Synthesis and Fluorescence Properties of $Tb_2Te_4O_{11}$

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A new compound, $Tb_2Te_4O_{11}$, with monoclinic symmetry was synthesized by the solid-state reaction of TeO_2 and Tb_4O_7 in the temperature range 700–800°C in air. Its lattice parameters were calculated to be $a = 12.54$ Å, $b = 5.124$ Å, $c = 16.08$ Å, and $\beta = 106.08°$. On heating at 800°C for a long time, the compound gradually changed its chemical formula to $Tb_2Te_{4-y}O_{11-2y}$ ($y \leq 0.25$) without any structural changes. Also, solid solutions of $(Y_{1-x}Tb_x)_2Te_4O_{11}$ were synthesized in the range $0.01 \leq x \leq 1.0$. When the amount of Tb^{3+} increased, the $^5D_4$ emission became intense, whereas the $^5D_3$ emission was quenched by cross-relaxation. Such fluorescence profiles were examined and discussed to provide an understanding of the energy transfer process with respect to the concentration of Tb^{3+} ion. © 1989 Academic Press, Inc.

Introduction

The rare-earth (RE) ion-doped compounds can be used for phosphors, solar concentrators, laser hosts, etc., because RE ions function as highly efficient luminescence centers. However, there are some difficulties in controlling crystal perfection and homogeneous distribution by doping with very small amounts of RE ions. Random substitution of RE ions can also decrease luminescence efficiency considerably. In addition, the increase of RE ion concentration frequently causes quenching phenomena in luminescence. In order to realize higher quantum efficiencies for photoluminescence, oxides containing RE ions as the main constituent elements must be developed. At present, only some phosphates and borates, e.g., NdP_5O_{14} (*1*), $LiNd_4P_4O_{12}$ (*2*), and $NdAl_3(BO_3)_4$ (*3*), are well known as possible candidate materials.

On the other hand, syntheses of tellurates containing RE ions, which were available for optical use, have been reported (*4*). Most of the previous investigations have only been concerned with phase equilibria in this system. Recently, several compounds such as $(RE)_2Te_4O_{11}$, $(RE)_2Te_3O_9$, and $Dy_4Te_3O_{12}$, were prepared and their fluorescence properties were reported (*5, 6*). Hence, we systematically examined the $(RE)_2O_3$–TeO_2 systems and found the new material, $Tb_2Te_4O_{11}$, to have highly efficient luminescence.

Experimental

Starting materials used in this study were Y_2O_3, Tb_4O_7 (purities of >99.99%), and TeO_2 (purity of >99.99%) purchased from Rare Metallic Co., Ltd. (Tokyo, Japan). After intimately mixing these powders in the desired proportions with ethanol, the mix-
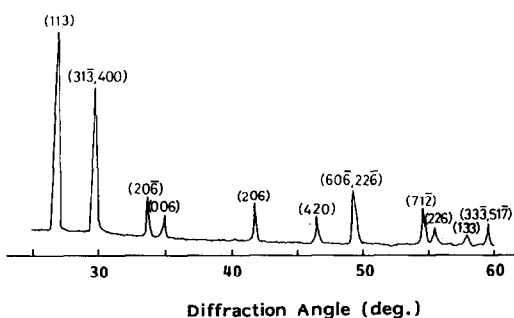
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FIG. 1. X-ray diffraction pattern of $Tb_2Te_4O_{11}$.

ture was dried at 100°C and ground. The powder mixture was calcined in an alumina or a platinum crucible in the temperature range 700–800°C for 2 hr in air. Occasionally, the procedure was followed by regrinding, repelleting, and refiring.

The contents of tellurium and rare-earth elements were measured using a Seiko Denshi Ind. SPS 1200 ICP emission spectroscope after dissolving the samples in a hot concn HCl. The phases of the samples were identified by means of a Rigaku X-ray diffractometer system with Ni-filtered $CuK\alpha$ radiation. The integrated intensities and positions of the reflections were measured at the scanning rate of 0.5°/min. Silicon powder was used as an internal standard. Also, the unit cell parameters of the recovered samples were correctly determined by a least-square refinement. TG–DTA measurements were performed using a Rigaku TG8110/TAS100 thermal analyzer. The sample was heated in air or in a stream of argon from room temperature to 800°C at a heating rate of 10°C/min. Al_2O_3 was used as a reference material.

