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Rare Earth Niobate Systems and the Phosphor $GdNbO_4$:Bi

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An investigation to determine the compounds present in the Ln_2O_3–Nb_2O_5 systems (Ln = La, Gd, and Y) and attempts to activate such compounds with Ti, In, Sb, Bi, Eu, and Tb revealed that only the orthoniobate ($LnNbO_4$) compound was a suitable host lattice and $LnNbO_4$:Bi under 2537 Å excitation produced the best phosphors. $GdNbO_4$:Bi is a brighter phosphor than the La and Y analogs, emitting at slightly higher energies. The position of the $GdNbO_4$:Bi peak emission at 4500 Å is independent of the activator concentration whereas peak emissions for $LaNbO_4$:Bi and $YNbO_4$:Bi move to lower energies with increasing Bi concentration.

Introduction

During the past decade numerous authors have published results concerning the structures and luminescent properties of rare earth niobates. Keller (*1*) reported that all of the lanthanide niobates of the $LnNbO_4$ types possessed the fergusonite ($YNbO_4$) structure and gave their lattice parameters. Wolten and Chase (*2*) reviewed the existing literature on $LnNbO_4$ structures and pointed out that while synthetic fergusonite structures were normally monoclinic at room temperature, a tetragonal form could also be prepared using the proper heat treatment. Later work by Keller and Walter (*3*) and Dyer and White (*4*) showed the large trivalent rare earth ions (La, Ce, Pr, and Nd) formed another niobate compound, $Ln_2O_3 \cdot 3Nb_2O_5$, which possessed a defect perovskite structure. The $La_2O_3 \cdot 3Nb_2O_5$ compound was also reported by Roth (*5*).

The luminescent properties in rare earth oxide–niobium pentoxide systems have generally covered the fergusonite structures, specifically lanthanum and yttrium orthoniobates as self-activated phosphors or activated by rare earth ions, e.g., Wanmaker et al. (*6*) and Bril et al. (*7*) or activated by bismuth, e.g., Blasse and Bril (*8*) and (*9*). Less information is available concerning the $GdNbO_4$ compound. Brixner (*10*) reported that unusually high concentrations of europium were required for optimum luminescence in yttrium and gadolinium niobates and tantalates. Blasse and Bril (*11*) have reported the absence of luminescence of $GdNbO_4$. The present note surveys the rare earth niobate compounds and in particular the $GdNbO_4$:Bi phosphor.

Experimental Procedures

Analytical, luminescent or optical grade oxides with purity levels ranging from 99.9 to 99.99% were used as starting materials for all phases of this work. The oxides and their suppliers include the rare earths (Molycorp, Michigan Chemical, American Potash), bismuth (Mallinckrodt), indium (Indium Corporation of America), antimony (Harshaw), titanium (Baker) and niobium (CIBA). The niobium hydroxide was prepared by (99.9+% purity, 36 wt% water) GTE Sylvania. Oxalates were prepared in the lab by dissolving the respective oxide(s) in concentrated nitric acid, filtering and then adding filtered oxalic acid solution to precipitate the respective oxalate. The precipitate was washed until a neutral pH

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was obtained. A weight factor was run on the dried oxalate to determine the effective molecular weight of each oxalate.

Appropriate amounts of starting materials were weighed to the nearest 0.0001 g, mixed dry or mortared in an acetone slurry and fired in fused silica (<1100°C) or alumina crucibles (>1100°C) to temperatures as high as 1500°C. To insure homogeneity, the materials were often remixed as described above and refired. X-ray diffraction was used to ascertain complete reaction and the phase(s) present. Excitation and emission spectra were measured on a Hitachi MPF-2A Fluorescence Spectrophotometer or a Perkin-Elmer spectrophotofluorimeter (Model 195). Diffuse reflectance spectra were obtained from a Beckman DK-2A ratio recording spectroreflectometer using a barium sulfate standard.

