PARTICLE MORPHOLOGY OF PEROVSKITE LANTHANUM TANTALATE PREPARED BY POLYMERIC COMPLEX SOL-GEL METHOD

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Abstract
Perovskite lanthanum tantalate La\(_{1/3}\)TaO\(_3\) (LT) precursors were prepared by a new polymeric complex sol-gel method using Ta-citrate or -tartrate complexes in different solvents (ethanol or methanol) and calcination between 750-1050°C. The structural properties of precursors were characterized by X-ray diffraction (XRD) analysis, Raman spectroscopy, scanning and transmission electron microscopy (SEM, TEM). The fluorite orthorhombic tungsten bronze (TB) of La\(_{4.67}\)Ta\(_{22}\)O\(_{62}\) and perovskite La\(_{1/3}\)TaO\(_3\) phases with a small amount of pyrochlore monoclinic LaTaO\(_4\) phase were formed after calcination at 900 and 1050°C respectively, irregardless of solvent. The particle morphology changed from larger agglomerates composed of spherical 5-20 nm amorphous clusters, without visible crystallization at 750°C, to plate-like well-ordered LT nanoparticles (ethanol) or individual spherical clusters with a fine inner structure (methanol) at 1050°C. The same effect of alcohol solvent on phase transformation during annealing was shown, but the effect of chelating agent was insignificant.

Keywords: sol-gel processes, phase transformation, perovskites, microstructure, La\(_{1/3}\)TaO\(_3\), nanoparticles

INTRODUCTION

Nowadays, a large number of ferroelectric oxides of four different structures (perovskite, tungsten bronze, pyrochlore type and layers structure) are available [1]. Perovskite tantalates of La\(_{1/3}\)TaO\(_3\) (LT), based on the La rare-earth element, represent progressive technological benefits in the form of ferroelectric ceramics and thin films for their dielectric, ferroelectric, electrolytic and magnetic properties, enabling applications in e.g. microelectromechanical systems (MEMS) and solid oxide fuel cells (SOFC) [2]. The orthorhombic structure at 25°C is transformed into the tetragonal at 650°C for La\(_{1/3}\)TaO\(_3\) [3]. Tungsten bronze (TB) is the second largest ferroelectric after perovskite [4]. The modified structure of TB type, where the charge balance is implemented by distinct ions, as in the case of Ag\(_8\)(Nb\(_{0.5}\)Ta\(_{0.5}\))\(_{26}\)O\(_{69}\) or La\(_{4.67}\)Ta\(_{22}\)O\(_{62}\) [5]. Pyrochlore orthotantalate LaTaO\(_4\), a solid electrolyte with monoclinic (M-type fergusonite and M’-type distorted) structure, transforms into orthorombic and tetragonal (scheelite) structure at elevated temperatures [6].

The conventional way to prepare La\(_{1/3}\)TaO\(_3\) ceramics is a solid-state reaction (SSR) characterized by mixing of La\(_2\)O\(_3\) and Ta\(_2\)O\(_5\) oxides and calcination at 800-1000°C (sintering at 1300-1500°C) [2,5]. The second preparation method is the sol-gel process, which occurs at low temperatures and the resulting LT ceramics have a high homogeneity. Standard alkoxide sol-gel method is based on mixing of organic alkoxides [7], but the
environmentally acceptable is the polymeric complex (PC) method from inorganic salts. PC method involves the preparation of Ta-citrate complex [8] and subsequent formation of the viscous sol transforming into gel, followed by calcination at lower temperatures (600-700°C) than in SSR to obtain final fine oxide phase, which can be sintered between 900-1100°C. The choice of appropriate starting reactants, solvents and molar ratio of chelating agent (citric acid (CA)) to ethylene glycol (EG) are important from the point of view of final procedure for preparation of LiTaO$_3$, Li$_{0.30}$Ca$_{0.35}$TaO$_3$ and LaTaO$_4$. Researchers have used different carboxylic acids, such as tartaric or oxalic, and solvents (alcohol) in PC synthesis and forming (by esterification between acid and EG) suitable gels. Results of the analysis of powder precursor morphologies synthesized by PC show that the chelating agent affects the shape, morphology and size of powder particles.

Therefore in this investigation we have utilized citric (CA) or tartaric acid (TA) as chelating agent to prepare polymeric Ta-CA or Ta-TA complex in the sol-gel process of LT precursors with different solvents (ethanol or methanol). The study was of their phase composition, nanoparticle morphology and substructure at different calcination temperatures. The present research focuses the direct transformation during thermal treatment from the amorphous precursor through intermediate fluorite TB phase to perovskite La$_{1/3}$TaO$_3$ nanocrystals.

