

High Throughput Preparation and Characterization of Pseudo-ternary Compounds by Combinatorial Wet-dry Process

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Pseudo-ternary compounds of $\text{LiO}_{0.5}\text{-X-TiO}_2$ (X: $\text{FeO}_{1.5}$, $\text{CrO}_{1.5}$ and NiO) system were prepared using fully automatic combinatorial robot system with the following functions: weighing and mixing of starting materials, heat treatment, and X-ray diffraction analysis. The composition range of the products with ramsdellite-type structure in $\text{LiO}_{0.5}\text{-X-TiO}_2$ (X: $\text{FeO}_{1.5}$, $\text{CrO}_{1.5}$ and NiO) showed to have a relationship to the ionic radii of the substitutional transition metals in octahedral site. Furthermore, in pseudo-ternary $\text{LiO}_{0.5}\text{-CrO}_{1.5}\text{-TiO}_2$ system, it was found that the ramsdellite-type compounds were obtained a wider composition range than the already reported in a short time.

Key words: Combinatorial wet and dry process, Combinatorial powder XRD, Electrode materials

1. INTRODUCTION

Combinatorial method has been developed in order to prepare and characterize a large number of materials in a short time, i.e. much faster than the conventional process. We have hitherto developed a fully automated combinatorial robot system for powder synthesis of inorganic materials and demonstrated its usefulness by preparing binary compounds [1].

We synthesized pseudo-ternary $\text{LiO}_{0.5}\text{-X-TiO}_2$ (X: $\text{FeO}_{1.5}$, $\text{CrO}_{1.5}$ and NiO) system as an example by using combinatorial robot system. $\text{LiO}_{0.5}\text{-FeO}_{1.5}\text{-TiO}_2$ system had already studied on the structure and phase relation by Grey [2], Yau [3] and Ma [4]. In this ternary system, six different structures; ramsdellite, spinel, pseudobrookite (Fe_2TiO_5), rock salt (Li_2TiO_3), hematite (Fe_2O_3) and rutile (TiO_2) structures; were reported. Also, Ma et al. reported that the Fe doped ramsdellite-type $\text{Li}_2\text{Ti}_3\text{O}_7$ showed excellent cycling performance as an electrode material in lithium batteries. Furthermore, Kajiyama et al. reported that Li-Cr-Ti-O with ramsdellite-type structure showed reversible deintercalation and intercalation of lithium ions at a potential of 4 V vs. Li/Li^+ [5]. In the same way, Li-Ni-Ti-O ramsdellite-type compounds expected as an electrode material because LiNiO_2 is a promising cathode material. However, Li-Ni-Ti oxides having ramsdellite structure were not reported.

2. EXPERIMENTAL

Figure 1 shows the fully automatic combinatorial robot system for the preparation of the ceramic powder. This system consists of the following sections: weighing and mixing of

starting materials, distributing of the mixtures to a reaction pallet, heating of these reactants, and characterizing of the products by powder X-ray diffraction. A robot hand (A-1) weighs, pipets and mixes starting materials by means of a micropipette, to which a disposable plastic chip (F) is attached. Starting materials used were solutions and slurries, which consist of nano-particles of oxides suspended in water or organic solvent. Such solutions or slurries are very useful for measuring and mixing the starting materials in this combinatorial processing. Starting materials in vials are placed at position (B). Predetermined amount of starting materials are pipetted from the vials to mixing vials (C) and then mixed. Pt reaction pallet (35×35×5mm) with 36 hollows of 4mm in diameter and 1.5 mm in depth is put on a hot plate (D). The mixture of the starting materials are poured into the hollows and then dried. The robot hand (A-2) carried the reaction pallet loaded with the samples to an electric furnace (E). The electric furnace (E) was developed for this combinatorial process. It can heat and cool the samples much faster than conventional ones. For example, it can heating the samples to 1573K within 15 minutes and cool them from 1573 to 473K, at which reaction pallet can be taken out from the electric furnace, within 25 minutes.

Products were characterized by powder X-ray diffraction. Powder X-ray diffraction was carried out by using a combinatorial X-ray diffractometer developed for the high throughput characterization of the products. Figure 2 shows the inside of the combinatorial X-ray diffractometer. This diffractometer is equipped with a slidable X-Y

stage and a position-sensitive proportional counter (PSPC). The reaction pallet is put on the X-Y stage, and the incident X-ray enters to one of the samples. The incident angle of X-ray (Cr-K α radiation: $\lambda = 0.22897\text{nm}$) is fixed at 10 degree, and the reflected X-ray is detected by PSPC. Consequently, the diffraction pattern is obtained without scanning a detector, and it takes only 2 minutes to obtain one pattern. After that, the X-Y stage slides for the measurement of the next sample.

