

## **A preparation of dysprosium monotitanate powder by mixed-oxide ceramics processing employing polymer carrier**

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### **Polymer carrier 효과에 의하여 단순화된 새로운 세라믹 분말 제조 방법**

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**Abstract** Dysprosium monotitanate ( $Dy_2TiO_5$ ) powder was synthesized by a simple mixed-oxide ceramics process using ethylene glycol (EG). Ethylene glycol, as the organic carrier for the metal cations, was used for polymerization mechanism. The successful use of a non-chelating polymer for the mixed-oxide ceramics process indicated that cation chelation is not the only route for creating stable ceramic precursors. Characterization of the powders by various thermal analysis, microscopy, and diffraction methods has been carried out.

**요 약** Ethylene glycol을 polymeric carrier로 사용한 새로운 화학적 세라믹 분말 제조 공정에 의하여  $Dy_2TiO_5$  분말을 제조하였다. Chelation 공정의 생략에도 불구하고, 고순도의 미세한 입자를 갖는 세라믹 분말 제조가 가능함을 확인하였다. 열분석, 미세구조분석, 회절분석 등으로 분말 특성을 평가하였다.

### 1. Introduction

Chemically-derived ceramic powders have excellent properties such as high purity, sub-micron size, high reactivity, and homogeneity on a molecular scale. However, they are expensive to produce and the throughput is low. Pechini has patented [1,2] a polymerized process which closely resembles the properties given above. The technique employs the Pechini resin as the polymeric carrier of the pre-ceramic powders. The resin consists of citric acid, as a chelating agent, and ethylene glycol, to promote polymerization during the esterification process. The cation sources are usually nitrate salts of the metals, mixed in stoichiometric proportions in the aqueous resin solution. Figure 1 presents the chemical reactions for the Pechini process. The heart of the process is chelation of the dissolved metal ions by the carboxylic acid end of the citric acid which has a configuration ideal for chelating (step I). Polyesterification follows as the temperature of mixture increase (step II). The chelation action of the organics is suggested to be responsible for the formation of a stable, atomistically homogeneous, pre-ceramic organometallic.

Modification of the Pechini method, which is based on the concept of mechanical entrapment of cations in an organic carrier, was suggested. A better inexpensive polymer, polyvinyl alcohol (PVA), was used as the organic carrier of the pre-ceramic powder [3] instead of the Pechini resin. The PVA polymer, which is a non-chelating polymer having large chain molecules as the polymeric carrier, has hydroxyl functional groups [4,5]. A steric entrapment of the metal ions was achieved by using these large chain molecules [4,6]. This was sug-

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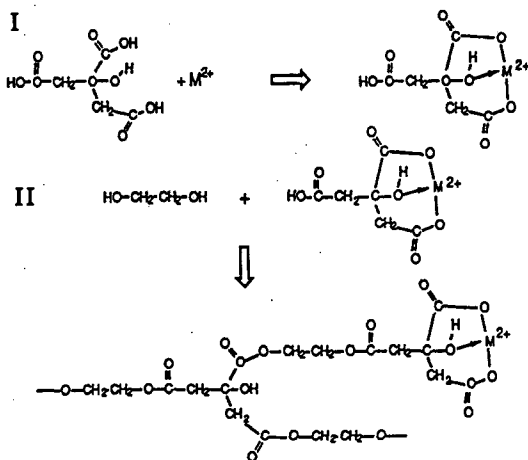


Fig. 1. Proposed chemical reactions for the Pechini process.

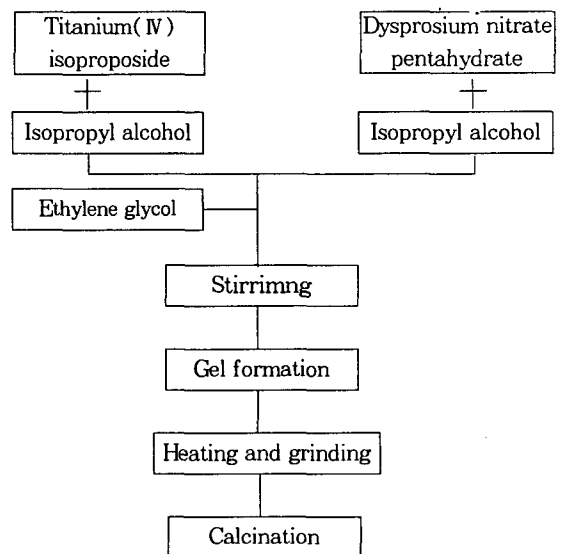


Fig. 2. Ethylene glycol flowchart for the synthesis of  $Dy_2TiO_5$  powder.

gested to form a soft and bulky ceramic precursor.

In this study, another simple-structured and inexpensive polymer, ethylene glycol (EG), is used as the organic carrier for the fabrication of dysprosium titanate ( $\text{Dy}_2\text{TiO}_3$ ) ceramic powder. The synthesis of the powder is reduced to a few simple steps rather than complex procedures such as in sol-gel. This work entails the use of ethylene glycol without any citric acid for chelation process to fabricate ceramics powder.

