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ARTICLE TYPE

The precursor manipulation of the $La_2Zr_2O_7$ epi-layers annealed by the Rapid Thermal Annealing

Yanling Cheng[1,2], Hongli Suo[2], Lin Ma[2], Zili Zhang[2],Yan Xu[2], Min Liu[2]

1.Guangdong University of Technology. 2. Beijing University of Technology

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This paper states the epitaxial growth of $La_2Zr_2O_7$(LZO) buffer layer on the cube textured Ni-5at.%W substrate with the nitrates as the precursor salts. The solution stability and the heat treatment routes were discussed in detail. In order to increase the stability of the nitrate solution, the dielectric constant of the solvent was discussed and the alcohol amine was used as the chelating agents. The decomposition route of the precursor salt for each solution system was studied systematically before and after the chelating. Consequently, a cube textured LZO epi-layer was obtained by the Rapid Thermal Annealing with the Full-Width-at-Half-Maximum (FWHM) values for in-plane and out-of-plane orientation are 7.0°and 5.0° respectively, the result of which shows the feasibility of the nitrate solution route and the importance of the precursor properties for the epitaxial growth of the LZO layers.

INTRODUCTION

Chemical Solution Deposition (CSD) method has been widely used for a variety of technologically important oxides such as $PbTiO_3$, $BaTiO_3$, $Pb(Zr,Ti)O_3$ and so on[1-3].CSD process requires that chemical stoichiometric metal cations dissolve in a solvent to produce an oxide layer of adequate thickness by the spinning or dipping deposition method. The heat treatments following the deposition must be optimized to yield films with the performance necessary for an application. The main attraction of this process is the flexibility and easy control in terms of stoichiometry, microstructure, and crystallographic texture. Some easy soluble salts such as acetylacetone, the propionate, the alkoxide, the nitrate and also the chlorate are acted as precursors in the Sol-gel and the Metal Organic Deposition (MOD) route. For the Sol-gel, the chelating agents always play a key role to keep the stability and control the reaction between the solutes.

CSD method is considered to be a cost effective way to deposit the superconductor layer and the related buffer layers in the structure of High Temperature superconductor (HTS).In this structure, the rolling assisted biaxially textured substrate (RABiTS) method has been developed to produce polycrystalline Ni tapes with a strong (001)[100] cube texture orientation, which serves as a template for the subsequent epitaxial growth of buffer layers and the $YBa_2Cu_3O_{7-x}$(YBCO) epi-layer. The buffer layers act as a transfer layer for the texture and an effective barrier. In order to avoid the oxidation of the substrate, a reductive protective ambience is needed in the process of buffer layer heat treatment.

Recently, it has been a mature technology to use the organic salts as the precursor to deposit the $La_2Zr_2O_7$ (LZO), CeO_2, $LaAlO_3$ and $SrTiO_3$ buffer layers. Besides, the inorganic nitrates can also be an advisable chooses to syntheses the ceramics and the oxides. So far, there has been no report to prepare the buffer layers on the textured metal substrate by the nitrate route.

However, D.E. Wesolowski et.al[4] used the aqueous nitrate as the precursor to deposit the CeO_2 layer on the YSZ single crystal, the polyvinyl alcohol(PVA) was also added as the binder. Man Fai Ng et.al [5] prepared $LaAlO_3$ layer on different single crystals by dissolving nitrates in methanol.

In this paper, the LZO buffer layers were deposited on the textured Ni-5at.%W (Ni5W) substrate with two solution systems. One is to dissolve the nitrate in the methanol, the other is to add the small molecular chelating agents in solution one. Due to the exothermic property of the nitrates, those two solution route should be prepared in an open atmosphere. The Rapid Thermal Annealing route was used for the epitaxial growth of the LZO layer deposited by the nitrate route and the modified chelating route. The solubility of the precursor solution and the orientation of the buffer layer were also characterized. The key point in this paper is to discuss the influence of the precursor property on the epitaxial growth of the CSD derived film.

1. Experimental

1.1 Precursor solution synthesis

The precursor solution for obtaining the LZO buffer layer was carried out under atmospheric condition in a clean room. The stoichiometric Lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$) and the Zirconium(Ⅳ) nitrate pentahydrate ($Zr(NO_3)_4{\cdot}5H_2O$) were dissolved in the methanol with the cations concentration of $[La^{3+}]=[Zr^{4+}]=0.25$M, and then stirred at the room temperature until obtaining the transparent solution. This route was denominated as the nitrate route.

