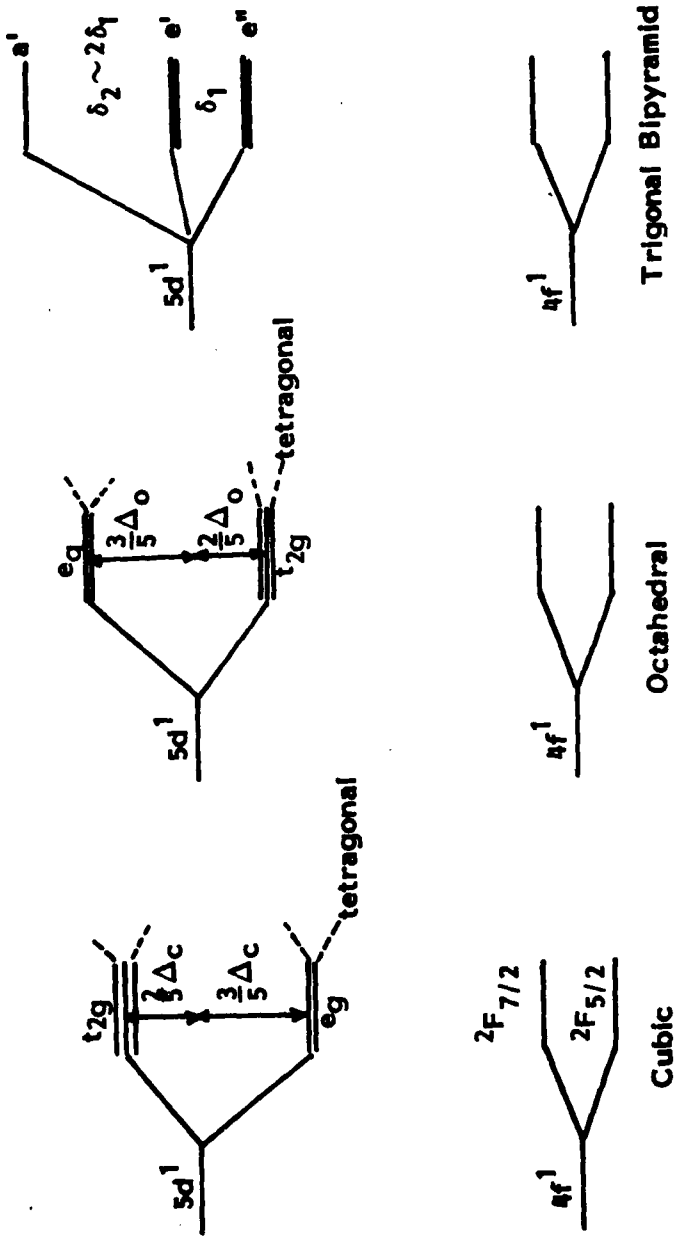


Figure 2. Splitting patterns for d-electrons of luminescing ion in hosts of various symmetry.

excited state to the conduction band of the host, an interpretation supported by the absence of such parasitic processes in fluoride hosts. A  $\text{Ce}^{+3}(1\%):\text{LiYF}_4$  laser operating at 325 nm has recently been reported by Ehrlich, Moulton and Osgood.<sup>6</sup> In order to avoid the possibility of this kind of excited state absorption, the host band gap should be greater than twice the fluorescence energy, or  $\geq 50,000 \text{ cm}^{-1}$ .

In summary, the overall goal of this program is to produce a high efficiency solid-state blue-green laser ( $\lambda_{\text{max}} \approx 480 \text{ nm}$ ) employing the luminescent  $d \rightarrow f$  transition of  $\text{Ce}^{+3}$ . In the 6-month Phase I period just completed, the objective has been to find a suitable host material that could form the basis of such a laser. This material must have the following features:

- 1) a band gap well in excess of 5 eV;
- 2) chemical inertness;
- 3) ability to incorporate  $\text{Ce}^{+3}$  substitutionally, without phase separation or oxidation to  $\text{Ce}^{+4}$ ;
- 4) place  $\text{Ce}^{+3}$  in a cubic site symmetry in order to yield luminescence in the 450-500 nm range;
- 5) give rise to high  $\text{Ce}^{+3}$  radiative lifetime and hence high fluorescence quantum yield; and
- 6) be adaptable to scaled-up crystal growth.

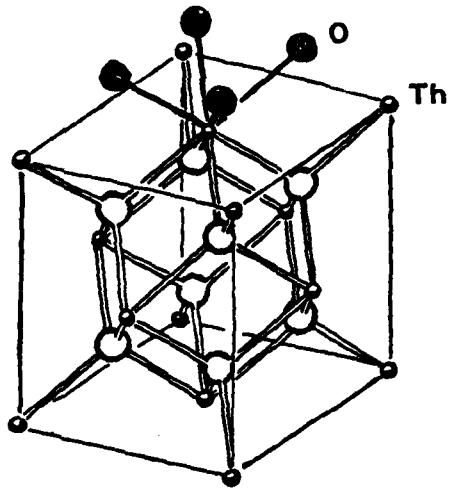
Two host lattices were chosen for investigation during this research period:  $\text{ThO}_2$  and  $\text{LaAl}_{1-x}\text{Sc}_x\text{O}_3$ . Both meet criteria 1) and 2) above as acceptable host materials. If Ce substitutes for Th in the same site, it will have an 8-fold coordination of  $\text{O}^{2-}$ , just as in YAG. In  $\text{LaAlO}_3$ , a perovskite lattice, the  $\text{La}^{+3}$  has a dodecahedral coordination of  $\text{O}^{2-}$ , but the symmetry is still cubic, as in YAG and  $\text{ThO}_2$ . Furthermore,  $\text{LaAlO}_3$  is almost perfectly cubic perovskite, with a rhombohedral angle of  $90^\circ 4'$ .  $\text{Sc}^{+3}$  (or  $\text{Ce}^{+3}$ ) is added to the lattice to correct even this small distortion.\* The structures of  $\text{ThO}_2$  and  $\text{LaAlO}_3$  are shown in Figure 3.

Criteria 3) and 4) should be naturally achieved for  $\text{LaAlO}_3$ , since  $\text{Ce}^{+3}$  and  $\text{La}^{+3}$  are isovalent. It is possible, however, that some separate

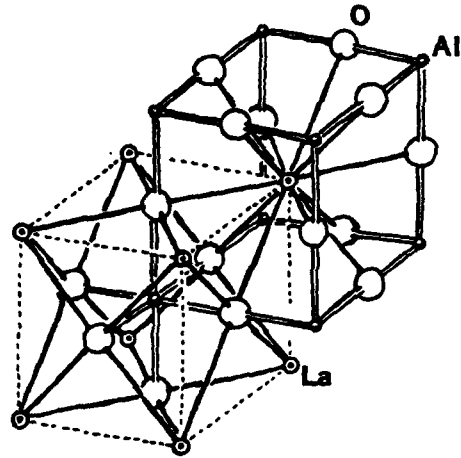
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<sup>6</sup>Ehrlich et al., loc. cit.

\*Goldshmidt has calculated that a tolerance factor for stability of a cubic perovskite structure, given by  $t = [(R_A + R_O)/\sqrt{2}(R_B + R_O)]$  has an approximate range of 0.8 to 0.9. For  $\text{LaAlO}_3$ ,  $t = 0.95$ ; thus, an increase in the average  $R_B$  will push  $t$  more into the desirable range. This may be accomplished by substituting some  $\text{Sc}^{+3}$  ( $R = 0.81\text{\AA}$ ) for  $\text{Al}^{+3}$  ( $R = 0.50\text{\AA}$ ). For  $t < 0.9$ , the mole fraction of  $\text{Sc}^{+3}$  should be greater than 0.3.



