Low-Temperature Synthesis of $\text{La}_2\text{Ti}_2\text{O}_7$ Nanocrystal by Metallorganic Decomposition Method

有機金属化合物分解法による $\text{La}_2\text{Ti}_2\text{O}_7$ ナノ結晶の低温合成

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Nanopowders of $\text{La}_2\text{Ti}_2\text{O}_7$ have been successfully prepared by metallorganic decomposition method (MOD). In comparison with the higher reaction temperature of conventional preparation methods, such as solid-state reaction (about 1100°C), the nanocrystal $\text{La}_2\text{Ti}_2\text{O}_7$ phase can be formed at an evidently lower temperature of 700°C by MOD. The resulting powders exhibit small and uniform grains. The images of FT-IR show that acetylacetone can associate with La^{3+} to form La-acetylacetone chelate complexes, and the absorption peak of La^{3+} in precursor solution disappears, while the peaks of chelate complexes located at 1580 and 1420 cm^{-1} are found correspondingly. The probable reason is that small precursor particles can be formed at a homogeneous and low La^{3+} concentration by control release from the complexes; these small, uniform and more active precursor particles probably make it possible to form $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal at significantly lower preparation temperature.

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1. Introduction

Perovskite structures of rare earth titanate oxides are of considerable interest in recent years. $\text{La}_2\text{Ti}_2\text{O}_7$ belongs to the family of perovskite layer structure compounds in monoclinic symmetry with a space group P2_1 , which is one of interesting ferroelectric substances characterized by high Curie temperatures and coercive fields.¹⁾ A series of new photocatalysts with layered perovskite structure such as $\text{Sr}_2\text{Nb}_2\text{O}_7$, $\text{La}_2\text{Ti}_2\text{O}_7$, $\text{Ca}_2\text{Nb}_2\text{O}_7$, and $\text{La}_4\text{CaTi}_5\text{O}_{17}$ has been newly investigated. Discovery of effective photocatalysis of $\text{La}_2\text{Ti}_2\text{O}_7$ has attracted more attention on these compounds. Very recently, Hwang et al have employed $\text{La}_2\text{Ti}_2\text{O}_7$ as a photocatalyst for water spitting reaction and degradation of volatile organic compounds, and obtained some exciting results, which indicate that these compounds have great potential for many new applications.^{2),3)} The synthesis of $\text{La}_2\text{Ti}_2\text{O}_7$ has been reported using solid-state reaction (SSR), polymerized complex, sol-gel, coprecipitation and hydrothermal synthesis methods.^{4)–8)} However, it still remains some drawbacks in the forgoing methods. For example, the solid-state reaction method needs to be carried out at fairly high temperature around 1100–1400°C, hydrothermal method spends a long synthesis period, and sol-gel method gives pure phase in bulk but relatively high cost. Therefore, it is essentially important to develop more efficient method of preparation of $\text{La}_2\text{Ti}_2\text{O}_7$ under mild conditions.

Up to now, there is a very few reports using metallorganic decomposition method (MOD) to synthesize $\text{La}_2\text{Ti}_2\text{O}_7$. In comparison with the conventional methods, MOD has the advantages of a simple process, low cost, easily adjusted composition,⁹⁾ especially the remarkably lower synthesis temperature. Jeon et al.¹⁰⁾ prepared $\text{La}_2\text{Ti}_2\text{O}_7$ thin films by MOD at 900–1000°C, but they revealed the presence of second phase, $\text{La}_4\text{Ti}_5\text{O}_{24}$. In this paper, the preparation of $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal by MOD at 700°C without any mesophase has been described, and the possible mechanism of successful

preparation at such lower temperature has also been discussed.

