Effect of LiF Addition on the Preparation and Transparency of Vacuum Hot Pressed Y_2O_3 [†]

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In the present work, the preparation of transparent yttria ceramics by vacuum hot pressing was investigated, using yttria powder whose mean diameter is $0.88\text{ }\mu\text{m}$ and whose purity is higher than 99.9%.

Transparent yttria ceramics were fabricated by vacuum hot pressing with small additions of LiF (about 1 mass%). Hot pressing temperature and pressure were kept at 1573 K and 44 MPa, respectively. The processed samples were observed to have transparencies up to 78% at the wavelength of 644 nm and over 80% in the range of 860 nm– $6\text{ }\mu\text{m}$.

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I. Introduction

Glass has played the leading role for a long time as a transparent material. Since the transparent Al_2O_3 ⁽¹⁾ has been developed, however, other transparent ceramics such as MgO ^{(2)–(5)} and ZrO_2 ^{(6)–(7)} have also been developed, and they have been used as the transparent materials for which the severe conditions such as high temperature and high pressure are demanded. Y_2O_3 has the highest melting point of 2668 K⁽⁸⁾ among the rare-earth oxides are chemically stable. The melting point and chemical stability of Y_2O_3 are superior to those of Al_2O_3 . Therefore, its application to the following two materials is expected; namely, one is a high-pressure sodium electric discharge light for which the heat resistance and corrosion resistance are demanded, and the other is a heat resistance transparent window material.

The preparation of transparent Y_2O_3 has also been investigated, and the methods for the preparation are divided into two classifications. One is the conventional sintering method and the other is the special method such as the hot pressing method in vacuum (Hereinafter, this method is denoted as VHP.). The former is further divided into two methods. One is the solid state sintering of pure Y_2O_3 , and the other is the liquid phase sintering using sintering additives.

Although Y. Tsukada *et al.*⁽⁹⁾ have reported that the transparent Y_2O_3 could be obtained by the conventional sintering method at an ambient pressure, it requires a sintering temperature as high as 2573 K and as high compacting pressure as 980 MPa. C. Greskoriech *et al.*⁽¹⁰⁾ have reported that the transparent Y_2O_3 could be prepared by the sintering, using ThO_2 as sintering additive. Since

ThO_2 , however, is a radioactive material, its usage is strictly restricted. In addition, the sintered compact with ThO_2 becomes black by high-temperature alkaline steam. This causes transparency loss. Toda *et al.*⁽¹¹⁾ have reported that the transparent Y_2O_3 could be obtained by the sintering using BeO as sintering additive. However, the sintering temperature as high as 2473 K is required. S. K. Dutta *et al.*⁽¹²⁾ have reported that the transparent Y_2O_3 could be prepared in the wavelength between 2– $6\text{ }\mu\text{m}$ by VHP using pure Y_2O_3 powders. Referring to their results, we also tried VHP at 1773 K in 1.33×10^{-2} – 1.33×10^{-3} Pa under the pressure of 98 MPa using graphite dies. But the transparent Y_2O_3 could not be obtained. In addition, it was confirmed that the Al_2O_3 tube was deformed after VHP under the above mentioned condition. This phenomenon was often recognized in the case of VHP at a higher temperature than 1673 K. Therefore, VHP at the temperature lower than 1673 K is recommended.

In order to lower the VHP temperature, the method using the sintering additive is tried. Lefever *et al.*⁽¹³⁾ have reported that the transparent Y_2O_3 could be prepared by hot-forging in the vacuum of 6.65×10^{-3} Pa under 79–82 MPa using 3–5 mass% LiF as the sintering additive. Although the VHP temperature in this case is as low as 1223 K, it requires as long VHP time as 172.8 ks. In addition, 79–82 MPa is a little bit too high for a graphite dies used in VHP. In this experiment, we investigated the development of a process to obtain transparent Y_2O_3 at a temperature as low as possible by VHP using LiF as a sintering additive.

II. Experimental Procedure

In this experiment, Y_2O_3 powder (purity > 99.9%) of Shin-Etsu Chemical Co. Ltd. is used, and its chemical composition is presented in Table 1. Mean particle di-

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Table 1 The chemical composition (mass%) of yttria powder used in this experiment.

