Low Temperature Synthesis of Sr₅Ta₄O₁₅ by Polymerizable Complex Method

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The powder of pure $Sr_5Ta_4O_{15}$ was synthesized by the polymerizable complex method based upon polymerization between citric acid (CA) and ethylene glycol (EG). Heating of the solution containing citric acid, ethylene glycol, $TaCl_5$ and strontium carbonate at 200°C yielded brown transparent gel without any precipitation. The gel after the pyrolysis and subsequent heating at $1000^{\circ}C$ in air transformed into $Sr_5Ta_4O_{15}$ powder. According to X-ray diffraction analysis and Raman spectroscopy, the obtained sample was single phase and did not contain even traces of carbonates. The UV-vis diffuse reflectance spectra revealed that $Sr_5Ta_4O_{15}$ has similar band gap energy with $Sr_2Ta_2O_7$ which shows high-photocatalic activity.

Key words: polymerizable complex method, photocatalyst, low-temperature synthesis, strontium tantalates

1. INTRODUCTION

Perovskite type compounds in the Sr-Ta-O system attract a lot of attention as prospective photocatalysts because the majority of these compounds possesses suitable band gap for photodecomposition of water, which is considered to be one of the most important photocatalytic reactions [1,2].

In general, the tremendous improvement of a catalytic activity in the heterogeneous catalysis can be achieved by increase of the material surface area even for the constant phase composition.

In the case of complex oxide photocatalytic materials the outstanding results were reported for the compounds prepared via Pechini-type process – so-called polymerizable complex (PC) method [3-8] - because it was possible to decrease substantially processing temperature and therefore to minimize sintering and grain growth processes [9-12]. For instance, recently it was reported that $Sr_2Ta_2O_7$ prepared by PC method exhibits strong enhancement of photocatalytic activity compared to the samples synthesized in the conventional way [13].

In the present work we attempted to find optimal conditions for preparation of $Sr_5Ta_4O_{15}$ by polymerizable complex method and carried out characterization of the samples. Reports on a crystal structure of $Sr_5Ta_4O_{15}$ have apparently not been published to date. The band gap energy of $Sr_5Ta_4O_{15}$ was obtained from the UV-vis diffuse reflectance spectrum, and the band gap structure was compared with one of $Sr_2Ta_2O_7$.

2. EXPERIMENTAL

2.1 Synthesis of Sr₅Ta₄O₁₅ powders

Powders of $Sr_5Ta_4O_{15}$ were synthesized by the PC method as schematically described in Fig.1. After dissolving TaCl₅ into methanol, anhydrous citric- acid (CA) and ethylene glycol (EG) with

Ta:CA:EG=1:15:60 ratio were added. The solution was magnetically stirred for 20 minutes at 100 °C, followed by the addition of SrCO₃. After dissolving SrCO₃ completely, the obtained solution has been kept at 200 °C for several hours to promote polymerization to obtain a polymeric gel. It is important that no visible formation of precipitation or turbidity was observed during the polymerization and after gel formation. The gel was pyrolyzed at 450°C to form a powder precursor for Sr₅Ta₄O₁₅, which was subsequently heat-treated in a furnace for 24-60 h at 700-1000 °C in air.



Fig.1 Flow chart for preparing $Sr_5Ta_4O_{15}$ by the polymerized complex method.



Fig.2 TG-DTA data of the precursor of $Sr_5Ta_4O_{15}$ in static air with a heating rate of 10° C · min⁻¹.



Fig.3 X-ray diffraction patterns of $Sr_5Ta_4O_{15}$ synthesized at 700°C for 24h (a), at 800°C for 24h (b), at 1000°C for 24h (c), at 1000°C for 60h (d).