The second route is adding the chelating agents at the end

procedure of the first route, which is named as the modified nitrate route.

1.2 Deposition of the buffer layers

The cube textured Ni-5at.%W(Ni5W) tapes made from the superconductor laboratory in Beijing University of Technology were used as substrates. The description of the Ni5W tapes and its properties were stated in detail elsewhere [6].

First, the 5mm ×5mm substrates were cleaned by methanol and acetone in ultrasonic bath for 20 min before coating. Second, the spinning method was performed to deposit films with different rotation speed for each solution system. The as-deposited films by the nitrate route are an even iridescent purple color, except at edges where the thickness increased. The as-deposited films by the modified route are with a single light yellow color, which shows a uniform distribution of the thickness. The annealing step was carried out at various peak temperatures (900-1150□) with a dwelling time in a continuous flowing Ar+4%H_2 gas atmosphere. This reducing atmosphere protects the Ni5W substrate from oxidation. After annealing, the samples were cooled in the furnace down to room temperature.

1.3 Characterizations

The microstructure was characterized by Scanning Electron Microscopy(JEOLJSM 6500F). The texture of the films and the epitaxial relations were determined by X-ray diffraction (Bruker D8 Advance) using CuKα radiation with a scan rate of 2°/min . The rocking curve and phi-scan are used to characterize the out-of-plane and the in-plane orientation of the LZO grains.

The thermal behaviour was measured by thermogravimetry (TG) and the Differential Scanning Calorimetry(DSC, NETZSCH STA 449C) with a heating ramp of 5-20°/min under argon flow.

2. Results and Discussion

In order to explore the decomposition behavior and the subsequent textured growth mechanism of such CSD-derived LZO layers, the property of the precursor solution and the LZO buffer layers were investigated in detail using various characterization techniques.

2.1 Preparation of the LZO epi-layers by the nitrate route

2.1.1 The stability of the precursor solution

When an adequate amount of alcohol is added to an aqueous inorganic salt solution, the solution becomes supersaturated and then the precipitation occurs. The theory for such phenomenon is that the alcohol of low dielectric constant decreases the salvation energy and thus the salt solubility of the mixed solvent. That is to say the solubility of an inorganic salt decreases with a decrease in the dielectric constant of the solvent [7]. The dielectric constant of an alcohol-water mixed solvent decreases with an increase in temperature as well as an increase in the volume ratio of alcohol to water.

The phenomenon happened in the nitrate route solution was in accordance with the theory stated above. A transparent solution could be obtained when dissolving the hydrated nitrates in the ethanol. As the increase of the temperature, the solution gradually changed to a Sol, and then precipitants occurred. It is believed that the dielectric constant of the solution was very sensitive to the temperature. An effective way to solve this problem is to increase the dielectric constant of the solution.

In order to keep the stability of the solution, the hydrated nitrates were dried in the vacuum oven for 6h at 60℃ to remove the crystal water to some extent, and the methanol with a high dielectric constant was chosen as the solvent(Table 1)

Table 1. Dielectric constants of different solvent

solvent	Water	methanol	ethanol	n-propyl alcohol	isopropyl alcohol	tert.-butyl alcohol
Dielectric constant(20℃)	80.37	32.35	25.00	20.81	18.62	8.44

2.1.1 The decomposition performance of the nitrate precursor

Wendlandt et al[8] studied the thermal decomposition of lanthanum nitrate and they found different pathways of decomposition in different atmospheres. But all the resultant of reaction will gradually lose water and transform to $La(NO_3)_3$ at 255℃. The latter further decomposes to La_2O_3 via $LaONO_3$ and $La_3O_4NO_3$ in inert atmosphere or $LaONO_3$ and $La_2O_2CO_3$, in air. The decomposition behavior of the nitrate precursor in this paper also confirms such results.

