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Solid-state Chemical Reaction Synthesis and Characterization of Lanthanum Tartrate Nanocrystallites Under Ultrasonication Spectra

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Abstract. Under near room temperature, by using sodium tartrate, lanthanum trichloride, lanthanum acetate, and lanthanum nitrate as reactants, we synthesize the lanthanum tartrate nanocrystals in one step under the condition that the infrared lamp is irradiated and the polyethylene glycol 400 is used as the surfactant, where the synthesis method of nanoparticles by solid phase chemical reaction is used. Deionized water after washing with ethanol washes. Tartaric acid lanthanum crystalline powder is gotten, respectively. Analyze solid products phase using X-ray diffraction (XRD) and electron diffraction; characterize the functional groups structure with infrared spectra, and analyzethe change of functional groups in drugs before and after reaction; observe the size, shape, and size distribution of particlesby transmission electron microscopy(TEM). Testing 3 types of tartaric acid crystal powder of lanthanum are nano-crystallization, solid products are granular and relatively uniform in size, with an average particle diameter of about 40 nm, and the yield rate is approximately 92.3%. Furthermore, during the synthesis, the solid-state reaction conditions including raw materials, matching proportion of reactants, additions of inert substance, addition of trace solvents, surfactants and porphyrization time, etc, all have some influence on the morphology, particle size and size distribution of the final products. During the synthesis of the lanthanum tartrate nanocrystallites, the solid state reaction conditions such as changing reactant, matching proportion of reactant, adding inert substance, joining a little solvent or surface active solvent and grinding at different times may influence morphology, particle size and the size distribution of final products.

1. Introduction

Nanocrystalline material has small size effect, quantum size effect, volume effect, surface effect and macroscopic quantum tunnel effect. It exhibits excellent characteristics in mechanics, catalysis, optics, electrics, magnetics, acoustics, calorifics, superconducting technology, chemical and biological activity, and so on. It also has high practical value in national defense, electronics, chemical industry, nuclear technology, metallurgy, astronautics, light industry, biological and medical industry. Recently it has become a foundation for developing special materials and has been active in the fields of physical, chemical and materials science research [1, 2, 3].

In the continuous extensive research on nanocrystallite, it has become especially important to obtain highly pure, super fine and uniform nanocrystallite with optional physical chemical characteristics, and produce new nanomaterials. The key to solving the demand lies in the research and development of new synthesis techniques. The study on the solid-state chemical reaction under ambient temperature and near ambient temperature has made great progress in recent years. Applying

solid-state chemical reaction to produce nanomaterials is a new method which was developed recently. The preparation of nanocrystallite generally requires: clean surface, controllable particle shape, size distribution that prevents particle agglomeration, easy collection, better stability and high productivity. The solid-state chemical reaction method can meet these needs and it is easy to operate with advantages of simple processes such as synthesis, high yield, high selectivity, uniform particle size distribution, controllable size and less pollution. It can prevent or reduce the phenomenon of agglomeration of the liquid phase and the phenomenon of particle agglomeration caused by intermediate step and high-temperature reaction[4,5,6]. The solid-state chemical reaction process consists of four steps: diffusion-reaction-nucleation-growth. When the nucleation rate is greater than the nucleus's growth speed, it is beneficial to the formation of nanocrystallite. But if the nucleus's growing rate is greater than the nucleation rate, a lump crystal forms [7, 8].

Lanthanum tartrate is an important rare earth coordination compound with practical mechanical properties and luminescent properties. The nanometer solid material composed of lanthanum tartrate nanoparticles has specific quantum size effect, volume effect, surface and interfacial effect, and presents a unique mechanics, optics, electrical, acoustics, magnetism, superconductivity, chemical and biological activity that differ from macroscopic objects and from single molecules. Lanthanum tartrate nanocrystals have very important research and use value in defense, electronics, chemical industry, metallurgy, aerospace and medicine. This paper discusses the application or the solid-state chemical reaction to synthesize the nanocrystalline lanthanum tartrate under near ambient temperature and ultrasonication. With characterization and observation of the solid phase, particle size and morphology performed through powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction (ED). It also discussed, the factors which the influence to the final product such as types of reactant, changing the proportions of reactant, addition of inert substances, mixing trace solvent or surfactant and time of porphyrizing [9, 10].