2. Experimental

Lanthanum nitrate (0.001 mol/L) and titanium butoxide (TBT) (the mole ratio of lanthanum nitrate/TBT = 1 : 1) were dissolved in 16 mL acetic acid. The solution was diluted with 20 mL 2-methoxyethanol (MOE), and 4 mL acetylacetone (0.0095 mol/L) was added so as to keep the precursor solution stable. The resulting mixture was heated at 60°C with constant stirring for half an hour, and then evaporated at 100°C. The solution gradually condensed and formed a gel-like matter. With the time elapsing, the gel turned to powder, the precursor. It was ground, and then was heated at different temperatures in the range of 600–1100°C for 6 h to obtain the desired products (heating rate = 10°C/min). For the purpose of comparison, $\text{La}_2\text{Ti}_2\text{O}_7$ was prepared by solid-state reaction. La_2O_3 (99.9%, Aldrich) and TiO_2 (99.9%, Aldrich) in 1 : 2 molar ratio were mixed. The samples were calcined at 700–1100°C for 8 h (heating rate = 10°C/min).

XRD patterns of the samples were recorded in the region of $2\theta = 10^\circ - 80^\circ$ on a XD-2 powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation of wavelength 0.15406 nm. The infrared spectra in transmission mode were obtained on a Fourier transform infrared spectrometer (Bruker Equinox 55) using KBr pellets. Morphologies of the resulting particles were observed on scanning electron microscopy (JEOL JSM-6330F). TG-DTA measurements (Shimadzu, DTG-60) were carried out with a heating rate of 10°C/min in air.

3. Results and discussion

The results of thermal analysis (TG and TDA) of the precursor are shown in Fig. 1. The TG trace shows one continuous weigh loss up to 600°C due to dehydration and decomposition of the organic matters. An endothermic peak in the DTA appears at around 57°C, corresponding to the loss of physically adsorbed water in the precursor network. The exothermic peaks center at 350°C, 405°C, and 440°C, respectively, and all can be attributed to the combustion of organic groups involved in the precursor. The broad endothermic peak

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Fig. 1. TG-DTA traces of $\text{La}_2\text{Ti}_2\text{O}_7$ precursor. Fig. 2. XRD patterns of $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by MOD at (a) 600, (b) 700, (c) 800, (d) 900, (e) 1000 and (f) 1100°C.

around 700°C in the DTA curve may be assigned to the phase transition, which is later confirmed by the XRD analysis.

XRD patterns of $\text{La}_2\text{Ti}_2\text{O}_7$ nanopowder prepared by MOD under different temperatures are shown in Fig. 2 within the 2θ range of 10 to 80°. The peak of powder heated at 600°C is very low intensities and broad, which demonstrate that dominating phase of the powder is still amorphous. $\text{La}_2\text{Ti}_2\text{O}_7$ crystalline phase has presented after the powder was heated at 700°C for 6 h, which is illustrated by the appearance of peaks corresponding to the characteristic peaks of $\text{La}_2\text{Ti}_2\text{O}_7$ as shown in Fig. 2. As the temperature is increased to 800°C, the stronger and sharper peaks can be observed. This indicates that the nanopowder crystallizes very well. When powders were heated at 900°C or above, all the peaks completely accord with those of pure $\text{La}_2\text{Ti}_2\text{O}_7$ phase reported in the standard XRD card (JCPDS 28-0517). Fuierer et al. and Milanova et al. have reported the same results.^{1),5),11)} Thus, pure $\text{La}_2\text{Ti}_2\text{O}_7$ with pyrochlore-related monoclinic structure is present when the precursor was heated at 900°C or above.¹¹⁾

The XRD patterns of $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by SSR are illustrated in Fig. 3. The influence of calcining temperature can be seen clearly. It is found that crystalline $\text{La}_2\text{Ti}_2\text{O}_7$ as the major phase was obtained at 1100°C. On the other hand, using Scherrer's equation, the sizes of crystal particle are 54.3 nm (sample prepared by MOD at 1100°C in Table 1) and 96.3 nm (sample prepared by SSR at 1100°C in Table 2), respectively. Therefore, comparing with the result of SSR, it is noticeable

Fig. 3. XRD patterns of $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by SSR at (a) 700, (b) 800, (c) 900, (d) 1000 and (e) 1100°C.