Diffuse reflectance UV–VIS spectra were obtained at room temperature on a Shimazu UV-265 spectrophotometer with an integrating sphere attachment. Fluorescence spectra were measured using a Shimazu RF-540 fluorophotometer (spectral resolution of a 2 nm). Luminescence life-

time measurements were made with a Horiba NAES-550 system.

Results and Discussion

Two kinds of compounds were obtained by the reaction of Tb_4O_7 and TeO_2 at 800°C for 24 hr. All products had a white color in powder. According to X-ray diffraction data, one product was identified as Tb_2TeO_6, reported by Natansohn (7), which has hexagonal symmetry with lattice parameters of $a = 10.53$ Å and $c = 10.18$ Å. Another product was found to be a new compound $Tb_2Te_4O_{11}$, which was isostructural with $(RE)_2Te_4O_{11}$ (5).

Figure 1 shows the X-ray diffraction pattern of $Tb_2Te_4O_{11}$. All the reflections could be satisfactorily assigned as indicated in this figure. The possible space group was considered to be $C_{2/c}$ or C_c. Also, the lattice parameters for the monoclinic cell was determined to be $a = 12.54(2)$ Å, $b = 5.124(2)$ Å, $c = 16.08(1)$ Å, and $\beta = 106.08(2)°$.

Figure 2 shows the TG–DTA data, which was obtained from the mixture of TeO_2 and Tb_4O_7 in the molar proportion of 8 : 1. An exothermic peak with a weight loss was observed near 665°C. The loss was estimated to be about 0.8 wt%, which almost corresponds to the theoretical value of 0.79 wt%
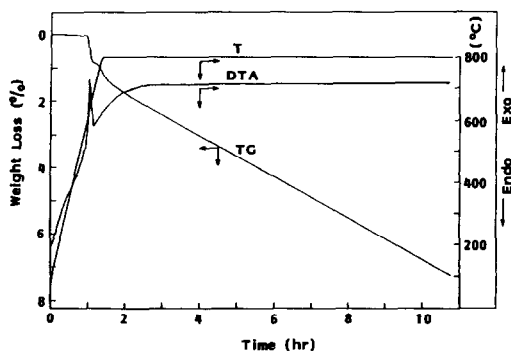

FIG. 2. TG–DTA curves obtained by the reaction of Tb_4O_7 with TeO_2.

obtained by the release of oxygen in the reaction of $8TeO_2 + Tb_4O_7 \rightarrow 2Tb_2Te_4O_{11} + \frac{1}{2}O_2$. Accordingly, the formation of stoichiometric $Tb_2Te_4O_{11}$ was assumed to proceed near 665°C. On the other hand, the weight of $Tb_2Te_4O_{11}$ linearly decreased with increasing holding time at 800°C. It appeared that the chemical composition $Tb_2Te_4O_{11}$ gradually varied due to the evaporation of TeO_2, and finally decomposed to Tb_2TeO_6 without the formation of $Tb_2Te_3O_9$. This result was also confirmed by experiments in which $Tb_2Te_4O_{11}$ was annealed in an evacuated silica tube at 800°C.

According to the chemical analysis and X-ray data of a sample annealed at 800°C in air, a phase $Tb_2Te_{4-y}O_{11-2y}$ was obtained in the range $0 \leq y \leq 0.25$; its lattice parameters were determined to be in the ranges $a = 12.29-12.54$ Å, $b = 5.19-5.124$ Å, $c = 16.04-16.08$ Å, and $\beta = 106.33-106.08°$. However, no systematic changes of lattice parameters and unit cell volume were found to depend on y. This suggested that the monoclinic symmetry persisted with irregular distribution of TeO_2 deficiencies.

Diffuse reflectance data indicated that the absorption edge of $Tb_2Te_4O_{11}$ occurred at about the same energy as that of TeO_2, and was estimated to be at 310 nm (about 4.00 eV). This edge was probably due to transitions between predominantly O^{2-} states and Te^{4+} states with little admixture of Tb^{3+} wave functions. Accordingly, direct excitation was possible into $Tb^{3+}4f^8$ (ca. 352 or 375 nm), but not into $Tb^{3+}4f^75d^1$ (ca. 270 nm).