2. Experimental

Composing experiment regents are all the analytical purity baking 10.0 mmol $La(Ac)_3 \cdot 3H_2O$ and 15.0 mmol $Na_2C_4H_4O_6 \cdot 2H_2O$ to grind in the agate pot with intrared light during grinding, the temperature is about 35 ~ 40° C, with the operate of ultrosonic, to wash the lomposing 3 times with distilled water, and then wash 2 times with alcohol, drying, finally the lanthanum tartrate nanocrystlline. The processes was repeated three separate times using $LaCl_3 \cdot 7H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $La_2(SO_4)_3 \cdot 9H_2O$ as the reactant in place of $La(Ac)_3 \cdot 3H_2O$. During each synthesis, the types of factors influencing the final product under different solid-state reaction conditions such as reactant, changing the proportions of reactant, addition of inert substances, mixing of trace solvent or surfactant and time of porphyrizing was also observed. The solid phase was characterized by powder X-ray diffraction (XRD) and electron diffraction (ED). The particle size and its distribution and morphology of the prepared nanocrystallite were observed by transmission electron microscopy (TEM). The TEM and ED patterns were obtained by utilizing a Japanese electronic type of JEM-200 CX transmission electric microscope at an accelerated voltage of 160 kV and an amplification of one hundred thousand times.

3. Results and Discussion

Table 1 shows the XRD patterns of lanthanum tartrate nanocrystallite synthesized according to the conditions of No.16 in table 2. Results of the synthesized lanthanum tartrate appears the XRD pattern of analytically pure lanthanum tartrate and the standard XRD pattern of lanthanum tartrate from JCPDS card, and which has no impurity peaks. However, the diffraction peaks of the synthesized product were significantly widened and conspicuously weaker. According to X-ray polycrystal diffraction theory, the widening of the peak diffraction is because of the superrefining of the particle size. This indicates that the particle size of the synthesized lanthanum tartrate is a single phase, ultrafine particle. According to the width of the peaks of the XRD pattern, and utilizing the formula of scherrer, the crystal's average particle size was calculated to be 40 nm. The particle size of the product is determined by the relative magnitude of the nucleation speed and the crystal nucleus's growing

speed. Results indicate that this condition enables the attainment of smaller nanocrystallites at ambient temperature, the nucleation speed is quicker than that of the nucleus's growth.

Table 1. X-ray diffraction result of the $La_2(C_4H_4O_6)_3$ nanocrystallite.

Reaction system	the liquid phase synthesis $La_2(C_4H_4O_6)_3$						Reaction system	$La(Ac)_3{\cdot}3H_2O + Na_2C_4H_4O_6{\cdot}2H_2O \rightarrow La_2(C_4H_4O_6)_3$					
2θ/(⁰)	15.9	16.2	21.7	36.1	45.3	55.1	2θ/(⁰)	15.6	17.8	20.2	36.1	45.1	53.2
d/Å	2.06	3.11	1.36	3.11	1.91	1.02	d/Å	2.07	3.21	1.30	3.21	2.01	1.03
Reaction system	$LaCl_3{\cdot}7H_2O + Na_2C_4H_4O_6{\cdot}2H_2O \rightarrow La_2(C_4H_4O_6)_3$						Reaction system	$La(NO_3)_3{\cdot}6H_2O+Na_2C_4H_4O_6{\cdot}2H_2O \rightarrow La_2(C_4H_4O_6)_3$					
2θ/(⁰)	14.7	17.7	20.1	35.8	45.2	54.9	2θ/(⁰)	15.3	16.9	20.3	36.3	46.2	53.8
d/Å	2.12	3.07	1.31	3.11	2.21	1.05	d/Å	2.08	3.23	1.32	3.32	2.11	1.12
Reaction system	$La_2(SO_4)_3{\cdot}9H_2O + Na_2C_4H_4O_6{\cdot}2H_2O \rightarrow La_2(C_4H_4O_6)_3$						Reaction system	the purity with analyses $La_2(C_4H_4O_6)_3$					
2θ/(⁰)	15.5	17.5	20.2	35.9	44.8	53.6	2θ/(⁰)	15.8	18.5	20.6	37.1	46.2	55.1
d/Å	2.09	3.08	1.27	3.22	2.17	1.05	d/Å	2.06	3.23	1.35	3.17	2.12	1.08

Figure 1 shows the ED pattern of this same sample (synthesized according to No.16 in table 2). The result shows that the round line of the diffraction is clear and is the result of multi-crystal diffraction. Calculation of the d value (table 1) of the corresponding diffraction, it shows that the product is the multi-crystal $La_2(C_4H_4O_6)_3$. Figure 2 shows the TEM result of the sample. The shape of the nanocrystalline $La_2(C_4H_4O_6)_3$ is approximately spherical in shape. The majority of the nanocrystallite's size is approximately 40 nm. This is consistent with the X-ray diffraction result.