Fluorite ( $\text{ThO}_2, \text{CeO}_2$ )



Perovskite ( $\text{LaAlO}_3, \text{LaScO}_3$ )

Figure 3. Structures of possible laser host crystals with cubic coordination of luminescing ion ( $\text{Ce}^{+3}$ ).

CeO<sub>2</sub> phase could form if the preparation of Ce<sup>+3</sup>-LaAlO<sub>3</sub> is conducted in air. For ThO<sub>2</sub>, substitution of Ce<sup>+3</sup> for Th<sup>+4</sup> is expected to be more difficult, requiring some additional valence compensation. Such compensation may be acquired via O vacancies, although these may also act as luminescence quenching sites. Substitutional compensation is therefore preferred.

Finally, crystal growth of ThO<sub>2</sub> from the melt would require extreme conditions, since its melting point is 3500°C. In both cases, crystal growth in an oxidizing atmosphere could result in partial oxidation of Ce<sup>+3</sup>. The crystal growth of LaAlO<sub>3</sub> has been reported from the melt, hydrothermally, and both LaAlO<sub>3</sub> and ThO<sub>2</sub> from fluxes.

## RESULTS

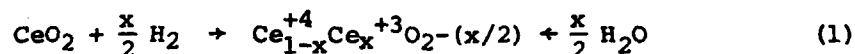
### Syntheses of Valency Compensated Reduced Oxides

All compounds used in oxide syntheses were of the highest available purity. They are listed in Table 1.

TABLE 1. MATERIALS USED IN OXIDE SYNTHESSES

<u>Compound</u>	<u>Supplier</u>	<u>Purity</u>
Al <sub>2</sub> O <sub>3</sub>	Spex	<2 ppm TMI
BaCO <sub>3</sub>	Cerac	99.999
BaF <sub>3</sub>	Spex	<10 ppm TMI
CeF <sub>3</sub>	Alfa	99.9
CeO <sub>2</sub>	Cerac	99.9
Ga <sub>2</sub> O <sub>3</sub>	Spex	99.9999
La <sub>2</sub> O <sub>3</sub>	Cerac	99.9999
Sc <sub>2</sub> O <sub>3</sub>	Spex	<10 ppm TMI

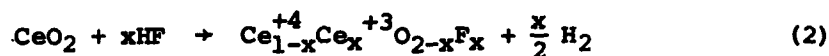
Several experiments were carried out to synthesize Ce<sup>+3</sup> in tetra-valent oxide hosts. Initial evaluation of conditions favoring reaction (1) was made using CeO<sub>2</sub> as the reactant:



Reductions were conducted under flowing H<sub>2</sub> in alumina boats set in a quartz reaction tube. A Lindberg 3-zone tube furnace was employed for heating, with the boats confined to the central zone. Reductions carried out for 3 hours at 600°C and for 3 hours at 800°C gave qualitatively the same result: the CeO<sub>2</sub> was black at the higher temperatures, turning to light brown on cooling (in H<sub>2</sub>). Thus, some reduction of Ce<sup>+4</sup> appears to be possible under mild conditions, which is not surprising since O diffuses in this lattice very rapidly.

A similar reduction was conducted for ThO<sub>2</sub> crystals (~2 mm/edge) doped with 1% Ce<sup>+4</sup>, which had been grown from a flux at Phillips Laboratories, and which were provided to us through the contractor. These were reduced at 600°C for 2 hours in flowing H<sub>2</sub>. The cubic crystals, which were light pink initially, seemed to lighten further in color as a result of the reduction, but several tiny black inclusions developed, their origin unknown.

Stabilization of O-deficient structures was sought by substitution of  $F^-$  for  $O^-$  vacancies, according to the reaction



The synthetic procedure of Subbarao et al.<sup>10</sup> was followed, which had been reported for producing several  $F^-$  compensated oxides, including  $TiO_{2-x}F_x$  and  $WO_{3-x}F_x$ . The apparatus is shown in Figure 4, and consists mainly of two Ni reaction tubes in separate tube furnaces connected by Teflon tubing. The first Ni tube is an HF generator, operated by thermally decomposing  $KHF_2$  at 250°C in a flow of 95% Ar/5%  $H_2$ . The second tube contains the oxide starting material in a Ni boat. The reaction temperature is limited to 700-800°C in order to prevent weakening of the reaction tube. A protective film of  $NiF_2$  forms on the inside of the Ni walls, passivating them against further corrosion. KOH traps are provided for decomposing excess HF.

Initially, the reaction with  $CeO_2$  was carried out at 670°C for 2 hours following thermal equilibration of the reaction zone and establishment of a steady flow of HF. The  $CeO_2$  starting material was pale yellow. Under these conditions, no color change in the  $CeO_2$  was noted after cooling to room temperature in  $H_2/Ar$ . The reaction was repeated using pure  $H_2$  as the carrier gas, for 8 hours at 670°C, then cooled to room temperature in flowing  $H_2$ . The resulting product was a pure white powder.

Both products were analyzed for  $F^-$  by dissolving them in 3:1 concentrated  $H_2SO_4/HNO_3$ , followed by dilution in 100 ml of  $H_2O$ , and measuring the potential of a fluoride specific ion electrode (Orion 94-09) in the resulting solution. Surprisingly,  $F^-$  incorporation appeared greater in the sample reacted under the milder conditions. Here, the mole fraction of  $[F]/[CeO_{2-x}]$  was  $\sim 0.2$ , while it was  $\sim 0.1$  in the white product. Since  $x$  is unknown, it is impossible to assign a precise formula to each sample. Nevertheless, this method for preparing  $F^-$  compensated  $CeO_{2-x}$  appears to have merit.

The reductive fluorination of the Ce doped  $ThO_2$  crystals was carried out using the more extreme conditions described above. The reacted crystals turned from light pink to yellow-brown, although they retained their transparency. Photomicrographs of the crystals before and after reaction are shown in Figure 5.

#### Syntheses of $LaAlO_3$ and $La_{1-x}Sc_xO_3$

Takeda et al.<sup>11</sup> have recently reported syntheses of  $Ce^{+3}$  doped YAG,  $YAlO_3$  and monoclinic  $Y_4Al_2O_9$  using fluxes based on  $BaF_2/BaCO_3$  mixtures.

<sup>10</sup>S. Subbarao, Y. Yun, R. Kershaw, K. Dwight and A. Wold, *Inorg. Chem.*, **18**, 488 (1979).

<sup>11</sup>T. Takeda, T. Miyata, F. Muramatsu and T. Tomiki, *J. Electrochem. Soc.*, **127**, 458 (1980).

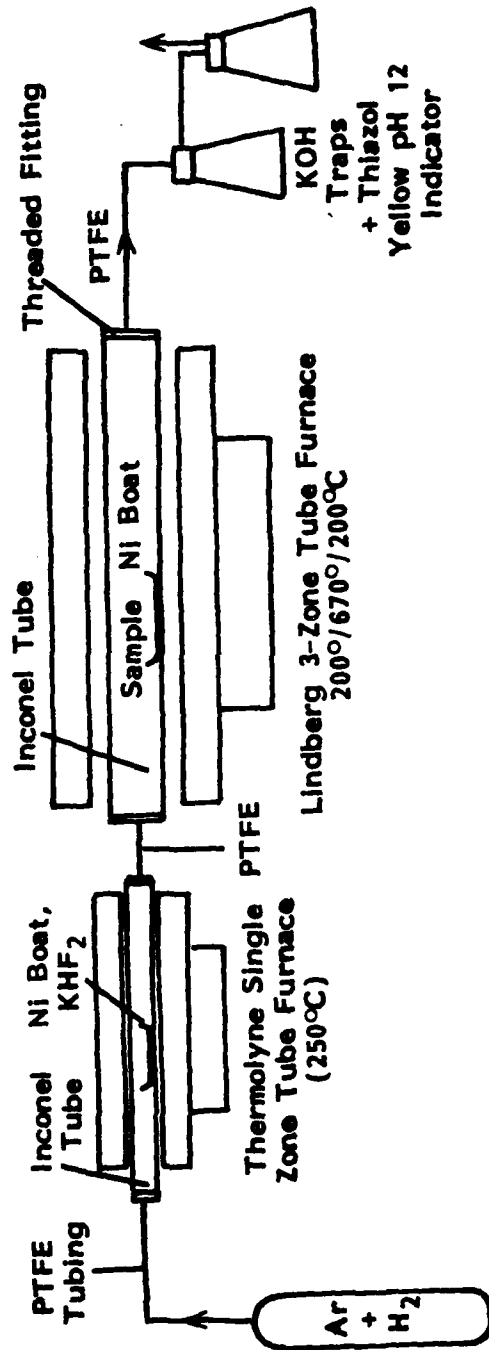


Figure 4. Apparatus for fluorination of oxides.



