Synthesis of $\text{La}_2\text{Sn}_2\text{O}_7$ Powder from Complex Colloid Prepared in Strongly Basic Solution

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強塩基性溶液中で調製した複コロイドからの $\text{La}_2\text{Sn}_2\text{O}_7$ 粉末の合成

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Amorphous complex colloid containing La^{3+} and Sn^{4+} ions with a stoichiometric ratio in a bulk solid particle was prepared by rapid hydrolysis of homogeneous aqueous solutions of tin (VI) and lanthanum chlorides under strongly basic conditions. Heating of the complex colloid at relatively low temperatures ($>800^\circ\text{C}$) resulted in the direct formation of $\text{La}_2\text{Sn}_2\text{O}_7$ active powder from the amorphous colloid particles without forming any intermediate phase. Some powder properties were measured for the amorphous and crystallized particles. Possible structural correlations between the amorphous colloid and the crystalline particles were discussed on the basis of the results obtained from infrared absorption spectroscopic examination on the structural change occurring during heat treatment of the amorphous particles. The simple procedure employed in the present work to prepare complex colloid consisting of La^{3+} and Sn^{4+} ions is applicable to powder formation of the family of $\text{Ln}_2\text{B}_2\text{O}_7$ ($\text{Ln} = \text{lanthanide atoms, B} = \text{Sn or Ti}$).

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1. Introduction

There were very few successes in the preparation of monodispersed inorganic sols because the properties of precipitated materials depend strongly on the conditions of the environment in which these solids are generated. However, considerable advances have been made in preparing monodispersed colloids by Matijević¹⁾. He has developed several procedures which can produce dispersions of metal oxides (hydroxides, hydrated oxides, etc.) particles exceedingly uniform in size and shapes. Since then ceramic chemical processing utilizing the inorganic colloids are in development to fabricate high-performance materials. For instance, so-called "sol-gel" processing starts with extremely small colloidal oxide particles obtained by hydrolysis of organic compounds of metals. They link together into a strong gel network and are converted to pore-free product by later drying and sintering²⁾. In the alternating process described as "densely packed uniform colloid process"³⁾, a body with pores as uniform as possible was obtained by packing of much larger, uniform, preferably spherical particles into a mold.

In addition to the considerable progress in the preparation of monodispersed inorganic colloids of simple composition, the practical application of complex colloids containing two or more kinds of cations is also expected because of an increasing importance of composite materials. The complex colloid systems generally consist either of particles of mixed compositions or of mixed dispersions of different materials⁴⁾. Some methods for preparing homogeneous particles of mixed compositions have been investigated by Matijević and co-workers⁴⁾. In most cases the colloidal particles of mixed compositions are initially produced as a mixture of extremely small particles of the corresponding metal hydroxides or hydrated oxides. Thus the formation of complex colloids with the incorporated metal ions to be a given cation ratio in an originally generated particle seldom occurs in multicomponent systems. It may be due to mostly the substantial difference in preparation conditions, in particular, pH region at which individual precipitation of each metal ions initiate separately.

The authors have attempted simultaneous precipitation of unlike cations, La^{3+} and Sn^{4+} ,

indicating extremely different properties in the formation of each precipitates to synthesize dielectric $\text{La}_2\text{Sn}_2\text{O}_7$ active powder applicable to the production of high-performance ceramics. In spite of the substantial difference between those cations, however, rapid hydrolysis procedure under very strong basic conditions could yield complex colloid for which constituting La^{3+} and Sn^{4+} are concurrently involved in a bulk solid particle. In the present paper, the effects of preparation conditions on formed complex colloid are examined and then various changes in some properties are also investigated for the colloidal particles and crystallized ones. Besides structural change occurring during heat treatment in the colloidal particles are discussed in relation to the atomic configurations of crystalline phases.

2. Experimental procedures

Hydrous tin(IV) and lanthanum chlorides ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7-10\text{H}_2\text{O}$) were used for the preparation of various starting solutions. Generally, in forming homogeneous multicomponent gels a major problem is the unequal hydrolysis of metal salts. Then a large number of precipitation experiments were carried out in order to determine the optimum conditions for completing the simultaneous precipitation of soluble La^{3+} and Sn^{4+} ions with a theoretical cation ratio. After the preliminary examinations, a procedure for obtaining the complex colloid was established as follows.

