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Synthesis of Mesostructured Materials Using Nb-containing Layered Perovskites and Cationic Surfactants

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Mesostructured composites of layered perovskites and cationic surfactants were synthesized. Layered perovskite $HCa_2Nb_3O_{10}$ and alkyltrimethylammonium (C_nTMA) or alkylpridinium (C_nPy) surfactants formed lamellar-type composites. The interlayer spacings of the composites increased with increasing carbon number of alkyl group in the surfactants. The spacings were also affected by the Nb:surfactant ratio in the reacting solutions. From comparison between size of molecule and interlayer spacing, it is suggested that two types of composites formed, which contain $C_{16}Py^+$ ions with mono- or bilayer arrangements.

Key Words : Layered perovskite, Mesostructured composite, Cationic surfactant

1 INTRODUCTION

Nb-containing layered perovskites have attracted attention from the scientific and applicational points of view because they exhibit photocatalytic activity, ion conductivity and intercalating behavior of organic molecules. Some Nb-containing layered perovskite-type compounds have been synthesized and investigated regarding their intercalation reaction with alcohols and alkylamines [1,2]. Recently, we reported the synthesis of mesostructured composites using single-layered perovskite, K_2NbO_3F and cationic surfactants as structure directing agents (SDA) [3]. In this case, 2-D-hexagonal- and lamellar-type mesostructured composites were obtained by adjusting pH of reacting solution. In the case of mesoporous materials synthesized from homogeneous solutions such as mesoporous silica, MCM-41, the mesostructure of the materials mainly depends on synthetic conditions and SDA[4]. While KSW-2 which is synthesized using a layered silicate, kanemite as starting material has a unique square shape pore, which is difficult to form from homogeneous solution[5]. This suggests that structure of layered compounds as starting materials is an important factor for controlling the mesostructure of the resultant composites.

In this study, we synthesized mesostructured composites using multi-layered perovskites, $KLaNb_2O_7$ and $KCa_2Nb_3O_{10}$ shown in Figure 1 as the starting materials and investigated the structure of the composites.

2 EXPERIMENTAL

2.1 Synthesis of layered perovskites and their protonate forms

Layered perovskites $KCa_2Nb_3O_{10}$ and $KLaNb_2O_7$ were synthesized by an ordinary solid state reaction. K_2CO_3, La_2O_3, $CaCO_3$ and Nb_2O_5 were weighed in the appropriate molar ratio and mixed in ethanol using a mortar and pestle. $KCa_2Nb_3O_{10}$ was obtained by heating at 1373 K for 24 h in air and $KLaNb_2O_7$ was obtained by heating at 1523 K for 18 h in air. The products were examined by the powder X-ray diffraction (XRD) method using a diffractometer (Rigaku RAD-PC, CuKα radiation). The protonated compounds, $HLaNb_2O_7$ and $HCa_2Nb_3O_{10}$, were prepared by ion exchange in 6 mol/dm^3 HNO_3 aqueous solution at 333 K for 24 h and in 6 mol/dm^3 HCl aqueous solution at 333 K for 16 h, respectively.

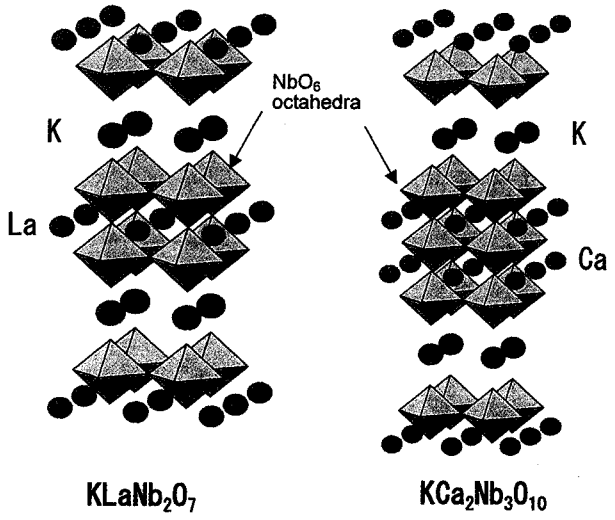

Figure 1 Structure models of Nb-containing layered perovskites, (a) $KLaNb_2O_7$ and (b) $KCa_2Nb_3O_{10}$