Figure 5.  $\text{ThO}_2/\text{Ce}$  doped crystals before (right) and after (left) reaction with  $\text{HF}/\text{H}_2$  for 8 hours at  $670^\circ\text{C}$ .

Conditions were chosen for synthesizing  $Ce^{+3}/LaAlO_3$  which yielded the most active  $Ce^{+3}/YAP$  phosphors. The starting mixtures were designated as  $x-y(CeF_3)-z(\text{flux})$ . Thus, the mixtures of desired stoichiometry contained  $[(x-0.01y)/2]$  mole  $La_2O_3$ , 0.01y mole  $CeF_3$ ,  $(x/2)$  moles  $Al_2O_3$ , and 0.01z gram equivalents of flux. Our optimal starting composition for preparing 1% doped  $Ce^{+3}/LaAlO_3$  was:  $x = 1$ ,  $y = 1$  and  $z = 1.5$  for a flux of 1:1  $BaF_2/BaCO_3$ . This mixture was ground repeatedly as a MeOH slurry, using an agate mortar/pestle. After  $\sim 1$  hour of grinding and mixing with constant renewal of the MeOH, the slurry had the consistency of a fine "jewelers' paste." The MeOH was then allowed to evaporate. The powder was transferred to a Pt crucible and placed in a muffle furnace at  $1175^\circ C$  for 12 hours. The product, which had an off-white appearance, was rinsed thoroughly with 3N  $HNO_3$  to remove flux and other Ba compounds, then several times with distilled  $H_2O$ , then dried. The product yield was  $>90\%$  for 2g of starting mixture.

The x-ray diffraction pattern of the product is shown in Table 2. Identical spectra were obtained for samples prepared with one sintering cycle and with three cycles (with intermediate grinding/mixing). The identification is definitely  $LaAlO_3$ , with  $\sim 1\%$  impurity phase, mostly  $Al_2O_3$ .

A similar synthesis was carried out for  $LaAl_{0.7}Sc_{0.3}O_3$ , containing various amounts of  $Ce^{+3}$ . The Sc was added stoichiometrically as  $Sc_2O_3$ . The x-ray diffraction data of the product are also presented in Table 2. A major second phase is typically present in these samples, which we identify as  $LaScO_3$ . Some shifts in the  $LaAlO_3$  d spacings indicate that limited incorporation of Sc may have occurred. However, under the present reaction conditions, the reaction to form the mixed oxide was obviously incomplete. An attempted synthesis of  $LaScO_3$  under the same conditions resulted in only  $\sim 25\%$  conversion to the desired compound, the rest being  $La_2O_3$  and  $Sc_2O_3$ . Further variation of the reaction temperature and/or flux composition may be necessary to produce this oxide.

#### Syntheses of Oxides from Oxalates

Syntheses of oxides by the oxidative sintering of the related oxalates is useful for preparing powders having very small particle size. These may, in turn, be used to produce ceramics with a very close interparticulate packing density and a high optical clarity (low scattering loss). The "optical ceramics" may be fabricated into laser rods, thus avoiding the necessity of growing large single crystals.

Ce-doped  $ThO_2$  was prepared by this method. Stoichiometric amounts of  $Th(NO_3)_4$  and  $Ce(NO_3)_3$  were dissolved in  $H_2O$ , and precipitated as oxalates by addition of excess oxalic acid solution. The fluffy white precipitate was dried at  $115^\circ C$  in air overnight, then placed in porcelain boats and calcined at  $850^\circ C$  for 6 hours in flowing air. The x-ray diffraction pattern of the final product was in excellent agreement with that published for  $ThO_2$ , with no identifiable impurities.

TABLE 2. EXPERIMENTALLY OBTAINED X-RAY DIFFRACTION PATTERNS OF SYNTHETIC ALUMINATES

Assignments: (1)  $\text{LaAlO}_3$  or  $\text{LaAl}_x\text{Sc}_{1-x}\text{O}_3$   
 (2)  $\text{LaScO}_3$   
 (3)  $\text{Al}_2\text{O}_3$   
 (4)  $\text{Sc}_2\text{O}_3$   
 (5)  $\text{CeF}_3$

$\text{LaAlO}_3$			$\text{LaAl}_{0.7}\text{Sc}_{0.3}\text{O}_3$		
$d$	$I/I_1$	Assignment	$d$	$I/I_1$	Assignment
			4.037	10.5	2
3.76	55	1	3.79	96	1
			3.62	3	2
3.21	2	5(?)	3.45	2	3
			2.86	27.2	2 or 4
2.66	100	1	2.68	100	1
2.53	-	3	2.55	2.5	3
2.37	-	3	2.38	1	2 or 3
			2.34	2.5	2
2.27	-	1	2.31	3.2	1
2.18	41	1	2.19	68	1
			2.10	1.5	-
2.08	2	3	2.08	3	3
			2.02	8	5(?)
			1.90	1.5	
			1.96	1	2
1.89	41	1	1.89	55.8	1
			1.80	1	2(?)
			1.77	1.5	2(?)
1.73	4	1	1.74	6	1
1.69	18	1	1.69	27	1
			1.65	3	2
			1.64	5.5	2
1.59	-	-	1.60	2	3
1.54	32	1	1.54	48	1
			1.48	2	-
			1.42	1	-
1.34	13	1	1.34	21	1
1.26	7	1	1.27	9.8	1
1.20	12	1	1.19	15	1
1.14	7	3	1.14	9.9	3

The oxalate method was also used to coat several samples of  $\text{LaAlO}_3$  with  $\text{MgO}$ , for later sintering to form optical ceramics. The purpose of the  $\text{MgO}$  is to prevent dendritic grain growth near the  $\text{LaAlO}_3$  melting point (the ceramic sintering temperature), thus allowing close packing of the small particles prepared initially. The coating was carried out by slowly adding a  $\text{Mg}(\text{NO}_3)_2$  solution to a rapidly stirred suspension of finely ground  $\text{LaAlO}_3$  in oxalic acid solution. The  $\text{Mg}$  oxalate-coated  $\text{LaAlO}_3$  was sintered for 7 hours at  $800^\circ\text{C}$  in flowing air.

A summary of the compounds prepared during this reporting period is given in Table 3.