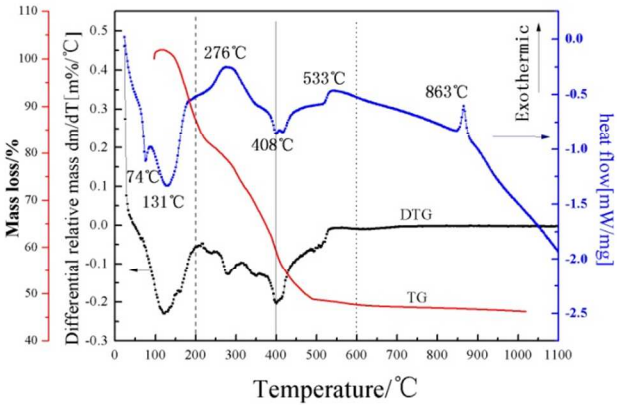

Fig. 1. DSC and DTG (derivation of the TG curve) curves of the nitrate route

Fig.1 is the DSC-DTG curves of the mixed nitrates. The heating rate for the test is 20°/min under the argon flow. The figure shows a multi-step decomposition performance. The fluctuant peaks before 200□ may due to the dehydration of the crystal water and the absorbed water. The ZrO_2 is formed before 400□[9], and the La_2O_3 is formed around 600□[10]. The weight loss is invariable after 600□, which indicates the synthesis of the stable LZO phase. The exothermic peaks at 863□ are the crystallization of LZO phase.

2.1.2 The preparation of the LZO buffer layer by the nitrate route

From a thermodynamic perspective, the driving force from the amorphous film to the crystalline ceramic is decreased as the increase of the temperature, so the heterogeneous nucleation is much more favorable than the homogeneous nucleation at the higher temperature. With high heating rates, the physical processes leading to densification and crystallization are delayed to higher temperatures. This causes nucleation to occur at a higher temperature than with conventional heating. Under these

conditions, crystallization occurs with lower driving forces [11]. So, lower energy heterogeneous nucleation events become more important. The Rapid Thermal Annealing (RTA) route means to reach at a high temperature with a rapid speed, which is preferred for the epitaxial growth. This method is widely used in the epi-film preparation.

In this paper, the RTA was used in the nitrate route. The furnace was first heated to a set temperature. The as-deposited samples made from the nitrate route were placed in a quartz tube, and then directly annealed at the temperatures between 900˚C to 1150˚C with a dwelling time of 60 min, then quenched to the room temperature. The annealing was implemented in a continuous flowing Ar+4%H_2 gas atmosphere. The XRD detection spectra of each sample are shown in Fig.2. From the figure, a pure LZO phase is shown for the diffraction peaks at 2θ=33.3° and 2θ=28.7°. As the increase of the temperature, the intensity of the LZO(222)(2θ=28.7°) peak increases obviously, a weak diffraction peak of LZO(400)(2θ=33.3°) is shown at 1150 ℃. The favorable LZO(222) is characteristic of powder diffraction, which shows a randomly oriented grains of LZO.

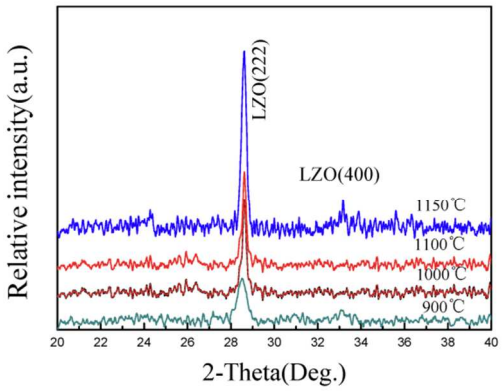

Fig.2. The XRD spectra of the precursor film coated on Ni5W substrate heat treated at different temperatures

The analysis from Fig.2 indicates that the LZO film made from the nitrate route annealed by RTA does not show a cubic texture growth along the texture of the substrate. It is believed that the annealing route is the main reason for such growth.

Because of the incomplete decomposition of the organic precursor, the remnant carbon were found in the surface of the LZO layers made from the Medal Organic Deposition method, which impeded the epitaxial growth seriously[12]. Fig.1 shows a multi-step decomposition character of the mixed nitrates, the subsalt and the compound salt are the entire intermediate product. The incomplete decomposition of these salts would act as a potential energy cost for the driving force of the heterogeneous nucleation. So, a decomposition route concerned annealing procedure is the key for the film growth. In view of the predominance of the RTA on the heterogeneous nucleation, it is conceivable to modify the property of the precursor salts to fit such sintering way.