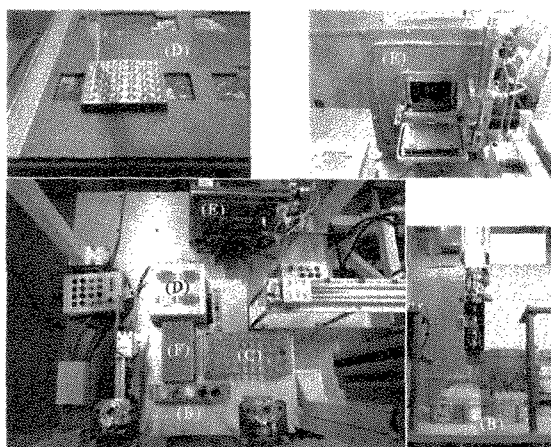


Fig.1 Photograph of the combinatorial robot system for preparing ceramic powders.

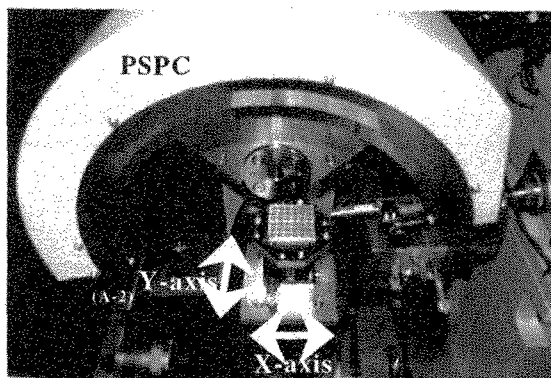


Fig.2 Photograph of the combinatorial X-ray diffractometer.

In this study, starting materials used were aqueous solutions of $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{Cr}(\text{OCOCH}_3)_3$ and $\text{Ni}(\text{NO}_3)_2$, and slurries of Fe_2O_3 and TiO_2 nano-particles suspended in water. These materials were placed in each vial, which was set at the starting position, and pipetted into mixing vials at the predetermined mixing ratio by using a micropipette attached to the robot hand. These liquids pipetted into mixing vials were mixed thoroughly by repetition of sucking and injecting for 50 times. These mixtures were molded into the hollows on reaction pallet. This plate was warmed

at about 373K by a heater, and the mixtures were dried on reaction plate. The molding and drying processes were repeated until the hollows were filled with powders. The chip of the micropipette attached to the head was disposed as needed in order to avoid contamination. Then, the reaction pallet was automatically transferred to an electric furnace, and heated at a temperature range from 1173 to 1373K for 5 hours.

3. RESULTS AND DISCUSSION

When the pseudo-ternary compounds were prepared with composition varying every 0.1 or 0.05, the number of ternary compounds to be synthesized leads to 66 or 213. First, we prepared 66 mixtures of the starting materials to synthesize the 66 kinds of oxides with compositions varying every 0.1 in order to find out the rough composition range where ramsdellite phase was observed.

Figure 3 shows phase diagrams of the samples heated at temperatures between 1173 and 1373K. The products that prepared from the starting materials with large contents of $\text{LiOH}\cdot\text{H}_2\text{O}$ did not give clear XRD patterns, because of Li_2O is hygroscopic to form a hydrate or likely to be sublimated at high temperature. Therefore, phases in the $\text{LiO}_{0.5}\text{-CrO}_{1.5}\text{-TiO}_2$ system were identified only in the composition range of $\text{Li}/(\text{Li}+\text{Cr}+\text{Ti}) \leq 0.3$. Plots in figure 1(a), (b), and (c) indicate compositions, where the structures are based on layer-type LiCrO_2 structure, spinel-type structure such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and rock salt-type Li_2TiO_3 structure, respectively. Figure 1(d) and (e) indicates composition ranges, where the other structures based on corundum (Cr_2O_3) and rutile (TiO_2) were observed, respectively. The structures of the products in the composition range indicated in figure 1(f) have not been identified. At a heating temperature of 1273K, ternary oxides with ramsdellite structure coexisting with other phases were obtained at compositions of Li: Cr: Ti = 4: 0: 6, 3: 3: 4, 3: 2: 5, 3: 1: 6, 3: 0: 7, 2: 1: 7 and 2: 0: 8 as shown in figure 1(g). When heated at 1373K, the samples with compositions of Li: Cr: Ti = 4: 1: 5 and 3: 4: 3 as well as the above compositions included the ramsdellite phase, and the single phase of ramsdellite structure appeared at compositions of 3: 2: 5 and 3: 1: 6.