Results and Discussion

As a preliminary step to luminescence studies, phases were determined in the La_2O_3–Nb_2O_5, Gd_2O_3–Nb_2O_5, and Y_2O_3–Nb_2O_5 systems. Ten mole % intervals in each system were fired at various temperatures and analyzed by X-ray diffraction. Reactions proceeded at a faster rate and better phosphors were generally obtained when rare earth oxalates and niobium hydroxide were used as starting materials instead of the respective oxides.

Complete reaction generally required heating at temperatures of 1200°C or higher for several hours. The rare earth side of these binary systems required higher temperatures to obtain equilibrium. For example, three compounds exist in the La_2O_3–Nb_2O_5 system; La_3NbO_7, $LaNbO_4$, and $LaNb_3O_9$. X-Ray diffraction pure $LaNbO_4$ and $LaNb_3O_9$ were prepared by heating at 1250°C for 6 hr. By contrast, La_3NbO_7 samples after firing at 1500°C, also for 6 hr, still contained small amounts of unreacted La_2O_3 and $LaNbO_4$. Similar trends were observed in the Gd_2O_3–Nb_2O_5 and Y_2O_3–Nb_2O_5 systems. For the preparation of Ln_3NbO_7 compounds, traces of sodium chloride were added to facilitate equilibrium. The intense sintering and in some cases melting of $LnNbO_4$ and niobia rich compositions respectively when fired at 1500°C shows the Ln_3NbO_7 compositions comprise the most refractory intermediate compounds in these systems. The above trend has also been reported by Timofeeva and Mordovin (*12*) in their investigation of the Gd_2O_3–Ta_2O_5 system. The absence of the gadolinium and yttrium analogs of $LaNb_3O_9$ agrees with the results of Keller and Walter (*2*) and Dyer and White (*4*). Although no solid solution limits were determined, X-ray diffraction suggested that extensive solid solution did not occur in these systems.

A luminescence survey was conducted in the rare earth niobate systems using some common activators including antimony, bismuth, indium, titanium, europium and terbium. In general, the Ln_3NbO_7 and $LaNb_3O_9$ compounds were poor host lattices for all of the activators under 3650 Å, 2537 Å, and, cathode-ray excitation. Even the luminescence of europium and terbium was very poor.

In the rare earth orthoniobates, the introduction of titania, e.g., $Ln_{.99}Ti_{.02}Nb_{.99}O_4$, produced no luminescence and rapidly quenched the niobate luminescence. When only 0.002 moles of titania were substituted into $YNbO_4$, the niobate luminescence under 2537 Å was lowered by half. Indium and antimony produced at best moderate luminescence, the brightest phosphor being $YNbO_4$: In.

The use of europium or terbium as activators in the lanthanum and yttrium orthoniobates is particularly interesting because the optimum brightness of the red and green emissions are obtained when 20 or more mole % of the activator replaces the host rare earth ion. Often the optimum activator concentration for rare earth-activated phosphors lies in the vicinity of 5 mole %. This difference is due to the interaction or energy transfer between the niobate and europium or terbium ions and has been observed and discussed by Wanmaker et al. (*6*) in the case of $YNbO_4$. The latter authors pointed out that the efficiency of transfer in the case of europium was much better in $YNbO_4$ than in the terbium-activated analog.