2.2 Preparation of the LZO epi-layers by the modified nitrate route

Chelating agents are molecules that have the ability to form more than one bond to a metal ion, thereby increasing the stability of the ion complex. The small molecular chelating agents were added in the nitrate solution as the modified nitrate route. There are Triethanolamine (TEA), the Triisopropanolamine (TIPA), and the Diisopropanolamine (DIPA). Alcohols with different dielectric constant can change the solubility of the nitrates seriously. If the mass of each chelating agent is more than a critical value, the precipitate occurs. The experimental critical values for TEA, TIPA, DIPA in the nitrates solution (0.5M) are 0.025g/L, 0.035g/L, 0.045g/L, respectively.

2.2.1 The decomposition of the modified nitrate precursor

The presence of strong nucleophilic centers (OH^- and NH^{-2}) on these three chelating agents make it a strong bidentate ligand with good chelating properties, which we believed would help to change the decomposition route of the precursor. Fig.3 is the DSC-TG analysis for the resultant of reaction. In order to observe the delicate chelating reactions, a heating rate of 5°/min was used for the test.

The test heating rate for Fig. 3a,3b, and 3c is 5°/min, and 20°/min for Fig. 3d. Fig.3b and 3d are TG-DSC curves for the sample with TIPA as the chelating agent tested with different heating rates. As shown in the Fig. 3a, 3c and 3d, except for the most violent exothermic peaks below 200℃, there are minor energy change happened, and the TG is invariable after this exothermic reaction. Fig. 3b shows an obvious multi-step decomposition route, which is different from the curve in Fig. 3d with the heating rate of 20 °/min. An accurate decomposition route for the nitrate with the chelating agent can be obtained with a low heating rate. In this paper, the RTA route with a rapid heating rate was applied, so the organic salts also decomposed under a rapid heating rate.

The chelating agents with more hydroxide radical nucleophilic centers induce the precursor salts with a low decomposition temperature. Compared with the multi-step decomposition in Fig.1, the nitrate with the chelating agents simplifies the decomposition route obviously.

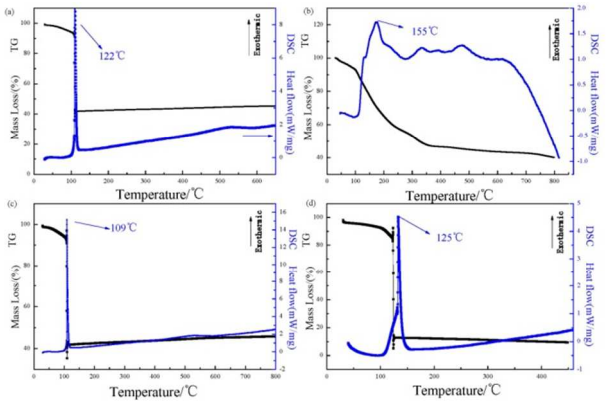

Fig.3 The DSC-TG curves of the nitrate with the chelating agent. (a) Triethanolamine :TEA, (b) Triisopropanolamine :TIPA, (c) Diisopropanolamine :DIPA, (d) Triisopropanolamine :TIPA(20°/min)

2.2.2 The preparation of the LZO buffer layer by the modified nitrate route

The precursor films were obtained on the textured Ni5W

substrate by the method of spinning. The rotation speed was in the range of 4000-6000 rotation per minute, which was varied for the films made from different chelating solution. The RTA route was implemented as described in 2.1.2. Fig.4 is the XRD spectra for the film samples annealed at different temperature made from the TEA chelating solution.