Mixed solutions of tin and lanthanum chloride ($\text{La}^{3+}/\text{Sn}^{4+}=1.0$) were prepared by dissolving required amounts of hydrous chlorides into given amounts of distilled water (50-500 cm^3). The total concentration of La^{3+} and Sn^{4+} salts, $[\text{M}]_T = [\text{LaCl}_3] + [\text{SnCl}_4]$, ranged from 0.052 to 1.04 M in the starting solutions. These homogeneous aqueous solutions were poured rapidly into a reaction vessel containing much excess aq. NH_3 . Then colloidal particles were instantaneously yielded in such a strongly basic environment. The systems were continuously agitated throughout the preparation of the complex colloids and subsequent aging for 30 min at room temperature. After repeated washings with distilled water by decantation technique, the coprecipitates were dried at 110°C for several days, and heat-treated at various temperatures.

The produced phases of as-coprecipitated (henceforth referred to as as-coppt) and heated

samples were identified by conventional powder X-ray diffractometry. Pore size distribution and specific surface area were measured by mercury porosimetry and BET gas adsorption, respectively, for some selected samples. In estimating apparent crystallite size of crystallized samples, purified germanium powder (5N) was used as internal standard. Infrared (referred to as ir) absorption spectra of samples heated at various temperatures were recorded in the range from 4000 to 300 cm^{-1} . The pressed disks of the finely powdered samples with potassium bromide were prepared for the measurement.

3. Results and discussion

3.1 Preparation of complex colloid

Both tin(IV) and lanthanum ions are precipitated as hydrated oxide or hydroxide gels by hydrolysis of aqueous solutions dissolving the corresponding metal salts. However, the conditions under which the colloidal precipitates are generated and the form of each precipitate are quite different. Hydrous tin(IV) oxide gel is readily produced above $\text{pH} \approx 1$, showing an amorphous character on the X-ray diffraction pattern. On the contrary, crystalline lanthanum hydroxide particles can be precipitated only under basic conditions. A decrease in pH of a reacting solution results in the incomplete precipitation of dissolving La^{3+} ions with a simultaneous prolonged deflocculation of formed $\text{La}(\text{OH})_3$ colloid. Hence to avoid the occurrence of compositional segregation due to the extremely different precipitation behavior between two kinds of colloidal particles, we examined several procedures for the preparation of complex colloid involving both cations simultaneously in the present system. As a result, it was found that rapid mixing of aqueous solutions containing given amounts of both cations with precipitating agent in strongly basic environment was the most suitable conditions for preparing the complex colloid. An increasing temperature of hydrolysis reaction generally causes a remarkable increase in the rate of hydrolysis. In the present system, the rapid hydrolysis required for the simultaneous precipitation of unlike cations was sufficiently achieved in the rapid mixing technique at room temperature. Therefore the preparation experiments were conducted at room temperature.

Figure 1 represents XRD results of individual precipitates obtained for selected coprecipitates

Fig. 1. Changes in XRD patterns of coprecipitates with atomic ratios La:Sn in starting aqueous solutions.

prepared by the rapid hydrolysis procedure from mixed chloride solutions in which La/Sn atomic ratio was varied between 1:0.1 to 0.1:1. Amorphous reflection which is substantially different from those of the precipitates having either Sn^{4+} -enriched or La^{3+} -enriched composition is observed for the coprecipitates with the atomic ratios between 1:0.7 to 0.7:1. Among coprecipitated colloids showing similar amorphous pattern, however, the production of $\text{La}_2\text{Sn}_2\text{O}_7$ single phase by subsequent heating at 1300°C was achieved only for a coprecipitate prepared from a solution containing the theoretical cation ratio (referred to as LSO hereafter).

Concentration effect of starting solution on the coprecipitation of the dissolving cations was also examined for the LSO solution. XRD analysis of a coprecipitate obtained from a concentrated solution (1.04 mol/dm^3 ; LSO-C) showed the same reflections as those of LSO powder from an original solution (0.26 mol/dm^3 ; LSO-O). On the other hand, crystalline $\text{La}(\text{OH})_3$ peaks superimposed on a broadened amorphous reflection appeared for a sample prepared from a diluted solution (0.052 mol/dm^3 ; LSO-D), indicating that a portion of dissolving La^{3+} ions precipitated separately as $\text{La}(\text{OH})_3$ particles. For most of cations dissolving in aqueous solution, electrically charged ions are essentially coordinated by a fixed number of molecular water, that is, well-known aqua-complex ions⁵⁾. In general, these complex ions exist as various polynuclear complexes (homonuclear species or heteronuclear ones) linked with hydroxyl anions, depending on the concentration of soluble cations. Addition of OH^- ions into an aqueous solution

Fig. 2. DTA-TG curves for a coprecipitate and individual precipitates composed of either La^{3+} or Sn^{4+} ions.

containing some cations promotes the removal of H_3O^+ from molecular water coordinating polynuclear complexes. A progressive increase in OH^- concentration decrease the solubility of the formed complex, finally resulting in the precipitation of polymerized hydroxide or hydrated oxide. The composition and structure of polynuclear complex also depend on the species of dissolving cations. Therefore heterogeneous coprecipitation observed in the diluted LSO-D solution system might be caused by some change in coordinated structure of aqua-complex with the concentration of dissolving La^{3+} and Sn^{4+} cations.

