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Zirconium titanate synthesis by diethanol amine based sol-gel route

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Abstract $ZrTiO_4$ powder are synthesized by a modified sol-gel route via bimetallic diethanol amine complex of zirconium and titanium alkoxides. Samples are cured at 140°C and calcined between 500–800°C. Powders are characterized with XRD, TGA, DTA, SEM and TEM methods. The $ZrTiO_4$ powders are obtained at 650°C from the amorphous form. No identified peaks can be attibuted to other phases, namely, zirconia and titania are not observed.

Keywords: Sol-gel · $ZrTiO_4$ · TEM

1. Introduction

In recent years a wide range of application areas have been reported for zirconium titanates ($ZrTiO_4$). Such as microwave dielectrics, dielectric resonators in telecommunication systems, high temperature pigments, refractory materials, sensors, thin film optics and also catalyst support for photoreduction and high temperature bifunctional applications [1–5].

$ZrTiO_4$ has α-PbO_2 orthorhombic structure and its crystal forms occurs via solid-state reaction between ZrO_2 and TiO_2 at the temperature range of 1200°C–1600°C. According to preparation route; morphological properties, crystal size, crystallization temperature and homogeneity are affected. The low temperature synthesis routes have been developed and reported in literature such as calcination of ball-milled of ZrO_2 and TiO_2 [6], co-precipitation from metal salts [7–9], aged and calcined from electrolyzed mixture of titanium and zirconium inorganic salts [10], dielectric tuning coprecipitation [1], polymeric precursor route [2], sol-gel route via hydrolysis of alkoxide precursors and their modifications [11–13], pyrolysis of organometallic aerosol precursor generated by ultrasonic spraying [14], modifications of 2-methoxyethanol for titanium and zirconium based perovskites [15], have been reported. All these routes are aimed to reduce synthesis temperature and to generate stoichiometric pure compound.

In this study modified sol-gel method are chosen to synthesis pure $ZrTiO_4$ at low temperature. In general sol-gel chemistry has some disadvantage in alkoxide hydrolysis route for bi- or multielemental mixtures through homogeneity, such as control of hydrolysis/condensation reactions and aging conditions due to different reactivity of various alkoxide compounds of related elements. Therefore the stability and reactivity of alkoxide compounds are very important for the special applications. In the peresent study it is aimed to produce $ZrTiO_4$ from a novel stable bimetallic sol-gel precursor. Recently, diethanol amine (DEA) complex of bimetallic zirconium and titanium alkoxides stable against to hydrolysis is reported [16]. From this point of view the potential use of DEA complex of zirconium and titanium for low temperature $ZrTiO_4$ formation are investigated.

2. Experimental

2.1. Preparation

70% Zirconium-n-propoxide-$Zr(OPr)_4$ in propanol solution (Fluka), tetra isopropyl ortho titanate-$Ti(iOPr)_4$ (Fluka), diethanol amine (DEA) (Merck) and bidistilled water are used as starting materials. As seen in Fig. 1 $Zr(OPr)_4$ and DEA

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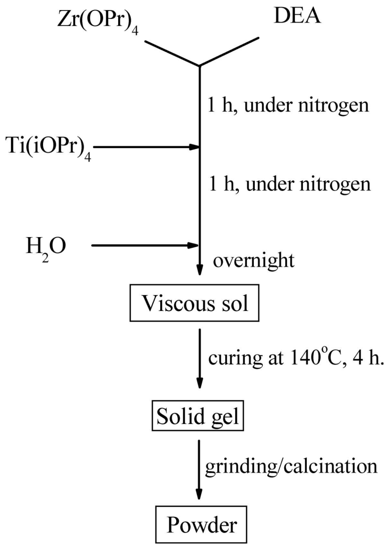