Table 1. Parameter of XRD Pattern of Sample Prepared by MOD at 1100°C

d	I/I ₀	d	I/I ₀
6.4246	7.3	2.1023	25.5
5.0568	3.7	2.0708	11.3
4.2169	37.9	2.0005	5.6
3.8696	9.5	1.9550	25.6
3.4054	9.1	1.9288	19.4
3.2241	46.5	1.8869	24.3
3.1779	25.6	1.7745	11.1
3.1106	12.4	1.6968	5.0
2.9998	100	1.6819	4.5
2.7822	50.5	1.6702	15.4
2.7186	51.6	1.6415	9.4
2.6788	16.4	1.5989	19.8
2.4137	3.4	1.5110	4.6
2.3393	4.4	1.4908	5.9
2.2553	19.8	1.4444	3.2
2.1324	10.4	1.4314	9.7

Table 2. Parameter of XRD Pattern of Sample Prepared by SSR at 1100°C

d(Å)	I/I ₀	d(Å)	I/I ₀
6.4224	6.8	2.0992	28.7
5.0808	5.7	2.0678	15.6
4.1966	45.7	2.0011	8.1
3.8590	12.2	1.9553	29.6
3.3976	9.7	1.9248	16.0
3.2130	47.1	1.8843	26.3
3.1765	27.9	1.7705	11.3
3.1169	9.9	1.7012	7.3
2.9906	100	1.6815	6.4
2.7738	47.3	1.6687	15.2
2.7154	52.6	1.6393	8.8
2.6740	23.1	1.5981	17.8
2.3386	2.4	1.5111	7.5
2.2505	21.1	1.4921	5.1
2.1290	14.2	1.4441	5.0
		1.4297	13.0

that the $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystalline phase by MOD is formed at much lower temperature and the crystal size is much smaller (Table 3).

The infrared spectra in the oxygen-metal stretching regime between 400 and 1000 cm^{-1} of $\text{La}_2\text{Ti}_2\text{O}_7$ heated at different temperatures are given in Fig. 4. The principal bands located in the regions of 1087–695 and 625–310 cm^{-1} may be assigned

Table 3. Standard Card (JCPDS 28-0517)

d(A)	Int	d(A)	Int
6.426	10	2.000	8
5.095	8	1.978	2
4.201	40	1.954	30
4.014	4	1.926	20
3.864	11	1.886	30
3.546	2	1.838	2
3.392	11	1.830	2
3.251	9	1.824	2
3.217	50	1.801	2
3.172	30	1.787	3
3.112	13	1.777	8
2.995	100	1.771	15
2.782	50	1.766	11
2.774	50	1.757	5
2.713	55	1.744	4
2.677	25	1.730	1
2.573	3	1.715	2
2.560	2	1.696	8
2.516	2	1.693	7
2.411	3	1.682	7
2.376	2	1.669	20
2.355	4	1.652	3
2.336	5	1.640	11
2.329	6	1.625	3
2.307	5	1.602	13
2.282	3	1.597	25
2.277	4	1.588	16
2.253	20	1.585	9
2.187	6	1.570	4
2.181	5	1.555	3
2.144	11	1.544	6
2.131	17	1.521	3
2.100	25	1.511	8
2.071	17	1.498	3
2.026	2	1.489	6
2.007	8

Fig. 5. Typical SEM of $\text{La}_2\text{Ti}_2\text{O}_7$ powder by MOD at 1100°C . Fig. 6. Typical SEM of $\text{La}_2\text{Ti}_2\text{O}_7$ powder by SSR at 1100°C . Fig. 4. IR spectra of $\text{La}_2\text{Ti}_2\text{O}_7$ prepared by MOD at (a) 600, (b) 700, (c) 800, (d) 900 and (e) 1000°C .

to the Ti–O bond stretching vibration. The band at 644 cm^{-1} with a shoulder at 516 cm^{-1} may be attributable to the La–O vibration.¹²⁾ As shown in the Fig. 4, the intensity of the band at about 644 cm^{-1} increases with increasing temperature. And the band at around 516 cm^{-1} is present when precursors were calcined above 700°C . It suggests that the La–O vibration at 516 cm^{-1} is present when the $\text{La}_2\text{Ti}_2\text{O}_7$ crystalline phase starts to form at 700°C . In addition, the rise in temperature results in the significant change of the Ti–O bond vibration. The absorption bands at around 760 and 460 cm^{-1} also present at 700°C and above. The absorption band at 760 cm^{-1} is assigned to the stretching vibration of TiO_4 tetrahedron and the band

about 460 cm^{-1} is due to the Ti (IV)–O stretching vibration. Hence, it is evident that $\text{La}_2\text{Ti}_2\text{O}_7$ can be formed at 700°C and above.