A comparison of DTA-TG data (heating rate: 10°C/min) is given in Fig. 2 for the individual precipitates of La^{3+} and Sn^{4+} and the coprecipitated LSO powder. The thermal behavior of the LSO powder clearly differs from those of other two precipitates. It presents a distinct exothermic peak corresponding to the formation of $\text{La}_2\text{Sn}_2\text{O}_7$ at about 900°C on the DTA curve. The characteristic nature of the LSO powder can be also seen in the result of TG experiment showing gradual elimination of physisorbed and combined water over wide temperature range. These results clearly indicated that the coprecipitate were generated not as a mixture of individual precipitates but as a complex colloid involving both unlike cations in a bulk solid particle by the simple procedure employed in this study. In Fig. 3 pore size

Fig. 3. Pore size distribution of LSO-O complex colloid using a logarithmic scale for pore size.

distribution of the LSO powder is shown. The sample was pre-heated at 300°C to eliminate physisorbed water prior to the measurement. The pores distributed in three-dimensional gel networks of the heated sample ranged in a relatively narrow size with a mode diameter of 5 nm. The symmetrical distribution curve suggested that hydrolysis of an aqueous solution containing unlike cations under strongly basic conditions yielded homogeneous complex colloid sols composed of relatively narrow-sized primary particles. From the result obtained in the pore size distribution, the dimension of the complex colloid particles seemed to be relatively large, ranging from about 10 to 20 nm in diameter, which was comparable to that calculated from the measured value of specific surface area reported in the following section.

3.2 Crystallization of complex colloid

Complex colloid particles prepared under different conditions were heated at various temperatures for given heating periods up to 24 h. At 1300°C all the LSO powders could be easily converted to $\text{La}_2\text{Sn}_2\text{O}_7$ single phase. Figure 4 represents the crystallization behavior of the complex colloid obtained from LSO-O solution. The temperature for $\text{La}_2\text{Sn}_2\text{O}_7$ single phase to be produced was found to be lowered to 800°C for the LSO-O powder under heating conditions employed in the present work. It is also seen that $\text{La}_2\text{Sn}_2\text{O}_7$ phase is directly formed from amorphous phase without any intermediate products. For LSO-C and LSO-D powders, the temperature required for the complete conversion to crystallized phase is usually above 900°C or

Fig. 4. XRD patterns of as-coppt and heated samples showing direct crystallization from amorphous phase.

Fig. 5. Changes in specific surface area, apparent crystallite size, and calculated d_{sp} with heat treatment.

more.

Changes in some powder properties, specific surface area (S_w) and apparent crystallite size, were examined for LSO-O powder. The former was estimated from N_2 gas adsorption at the liquid-nitrogen temperature and the latter from broadening of crystalline peaks. They are plotted against heating temperatures (for 24 h at each temperatures) in Fig. 5. Surface area diameter, d_{sp} which could be calculated from the S_w by assuming that complex colloid consisted of spherical particles with equal size, is also shown in Fig. 5. A pronounced decrease in S_w observed in

the temperature range 700°–900°C was clearly ascribed to the crystallization of amorphous particles. In contrast to this steep change, a sluggish decrease in S_w below 700°C was likely due to gradual dehydration of surface hydroxyl group over wide temperature range as indicated in TG result. The restricted dehydration between amorphous primary particles may be caused by random configuration of constituent unlike cations without any structural regularity. The structural correlation between amorphous particles and crystallized ones is discussed in detail at section 3.3.

It was of interest that an apparent crystallite size of a sample heated at 800°C is nearly comparable to the estimated value of d_{sp} . This means that an amorphous primary particle of about 20 nm in size may be converted to an ultimate crystalline particle with a fixed atomic orientation. Since it is unlikely to occur that only a single nucleus is formed in such a primary particle, structurally equal environment would be constructed over the whole particle by diffusion process during heating up to temperature just above which the crystallization of amorphous phase initiates, resulting in the growth of many nuclei in a fixed direction.