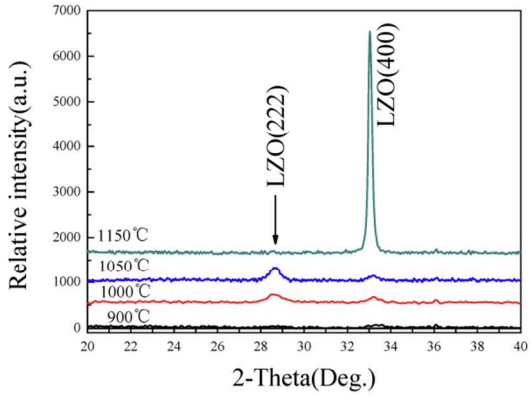

Fig.4 The XRD patterns of the LZO films annealed under different temperatures

From the figure, the film was still amorphous at the lower temperature, the (400) peak (2θ =33.3°) and (222) peak (2θ=28.7°) of the LZO phase appears when annealing at 900℃. With increasing temperature, the intensity of (400) peak increases, while the (222) peak of the LZO film decreases at the background level. When the annealing temperature increased to 1150℃, only (400) reflection is observed, which indicates that the LZO film grows along the c-axis when the temperature is above 1150℃. Films made from the other chelating solution also show the same trend.

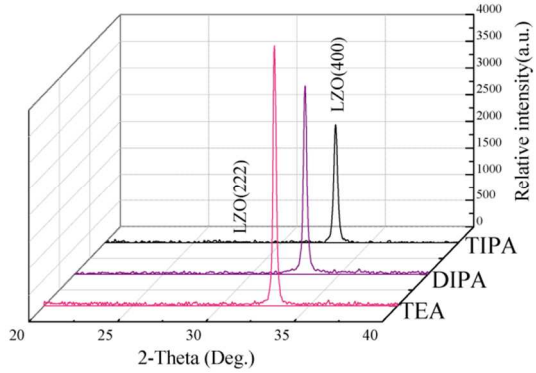

Fig.5 The XRD patterns of LZO films sintered at 1150℃

Fig.5 is the XRD spectra for films annealed at 1150℃. The dwelling time for each chelating solution was 60min. Each spectra exhibits only (00l) peaks corresponding to the LZO phase, indicating that the LZO films have a lattice alignment along (400), which shows a sharp c-axial orientation. The XRD analysis confirms that the RTA route is suitable for the c-axis growth of LZO films made from the chelating agents modified nitrate route. The key is that the chelating reaction simplifies the decomposition step of the nitrate salts, and also decreases the resistance of the oriented growth of the LZO film.

(400) rocking curve and (222) phi-scan are used to characterize the out-of-plane and the in-plane orientation of the LZO grains. Fig.6 is the (400) rocking curve and (222) phi-scan for LZO layers made from different chelating solution. A four peak symmetry with a 90° interval is clearly seen, which is an indication of cube-on-cube textured growth on the Ni5W substrate.

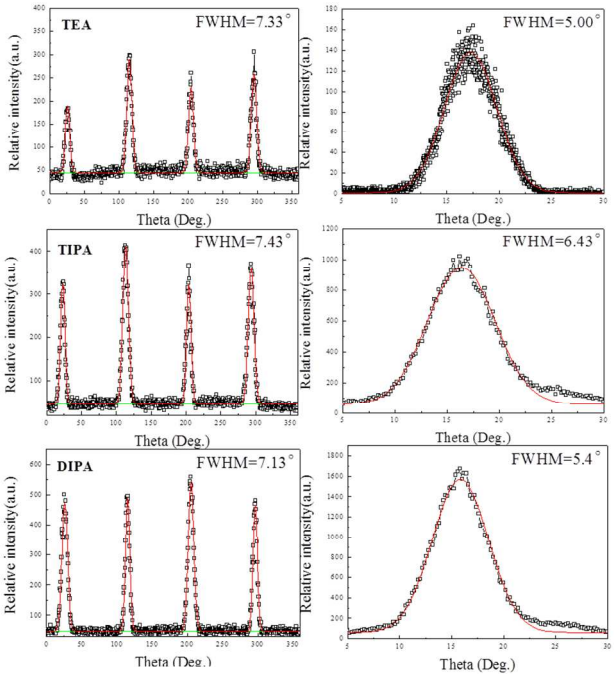

Fig. 6 The (222)phi-scan (left column)and (400)rocking curve(right column) of the LZO layers made from TEA,TIPA, DIPA chelating solution

Table 2 is the summary of Full-Width-at-Half-Maximum (FWHM) values of the LZO layer made from different precursor salts, the values for Ni5W is used as a reference. As summarized in the Table 2, The FWHM values of the rocking curve and the phi-scan are in the round of 5° and 7° respectively, which is in good accordance with the values of the Ni5W substrate, especially for the FWHM values of the rocking curve, which indicates that the LZO layers made from different chelated nitrate solution show epitaxial growth on the Ni5W substrate by the RTA route.