2.2 Characterization

thermogravimetry-differential The thermal analysis (TG-DTA; Type-2020, MAC Science Company) was carried out to follow the decomposition of the powder precursor in static air with a heating rate of 5 $^{\circ}$ C \cdot min⁻¹. The products were characterized by X-ray diffraction (XRD) using CuK α radiation (Model MXP^{3VA}, Mac Science) and Raman scattering with excitation by the 514.5 nm line of an Ar laser (Jobin Yvon T64000) for phase identification. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured for the products using a Shimazu UV-2400PC spectrometer to evaluate their absorption edges and thereby band gap energies. The specific surface area of the sample was measured by the conventional Brunauer-Emmett-Teller (BET) method (ASAP 2010, SHIMADZU). Sr₅Ta₄O₁₅ particles were observed by scanning electron microscope (SEM).



Fig.4 Raman spectrum of $Sr_5Ta_4O_{15}$ synthesized at 1000°C for 60h. The position of the Raman peak characteristic to CO_3^{2-} group is pointed out by the circle.



Fig.5 Diffuse reflectance spectra of $Sr_5Ta_4O_{15}$ synthesized at 1000 °C for 60h (a), $Sr_2Ta_2O_7$ synthesized at 900 °C for 5h (b).

3. RESULTS AND DISCUSSION

Figure 2 presents the TG-DTA curve for $Sr_5Ta_4O_{15}$ precursor heated up in air. The TG curve shows a continuous weight loss till 990 °C, which we explain as due to the dehydration and decomposition of the remained carbonates. The relatively abrupt weight decrease at 900 °C accompanied by the exothermic peak on the DTA curve at 912°C is probably due to a discharge of carbon dioxide and the crystallization of amorphous phase, which should be considered as the optimal temperature for $Sr_5Ta_4O_{15}$ synthesis.

This conclusion is in an agreement with the XRD patterns in Fig.3, which correspond to the powder precursors, calcined in air at different temperatures for 24-60 h. The product after the



Fig.6 SEM images of $Sr_5Ta_4O_{15}$ prepared at 1000 °C for 60 h.

calcination at 700 °C for 24 h was mainly amorphous. It is characterized by the broad reflections of small intensity (Fig.3 (a)) that correspond to $Sr_4Ta_2O_9$. This phase completely disappeared above 800 °C. Some weak unidentified peaks are showed up at 1000 °C for 24 h ($\mathbf{\nabla}$ in Fig.3 (c)). The XRD pattern of the sample prepared at 1000°C for 60h is similar to that of $Ba_5Ta_4O_{15}$ [14], and the XRD pattern could be indexed in the crystal system which is the same as $Ba_5Ta_4O_{15}$ (trigonal). Therefore, this sample was identified as $Sr_5Ta_4O_{15}$.

The Raman spectrum of $Sr_5Ta_4O_{15}$ sample prepared at 1000°C shows no evidence of impurities containing CO_3^{2-} groups (Fig.4). For carbonate group one should expect very strong Raman active mode at 1000-1100cm⁻¹, which is referred to the fully symmetric mode of CO_3^{2-} ion.

The UV-vis diffuse reflectance spectrum of $Sr_5Ta_4O_{15}$ prepared at 1000 °C for 60 h is shown in Fig.5 (a). The band gap energy derived from the absorption edge of $Sr_5Ta_4O_{15}$ and $Sr_2Ta_2O_7$ are 4.75 eV and 4.55 eV. Thus it was found that the band gap of $Sr_5Ta_4O_{15}$ is slightly larger than that of $Sr_2Ta_2O_7$. The BET specific surface area of $Sr_5Ta_4O_{15}$ powder is 2.2332 m²/g. Figure 6 shows a SEM photograph of $Sr_5Ta_4O_{15}$ obtained by this photograph is about 0.5 μ m.

4. CONCLUSION

Single phase $Sr_5Ta_4O_{15}$ samples were prepared by heat-treating the PC powder precursor in air at 1000 °C for 60 h. The XRD and Raman scattering measurements revealed no traces of impurities. We believe that $Sr_5Ta_4O_{15}$ could be a potential photocatalyst because it has close chemical composition and, according to UV-vis diffuse reflectance spectra, comparable band gap to another well-established photocatalyst in the Sr-Ta-O system - $Sr_2Ta_2O_7$.

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