TABLE 3. MATERIALS SYNTHESIZED FOR EVALUATION AS BLUE-GREEN LASER CANDIDATES

	<u>X-Ray</u>	<u>Chemical</u>	<u>Total Luminescence</u>	<u>Excitation</u>
$\text{CeO}_2\text{-x}$				
$\text{CeO}_2\text{-xF}_x$		[F <sup>-</sup> ]		
$\text{ThO}_2$ , 1% Ce	✓		✓	✓
$\text{ThO}_2\text{-x}$ , 1% Ce (reduced)	✓		✓	✓
$\text{ThO}_2\text{-xF}_x$ , 1% Ce			✓	
$\text{LaAlO}_3$	✓		✓	✓
$\text{LaAlO}_3$ , 1% Ce (as $\text{CeF}_3$ )	✓		✓	✓
$\text{LaAlO}_3$ , 0.1% Ce (as $\text{CeF}_3$ )	✓		✓	✓
$\text{LaAl}_{1-x}\text{Sc}_x\text{O}_3$ , 1% Ce (as $\text{CeF}_3$ )	✓		✓	✓
$\text{LaAl}_{1-x}\text{Sc}_x\text{O}_3$ , 1% Ce (as $\text{CeF}_3$ )	✓		✓	✓
$\text{LaScO}_3$ , 1% Ce (as $\text{CeF}_3$ )	✓			
$\text{LaAl}_{1-x}\text{Ga}_x\text{O}_3$ , 1% Ce (as $\text{CeF}_3$ )	✓			

#### Luminescence Spectra

Luminescence spectra were recorded on two different instruments. One arrangement employed a Molectron UV12 pulsed  $\text{N}_2$  laser which provided excitation at 337.1 nm. Detection was accomplished with an SA H-20 monochromator equipped with a Pacific Precision photomultiplier tube. The laser trigger signal was also used as an input to the reference channel of a Princeton Applied Research Model 5804 lock-in amplifier, which was used to process the signal from the photomultiplier tube. The outputs from the amplifier and the monochromator drive were recorded in digital form using a Bascom-Turner Series 8000 "Intelligent Recorder," and stored in its memory. The wavelength sensitivity of the monochromator/phototube combination was calibrated with a spectral standard tungsten-halogen lamp, and was also stored in the memory. The recorder could perform the function of multiplying the luminescence spectrum by the sensitivity spectrum, thus yielding corrected luminescence curves.

Excitation spectra were recorded on another luminescence spectrometer of conventional design. This instrument employed two monochrometers, one for excitation and one for emission. UV excitation spectra were recorded using a 100W D<sub>2</sub> light source.

Samples were prepared for luminescence analysis by pressing as pellets (0.5" diameter) in a commercial hardened steel die at 25,000 psi for 5 minutes. The pellets had sufficient green strength to survive dropping 2-3 feet onto a hard surface. Some pellets containing Ce were reduced at 1000°C for 6 hours under flowing 95% Ar/5% H<sub>2</sub>. For LaAlO<sub>3</sub>, this treatment increased the pellet density from 2.66 to 4.35 g/cm<sup>3</sup>.

Total luminescence and excitation spectra were recorded for 1) LaAlO<sub>3</sub> containing 0.1 and 1.0% Ce<sup>+3</sup>; 2) LaAl<sub>1-x</sub>Sc<sub>x</sub>O<sub>3</sub> containing 0.1 and 1.0% Ce<sup>+3</sup>; 3) ThO<sub>2-x</sub>, 1% Ce (crystal and oxalate-synthesized powder); 4) LaScO<sub>3</sub> + 1% Ce<sup>+3</sup>. Representative spectra are reproduced in Figures 6 through 12. The numerical values of emission and excitation peak maxima are summarized in Table 4. Samples of CeO<sub>2</sub> and CeO<sub>2-x</sub>F<sub>x</sub> were nonluminescent. Reduced ThO<sub>2</sub>/Ce single crystals gave spectra which were similar to the starting material, although reduction made the luminescence slightly more intense. Fluorination of these crystals appeared to quench the luminescence.

All the luminescence spectra display two major emission peaks with  $\lambda_{\max}$  between 430 and 500 nm, and two major excitation peaks between 320 and 365 nm. Excitation into the higher energy manifold results in favoring of the higher energy emission band. The lower energy excitation and emission bands are similarly related. However, both excitation and emission bands are always present. No excitation was detected below 300 nm for any of the samples. The splittings are on the order of 1000 cm<sup>-1</sup>, so cannot be ascribed to the major e<sub>g</sub>-t<sub>2g</sub> splitting of the d manifold, which would be closer to 10,000 cm<sup>-1</sup> (14,000 cm<sup>-1</sup> in YAG). The splittings are reasonable for the Ce<sup>+3</sup> (2F<sub>7/2</sub>, 2F<sub>5/2</sub>) ground state, but the same emission spectrum should be attained for each, which is not observed.

Several other transitions are possible which may complicate the spectra. The slight yellow color of CeO<sub>2</sub> has been attributed to an O(2p) → Ce<sup>+4</sup> charge transfer transition. Thus, Ce<sup>+4</sup> may have an excitation/fluorescence spectrum overlapping that of Ce<sup>+3</sup>. The sensitivity of the Ce<sup>+3</sup>/ThO<sub>2</sub> spectra to reduction suggests such a mechanism. Furthermore, if both Ce<sup>+3</sup> and Ce<sup>+4</sup> are present in the crystal, and if there is significant ion pairing (as has been suggested by Blasse<sup>12</sup>), then new charge transfer transitions can arise. The Ce concentration dependence of the Ce-LaAlO<sub>3</sub> spectra indicate that such pairing may be present.

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<sup>12</sup>G. Blasse, J. Electrochem. Soc., 128, 2694 (1981).