Table 2 The orientation analysis of LZO films made from different chelating solution

	FWHM values of phi scan	FWHM values of rocking curve (RD)
TEA	7.01°	5.00°
TIPA	7.43°	6.43°
DIPA	7.13°	5.40°
Ni5W	6.80°	5.70°

The FWHM values of the sample with TIPA as the chelation agent are bigger than that of the other sample. That is to say, TEA and DIPA chelated nitrate precursor solution is superior for the epitaxial growth of the LZO layer. Compared with the single-step decomposition route of TEA and DIPA chelated precursor solution, multi-step decomposition (Figure 3b) of TIPA chelated precursor is responsible for the results.

Fig. 7 is the SEM images of the LZO buffer layer made from

the modified nitrate route. The images show a homogeneous grain size distribution of about 50nm. Except for the Fig.7a, there are obvious holes for the samples with TIPA and DIPA as the chelating agents. It is believed that such morphology is also deduced from the decomposition procedures of the precursor salts. For all the samples, the film thickness is enough to cover the grain boundaries of the substrate. The LZO buffer layer with TEA as the chelating agent shows a dense and smooth morphology.

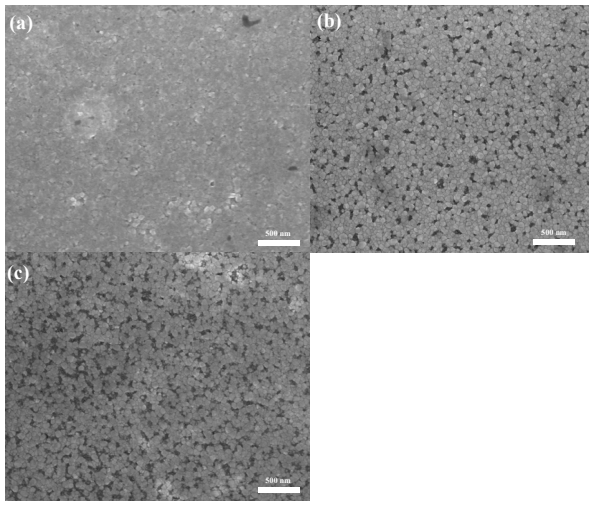

Fig.7 SEM images of LZO films made from different chelating agents. (a) TEA, (b) TIPA, (c) DIPA.

In the thermodynamic opinion, unless rapid thermal processing technique is used, film crystallization usually begins during heating to the anneal temperature. Therefore, as the temperature increasing, more energy becomes available to surmount the barriers for nucleation events in addition to the energetically most favorable nucleation event. This can lead to film microstructures defined by nucleation and growth processes associated with more than one nucleation event [13-16].

In order to obtain the epitaxial growth, the heterogeneous nucleation should be promoted, and the Rapid Thermal Annealing is a favorable route. Due to the nature of this approach and the use of relatively high temperatures, a number of complex and potentially overlapping processes may occur during this processing. The preparation of the buffer layer on the metal alloy substrate needs a reductive protecting atmosphere, which will impede the decomposition of the precursor thoroughly. The products of the incomplete decomposition always embed into the grain boundary and then astrict the moving of the grains. In order to promote the heterogeneous nucleation in this processing, the decomposition steps of the precursor need to be modified as simple as possible.

3. Conclusions

In this paper, cube textured LZO buffer layers were deposited on the Ni5W substrate by the nitride route. A transparent and stable precursor solution was obtained by the manipulation of the solvent dielectric constants. The methanol with higher dielectric constants was substitute with the ethanol. The chelating agent modified precursor was obtained with a simplified decomposition route, by which, the Rapid Thermal Annealing route could be implemented to drive an epitaxial growth of the LZO buffer layers. The orientation characterizations and the decomposition route for the LZO precursors with and without the chelating agents confirm the importance of the decomposition route for the epitaxial growth of the LZO layers. Finally, a cube textured LZO epi-layer was obtained by the Rapid Thermal Annealing with the Full-Width-at-Half-Maximum (FWHM) values for in-plane and out-of-plane orientation are 7.0° and 5.0° respectively. Dense and smooth film morphology is obtained with the TEA as the chelating agent.

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