SEM photographs of the $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystals prepared by MOD and SSR are shown in Figs. 5 and 6, respectively. As seen in Fig. 5, the result of SEM demonstrates that the sample consists of small and uniform primary rice-like particles with a size of $30\text{--}120\text{ nm}$, however, it exhibits a slight agglomeration, probably resulting from the sintering at high temperature. Figure 6 reveals that sample consists of well-rounded particles that have an average size of $0.1\text{--}0.5\text{ }\mu\text{m}$. It can be seen that the average particle size for $\text{La}_2\text{Ti}_2\text{O}_7$ formed by MOD is much smaller and the morphology is more uniform than those prepared by SSR.

Acetylacetone is an excellent ligand and its cumulative stability constants of complexes with La^{3+} are $K_1 = 10^{5.1}$, $K_2 = 10^{8.9}$, $K_3 = 10^{11.9}$, respectively.¹³⁾ Figure 7 shows distribution of La–AcAc complexes with different ligand concentration. It is well known that La^{3+} ion can react with AcAc to form three chelate complexes, namely $\text{La}(\text{AcAc})$, $\text{La}(\text{AcAc})_2$ and $\text{La}(\text{AcAc})_3$. There exists a succession of equilibria as follow:

The initial concentration of AcAc is 0.0095 mol/L , after reacting with La^{3+} ion, the equilibrium concentration would drop to the range of $0.0065\text{--}0.0085\text{ mol/L}$ (assume that the complexes with coordination number of 1, 2 or 3). As clearly shown in Fig. 7, at this range of AcAc concentration, the most

Fig. 7. Distribution curves of La-AcAc.

Fig. 8. IR Spectra of precursors of $\text{La}_2\text{Ti}_2\text{O}_7$ (a) with AcAc, (b) without AcAc.

of the La^{3+} ions are exist as the complexes, whereas, the free La^{3+} concentration is quite low. Therefore, the precursor can be formed under homogeneous, low La^{3+} ion concentration. Since the existence of equilibrium between La^{3+} ion and the complexes, the consumed free La^{3+} can be reinforced by the complexes with the shift of the equilibrium reaction, so-called control release of La^{3+} , leading to nearly constant La^{3+} concentration during the whole reaction. Thus, it can be predicted that the small and uniform precursor particles may be formed with the low concentration of free La^{3+} in the precursor solution. Therefore, these small, uniform and more active precursor particles probably make it possible to form $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal at significantly lower preparation temperature.

To further confirm the formation of La-AcAc complexes, the FT-IR of precursors are carried out. FT-IR spectra of precursors at different conditions are shown in Fig. 8. The strong peak at 1383 cm^{-1} is described to La-O bond,¹⁴⁾ and it decreases significantly when AcAc was added into the precursor. In particular, the absorption peaks at 1580 and 1420 cm^{-1} are characteristic for chelate ligands—the asymmetrical and symmetrical vibration mode of carboxyl groups. The existence of La-AcAc complexes and two types of ligands (the acetylacetone and acetic acid) lead to broaden the peaks.¹⁵⁾ It can be concluded that the success in dramatically lowering the synthesis temperature may be concerned with formation of La-AcAc complexes.

4. Conclusions

Pure $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal was successfully prepared by the metallorganic decomposition method. The results of XRD, FT-IR, and TG-DTA characterization strongly indicated that the formation of $\text{La}_2\text{Ti}_2\text{O}_7$ crystals was occurred around 700°C . The synthesis temperature for $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal by MOD is significantly lower and the average size is remarkably smaller compared to those synthesized by SSR. The possibility of obtaining $\text{La}_2\text{Ti}_2\text{O}_7$ nanocrystal without any second phase at such lower temperature is relevant to the uniform precursor particles prepared by MOD. In other words, the small and uniform particles strongly depend on the existence of La-

AcAc chelate complexes.

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