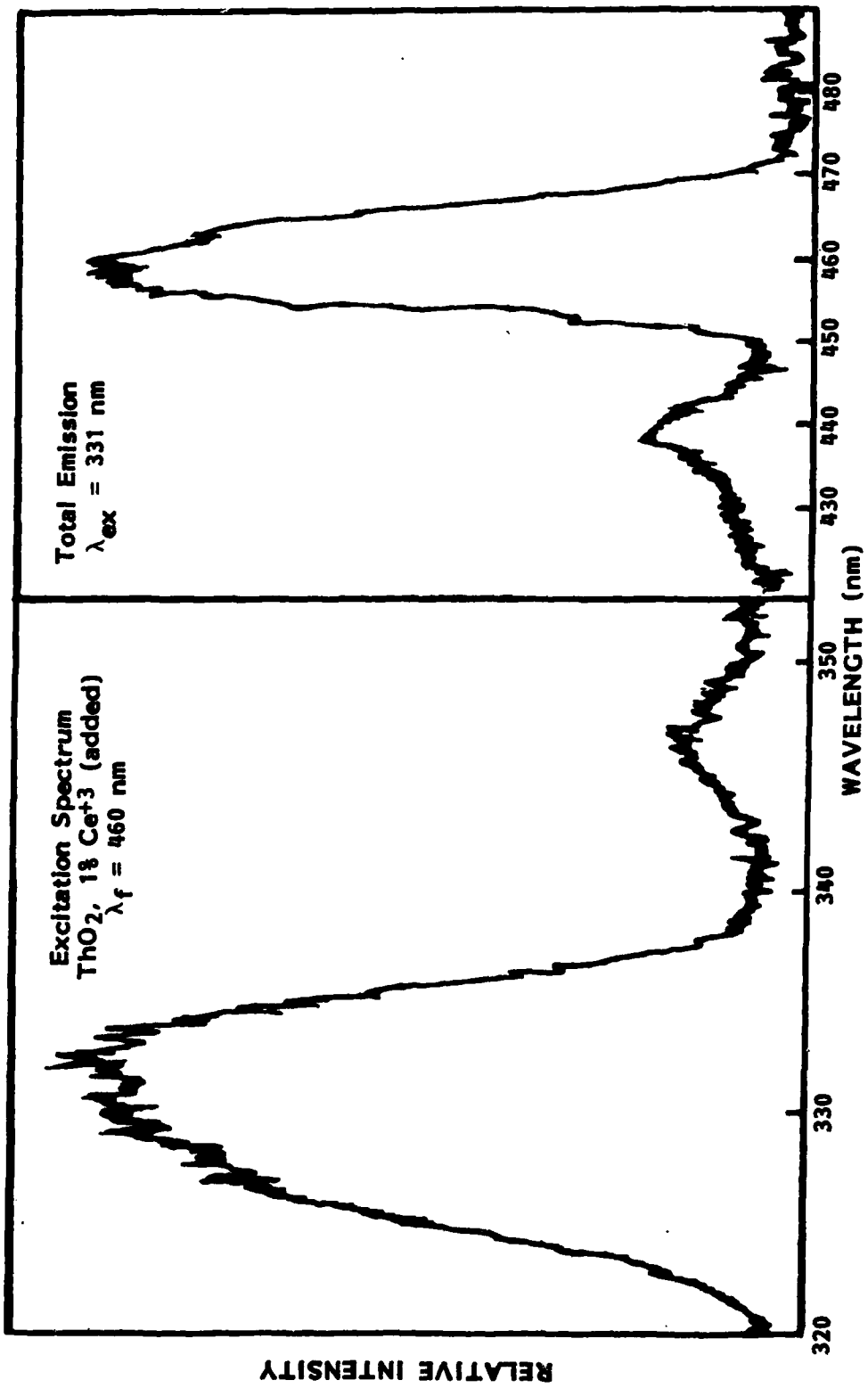


Figure 6. Total excitation and emission spectra for ThO<sub>2</sub> doped with 1% Ce<sup>+3</sup>, powdered sample, 25°C (unreduced).

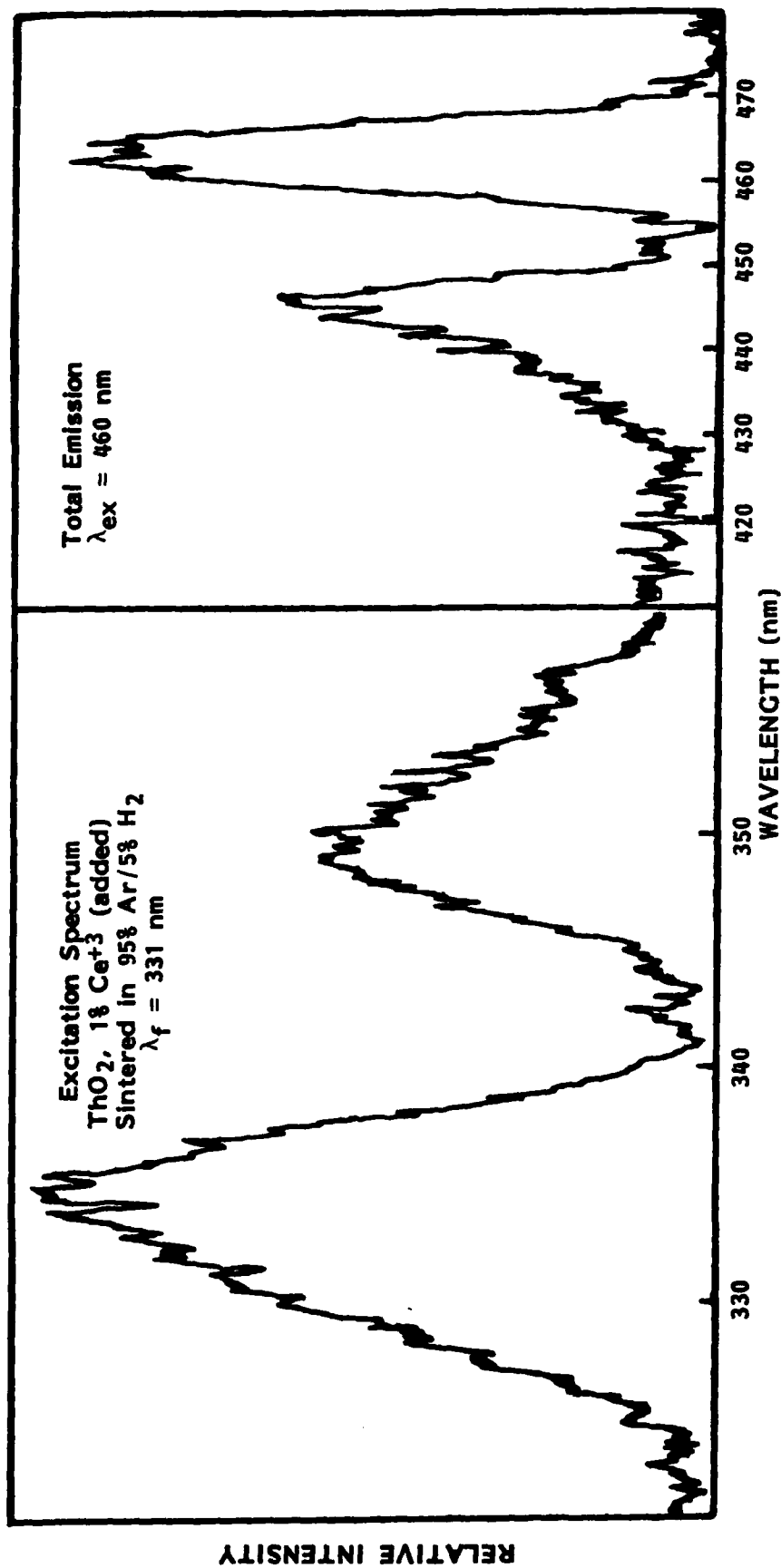


Figure 7. Total excitation and emission spectra for ThO<sub>2</sub> doped with 1% Ce<sup>+3</sup>, powdered sample, 25°C (reduced in Ar/5% H<sub>2</sub>).