To clarify the fluorescence properties of $Tb_2Te_4O_{11}$, extensive substitution of Tb for yttrium (Y) in $Y_2Te_4O_{11}$ was carried out as a solid solution of $(Y_{1-x}Tb_x)_2Te_4O_{11}$ ($0 \leq x \leq 1$). The substitution of Tb^{3+} (ionic radius for 8 coordination: 1.09 Å) for Y^{3+} (1.05 Å), however, caused the discontinuous changes of lattice parameters as a function of x. In addition, the crystal symmetry appeared to be only lowered in the range 0.3
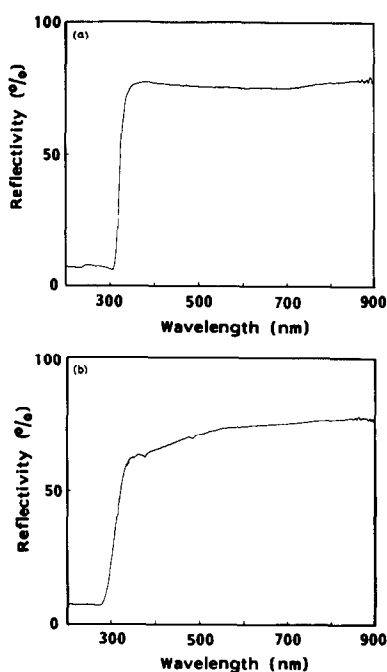

FIG. 3. Diffuse reflection spectra of TeO_2 (a) and $Tb_2Te_4O_{11}$ (b).

$\leq y \leq 0.7$ because of the fractional splitting in X-ray reflections.

The excitation and emission spectra of $(Y_{0.99}Tb_{0.01})_2Te_4O_{11}$ measured at room temperature are shown in Fig. 3. The excitation spectrum (Fig. 3a) measured at 544 nm shows two intense bands at 352 and 375 nm, corresponding to the transitions within the $4f$ shell of Tb^{3+}. Hereafter, all the emission spectra were measured by the excitation at 375 nm because of its intensity. The emission spectrum shown in Fig. 3b consists of several narrow peaks which are attributed to the $^5D_3-^7F_{5,4}$, and $^5D_4-^7F_{6,5,4}$ transitions. The most intense peak for the $^5D_4-^7F_5$ transition occasionally had very small shoulders due to a slight distortion around Tb^{3+}. However, the number and the magnitude of these components failed to be correctly evaluated within the spectra resolution of 2 nm. When using a fluorophotometer (excited by Ar laser) of our own making with a
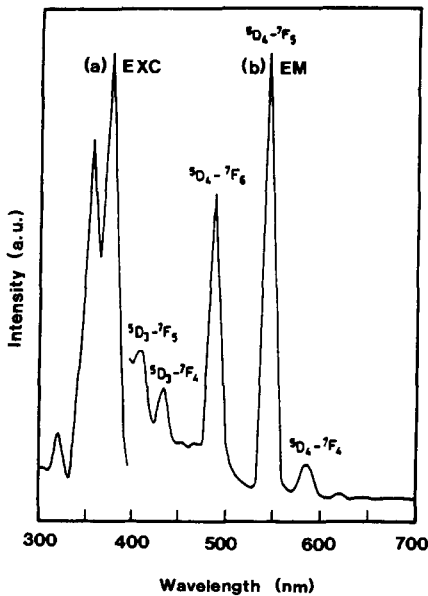
FIG. 4. Excitation (a) and emission spectra (b) of Tb^{3+} luminescence in $(Y_{0.99}Tb_{0.01})_2Te_4O_{11}$ at room temperature ($\lambda_{exc} = 375$ nm).

resolution of 1 cm^{-1}, all the peaks of Tb_2 $Te_{4-y}O_{11-2y}$ seemed to consist of more than seven crystal field components, depending on the composition. Such experiments are now under investigation.