La_2O_3	Ce_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3
<0.001	<0.0005	<0.0003	<0.0003	<0.001	<0.001	<0.003	<0.003	<0.005	<0.005	<0.005	<0.0005	<0.005	<0.0005	>99.9

ameter of primary grain is several 10 nm, and that of the secondary grain is about $0.88\text{ }\mu\text{m}$. 0.5–3.0 mass% LiF powder (purity > 99.9%) of -70 mesh was added to the above-mentioned Y_2O_3 powder. This mixed powder was packed in a graphite dies whose size is 15 mm in inside diameter and 33 mm in outside diameter by 45 mm long, and cold-pressed by graphite punches at 98 MPa, where the W film of $50\text{ }\mu\text{m}$ was inserted between graphite punch and Y_2O_3 powder to prevent the reduction of Y_2O_3 by graphite. Then the VHP was carried out at 1573 K under a vacuum of 1.33×10^{-2} – 1.33×10^{-3} Pa, where the heating rate was 138.9 K/ks (500 K/h) to 873 K, 111.1 K/ks (400 K/h) from 873–1273 K and 69.4 K/ks (250 K/h) from 1273 to 1573 K, respectively. Two methods of pressing were applied in this experiment; one was the rapid pressing of 44 MPa and the other was the stepwise pressing to 44 MPa. The thickness of the specimen obtained in this way was about 2.5 mm, and it became 1 mm by diamond polishing. The transmittance was measured on these specimens at the constant wave length of $0.644\text{ }\mu\text{m}$ in order to compare the transmittance among the different specimens, and the wavelength dependence of transmittance was measured in the wavelength between 200 nm and $25\text{ }\mu\text{m}$.

III. Results

1. Rapid pressing method

At first, the vacuum hot pressed Y_2O_3 specimen with

3.0 mass% LiF was prepared, where 44 MPa was rapidly applied at 1573 K. The transmittance of the prepared specimen was 20% and SEM photograph is shown in Fig. 1. The grains were uniformly $3\text{--}4\text{ }\mu\text{m}$ in diameter as shown in Fig. 1(a), which is profitable for developing high transmittance. However, the presence of impurity is indicated by an arrow in the enlarged image of Fig. 1(b). It was confirmed by EPMA that F is enriched in the impurity. Therefore, the added LiF has remained after VHP

Fig. 2 Schematic diagram showing the relationship between vacuum hot pressing temperature and pressure for the stepwise pressing method.

Fig. 1 SEM fractographs of vacuum hot-pressed Y_2O_3 specimen. The pressure of 44 MPa was applied rapidly at 1573 K and kept during isothermal holding at 1573 K for 3.6 ks. 3.0 mass% LiF was added.

treatment.

2. Stepwise pressing method

By considering the above-mentioned result, we investigated the effect of stepwise pressing as shown in Fig. 2. Transmittance of the specimen with 3.0 mass% LiF vacuum hot-pressed under the condition of Fig. 2 was 24% in the center of the specimen and 58% in the edge of the specimen, respectively. Therefore, it was confirmed that the transmittance was fairly improved by the stepwise pressing method compared with the rapid pressing method.

Figure 3 shows the SEM fractographs of this specimen. As seen in Fig. 3(a) and (b), LiF is not detected and the grain sizes are uniformly 3–4 μm in the edge region. Although LiF is not detected in either regions, abnormal-

ly coarsened grains are observed in the center region as shown in Fig. 3(c) and (d). Therefore, we can conclude that these coarsened grains deteriorate the transmittance in the center region compared with that in the edge region.

Figure 4 shows the relationship between transmittance and the addition of LiF in amounts from 0.5 to 3 mass% for the Y_2O_3 specimens vacuum hot-pressed under the condition presented in Fig. 2. All of the specimens obtained showed a density ratio higher than 99.5% of the theoretical value. The transmittance has been recognized to be much higher in the edge region than in the center region, irrespective of the added amount of LiF. It became obvious that the specimen with 1.0 mass% LiF shows the highest transmittance of 78% in the edge region and 59% in the center region. It was impossible to

Fig. 3 SEM fractographs of Y_2O_3 specimen vacuum hot-pressed under the condition shown in Fig. 2. 3.0 mass% LiF was added. (a) and (c) the edge region, and (c) and (d) the center region. (b) and (d) are the enlarged images of (a) and (c), respectively.

Fig. 4 Relationship between transmittance and adding amount of LiF for the Y_2O_3 specimen vacuum hot-pressed under the condition shown in Fig. 2.

measure the transmittance in the center region of the specimen with 0.5 mass% LiF.

As may be seen from the SEM photograph of Fig. 5, the grain size in the center region of the specimen with 0.5 mass% LiF is as small as $1\ \mu m$. Therefore, the liquid phase sintering cannot be effective for the specimen with 0.5 mass% LiF. This may cause the degradation of transmittance. It was also confirmed that the grain size in the transparent region of the specimen with LiF was about $3\text{--}4\ \mu m$.

Figure 6 shows the SEM photograph for the center region of the specimen with 1.0 mass% LiF. Although the grain size was mostly $3\text{--}4\ \mu m$ as presented in Fig. 6(b), we can detect the coarsened grains in some parts of the specimen as presented in Fig. 6(a). From the above-mentioned result, it was confirmed that the specimen with

1.0 mass% LiF showed the highest transmittance of 78% in the edge region. However, the transmittance in the center region was 59% being much lower than 78% in the edge region. The way to improve the lower transmittance in the center region compared with that in the edge region should be investigated in the future.