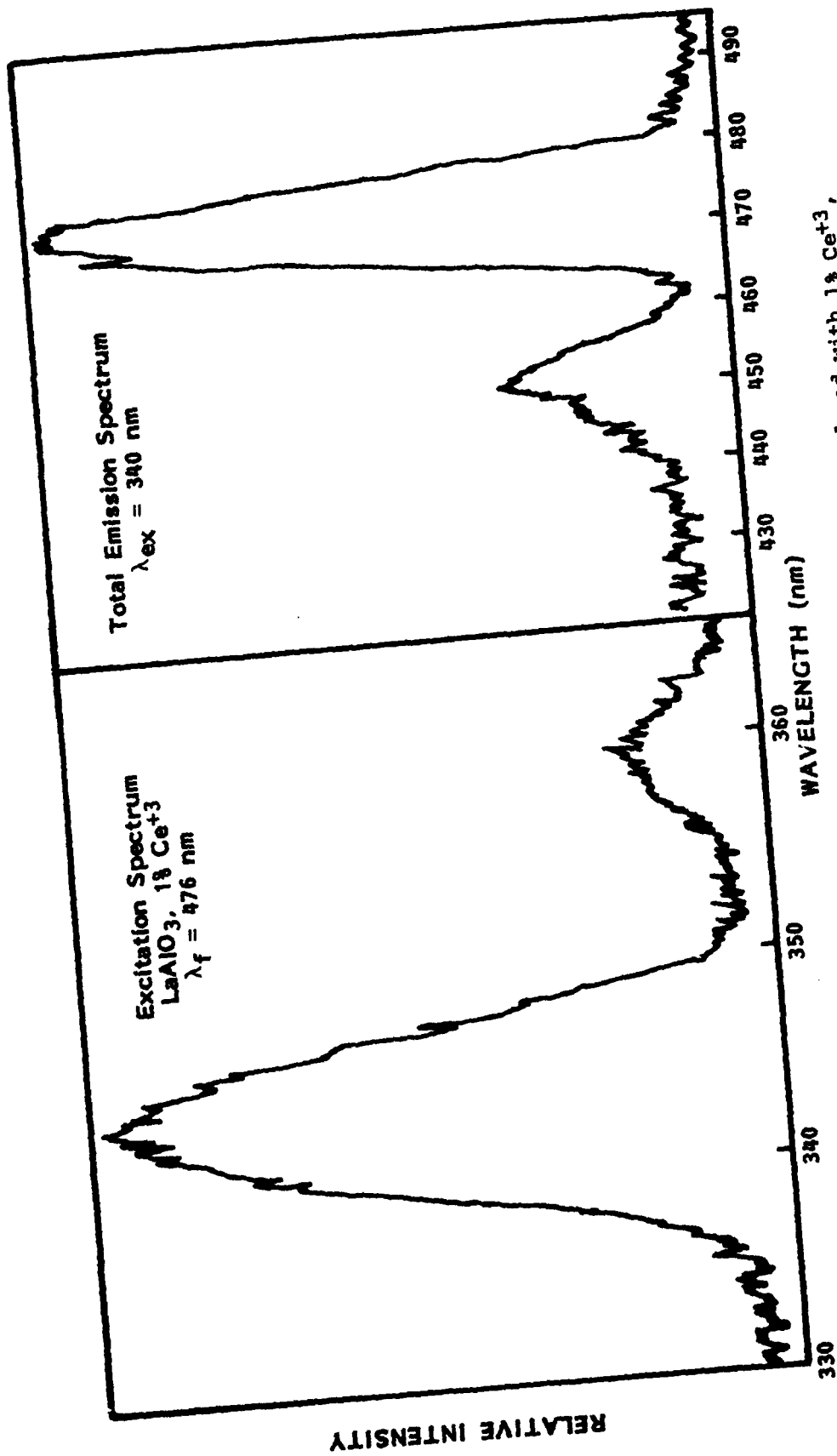


Figure 8. Total excitation and emission spectra for  $\text{LaAlO}_3$  doped with 1%  $\text{Ce}^{+3}$ , powdered sample, 25°C.

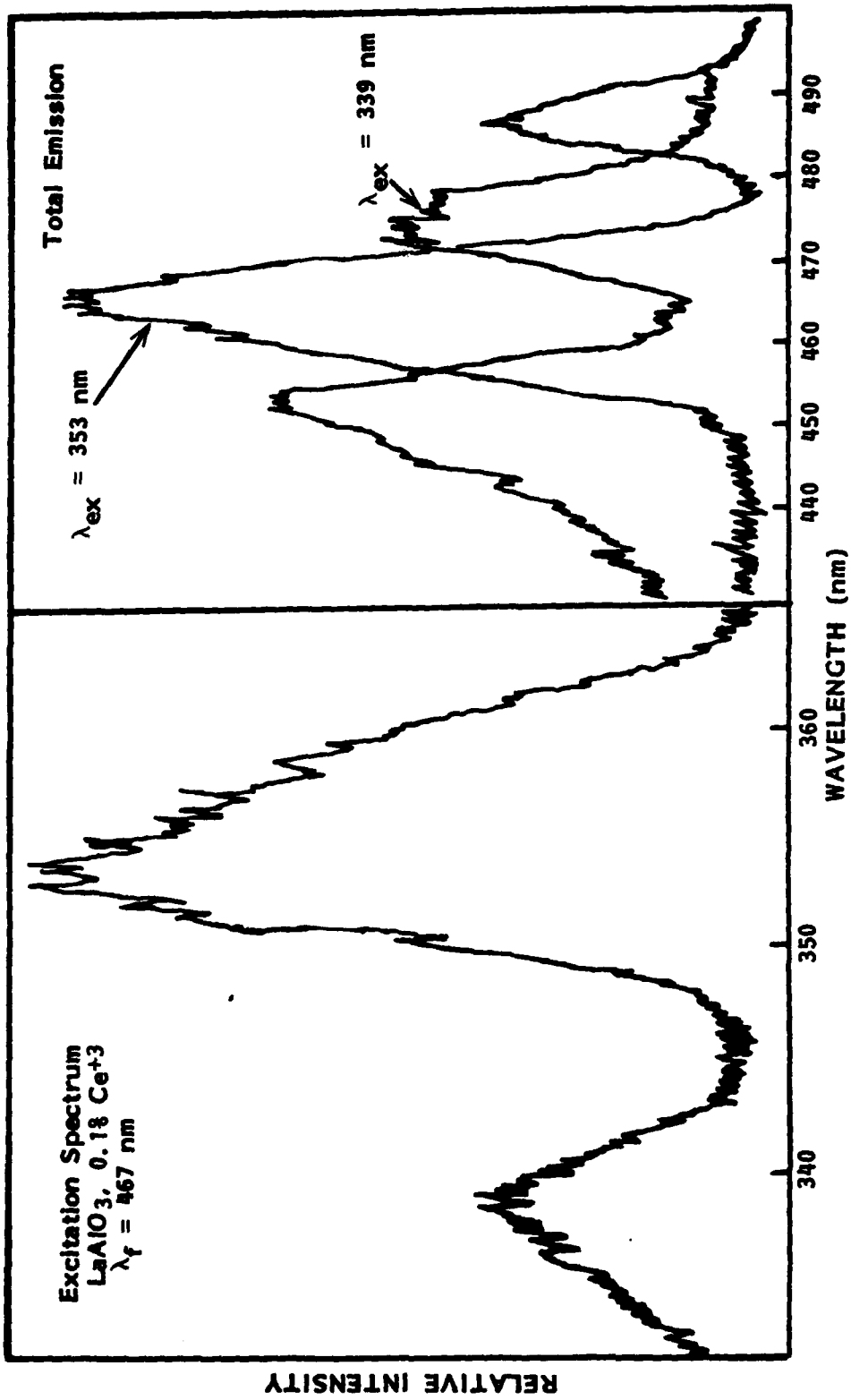


Figure 9. Total excitation and emission spectra for LaAlO<sub>3</sub> doped with 0.1% Ce<sup>3+</sup>, powdered sample, 25°C.