Because of highly active properties of the synthesized $\text{La}_2\text{Sn}_2\text{O}_7$ powder ($S_w=8.5 \text{ m}^2/\text{g}$ for a powder heated at 1000°C for 24 h), it is expected that, for example, dielectric materials having high quality can be easily fabricated by using the $\text{La}_2\text{Sn}_2\text{O}_7$ powder. In fact, a dense body of $\text{La}_2\text{Sn}_2\text{O}_7$ with relative sintered densities more than 90% was yielded by the conventional press-

ureless sintering. Investigations on the practical applications of the synthesized $\text{La}_2\text{Sn}_2\text{O}_7$ powder will be reported elsewhere.

3.3 Structural change induced in heating process for amorphous complex colloid

As has been mentioned in the preceding section, La^{3+} and Sn^{4+} dissolving in aqueous chloride solutions coprecipitated not in the form of a mixture of each colloidal precipitates. Then ir spectroscopic analysis was performed for LSO colloid system to elucidate the form of the complex colloid, namely whether the coprecipitate having a specific ordered configuration formed with two types of cations would be produced or not. In Fig. 6 changes in the ir absorption spectra of as-coppt and several samples successively heated up to 700°C are shown with a comparative representation of those of SnO_2 (hydrated gel and heated sample) and $\text{La}(\text{OH})_3$. Figure 7 indicates similar ir spectral changes (a) and XRD patterns (b) of various samples heated at higher temperatures, showing gradual structural ordering via crystallization process.

An extensive investigation of systematic variations in the structures and some properties has been carried out for a number of rare-earth stannates having a very regular pyrochlore structure⁶. The ideal pyrochlore structure, for example in double oxides represented by the general formula of $\text{A}_2\text{B}_2\text{O}_6\text{O}'$, is composed of two types of cation coordination polyhedra. The smaller B cations are six coordinated, forming a network of BO_6 trigonal antiprisms. The BO_6 polyhedra are linked on corners only with hex-

Fig. 6. Infrared absorption spectra of (a) LSO complex colloid heated up to 700°C and (b) individual precipitates for La^{3+} and Sn^{4+} ions.

Fig. 7. Changes in (a) infrared spectra and (b) XRD patterns of heat-treated LSO powder occurring during crystallization process.

agonal interstices, where $\text{AO}_6(\text{AO}_6\text{O}'_2)$ scalenohedra⁷⁾ containing six equally spaced O^{2-} ions and two additional axial O'^{2-} ions are situated. Thus O'^{2-} ions bonded to only A cations constitute an alternative network of $\text{A}_4\text{O}'$ tetrahedra. Because the BO_6 network is essential to the cohesion of the crystal, significant perturbation of the $\text{A}_4\text{O}'$ network has a weak influence on the BO_6 network⁸⁾.

Most of the ir spectra of rare-earth pyrochlores exhibit seven well-resolved absorption bands^{9),10)}. For rare-earth stannates, absorption bands centered at 650–580 cm⁻¹ and broader bands in the frequency range 500–350 cm⁻¹ are assigned to B–O stretching modes and couplings between B–O stretching and O–B–O bending modes, respectively. A weak band in the vicinity of 320 cm⁻¹ are due to vibrational modes of $\text{A}_4\text{O}'$ network. Although an appreciable change in XRD pattern was observed only for samples in which crystallization proceeded (Fig. 7 (b)), various informations about the short-range ordering in, particularly, amorphous state were given from ir spectral change as seen in Figs. 6 and 7.

Colloidal particles of hydrated SnO_2 precipitated from an aqueous solution containing Sn^{4+} ions reveal specified amorphous character in its XRD profile; the appearance of the very broadened peaks located at the corresponding diffraction angles to crystallized SnO_2 . Thus the hydrous SnO_2 gel was probably composed of extremely fine primary particles in which “ SnO_2 -like” atomic configuration existed¹¹⁾. Such a close correlation of the gel structure with crystallized one is also represented in the ir spectra of both materials shown in Fig. 6 (b). For the complex

colloid prepared in this work, however, ir spectra of as-coppt greatly differed from that of well-crystallized $\text{La}_2\text{Sn}_2\text{O}_7$, indicating the absence of structural correlation between them. After heating of prepared colloidal particles at 300°C a broad band at 320 cm⁻¹ became substantially disturbed with an appreciable change in another broad band at 540 cm⁻¹. The drastic change of the broad band centered at 320 cm⁻¹ are probably due to dehydration process occurring in $\text{La}(\text{OH})_3$ over the temperature range 300°–400°C. Although much information are required for rigid assignment, the bands at 540 and 320 cm⁻¹ were presumably due to “Sn–O”-related and “La–O”-related vibration mode, respectively, for the as-coppt sample. Heating of the amorphous colloid at higher temperatures resulted in the appearance of ir spectra different from those of heated samples below 300°C and in the increasing absorbance of a broad band at about 360 cm⁻¹ with its gradual shifting to higher frequency.