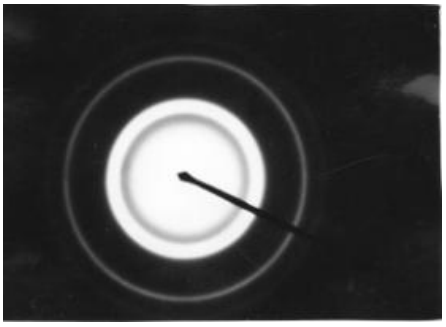

Figure 1. The ED pattern of the $La_2(C_4H_4O_6)_3$ nanocrystallite

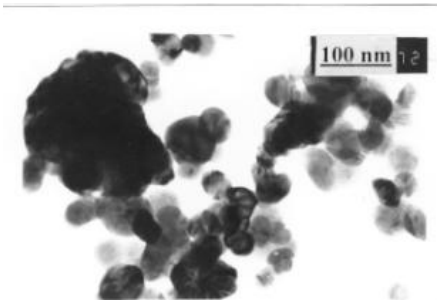

Figure 2. TEM photograph of the $La_2(C_4H_4O_6)_3$ nanocrystallite

Results indicate that separately using $LaCl_3{\cdot}7H_2O$, $La(NO_3)_3{\cdot}6H_2O$ and $La_2(SO_4)_3{\cdot}9H_2O$ in place of $La(Ac)_3{\cdot}3H_2O$ as the reactant as synthesized according to the conditions of No.1 to 4 in table 2, yield similar XRD patterns, TEM results and the ED patterns as when using the latter. All these experiments resulted in the synthesis of single nanocrystalline $La_2(C_4H_4O_6)_3$. The X-ray diffraction analysis results are indicated in table 1. But it can be seen from the TEM graph that the particle for nanocrystalline $La_2(C_4H_4O_6)_3$ of different reactants are eavenly dispersed and the order of granular sizes is: $La(Ac)_3{\cdot}3H_2O < La_2(SO_4)_3{\cdot}9H_2O < LaCl_3{\cdot}7H_2O < La(NO_3)_3{\cdot}6H_2O$ (table 2), among which the particle size of nanocrystallite $La(Ac)_3{\cdot}3H_2O$ is the smallest. During experimentation, observing from changing rate of the mixture's color after reactants are mixed and porphyrized indicates the speeds of reaction are different. Using $La(Ac)_3{\cdot}3H_2O$ as the reactant, yielded the fastest rate of reaction and the faster the reaction speed is, the faster the speed of nucleation growth.

Table 2. Morphology and particle size of nanocrystalline $La_2(C_4H_4O_6)_3$ under different conditions by solid-state reaction.

No.	Mole ratio	Inert substance and ratio of mixture (between La)	Solvent (1 mL)	Reaction time/min	Morphology	Particle size/nm	Yield /%
1	$LaCl_3{\bullet}7H_2O$,$Na_2C_4H_4O_6$(1:1.5)			30	Approx ball shape	80	89.1
2	$La(NO_3)_3{\bullet}6H_2O$,$Na_2C_4H_4O_6$(1:1.5)			30	Approx ball shape	90	90.2
3	$La_2(SO_4)_3{\bullet}9H_2O$,$Na_2C_4H_4O_6$(1:1.5)			30	Rhombus shape	70	90.2
4	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:1.5)			30	Rhombus shape	60	92.6
5	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)			30	Rhombus shape	60	93.8
6	$La(Ac)_3.3H_2O$, $Na_2C_4H_4O_6$ (1:3)			30	Rhombus shape	80	91.2
7	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:3)	NaCl (8:1)		30	Rhombus shape	70	92.2
8	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(1:1)		30	Rhombus shape	80	91.3
9	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(2:1)		30	Rhombus shape	70	90.2
10	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(4:1)		30	Rhombus shape	80	91.0
11	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)		30	Rhombus shape	80	91.6
12	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(16:1)		30	Rhombus shape	70	91.8
13	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(32:1)		30	Rhombus shape	80	92.9
14	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	Alcohol	30	Approx ball shape	70	93.2
15	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	Acetonitrile	20	Approx ball shape	40	89.2
16	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	Acetonitrile	30	Approx ball shape	40	92.3
17	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	Acetonitrile	60	Rhombus shape	50	92.2
18	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	Phenthiol	30	Rhombus shape	50	92.7
19	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	OP	30	Approx ball shape	60	91.2
20	$La(Ac)_3{\bullet}3H_2O$, $Na_2C_4H_4O_6$ (1:2)	NaAc(8:1)	H_2O	30	Approx ball shape	90	90.1