Fig. 1 Preparation scheme of $ZrTiO_4$ by DEA modified sol-gel route

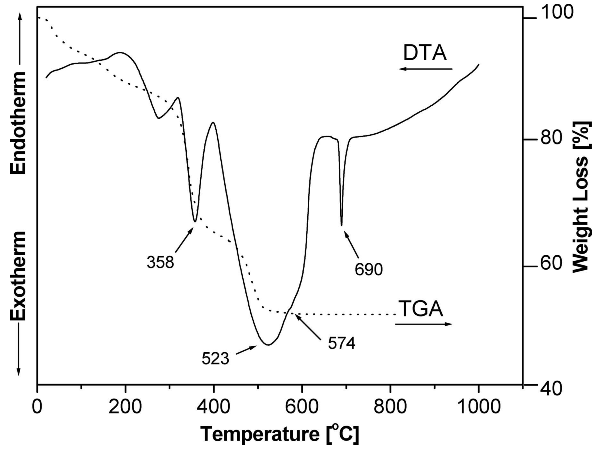


Fig. 2 TGA and DTA curves of sample cured at 140°C

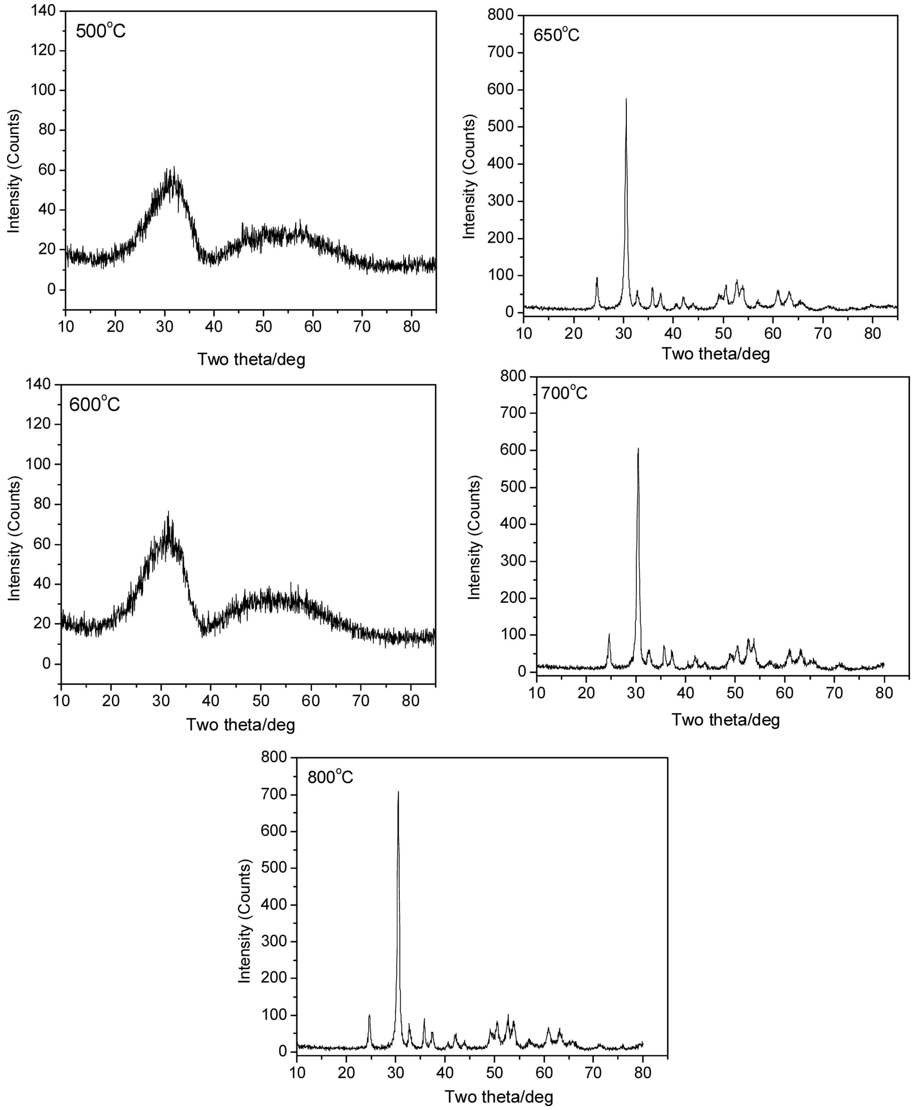


Fig. 3 XRD diffractograms of samples calcined between 500–800°C

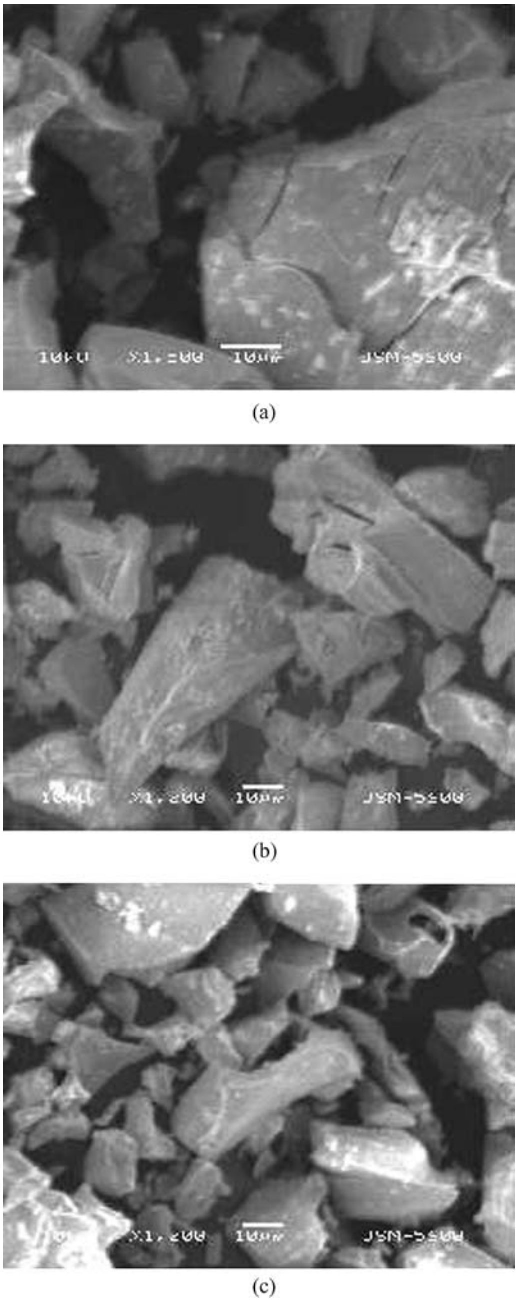
are mixed with the molar ratio of 1 to 2 in nitrogen atmosphere and stirred for 1 h Then Ti(*i*OPr)$_4$ is added to this mixture with the same molar ratio of Zr(OPr)$_4$ and stirred for 1 h again. Water is added to this bimetallic homogeneous mixture with the ratio of 20/1 to Zr(OPr)$_4$. The viscosity is slightly increased under stirring without precipitation in a few minutes. After overnight in nitrogen atmosphere the viscous solution is cured at 140°C for 4 h Solid yellowish transparent gel is obtained and grinded in agite mortar. Powders are calcined between 500 and 800°C for 3 h in air flow.

2.2. Characterization

The X-ray Diffraction (XRD) patterns of calcined samples are obtained by Rigaku machine using Cu Kα radiation ($\lambda = 1.54056$ Å). Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) measurements are made by Shimadzu 50 TGA and Linseis (L62) instruments with conditions of 50 ml/min air flow and 10°C/min heating rate up to 1100°C. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) photographs are observed by JEOL JSM 5600 at 10 kV and JEM 3010 at 300 kV, respectively.

3. Results and discussion

TGA and DTA curves are shown in Fig. 2. Approximately 50% weight loss is observed in total between 140°C and 800°C. The endothermic peak at around 200°C and an exothermic peak at 290°C are observed, respectively. Since boiling point of DEA is over 200°C the endothermic peak can be attributed