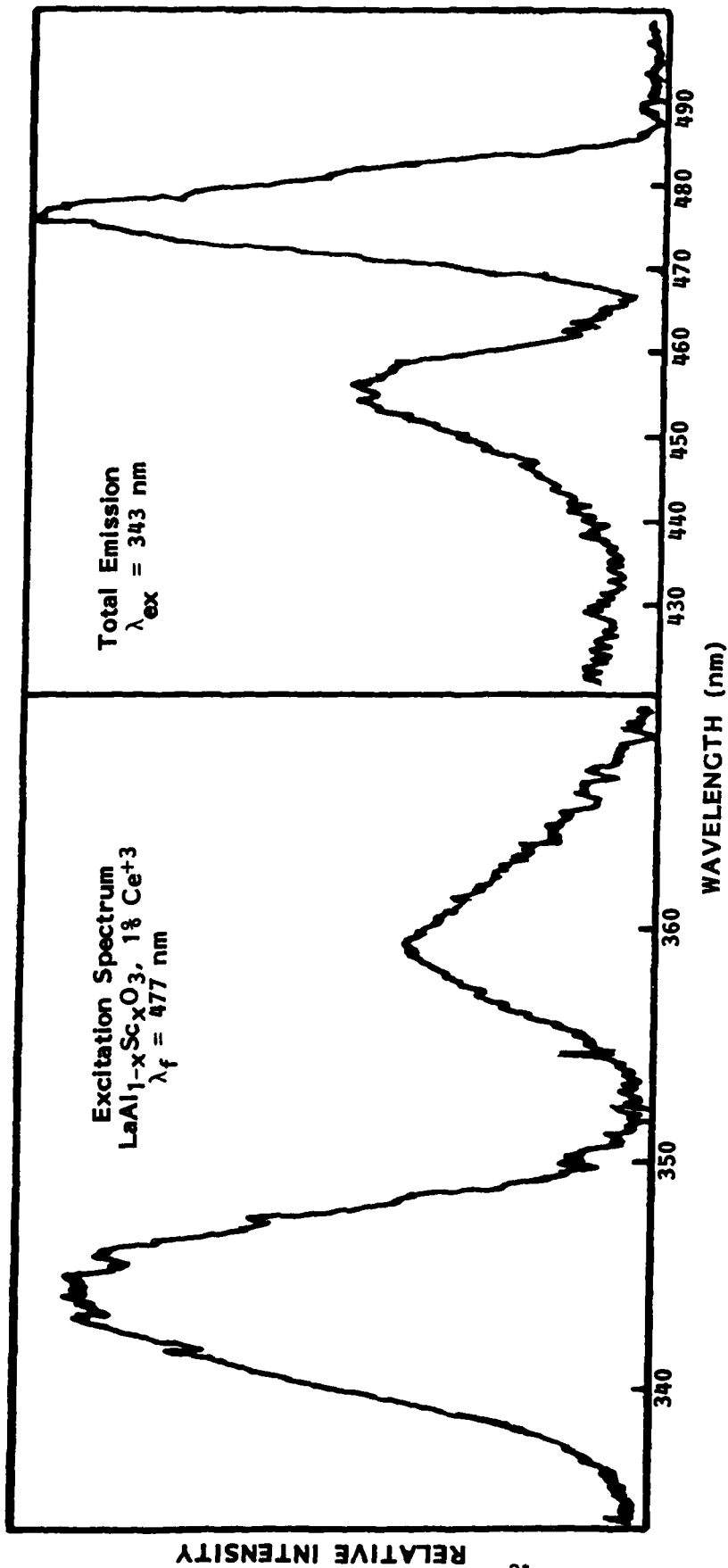


Figure 10. Total excitation and emission spectra for LaAl<sub>1-x</sub>Sc<sub>x</sub>O<sub>3</sub> doped with 1% Ce<sup>+3</sup>, powdered sample, 25°C.

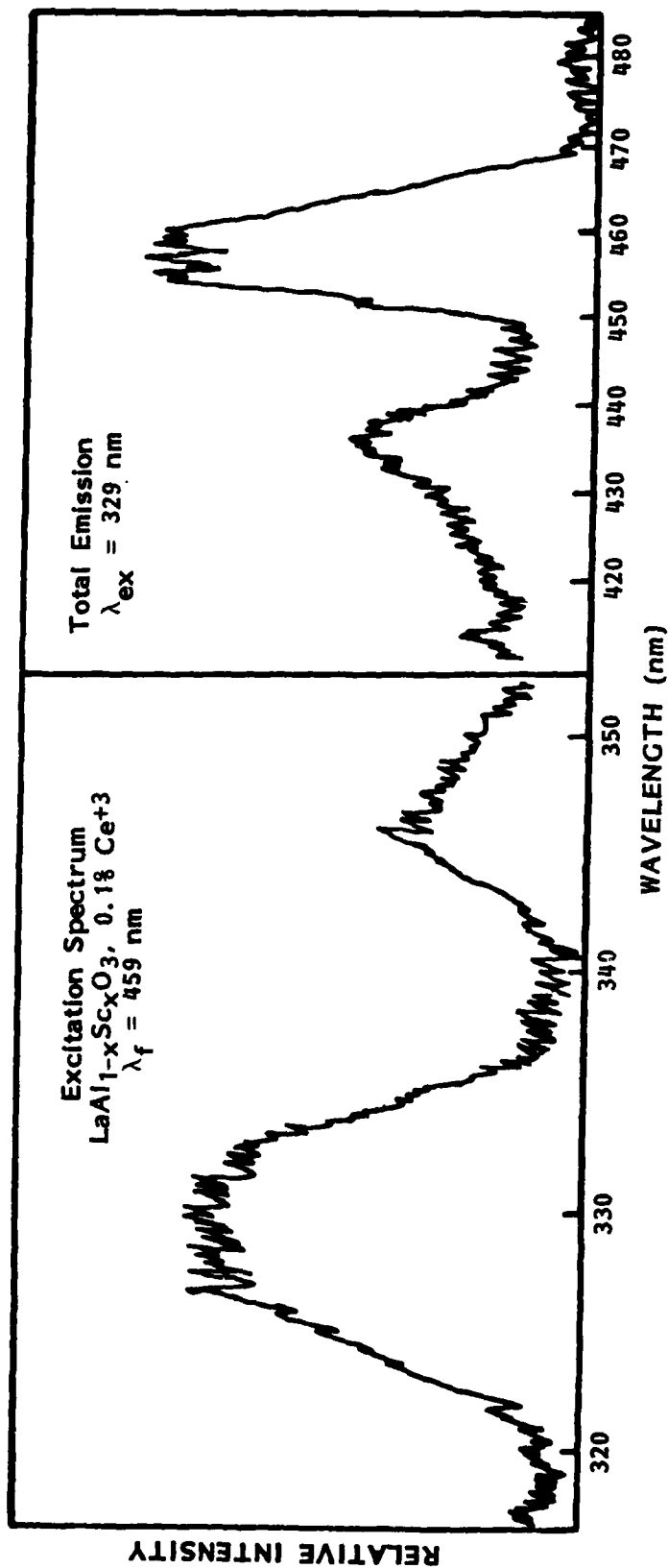


Figure 11. Total excitation and emission spectra for  $\text{LaAl}_{1-x}\text{Sc}_x\text{O}_3$  doped with 0.18  $\text{Ce}^{+3}$ , powdered sample, 25°C.