2.2 Synthesis of layered perovskite-cationic surfactant composites

The surfactants used as the SDA in this study were alkyltrimethylammonium chloride (C_nTMACl, n=12, 14, 16, 18) and alkylpyridinium chloride (C_nPyCl, n=12, 16), where n is number of carbon atoms in alkyl chain. 0.3 g of $HLaNb_2O_7$ or $HCa_2Nb_3O_{10}$ powders were dispersed into distilled water (100 cm^3 for $HLaNb_2O_7$ or 110 cm^3 for $HCa_2Nb_3O_{10}$) and then 0.1 mol/dm^3 C_nTMACl or C_nPyCl aqueous solution was added. Nb:SDA ratios in the suspensions were 1:1-12:1. The suspension was stirred with a magnetic stirrer at 343 K for 3 h. The resulting white precipitate was recovered by filtration and dried. Structural characterization of the products was performed using XRD. Thermogravimetry and differential thermal analysis (TG-DTA) of the composites were performed from room temperature to 1000℃ (Rigaku TG8120, heating rate; 10 K/min).

3 RESULT AND DISCUSSION

Figure 2(a) and (b) shows XRD patterns for $HLaNb_2O_7$-C_nTMA and $HCa_2Nb_3O_{10}$-C_nTMA composites. In the case of n=14-18 for $HLaNb_2O_7$ and n=12-18 for $HCa_2Nb_3O_{10}$, the (001) peaks of the composites observed at angles lower than those of the protonate forms, $HLaNb_2O_7$ or $HCa_2Nb_3O_{10}$. And these peaks shifted to lower angle with increasing number of carbon atoms in alkyl chain. These results indicate formation of lamellar type composites and expansion of interlayer space due to intercalation of the surfactants. Figure 3 shows relationship between the number of carbon atoms and the d-spacings of (001) plane, d_{001} for $HLaNb_2O_7$-C_nTMA and $HCa_2Nb_3O_{10}$-C_nTMA composites. Difference in d_{001} between $HLaNb_2O_7$-C_nTMA and $HCa_2Nb_3O_{10}$-C_nTMA composites containing the same surfactant was about 0.4 nm. As shown Figure 1, $HLaNb_2O_7$ and $HCa_2Nb_3O_{10}$ consist of double and triple NbO_6 octahedra sheets, respectively. This difference in d_{001} is corresponding to a thickness of a single NbO_6 octahedra sheet. In addition, the d_{001} increased linearly with increasing number of carbon atoms, n for both composites and the slopes were nearly equal to each other. These results indicate that arrangements of C_nTMA ions in the interlayer are same for these composites. On the other hand, the XRD pattern of $HLaNb_2O_7$-$C_{12}TMA$ composite was different from that of lamellar or 2-D-hexagonal type mesostructured materials, suggesting a formation of an unidentified type composite.

Figure 4 shows the XRD patterns of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites synthesized at various Nb:$C_{16}PyCl$ ratios. It was found that two types of lamellar phases formed for 3:1 and 12:1. The product for 6:1 was a mixture of these lamellar phases. While the XRD patterns of the products for Nb:$C_{12}PyCl$=12:1, 6:1 and 3:1 in the reacting suspensions showed that lamellar-type $HCa_2Nb_3O_{10}$-$C_{12}Py$ composites formed in single phases, respectively. Relationship between d_{001} values of the $HCa_2Nb_3O_{10}$-