**EXPERIMENTAL**

The polymer Ta-citrate (Ta-CA) or Ta-tartrate (Ta-TA) complexes were synthesized by polymer complex method, where NbCl$_5$ was dissolved in ethanol and mixed with citric (C$_6$H$_8$O$_7$) or tartaric (C$_4$H$_6$O$_6$) acid (chelating agent) and ethylene glycol C$_2$H$_6$O$_2$ (EG) at molar ratio CA or TA:EG = 3:1. Subsequently, the modified PC method was used, in which the methanol was applied as TaCl$_3$ solvent [9,10]. LT sols were prepared by sol-gel synthesis from La(NO$_3$)$_3$.6H$_2$O ethanol (et) or methanol (met) solutions and Ta-CA or modified polymeric Ta-TA complex solutions with stoichiometric ratio of La:Ta=0.33:1.0. EG and CA or TA were used as polymerization/complexation agents. All chemicals were analytical grade and were purchased from Merck (Darmstadt, Germany). After homogenization at 80°C, the solutions were magnetically stirred and heated at 130°C for 6 hours resulting in the formation of transparent viscous sols and yellow gels after drying at 135°C for 12 hours. PC sol-gel process of La$_{1/3}$TaO$_3$ (LT) precursor preparation can be described by the equation (1):

$$\text{TaCl}_5 + \text{CA(TA)} - \text{et(met)} \rightarrow \text{Ta} - \text{CA(TA)} - \text{complex} + \text{La(NO}_3)_3 - \text{et(met)} + \text{EG} \rightarrow \text{LT} - \text{CA(TA)}\text{sol} \rightarrow \text{LT} - \text{CA(TA)}\text{gel}$$

Consequently LT powder precursors (citrate LT$_{(CA)\text{et}}$ or LT$_{(CA)\text{met}}$ and tartrate LT$_{(TA)\text{et}}$ or LT$_{(TA)\text{met}}$) were obtained by calcination of xerogels at selected temperatures (750-1050°C and times 1-6 hours).

The phase composition and thermal decomposition of samples were analyzed by X-ray diffraction (XRD, Philips X’ PertPro, Cu K$_\alpha$ radiation), differential scanning calorimetry and Raman spectroscopy (HORIBA BX 41TF). The morphology and particle size of powder samples were observed by scanning electron microscopy (SEM), (JEOL JSM 7000F) and transmission electron microscopy (JEOL JEM 2100F).
RESULTS AND DISCUSSION

XRD diffractograms of LT powder precursors after calcination at 750-1050°C are shown in Fig. 1. XRD analyses verified the formation of fluorite orthorhombic $\text{La}_{4.67}\text{Ta}_{22}\text{O}_{62}$ (JCPDS 46-0062) phase, monoclinic $\text{LaTaO}_4$ (JCPDS 72-1808) and perovskite tetragonal of $\text{La}_{0.33}\text{TaO}_3$ (JCPDS 42-0061) phases. XRD diffractograms (Fig. 1a and 1b) revealed the major perovskite $\text{La}_{0.33}\text{TaO}_3$ and a small amount of monoclinic $\text{LaTaO}_4$ phases in LT precursors after calcination at 1050°C, independently both of the complexing agent and applied solvent (see detail in Fig. 1a). The transformation process started at 750°C, where the amorphous $\text{La}_{4.67}\text{Ta}_{22}\text{O}_{62}$ phase was found only. The gradual crystallization to orthorhombic tungsten bronze (TB) structure of $\text{La}_{4.67}\text{Ta}_{22}\text{O}_{62}$ followed at about 800°C and continued up to 900°C. After annealing at 900°C for 1 hour, the metastable $\text{La}_{4.67}\text{Ta}_{22}\text{O}_{62}$ clearly partially crystallized, but some fraction of the amorphous phase was still found in patterns, and was practically not changed by the prolongation of annealing up to 6 hours. Created $\text{La}_{1/3}\text{TaO}_3$ exhibits a perovskite tetragonal superstructure, in which two of the La-sites should remain vacant [11].

Fig. 1. XRD patterns of (a) citrate CA(et) or CA(met) and (b) tartrate TA(et) or TA(met) LT precursors prepared in different solvents (ethanol or methanol) after calcination at 750°C for 1 hour, 900°C for 1 and 6 hours and 1050°C for 6 hours.