## 2. Experimental Procedure

### 2.1. Powder preparation

Dysprosium titanate ( $\text{Dy}_2\text{TiO}_5$ ) powder was prepared using ethylene glycol (EG,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , Fisher Chemicals, Pittsburgh, PA) as the cation carrier. The precursors used were titanium (IV) isopropoxide (TISO,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , Alfa Aesar, Ward Hill, MA) and dysprosium nitrate pentahydrate ( $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , Rhone-Poulenc Basic Chemical Co., Shelton, CT). Due to the reactive nature of the TISO in water, its decomposition was delayed by mixing it with isopropyl alcohol (IPA). The decomposition reaction is below:

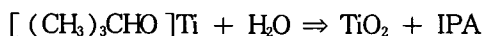


Figure 2 details the preparation process. After mixture of these precursors with isopropyl alcohol in stoichiometric proportion,

the ethylene glycol was added. And then, the mixture was stirred and heated up to  $200^\circ\text{C}$ . Upon heating, gases evolved very exothermically and a charred foam resulted. The foam was then ground with a mortar and pestle. The ground foam was calcined at various temperatures.

### 2.2. Characterization

The crystallization temperature and weight loss of the precursor of  $\text{Dy}_2\text{TiO}_5$  were studied with simultaneous differential thermal analysis and thermogravimetric analyzer (DTA/TGA, Model STA 409, Netzsch GmbH, Selb, Germany) to monitor the conversion from pre-ceramic to mixed oxide powder. The DTA/TGA results exhibited that the crystallization temperature was around  $830^\circ\text{C}$ . Therefore, calcination of the powder started at  $830^\circ\text{C}/1$  h. Other calcination temperatures/holding times were  $1000^\circ\text{C}/1$  h,  $1100^\circ\text{C}/1$  h,  $1300^\circ\text{C}/1$  h,  $1400^\circ\text{C}/1$  h and  $1600^\circ\text{C}/1$  h. The amorphous and crystalline structures were determined by the X-ray powder diffractometer (XRG 3100 X-ray Generator, Phillips Electronic Instruments, Mahwah, NJ) used a  $\text{CuK}\alpha$  source. The morphology and particle size of the powder were studied using a scanning electron microscope (SEM, Model S-530, Hitachi, Conroe, TX). The transmission electron microscope (TEM, Philips CM-12, Philips Instruments, Inc., Mahwah, NY) was used to characterize the phase of dysprosium titanate at  $1300^\circ\text{C}$ .

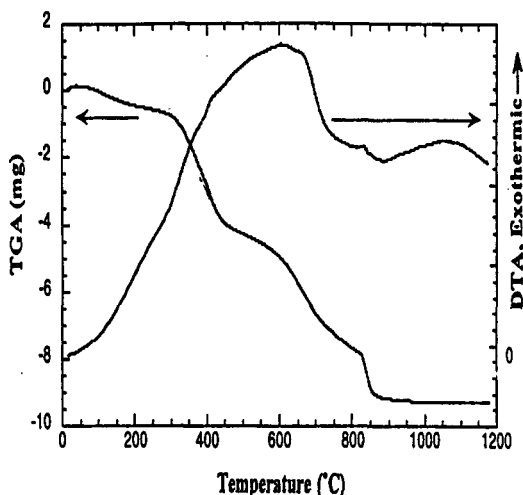


Fig. 3. DTA/TGA curves of the  $Dy_2TiO_5$  precursor made by the EG method.

### 3. Results

In the synthesis of the dysprosium mon titanate, an arbitrary amount of EG with a ratio of cations to moles of ethylene glycol of 1 : 3 was adopted. Upon the addition of the TISO to the dysprosium nitrate, precipitates were formed due to the water contained in the nitrate [ 7 ] but were dissolved after stirring. After 1 h , the solution became very viscous and a gel resulted. The gel is probably due to the evaporation of isopropyl alcohol and the crosslinking of the EG and TISO. Application of heat to the gel resulted in a charred foam structure. The exothermic reaction was due to the oxidation of ethylene glycol by the nitrate ions.

Simultaneous DTA/TGA result of the powder precursor from room temperature to 1200°C is shown in Fig. 3. Exothermic reactions

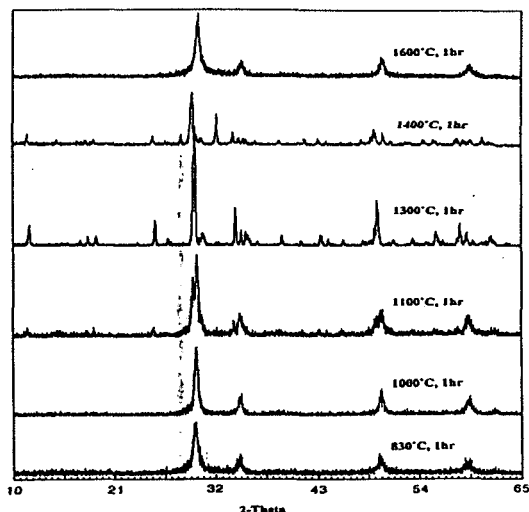


Fig. 4. X-ray diffraction patterns of  $Dy_2TiO_5$  powder at different temperatures.