to remained DEA removal during heating. The exothermic peak at 290°C may belongs to first decomposition of organics. This observation reported also for aluminum alkoxide based systems in our previous study [17]. The secondary weight loss region are observed in two steps nearly at 270–370°C and 420–490°C, respectively. In combine with TGA and DTA results in the same temperature region, the exothermic peak at 358°C and in the second higher weight loss region, the biggest exothermic peaks at 523 and 574°C are observed, respectively. They can be attributed to the removal of organics. It can be said that removal of organics occurs via steps in this system namely the remained alkoxides and particularly the diethanol amine groups, respectively. The clearly observable sharp peak at 690°C can be attributed to ZrTiO$_4$ crystallization temperature.



(a)
(b)
(c)

Fig. 4 SEM photographs of samples calcined between 500 and 800°C, respectively. (a) 500°C; (b) 650°C; (c) 800°C

XRD pattern of samples calcined between 500°C and 800°C are shown in Fig. 3. As it is seen in 500 and 600°C diffactograms despite the being a small broad shoulder nearly at $2\theta \approx 30$ it can be said that the sample is almostly in amorphous form and no any segregated tetragonal/monoclinic zirconia or anatase/rutile phases are identified. The ZrTiO$_4$ peaks appear in sample calcined even at 650°C (JCPDS/34-415). In these conditions the crystallization of ZrTiO$_4$ occurs in a close temperature region. This indicates that the bimetallic precursor of zirconium and titanium diethanol amine complex produces amorphous mixture and is directly converted to ZrTiO$_4$ phase during calcination. This is comparable with the results of Hu et al. as

