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# Flux Growth of Rare-earth Niobates with Fergusonite Structure

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**Synopsis.** Single crystals of rare-earth niobates $RNbO_4$ (R denotes a rare-earth element) were grown from a melt of $PbF_2$–PbO flux. They are monoclinic and isostructural with natural and synthetic fergusonites. These crystals, except those containing Pr, Nd, Sm, and Ho were found to emit luminescent colors under UV irradiation.

Yttrium niobate $YNbO_4$, a member of mineral fergusonite (Y, Er, U) (Nb, Ta, Ti,···)$O_4$, belongs to a monoclinic system having a pseudo-sheelite type structure.[1] Natural fergusonite occurs mostly in metamict form due to the inclusion of radioactive elements such as uranium and thorium, so that its original structure had long been believed to be tetragonal from studies on samples recrystallized by heating to over 400 °C.[2] Studies of refractory materials such as $YNbO_4$ have been made mainly on powder samples prepared by the sintering or arc fusion method.[3]

Recently, Sugitani and Nagashima have grown crystals of $YNbO_4$ of macroscopic size by the flux method,[4] and have found that the monoclinic form of $YNbO_4$ is also supported by optical observations in addition to X-ray studies. In this note, the preparation of rare-earth niobate crystals which have monoclinic forms are reported. It was found that most of these crystals produce luminescent emission of various colors which is considered to be rare for "pure type" oxide phosphors.

As a typical case, the method of growing yttrium niobate is given here. Other rare-earth niobates can be grown, in general, in a manner similar to that for $YNbO_4$, with some minor changes in the growing conditions, such as the cooling rate, solute-flux ratio, *etc.* Equimolar $Nb_2O_5$ (purity 3N) and $Y_2O_3$ (purity 4N) were mixed in a platinum crucible together with the flux material $PbF_2$–PbO (purity 3N, the flux ratio $PbF_2$: PbO=80: 20) of an amount several times the molar ratio. All of the rare-earth oxides used as starting materials were sesquioxides $R_2O_3$, except for $Pr_6O_{11}$ and $Tb_4O_7$. The crucible was tightly covered by a lid and was placed in an alumina-box filled with alumina powder. This system was placed in an electric furnace maintained at 1300 °C. After about two hours at that temperature, it was cooled down to 1100 °C at the rate of 1.2 °C/h by a programmed controller. At the final temperature the system was removed from the furnace and was allowed to cool down to room temperature. The products in the crucible were removed and washed with hot 6M–$HNO_3$ for several hours. The crystals thus obtained were confirmed to have the desired $RNbO_4$ composition by chemical analysis and/or by X-ray analysis. They are mostly in the shape of slightly elongated octahedra, and their sizes range from 0.2 to 3 mm for their largest dimension.

Table 1 shows a list of the rare-earth niobates prepared, together with their colors, cell parameters, and luminescent colors under UV irradiation. The values of the cell parameters were calculated from the $\bar{1}21$, 031, 121, 040, 200, 002, 112, and 240 reflections.

It was found that $Bi_2O_3$–$V_2O_5$ flux (the flux ratio

TABLE 1. CELL PARAMETERS AND LUMINESCENT COLORS OF SYNTHETIC RARE-EARTH NIOBATES

| | Color | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\beta$ (deg.) | Luminescent color (3650 Å irradiation) | | Luminescent color (2537 Å irradiation) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | at room temperature | at 77 K | at room temperature | at 77 K |
| $YNbO_4$ | colorless | 5.30 | 10.96 | 5.07 | 94.60 | dark orange w | yellowish orange m | bluish white m | white w |
| | yellow[a] | | | | | greenish brown w | — | greenish brown w | — |
| $LaNbO_4$ | pale yellow | 5.57 | 11.55 | 5.21 | 94.07 | brown w | orange w | green m | yellowish green w |
| $PrNbO_4$ | green | 5.51 | 11.35 | 5.17 | 94.52 | — | — | — | — |
| $NdNbO_4$ | violet | 5.48 | 11.31 | 5.16 | 94.75 | — | — | — | — |
| $SmNbO_4$ | yellow | 5.42 | 11.18 | 5.12 | 94.48 | — | — | — | — |
| $EuNbO_4$ | colorless | 5.39 | 11.13 | 5.12 | 94.68 | light red s | red s | dark red m | red m |
| $GdNbO_4$ | pale brown | 5.37 | 11.10 | 5.11 | 94.45 | yellow w | yellow w | yellow w | yellow w |
| $TbNbO_4$ | orange | 5.33 | 11.07 | 5.10 | 94.03 | greenish brown w | — | brown w | — |
| $DyNbO_4$ | yellow | 5.31 | 11.02 | 5.10 | 94.01 | green w | — | green w | — |
| $HoNbO_4$ | colorless | 5.31 | 10.97 | 5.08 | 94.62 | — | — | — | — |
| $ErNbO_4$ | pink | 5.21 | 10.95 | 5.07 | 94.81 | — | yellow w | — | greenish yellow w |

s: strong, m: medium, w: weak. —: not observed. a) $Bi_2O_3$–$V_2O_5$ flux.

$Bi_2O_3$: $V_2O_5$=120: 8) was also useful in growing these niobates, though the sizes of the crystals obtained were usually smaller than those obtained using $PbF_2$–PbO flux, for the same growing conditions. The color of $YNbO_4$ grown in $PbF_2$–PbO flux is pale yellow with a tint of brown, while that grown in $Bi_2O_3$–$V_2O_5$ flux is yellow (Table 1). This is considered to be due to contamination by the flux material, but details remain unknown.

Crystals which were obtained as by-products during the growing runs are $CeO_2$, $Pb_2Nb_2O_7$, $Pb_3Nb_2O_8$, PbO and other unidentified crystals.

Brixner[5] has reported the emission colors of sintered pellets of several niobates of $RNbO_4$ composition. His results are considered to agree with the present results within a small discrepancy in color description. Suemune[6] has reported coloring and bleaching of several $RNbO_4$ materials which had been exposed to UV light for 5 min at 25 °C and maintained at 100 °C for 24 h after the exposure. From the present experiments, it is apparent that the coloring for UV irradiation does not remain but the samples immediately return to their original colors when the irradiation ceases.

Spectroscopic studies as well as other studies, are needed to understand the luminescence and photochromism of fergusonite-type niobates. Such studies are now in progress.

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