Fig. 2. Raman spectra of citrate and tartrate LT precursors after calcination at (a) 900°C for 6 hours and (b) 1050°C for 6 hours.
The Raman spectra of citrate or tartrate LTet and LTmet precursors after calcination at 900°C and 1050°C for 6 hours exhibit bands at 247, 458, 778 and 900 cm⁻¹ (Fig.2a) and sharp peaks of different intensity at 280, 355, 410, 476, 738, 875 and 975 cm⁻¹, Fig.2b, respectively. The other LT precursors exhibit very similar Raman modes. The frequencies in the range 230-450 cm⁻¹ are influenced by La cation displacements [50]. The bands in the range of 450-900 cm⁻¹ were assigned to the stretching modes of Ta-O bands with different strengths. Figure 2a indicates that the Raman spectra of La₄.₆₇Ta₂₂O₆₂ exhibits amorphous pattern with two very broad peaks at ~455 and 775 cm⁻¹ [12]. Figure 2b clearly shows that the Raman spectra of La₁/₃TaO₃ precursors differ significantly in peaks at ~355, 415, 475, 875 and 975 cm⁻¹ (vibration mode Eg(1), Eg(2), A1g(1), B1g(1) and B1g(1)). In contrast to La₄.₆₇Ta₂₂O₆₂, the La₁/₃TaO₃ samples exhibit very strong intensities of Raman modes, especially for peaks at ~605 and 670 cm⁻¹, representing the Eg(3) and A1g(2) vibration modes. Chelating agent had little effect on the Raman spectra of products synthesized in both solvents, whereas more intensive peaks were found in powder precursor prepared in the methanol solvent. Strong differences in Raman spectra of LT precursors at different calcination temperatures resulted from the various molecular arrangements of final phases (La₄.₆₇Ta₂₂O₆₂ and La₁/₃TaO₃).

SEM observations clearly verify the formation of amorphous La₄.₆₇Ta₂₂O₆₂ phase during annealing at 750°C (Fig. 3a,b). The micrographs of the LT precursors calcined at 750°C for 1 hour demonstrate the formation of extremely fine particles forming large agglomerates, while at 900°C, with prolonged annealing up to 6 hours, particle coarsening to around 50 nm size (Fig.3 c,d) and 80 nm (Fig.3 e,f) was observed. Note that the complexing agents (carboxylic acids) used did not significantly affect agglomerate morphologies. In Figure 4, the morphologies of particle agglomerates in powder tartrate samples (in ethanol LT(TA)et and methanol LT(TA)met), after annealing at 1050°C for 6 hours, are shown. LTet particle agglomerates (up to 1µm size) have a more compact irregular morphology and plate-like shape. They consist of small, approximately 100 nm, globular clusters with very fine structure containing 10-20 nm particles (Fig.4a). On the other hand, LTmet agglomerates are characterized by a higher degree of microporosity, with the separation of individual spherical clusters, but with a similar extremely fine inner structure (Fig.4b).

TEM observations clearly verified the formation and crystallization of nanosized, about 50 nm, particles of the perovskite tetragonal La₁/₃TaO₃ phase. In the case of LT(TA)met sample (Fig.5a), the higher amount of fine particles of rectangular shape was found in agglomerates and a more detailed study by HRTEM (Fig.5b) showed the presence of La₁/₃TaO₃ phase and multidomain regions [13]. The analysis and calculation of lattice plane distances from HRTEM images confirmed the presence of tetragonal perovskite structure of La₁/₃TaO₃ phase (JCPDS 42-0061), which is in accord with the XRD results.
Fig. 3. SEM microstructures of (a,c,e) citrate LT_{(CA)\text{met}} and (b,d,f) tartrate LT_{(TA)\text{met}} precursors after calcination at (a,b) 750°C for 1 hour, (c,d) 900°C for 1 hour and (e,f) 900°C for 6 hours.
CONCLUSIONS

$\text{La}_{1/3}\text{TaO}_3$ (LT) precursors were prepared using a new polymeric citrate or tartrate complex by sol-gel process in ethanol or methanol solvents. XRD analyses indicate that the same mechanism of transformation from amorphous and fluorite orthorhombic $\text{La}_{4.67}\text{Ta}_{22}\text{O}_{62}$ at 900°C to perovskite tetragonal $\text{La}_{1/3}\text{TaO}_3$ phase at 1050°C takes place in both media.

SEM observations showed formation of spherical, 5-20 nm, amorphous clusters during annealing at 750°C, particle coarsening (to size around 50 nm) at 900°C and plate-like shaped LT nanoparticles (ethanol) or individual spherical clusters with the fine inner structure (methanol) at 1050°C. XRD analysis and HRTEM images confirmed the presence of tetragonal perovskite structure of $\text{La}_{1/3}\text{TaO}_3$ phase at 1050°C.

The presence of methanol as ligand in the complex caused the formation of larger particles, in contrast to powders synthesized in ethanol. Note that no significant effect of chelating agent on phase composition or particle morphology was observed.

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