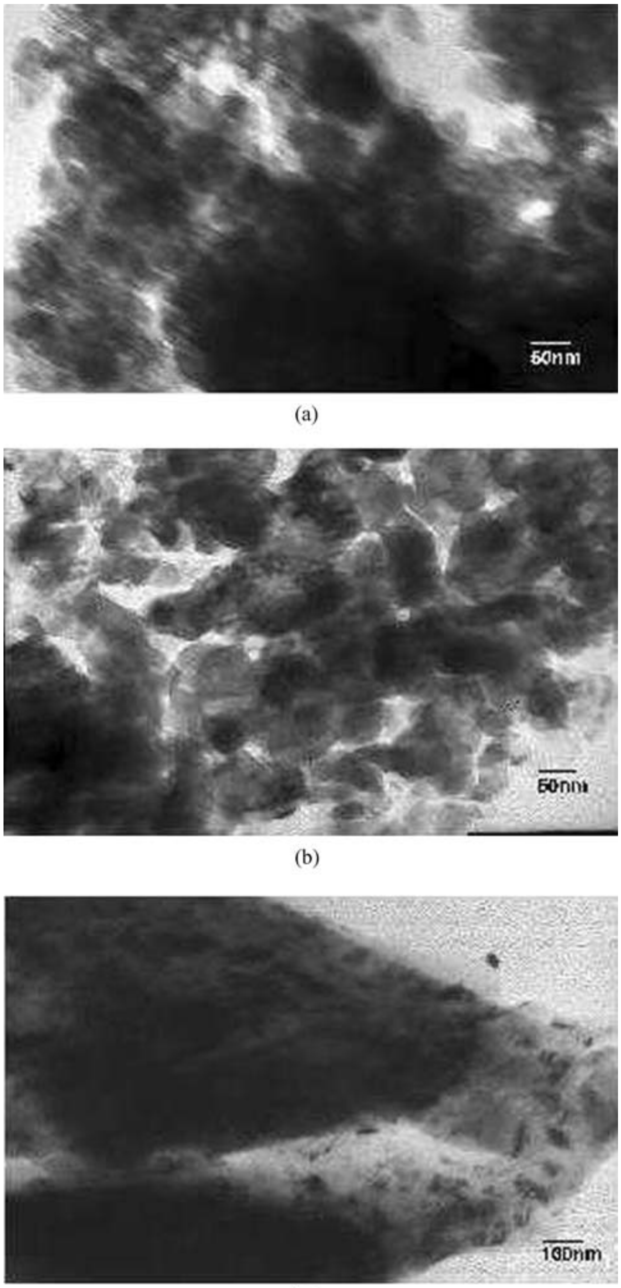


Fig. 5 TEM photographs of samples calcined at 650 and 800°C, respectively: (a) 650°C; (b) and (c) 800°C

reported via dielectric-tuning coprecipitation route [1]. The crystallization temperature of $ZrTiO_4$ is changed with preparation conditions. While Ananta et al. has reported 1300°C with ball-milling of TiO_2 and ZrO_2 precursors [6], Lucena et al. has reported 700°C with ethylene glycol and citrate precursors of zirconium and titanium [18]. Karakchiev et al. has reported synthesis temperature as between 600–700°C [10]. Hu et al. has reported that crystallization begins at 600°C and more sharper peaks appear at 700°C [1].

The peak intensities attributed to $ZrTiO_4$ increased slightly for samples calcined at 700 and 800°C, respectively. These results are comparable with DTA results indicating crystallization peak at 690°C. The difference of crystal formation temperatures of DTA and XRD results is almostly due to heating regimes of samples.

SEM and TEM photographs are seen in Figs. 4 and 5, respectively. As it is seen in SEM results powder uniformity slighlty increased with calcination temperature between 500–800°C, respectively. And particles are bigger at lower temperatures than that of 800°C. It can be due to agglomeration effect through decomposition of residual organics between 500 and 650°C temperature region similarly reported by Bianco et al. [19]. The nano particles of $ZrTiO_4$ are more observable in TEM results of 650 and 800°C samples.

4. Conclusion

$ZrTiO_4$ powder is synthesized by a modified sol-gel route via hydrolytically stable bimetallic diethanol amine complex of zirconium and titanium alkoxides. The $ZrTiO_4$ crystals are formed at 650°C from amorphous phase. No identified peaks can be attibuted to other phases, namely, zirconia and titania are not observed. The nano particle forms are observed with TEM results. The cation compatibilities and the effect of dopant cation on crystalization behaviours are investigated with the same precursor.

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