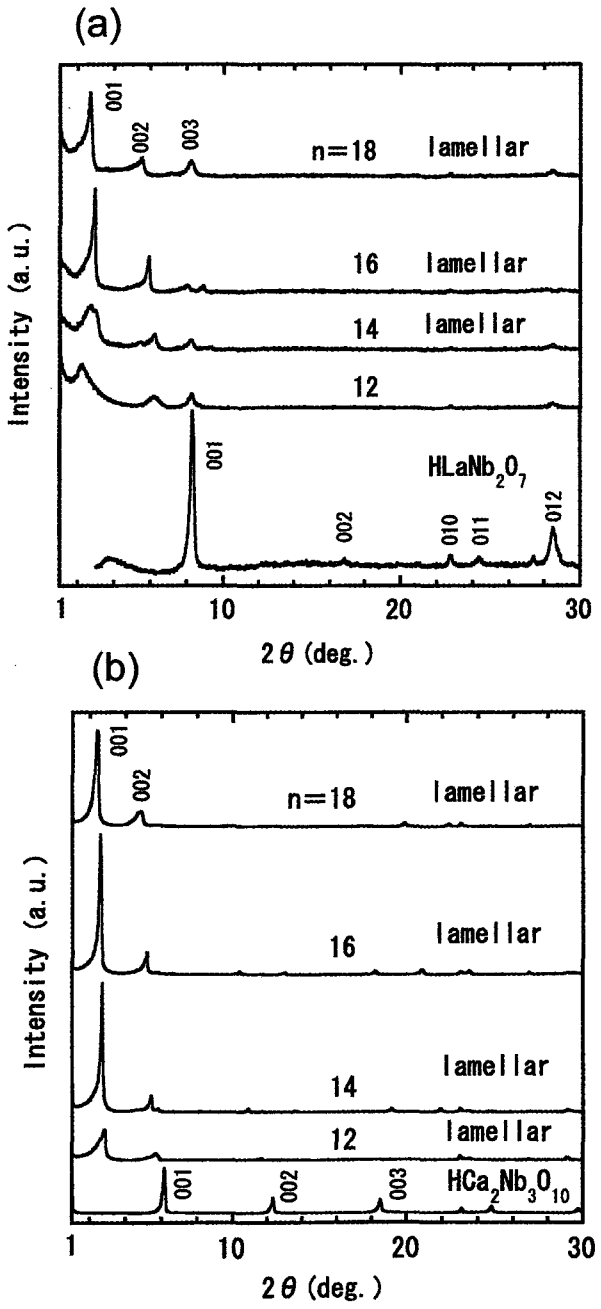

Figure 2 XRD patterns for (a) $HLaNb_2O_7$-C_nTMA and (b) $HCa_2Nb_3O_{10}$-C_nTMA composites

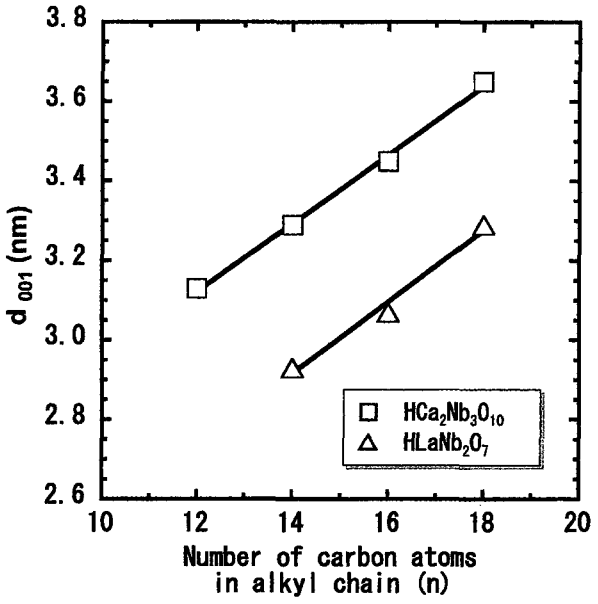

Figure 3 Relationship between number of carbon atoms and d_{001} values for $HLaNb_2O_7$-C_nTMA and $HCa_2Nb_3O_{10}$-C_nTMA composites