The results obtained from the ir spectroscopic analysis suggested that an amorphous primary particle of the complex colloid (as-coppt) was constructed with an atomic configuration of a mixed linkage of distorted SnO_6 and LaO_9 polyhedra (assuming on the basis of a hydration number with which each cations in an aqueous solution are surrounded by molecular water¹²⁾) without any close relation to the corresponding crystalline $\text{La}_2\text{Sn}_2\text{O}_7$ phase. The “amorphous” configuration in a primary particle was destroyed by dehydration of bonded OH^- ions and converted to an another amorphous precursor having $\text{La}_2\text{Sn}_2\text{O}_7$ -related structure. An increase in heat-

ing temperature promoted atomic diffusion in the precursor, resulting in the progressive ordering between two types of the constituting network, SnO_6 and $\text{La}_4\text{O}'$. This structural ordering is supported by the increasing sharpening of ir absorption bands in the range from 700 to 300 cm^{-1} , which is closely related to a transition from the disordered to the ordered state¹³⁾. Finally we may conclude that La^{3+} and Sn^{4+} ions initially incorporated in a bulk solid particle of the complex colloid without any structural correlation between them (primary amorphous precursor) were rearranged to some structurally ordered precursor (secondary amorphous one) by heating at relatively low temperatures. Then further heating at appropriate temperatures resulted in the direct formation of $\text{La}_2\text{Sn}_2\text{O}_7$ powder from the secondary amorphous precursor, depending on the structural ordering of the precursor induced in heating operation.

4. Conclusion

An attempt to precipitate unlike cations simultaneously, La^{3+} and Sn^{4+} , dissolving in an aqueous solution, which show extremely different precipitation behavior, was made to synthesize dielectric $\text{La}_2\text{Sn}_2\text{O}_7$ active powder applicable to the fabrication of high-performance ceramics. From extensive examinations of preparation conditions it was found that rapid hydrolysis in strongly basic solutions yielded amorphous complex colloid composed of not a mixture of individual precipitates containing either La^{3+} or Sn^{4+} ions, but relatively narrow-sized primary particles in which stoichiometric ratio of both unlike cations were incorporated. Heating of the complex colloid at a relatively low temperature (800°C for LSO-O sample) directly converted the amorphous colloid to crystallized $\text{La}_2\text{Sn}_2\text{O}_7$ powder without any intermediate product. Possible

structural change of the complex colloid occurring during heating operation was discussed on the basis of ir spectroscopic analysis. The results suggested that both cations initially randomly incorporated in a bulk solid particle of the complex colloid were rearranged to some structurally ordered precursor (still amorphous) by heating at lower temperatures and then the precursor was easily converted to the corresponding crystalline phase by subsequent heating at elevated temperatures. The simple procedure employed in the present study to prepare homogeneous complex colloid consisting of La^{3+} and Sn^{4+} ions can be clearly applied to the powder preparation of $\text{Ln}_2\text{B}_2\text{O}_7$ (Ln =lanthanide atoms, B =Sn or Ti).

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References

- 1) E. Matijević, *Acc. Chem. Res.*, **14**, 22-29 (1981).
- 2) for example, Sol-Gel Processing in "Ultrastructure Processing of Ceramics, Glasses, and Composites", Ed. by L. L. Hench and D. R. Ulich, John Wiley & Sons, New York (1984) p.15-231.
- 3) R. K. Iler, "Science of Ceramic Chemical Processing", Ed. by L. L. Hench and D. R. Ulich, John Wiley & Sons, New York (1986) p.3-20.
- 4) E. Matijević, *ibid.*, p.463-81.
- 5) H. Ootaki, "Youeki Kagaku", Syokabo (1985) p.198-218.
- 6) F. Brisse and O. Knop, *Can. J. Chem.*, **46**, 859-73 (1968).
- 7) R. A. McCauley, *J. Appl. Phys.*, **51**, 290-94 (1980).
- 8) M. T. Vandenborre and E. Husson, *J. Solid State Chem.*, **53**, 253-59 (1984).
- 9) J. F. McCaffrey, *J. Opt. Soc. Am.*, **61**, 209-12 (1971).
- 10) M. T. Vandenborre and E. Husson, *J. Solid State Chem.*, **50**, 362-71 (1983).
- 11) S. Kaneko, J. Kanamori and F. Imoto, *Nippon-Kagaku-Kaishi*, **1976**, 906-10 (1976).
- 12) Ref 5), p.110-57.
- 13) W. E. Klee and G. Weitz, *J. Inorg. Nucl. Chem.*, **31**, 2367-72 (1969).