Then, the other pseudo ternary compounds, which substituted $\text{CrO}_{1.5}$ for other transition metal oxides, i.e., $\text{FeO}_{1.5}$ and NiO , were prepared by the combinatorial robot system. Figure 4 shows ternary phase diagrams of $\text{LiO}_{0.5}\text{-X}$ (X: $\text{CrO}_{1.5}$, $\text{FeO}_{1.5}$ and NiO)- TiO_2 heated at 1373K.

Most of the products with compositions of $\text{Li}/(\text{Li}+\text{Fe}+\text{Ti}) \geq 0.3$ had spinel structure, and the rest had that based on for the rock salt-type Li_2TiO_3 . On the other hand, the products with compositions of $\text{Li}/(\text{Li}+\text{Fe}+\text{Ti}) \leq 0.2$ were single or multi phase of the following structures: spinel, pseudobrookite, rutile and hematite. In addition, the ramsdellite-type structure appeared in the

products heated at 1273K and 1373K in the following mole ratio: $\text{LiO}_{0.5}$: $\text{FeO}_{1.5}$: TiO_2 = 4: 1: 5, 4: 0: 6, 3: 2: 5, 3: 1: 6, 3: 0: 7 and 2: 0: 8.

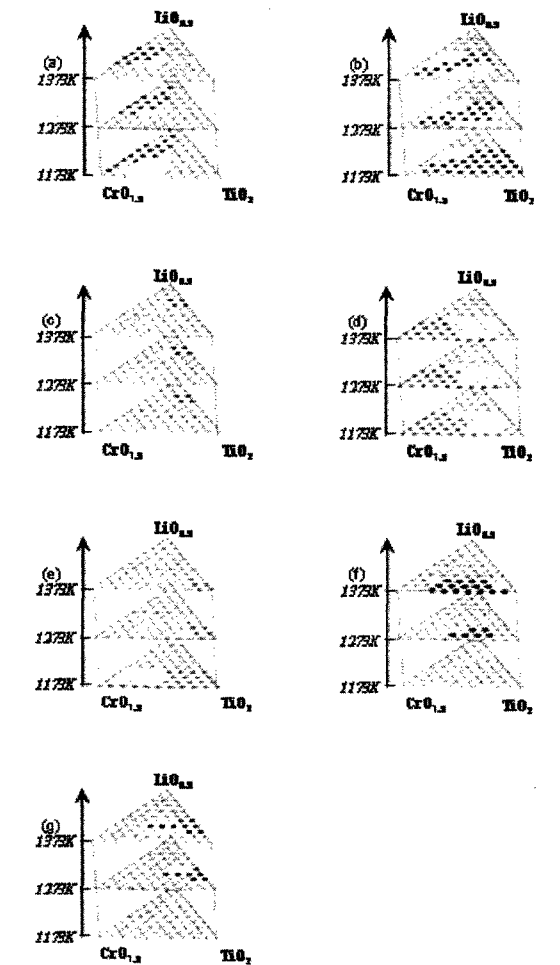


Fig.3 Phase diagrams of $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{TiO}_2$ ternary compounds.

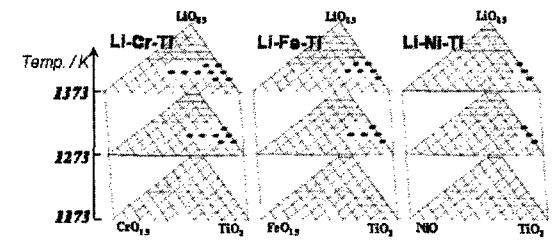


Fig.4 Phase diagrams of $\text{LiO}_{0.5}-\text{X}-\text{TiO}_2$ (X: $\text{FeO}_{1.5}$, $\text{CrO}_{1.5}$ and NiO) ternary system, which were made range from at 1173 to 1373K for 5 hours.