In the present study using 2537 Å excitation, $Y_{.8}Eu_{.2}NbO_4$ was a brighter phosphor than the lanthanum analog whereas the opposite was true using terbium. $La_{.8}Tb_{.2}NbO_4$ possessed a relatively bright green emission after treatment in a reducing atmosphere (99% N_2–1% H_2) and was a much better phosphor than the yttrium analog as well as Y_2O_3:Tb. Figure 1 shows typical emission curves for $LaNbO_4$:Tb and Y_2O_3:Tb under 2537 Å excitation. Although the optimum brightness was not exactly determined, europium and terbium were substituted for yttrium, gadolinium and lanthanum in the orthoniobate compounds. In the yttrium and lanthanum cases, optimum rare earth emission occurred in the 20 to 30 mole% range. The phosphors $GdNbO_4$:Eu and $GdNbO_4$:Tb acted differently with the optimum activator concentration being in the 8 to 10 mole% range. For a given concentration of europium or terbium up to 10 mole%, the rare earth emission was much brighter in gadolinium niobate relative to the yttrium and lanthanum analogs. This difference in character of the gadolinium compounds is explained by the fact that in the yttrium and lanthanum niobates, both the rare earth activator and host lattice give rise to luminescence whereas on such phenomenon occurs in gadolinium niobate.

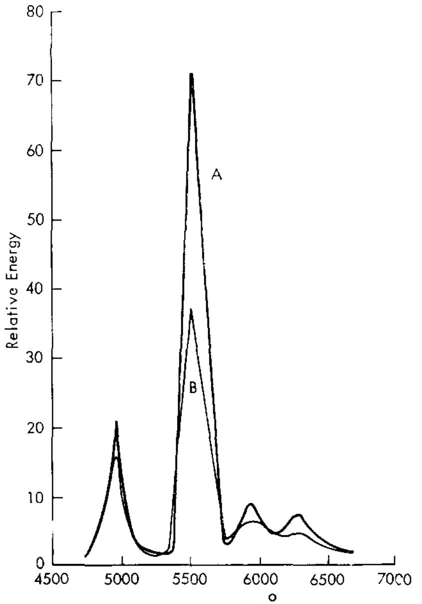

FIG. 1. Emission spectra of (A) $LaNbO_4$:Tb and (B) Y_2O_3:Tb under 2537 Å excitation.

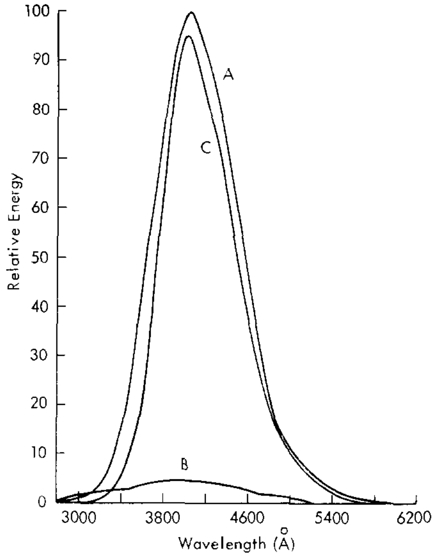

FIG. 2. Emission spectra of (A) $YNbO_4$, (B) $GdNbO_4$ and (C) $LaNbO_4$ under 2537 Å excitation.

$GdNbO_4$ is essentially inert in the visible region under 2537 Å while the corresponding lanthanum and yttrium compounds are a bright deep blue. Corrected emission spectra of the host lattice orthoniobates under 2537 Å excitation are shown in Fig. 2. The brightness of $LaNbO_4$ is about 95% that of $YNbO_4$. The formation of solid solutions of the rare earth orthoniobates showed that replacing as little as 2 mole% yttrium or lanthanum by gadolinium decreases their visual brightness. The effect was quite pronounced, e.g., the brightness of the niobate emission in $Y_{.95}Gd_{.05}NbO_4$ was only 80% of $YNbO_4$ under 2537 Å excitation. Blasse and Bril (*11*) offer a logical explanation for the absence of luminescence in $GdNbO_4$, namely that energy transfer does occur from niobate to gadolinium ions but the latter shows no luminescence due to concentration quenching. The visually inert nature of $GdNbO_4$ to ultraviolet or cathode ray excitation questions the results of Dyer and White (*4*) who state all rare earth niobates show cathodoluminescence of various colors. It is likely that the latter authors observed luminescence originating from a trace impurity in their starting materials.