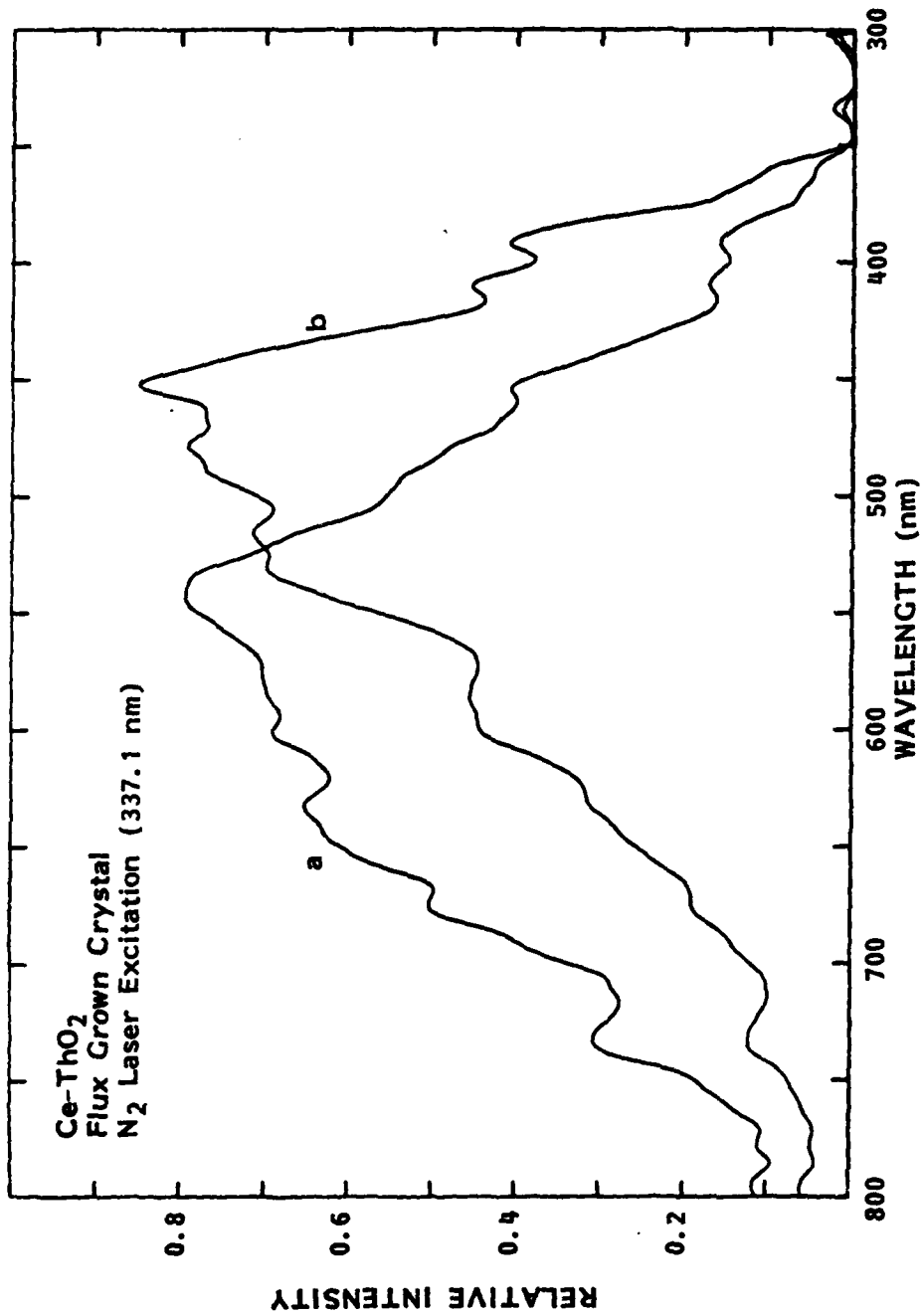


Figure 12. Luminescence from Ce doped ThO<sub>2</sub> crystal excited at 337.1 nm.  
Curve a: uncorrected spectra; Curve b: spectrum corrected  
for multiplier and monochromator sensitivity.

TABLE 4. SUMMARY OF TOTAL LUMINESCENCE SPECTRA OF Ce-DOPED ThO<sub>2</sub> AND LaAlO<sub>3</sub>. ALL SAMPLES WERE ANNEALED AT 1000°C IN FLOWING 95% Ar, 5% H<sub>2</sub> FOR SIX HOURS, UNLESS OTHERWISE INDICATED (\*) (SEE TEXT).

	Fluorescence		Excitation	
	Excitation $\lambda$	$\lambda_f$ (max)	Fluorescence $\lambda$	$\lambda_{ex}$ (max)
ThO <sub>2</sub> , 1% Ce* (crystal)	337.1 (N <sub>2</sub> laser)	450 (broad)	>470	365 385
ThO <sub>2</sub> , 1% Ce* (ox)	331.1	440 459	459	332.1 346.6
ThO <sub>2-x</sub> , 1% Ce	343	446 462	462	334.8 <u>349.4</u>
LaAlO <sub>3</sub> , 1% Ce	340	451 473	476	343.5 360.1
LaAlO <sub>3</sub> , 0.1% Ce	338.8  353	450 470 467 487	467	338.8  <u>353.7</u>
LaAl <sub>1-x</sub> Sc <sub>x</sub> O <sub>3</sub> 1% Ce	343.4	456 477	476.7	<u>344.6</u> <u>359.8</u>
LaAl <sub>1-x</sub> Sc <sub>x</sub> O <sub>3</sub> 0.1% Ce	329	435 458	459	346.9 <u>329.6</u>
LaAl <sub>0.7</sub> Ga <sub>0.3</sub> O <sub>3</sub> 1% Ce	328	(430) 458	458	327
LaScO <sub>3</sub> , 1% Ce (incomplete reaction)	322	428 452	452.5	321

Contributions to the total emission from lattice defect centers are another possibility. "Pure"  $\text{LaAlO}_3$  shows some weak emission bands at  $\sim 400$  nm. It is possible that the addition of Ce to the lattice could influence the concentration or type of such "impurity" luminescent sites. If luminescence were associated with bonding defects in grain boundaries, then differences might be observed between monocrystalline and powder luminescence. Significantly, a luminescence spectrum which we recorded of the Ce-doped  $\text{ThO}_2$  single crystals, shown in Figure 12, does differ from that of the corresponding powder synthesized by the oxalate method (Figures 6 and 7).

## CONCLUSIONS

This preliminary study has documented several wide band gap oxides containing Ce which luminesce in region from 450-500 nm. These oxides should all contain Ce in a nearly cubic coordination. Thus, a compromise should be reached between the low energy Ce<sup>+3</sup>/YAG emission (cubic with tetragonal distortion) and the UV emission from octahedrally coordinated Ce<sup>+3</sup>. Furthermore, the system based on LaAlO<sub>3</sub> is amenable to a low temperature synthesis based on a BaCO<sub>3</sub>/BaF<sub>2</sub> flux. Unlike the commonly used Pb based fluxes, the Ba compounds should not introduce low energy optical excitation, emission or quenching centers. Hence, they should be useful in crystal growth of La aluminates from high temperature solvents.

Several questions arise concerning the analysis of the emission and excitation spectra obtained from these oxides. Their two-component structure comprised of relatively narrow lines is somewhat different from the broad luminescence usually observed. If indeed the emission all arises from Ce<sup>+3</sup>, the narrow spectra may mean that the Ce ion is tightly bound in the lattice. Furthermore, the variations in fluorescence with emission wavelength may indicate multiple sites, oxidation states, the presence of impurities, or emission from upper states.

Several experiments remain unfinished due to the time limitations of the project Phase I. In particular, MgO coated LaAlO<sub>3</sub> has been prepared, but equipment malfunctions prevented us from sintering at 2200°C in a reducing atmosphere to yield optical ceramic samples. These would permit a study of the Ce and host absorption spectra, and an identification of the crystal field transitions associated with the Ce<sup>+3</sup> ion. It would further permit the fabrication of samples for laser testing, if scattering losses could be kept low enough.

## RECOMMENDATIONS

Since  $\text{LaAlO}_3$  and related compounds appear to be potential hosts for  $\text{Ce}^{+3}$  solid-state lasers, optical samples - ceramics or single crystals - must be produced next for more detailed investigation. A further goal is to produce samples large enough for detailed laser characterization, as well as with a cubic geometry suitable for excited state absorption measurements. Any crystal growth procedure should be designed for a reducing atmosphere, in order to prevent oxidation of the  $\text{Ce}^{+3}$ . Since crystal growth of  $\text{LaAlO}_3$  has been reported from fluxes<sup>13,14</sup>, it may be possible to control the crystal geometry using a traveling solvent zone method. This is similar to zone refining, where a molten flux/dissolved oxide zone is made to travel up a ceramic cylinder of the oxide, the emerging solid being a single crystal. This technique has been demonstrated for growing  $\text{ZnO}$ ,  $\text{BaTiO}_3$  and other crystals. It would also be useful in growing crystals of the highly refractory  $\text{ThO}_2$ .

Another option, as mentioned above, is to fabricate optical ceramics. Greskovich and Chernoch<sup>15</sup> have reported  $\text{Nd}^{+3}$  doped  $\text{Y}_2\text{O}_3$  optical ceramic laser rods of 7.6 x 0.46 cm dimensions with attenuation coefficients of only 2% per cm. The melting of  $\text{LaAlO}_3$  is reported by Coutures<sup>16</sup> to be congruent and takes place at 2110°C. Thus, a sintering temperature of ~1900°C would be appropriate. Optical ceramics may be particularly attractive for  $\text{LaAlO}_3$  which undergoes a rhombohedral to cubic phase transition above 450°C, a fact which may make the growth of large defect-free crystals difficult.

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<sup>13</sup>G. Garton, B. Haun, B. Wanklyn and S. Smith, *J. Crystal Growth*, 12, 66 (1972).

<sup>14</sup>S. Smith and P. Walker, *J. Crystal Growth*, 47, 315 (1979).

<sup>15</sup>C. Greskovich and J. P. Chernoch, *J. Appl. Phys.*, 45, 4495 (1974).

<sup>16</sup>J. Coutures et al., *High Temp. Sci.*, 13, 331 (1980).

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- <sup>15</sup>C. Greskovich and J. P. Chernoch, J. Appl. Phys., 45, 4495 (1974).
- <sup>16</sup>J. Coutures et al., High Temp. Sci., 13, 331 (1980).

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