C_nPy composites and number of carbon atoms of the surfactants is shown in Figure 5. The d_{001} data of $HCa_2Nb_3O_{10}$-C_nTMA composites are also shown for comparison. The d_{001} of $HCa_2Nb_3O_{10}$-$C_{12}Py$ and $HCa_2Nb_3O_{10}$-$C_{16}Py$ (12:1) composites are close to the straight line drawn for the $HCa_2Nb_3O_{10}$-C_nTMA composites. This result suggests that C_nPy^+ ions were incorporated into $HCa_2Nb_3O_{10}$-$C_{12}Py$ and $HCa_2Nb_3O_{10}$-$C_{16}Py$ (12:1) with an arrangement similar to the interlayer of $HCa_2Nb_3O_{10}$-C_nTMA composites. On the other hand, $HCa_2Nb_3O_{10}$-$C_{16}Py$ (3:1) composite has larger d_{001} than $HCa_2Nb_3O_{10}$-$C_{16}Py$ (12:1) composites in spite of containing the same surfactant. The difference in d_{001} implies that the composites for Nb:$C_{16}PyCl$=3:1 and 12:1 incorporate $C_{16}Py$ ions in a different arrangement in the interlayer. Figure 6 shows TG curves of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites. Weight losses were observed around 300, 400 and 600℃, which are attributed to combustion and/or decomposition of the surfactant. Total weight loss for the 3:1 composite is larger than that for the 12:1 composite, indicating that the amount of the $C_{16}Py^+$ ion incorporated in the 3:1 composite is larger than that in the 12:1 composite. From this result, it is suggested that the amount of $C_{16}Py$ ion in the composites affects the arrangement of the surfactant.

Structure models of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites for Nb:$C_{16}PyCl$=3:1 and 12:1 are shown in Figure 7. The thickness of the $[Ca_2Nb_3O_{10}]$ layer is estimated to be 1.2 nm from the structure of

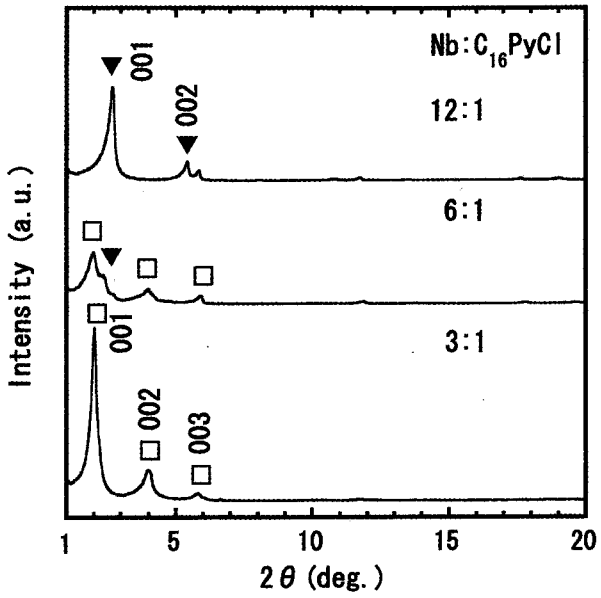

Figure 4 XRD patterns of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites synthesized at various Nb:$C_{16}PyCl$ ratios

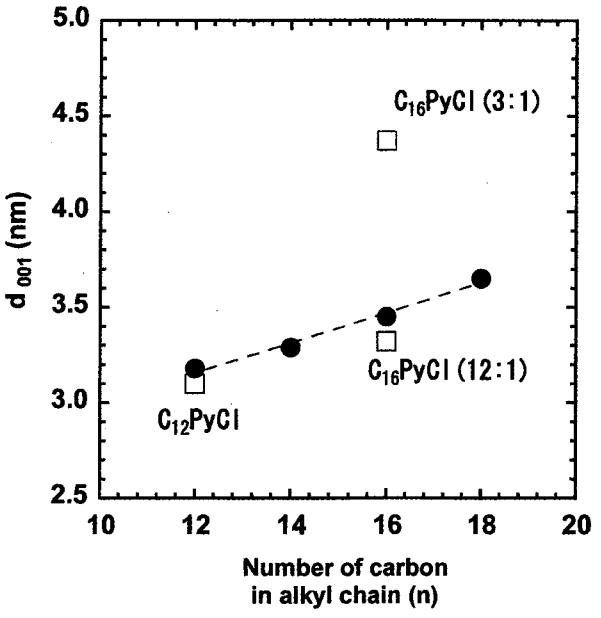

Figure 5 Relationship between d_{001} values of the $HCa_2Nb_3O_{10}$ -surfactant composites and number of carbon atoms of the surfactants. □; C_nPy, ●;C_nTMA