In contrast to the inertness of $GdNbO_4$ under 2537 Å excitation is the fact that of the bismuth-activated orthoniobates, $GdNbO_4$: Bi is the best phosphor. The effect of two mole bismuth additions on the diffuse reflectance spectra of $YNbO_4$ and $GdNbO_4$ is quite pronounced as shown in Fig. 3. The absorption edge is shifted to longer wavelengths by the addition of bismuth, a characteristic which has been reported in rare earth vanadates and oxides by Datta (*13*) and (*14*) and Blasse and Bril (*8*).

The absorption peak at 2900 Å for $YNbO_4$ is presumably due to the $NbO_4{}^{3-}$ ion absorption while the absorption due to bismuth additions is most pronounced by the absorption maximum in the vicinity of 3400–3450 Å. Because of the overlap between the outer Bi^{3+} orbital and their surrounding oxygen neighbors, the absorption at 3400 Å can be better described as due to Bi–O groups. Datta (*14*) mentions that the 3200 Å absorption in Y_2O_3: Bi may also be due to a charge transfer mechanism involving bismuth and oxygen. Excitation and emission spectra of $YNbO_4$ and $GdNbO_4$ are shown in Figs. 4 and 5 respectively along with spectra of $Sr_2P_2O_7$: Sn used for comparison. Since $YNbO_4$ and $YNbO_4$: Bi are brighter phosphors than their lanthanum analogs, the former were used as standards of comparison. As shown in Fig. 5, $GdNbO_4$: Bi is a slightly bluer and better phosphor than $YNbO_4$: Bi. The brightness and chromaticity coordinates of the phosphors (obtained from lamp tests) are presented in Table I.

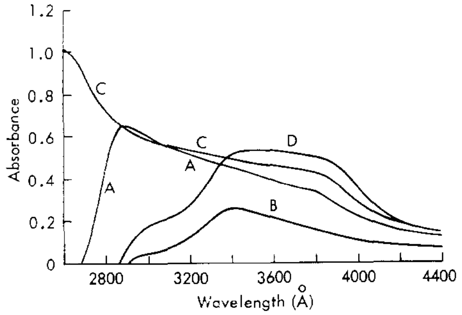

FIG. 3. Diffuse reflectance spectra of (A) $YNbO_4$, (B) $YNbO_4$: Bi, (C) $GdNbO_4$, and (D) $GdNbO_4$: Bi.

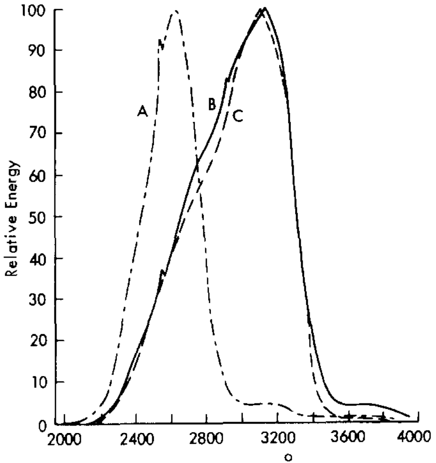

FIG. 4. Excitation spectra of (A) $Sr_2P_2O_7$:Sn, (B) $GdNbO_4$: Bi, and (C) $YNbO_4$: Bi.

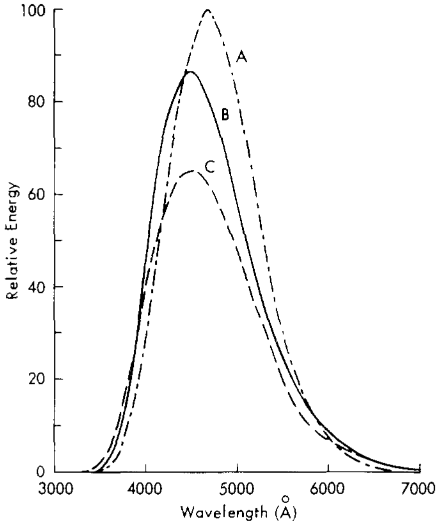

FIG. 5. Emission spectra of (A) $Sr_2P_2O_7$:Sn, (B) $Gd_{.98}Bi_{.02}NbO_4$, and (C) $Y_{.98}Bi_{.02}NbO_4$ under 2537 Å excitation.