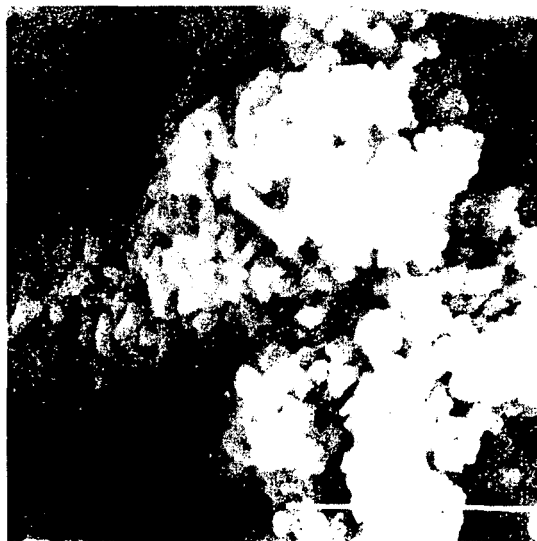


Fig. 5. SEM micrograph of  $Dy_2TiO_5$  powder calcined to 1300°C for 1 h.

occurred at 600°C, 830°C, and 1050°C. The temperature zones of decomposition were:(i) 100°C-300°C, (ii) 300°C-400°C, (iii) 400°C-600°C, (iv) 600°C-850°C. Beyond 850°C, the percent of decomposition

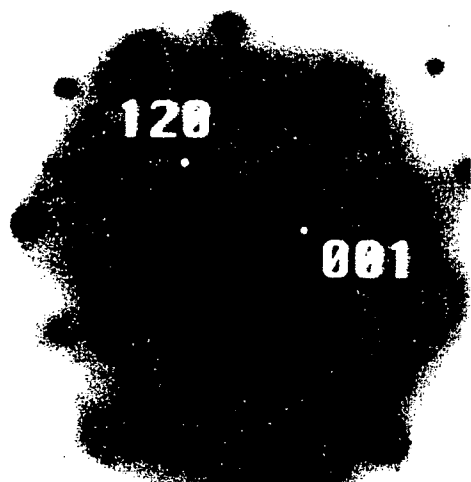


Fig. 6. Electron diffraction pattern of  $Dy_2TiO_5$  calcined to  $1300^\circ C$  for 1 h showing orthorhombic symmetry.

was less than 1 %. The initial weight loss was due to the water from the precursor. This was followed by the release of nitrates. Pyrolysis of  $NO_x$  gases from nitrate source and of polymer chain from EG were observed in the temperature range of  $300^\circ C$ - $400^\circ C$ . At  $600^\circ C$ , oxidation of the residual carbon from pyrolysed organics with complete disappearance by  $850^\circ C$  was observed. Furthermore, the DTA curve exhibited an exothermic curve at  $830^\circ C$  which is the crystallization temperature.

The phases at the different calcined temperatures were identified by the X-ray diffraction technique (Fig. 4). The powder samples were calcined for 1 h at each temperature. Crystalline phase was observed at  $830^\circ C$ , while amorphous phase was detected below  $800^\circ C$ . Cubic symmetry-type dysprosium titanate was observed for pre-

cursor powder calcined up to  $1100^\circ C$ . The exotherm at  $1050^\circ C$  indicated that the transformation from cubic to orthorhombic [8] occurred as shown in the diffraction pattern at  $1100^\circ C$ . Complete conversion to the orthorhombic phase was observed at  $1300^\circ C$ . At  $1400^\circ C$ , a mixture of orthorhombic and hexagonal symmetry was observed. The high temperature cubic phase [9] returned at  $1600^\circ C$ .

Subsequent calcination of the dysprosium titanate powder at  $1300^\circ C$  showed submicron particle size (Fig. 5). TEM investigation of the powder at  $1300^\circ C$  indicated the presence of orthorhombic phase (Fig. 6).

#### 4. Discussion

The reduction of the citric acid from the Pechini resin and the use of only ethylene glycol showed that powders can be synthesized and chelation is not a key factor. Although some precipitation occurred, the solution tended to dissolve it away. Without the chelating action of the citric acid, the ethylene glycol has no other function than to trap the cations mechanically when it polymerizes, however, further studies on the bonding are underway to elucidate if there are any actual bonds being formed.

#### 5. Conclusions

A new polymer route to the synthesis of mixed oxide ceramic powder was developed

successfully. The powder showed atomistically homogeneity and submicron-size particles. This indicated that polymerization mechanism by ethylene glycol acted as an effective organic carrier without chelation action.

#### References

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