The intensity of the $^5D_3$–$^7F_{5,4}$ emissions are relatively weaker than those of $^5D_4$–$^7F_{6,5}$. With the increase of x, i.e., increase of Tb^{3+} content, the $^5D_3$ emission intensity decreased and almost disappeared at $x = 0.1$. According to the energy level diagram reported by Ofelt (8), the interval of $^5D_3$ and $^5D_4$ was very close to that of $^7F_6$ and $^7F_0$. At higher concentrations of Tb^{3+} in $(Y_{1-x}Tb_x)_2$ Te_4O_{11}, Tb^{3+} ions in the $^5D_3$ level were likely to transfer the energy to the neighbor Tb^{3+} ions in $^7F_0$ levels. Otherwise, Robbins et al. (9) reported that the critical distance between Tb^{3+} ions for cross-relaxation was about 13 Å as described in the garnet structure. In the structure of $Tb_2Te_4O_{11}$, it was expected that a large number of Tb^{3+} ion sites would be occupied in a sphere with a

13-Å radius around a Tb^{3+} ion. Tb^{3+} emission, which usually consists of the $^5D_3$ level which is quenched by such cross-relaxation, resulted in more $^5D_4$ emission by direct excitation into the $Tb^{3+}4f^8$ levels (10). Also, no transition process which quenched the $^5D_4$ emission was observed.

Figure 4 shows the relationship between the relative intensity of fluorescence for the transition $^5D_4$ to $^7F_5$ and x of $(Y_{1-x}Tb_x)_2$ Te_4O_{11}. The $^5D_4$ emission increased with increasing x up to the concentration of $x = 0.1$. This can be explained by the results of cross-relaxation of $^5D_3$ emission already described. However, at concentrations of $x > 0.1$, intense $^5D_4$ emission was observed. This cannot be understood by the effect of cross-relaxation on the emission. Likewise, it was confirmed that such a profile was indeed observed in the solid solution of $(Gd_{1-y}Tb_y)_2Te_4O_{11}$. Therefore, the emission is considered to be substantially governed by the content of Tb^{3+} ions themselves without a concentration quenching process. As shown in Fig. 4, the most favorable in-
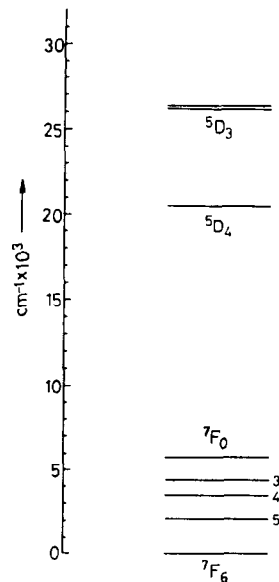

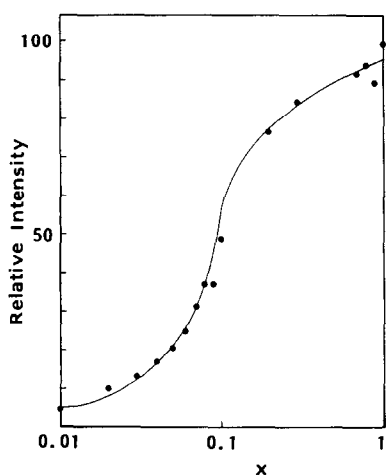FIG. 5. Energy level diagram of the Tb^{3+} ion in $Tb_2Te_4O_{11}$ as deduced from the emission spectra.

FIG. 6. Concentration dependence of the relative emission intensity of the luminescence ($^5D_4-^7F_5$) at room temperature in $(Y_{1-x}Tb_x)_2Te_4O_{11}$ upon excitation at 375 nm.

tensity of phosphor was obtained in $Tb_2Te_4O_{11}$. (See also Figs. 5 and 6.)

Luminescence lifetimes were estimated to be about 430 psec, 290 nsec, and 97 μsec from at least double- and sometimes triple-exponential decay patterns. The number of lifetimes seemed to be related to the total number of Tb^{3+} sites in $Tb_2Te_{2-y}O_{11-2y}$. The detailed fluorescence and structural data will be published elsewhere after the preparation of well-crystallized $Tb_2Te_4O_{11}$.

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