Figure 6 shows the percent brightness as a function of the bismuth concentration in the yttrium and gadolinium orthoniobates. In both cases, the optimum bismuth concentration is 2 mole%.

TABLE I

COMPARISON OF $YNbO_4$:Bi, $GdNbO_4$:Bi AND $Sr_2P_2O_7$:Sn UNDER 2537 Å EXCITATION

Phosphor	Peak emission Å	Percent relative brightness	Chromaticity coordinates x	y
$Gd_{.98}Bi_{.02}NbO_4$	4500	82	.184	.170
$Y_{.98}Bi_{.02}NbO_4$	4520	60	.194	.195
$Sr_2P_2O_7$:Sn (Sylvania type 243)	4620	100	.178	.186

With increasing bismuth concentration in $YNbO_4$ (and $LaNbO_4$) the peak emission shifts to longer wavelengths (around 4750 Å). By contrast, the $GdNbO_4$:Bi peak emission remains around 4500 Å and the brightness above 2 mole % bismuth does not decrease as rapidly as in the yttrium phosphor. Presumably, the variation in peak emission of the latter is due to interaction of the Bi^{+3} and host lattice emissions. $GdNbO_4$ is not self-luminescent and the peak position of the bismuth emission remains relatively constant relative to the yttrium analog.

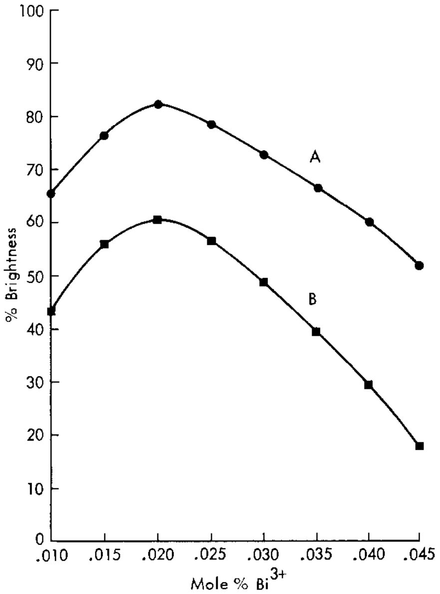

FIG. 6. Percent brightness as a function of the bismuth concentration in (A) $GdNbO_4$:Bi and (B) $YNbO_4$:Bi under 2537 Å excitation using $Sr_2P_2O_7$:Sn (Sylvania type 243) as a standard.

Summary

In summary, a survey of the yttrium, gadolinium and lanthanum niobate systems showed that: (1) three intermediate compounds, Ln_3NbO_7, $LnNbO_4$, and $LnNb_3O_9$ exist with the latter existing only in the lanthanum system and the former having the most refractory nature; (2) only the $LnNbO_4$ compound was a suitable host lattice for the activators studied; (3) the phosphors prepared were best under 2537 Å excitation; (4) unlike $YNbO_4$ and $LaNbO_4$, both self-luminescent, $GdNbO_4$ was inert to ultraviolet and cathode-ray excitation; (5) of the activators studied, bismuth gives the best phosphors; (6) $GdNbO_4$:Bi is a slightly bluer and brighter phosphor than the yttrium and lanthanum analogs. Furthermore, the bismuth peak emission in $GdNbO_4$:Bi is independent of the activator concentration whereas the emission shifts to longer wavelengths with increasing bismuth in $YNbO_4$:Bi and $LaNbO_4$:Bi, presumably due to interaction between the Bi^{+3} and host lattice emission.

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