On the other hand, the ramsdellite-type compounds in ternary system $\text{LiO}_{0.5}-\text{NiO}-\text{TiO}_2$ were only binary system of $\text{LiO}_{0.5}$: NiO : TiO_2 = 4: 0: 6, 3: 0: 7 and 2: 0: 8. The closed and open circles indicate the compositions, at which the

single phase of ramsdellite-type structure and the multi phase with ramsdellite phase were obtained, respectively. From these results, it was considered that the difference of composition range for ramsdellite-type structure in pseudo-ternary system $\text{LiO}_{0.5}-\text{X}$ (X: $\text{CrO}_{1.5}$, $\text{FeO}_{1.5}$ and NiO)- TiO_2 was caused by larger than ionic radii in octahedral site of Fe^{3+} and Ni^{2+} than Cr^{3+} , because the ionic radii of Cr^{3+} is close to that of Ti^{4+} .

Then, in the secondary step, we prepared the oxides with compositions varying every 0.05 around the region in order to find out the composition range for the formation of ramsdellite-type structure in detail. Figure 5 is the finally-obtained ternary phase diagrams of the Li-Cr-Ti oxides heated at temperatures between 1273 and 1373K for 5 hours. The closed and open circles indicate the compositions, at which the single phase of ramsdellite-type structure and the multi phase with ramsdellite phase were obtained, respectively. In the previous study [5], formation of ramsdellite structure was investigated for the compounds with compositions of $\text{Li}_{2-x/3}\text{Cr}_x\text{Ti}_{3-2x/3}\text{O}_7$ ($0 \leq x \leq 1.5$), i.e. only on a tie line where the ratio of cation to anion was 5 to 7.

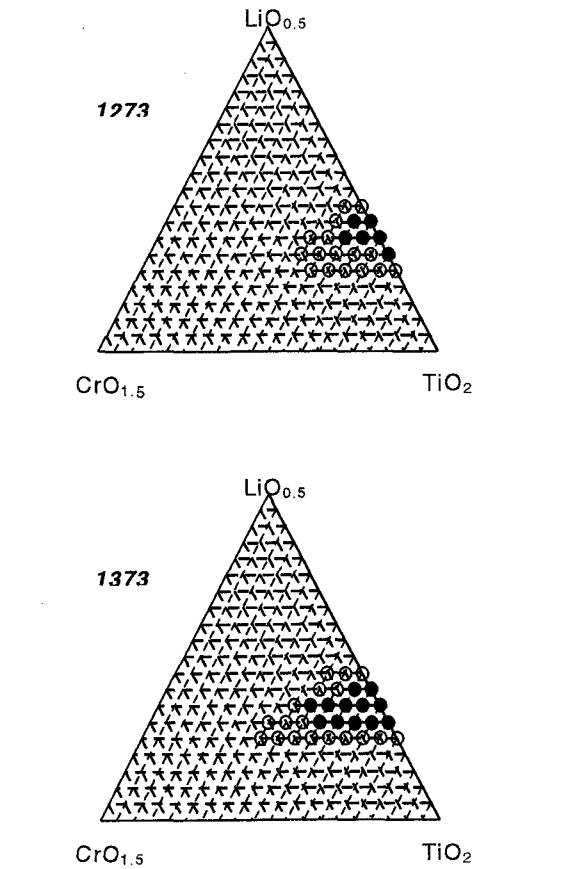


Fig.5 Phase diagrams of $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{TiO}_2$ pseudo ternary system.; ○: ramsdellite and other structure, ●: ramsdellite structure

Our developed system complete about 2 hours for weighing and mixing starting materials, and heating the mixtures, about 5 hours for heat treatment, and about 1 hour for XRD measurement for about 70 samples. As a result, preparation and characterization about 200 combinations can be obtained in one day. These results demonstrated that combinatorial process is very useful for exploration of new and functional materials and establishment of phase diagrams in a short time.

REFERENCES

- [1] I. Yanase T. Ohtaki and M. Watanabe, *Applied Surface Science*, 189, 292-299 (2002)
- [2] I. E. Grey, C. Li and T. Ness, *Journal of Solid State Chemistry*, 141, 221-228 (1998)
- [3] Y. C. Yau and J. M. Hughes, *Journal of the American Ceramic Society*, 66(7), 479- (1983)
- [4] S. MA and H. Noguchi, *Electrochemistry*, 69(7), 526-529 (2001)
- [5] A Kajiya, K. Takada, K. Arihara, T. Inada, H. Sasaki, S. Kondo and M. Watanabe, *Journal of Electrochemical society*, 150(2), A157-A160 (2003)

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