Figure 7 presents the appearance of the specimen (1.0 mass% LiF) of 1.0 mm thick polished with diamond. We can read the letter of Y_2O_3 through this vacuum hot pressed Y_2O_3 specimen.

Assuming the shape of Y_2O_3 powder with 1.0 mass% LiF is sphere, the thickness of the LiF film around Y_2O_3 powder is considered as follows. Let D (μm) be the mean radius of Y_2O_3 powder, ρ (Mg/m^3) the density of Y_2O_3 and ρ' (Mg/m^3) the density of LiF, respectively. Then the LiF film of $t\ \mu m$ will cover the Y_2O_3 powder surface. One hundred grams of the specimen with 1.0 mass% LiF consists of 99 g of Y_2O_3 and 1 g of LiF. Since the volume of one particle of Y_2O_3 is $\pi D^3/6$, the number (N) of Y_2O_3 is $99/(\pi D^3 \rho/6)$. The equation of $t \cdot \pi D^2 \cdot N \cdot \rho' = 1$ holds because the surface area of Y_2O_3 powder is πD^2 . Substitution in this equation of $D = 0.88\ \mu m$, $\rho = 4.84\ Mg/m^3$ and $\rho' = 2.64\ Mg/m^3$, produces $t \approx 2.7 \times 10^{-3}\ \mu m = 2.7\ nm$. LiF has NaCl structure of cubic system, and its lattice constant is $a = 0.40173\ nm^{(14)}$. When 1 mass% LiF spreads over the surfaces of Y_2O_3 powders homogeneously, the LiF film composed of about 7 atomic layers exists over the Y_2O_3 powder surfaces. And assuming half of the added amount of LiF works effectively, the thickness of LiF covering the Y_2O_3 powder surface becomes three atomic layers. This value is quite reasonable. Therefore, the effectiveness of the addition of 1 mass% LiF is admitted from the point of calculation.

Figures 8 and 9 show the transmission spectra between the wavelength from $0.2\ \mu m$ to $25\ \mu m$ for the polished Y_2O_3 specimen of 1.0 mm thick. In the ultraviolet re-

Fig. 5 SEM fractographs for the center region of the Y_2O_3 specimen vacuum hot-pressed under the condition shown in Fig. 2. 0.5 mass% LiF was added.

Fig. 6 SEM fractographs for the center region of the Y_2O_3 specimen vacuum hot-pressed under condition shown in Fig. 2. 1.0 mass% LiF was added.

Fig. 7 Photograph showing the transparency for the polished Y_2O_3 specimen of 1.0 mm thick, vacuum hot-pressed under the condition shown in Fig. 2. 1.0 mass% LiF was added.

Fig. 8 Transmission spectra between the wavelength from 0.2 to 2.5 μm for the polished Y_2O_3 specimen 1.0 mm thick, vacuum hot-pressed under the condition shown in Fig. 2. 1.0 mass% LiF was added.

Fig. 9 Transmittance spectra between the wavelength from 2.5 to 25 μm for the polished Y_2O_3 specimen 1.0 μm thick, vacuum hot-pressed under the condition shown in Fig. 2. 1.0 mass% LiF was added.

gion, the transmittance increases with increment of wavelength, and it reaches the highest value of 82% at 0.86 μm . This value continues until the wavelength becomes 6 μm . In the wavelength longer than 6 μm , the transmittance begins to drop, and it reaches 0% at 10 μm . Therefore, the vacuum hot-pressed Y_2O_3 specimen with 1.0 mass% LiF has the ultraviolet absorption limit of 0.24 μm and the infrared absorption limit of 10 μm . And this specimen has the ideal wavelength dependence of transmittance without absorption edge in the visible light region (0.38–0.77 μm).

Although there exist many problems to investigate in the future, it may be concluded that the transparent Y_2O_3 can be prepared at a fairly low temperature such as 1573 K by the vacuum hot pressing method through the step-wise pressing.

IV. Conclusions

The results obtained are summarized as follows.

(1) Rapid pressing caused LiF to remain in the specimen, especially in the center region of the specimen, and resulted in low transmittance. On the other hand, step-wise pressing caused LiF to move from the center to the edge region and improved transmittance.

(2) The effect of adding LiF on the transmittance was most favorable at 1.0 mass%. When the amount of LiF was more than 1.0 mass%, the grains were coarsened in the center region. When it is less than 1.0 mass%, the grains were too small (about 1 μm) to show high transmittance because of insufficient sintering.

(3) Because of the microstructure mentioned above, the transmittance was lower in the center region and higher in the edge region of the specimen. The optimum transmittance of 78% was obtained in the edge region of the specimen with 1.0 mass% LiF, and it was 59% in the center region of this specimen. The ultraviolet absorption edge and the infrared absorption edge were 0.24 and 10 μm , respectively.

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