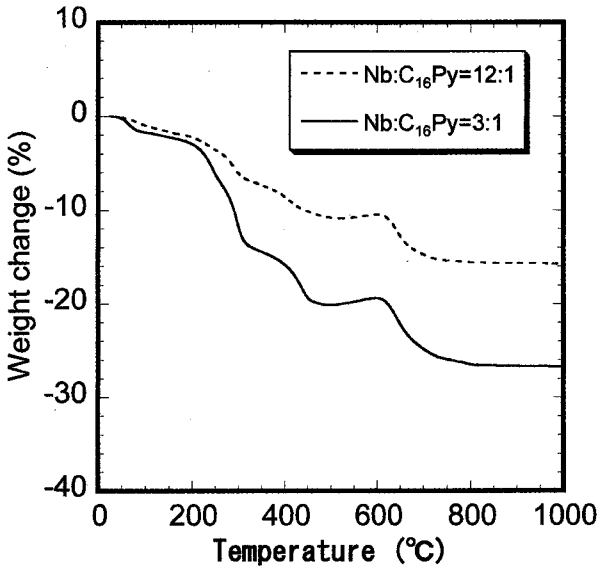

Figure 6 TG curves of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites

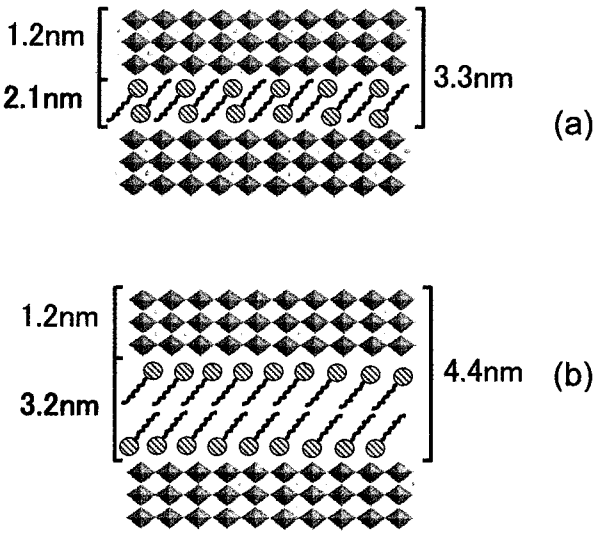

Figure 7 Structure models of $HCa_2Nb_3O_{10}$-$C_{16}Py$ composites for Nb:C_{16} PyCl= (a)12:1 and (b) 3:1

$KCa_2Nb_3O_{10}$ and the length of a $C_{16}Py^+$ ion is 2.4 nm. Taking into account of these dimensions and d_{001} of the composite for Nb: $C_{16}PyCl$=3:1, the interlayer spacing of the composite is estimated to be 3.2 nm, which is larger than the length of a $C_{16}Py^+$ ion. This suggests that the organic species in the interlayer would be form a bilayer arrangement with tilting. In the case of Nb:$C_{16}PyCl$=12:1, the interlayer spacing is estimated to be 2.1 nm, which is smaller than the length of a $C_{16}Py^+$ ion, suggesting that the organic species in the interlayer form a monolayer arrangement with tilting.

4 CONCLUSIONS

In the present study, we synthesized the composites consisting of multi-layered perovskite and cationic surfactants. The lamellar-type composites formed for the combinations of $HLaNb_2O_7$- or $HCa_2Nb_3O_{10}$-C_nTMA and $HCa_2Nb_3O_{10}$-C_nPy. The interlayer spacings of the composites were affected by the size of the surfactant and Nb:surfactant ratio in the reacting suspensions. From the results of XRD analysis for the composites, structural models of the $HCa_2Nb_3O_{10}$-C_{16}Py composites were proposed. From the comparison between size of the molecule and the interlayer spacing, it is suggested that two types of composites formed, which contain $C_{16}Py^+$ ions with mono- or bilayer arrangements. The arrangement would be controlled by the amounts of surfactants in the interlayer.

Acknowlegement

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