OP: poly ethylene glycol dioctyl ether

The XRD patterns of nanocrystalline $La_2(C_4H_4O_6)_3$ synthesized according to different matching proportions of reactants (synthesized according to No.4 to 6 in table 2) are similar. It is shown in the TEM pattern that by increasing the anion proportion of the reactant, the granularity of particles is reduced and its dispersity is improved. This is because with increasing density of the reactant, the nucleation speed is accelerated therefore decreasing particle size. Results indicate that by adding inert substances like NaCl and NaAc can produce smaller particle sizes, X-ray powder diffraction (XRD) of the products with the latter yielding results slightly better. X-ray powder diffraction (XRD) results of

different matching proportions (synthesized according to No.7 to 13 in table 2) shows that the XRD pattern of $La_2(C_4H_4O_6)_3$ is similar to the standard XRD pattern of $La_2(C_4H_4O_6)_3$, and that the product is a nanocrystalite. It can be seen from the TEM photograph that the particle of $La_2(C_4H_4O_6)_3$ is in the shape of a rhombus. Moreover, the larger the matching proportion of NaAc is, the smaller the produced particle size of $La_2(C_4H_4O_6)_3$ becomes. When the matching proportion reaches 16:1, the size of the particle diameter will be about 70 nm. In solid-state reaction those substances that do not take part in the reaction all belong to inert substances, and the appropriate amount of inert substances, the ones which can be added in order to change the speed of nucleation and the nucleus's growth. On one hand, the added insert substances can make the reactant be more dispersive and mix more evenly, and make the growing speed of the product particle slow down and the produced particle becomes less. On the other hand, by adding insert, the reaction speed of the system and the speed of nucleation would slow down. Therefore, the matching proportion should be appropriately controlled so as to achieve the best result.

The XRD pattern of $La_2(C_4H_4O_6)_3$ synthesized by adding various kinds of trace solvents or surfactants (synthesized according to No.14 to 19 in table 2) all yielded similar results as well. All the products from these reactions were single phase nanocrystalline $La_2(C_4H_4O_6)_3$. It can be seen from the TEM graph that by adding trace solvent or surfactant, the product particle size becomes slightly smaller and the particle diameters are more evenly dispersed. Solvents or surfactants can promote the contact and dispersion of the reactants in solid-state reaction system, and quicken the reaction speed.

Among the solvents and surfactants tested the best result yielded acetonitrile.

Different time spent on porphyrizing the reactant,the XRD pattern of $La_2(C_4H_4O_6)_3$ are similar.However, the size differences of the $La_2(C_4H_4O_6)_3$ nanocrystallite particles are minimal between a porphyrization time of 20 min and 30 min. However, after porphyrizing the reactants for 60 min, the nanocrystallite particle sizes becomes larger (synthesized according to No.15, 16, 17 in table 2). After 30 min of porphyrizing, the chemical reactions is basically complete and if porphyrization continues, the growth of the nanocrystalline nucleus becomes the main reaction process. Therefore, resulting in a larger diameter of the nanocrystalline particle. Table 2 shows the TEM graph of the nanocrystalline $La_2(C_4H_4O_6)_3$ (synthesized according to No.17 in table 2). The graph indicates that the produced nanocrystalline $La_2(C_4H_4O_6)_3$ is rhombus spherical, most of which are about 50 nm in size.

4. Conclusions

In conclusion, under near ambient temperature and ultrasonication, nanocrystalline $La_2(C_4H_4O_6)_3$ can be synthesized by solid-state reaction. The resulting particle sizes are relatively uniform, the morphology of the crystal is spherical, and the average particle diameter is about 40 nm.

Furthermore, during the synthesis of nanocrystalline $La_2(C_4H_4O_6)_3$, varying the solid-state reaction conditions such as the types of reactants, matching proportion of reactants, additions of inert substance, addition of trace solvents or surfactants and porphyrization time may influence the morphology, particle size and size distribution of the final products. The best condition for solid-state synthesis nanocrystalline $La_2(C_4H_4O_6)_3$ involves the utilization of $La(Ac)_3 \cdot 3H_2O$ and $Na_2C_4H_4O_6 \cdot 2H_2O$ (1:1.5) as reactants, addition of inert substance at a ratio of 8 to 1 acetonitrile (1 mL). The synthesis is achieved during a porphyrization period of 30 min under heatred conditions. Finally, the yield rate of nanocrystalline $La_2(C_4H_4O_6)_3$ is approximately 92.3%.

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