

# Effective algorithm for material exploration in ceramics with combinatorial technology

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## Abstract

A reaction phase diagram of pseudo-ternary  $\text{LiO}_{0.5}\text{--CrO}_{1.5}\text{--TiO}_2$  compounds was established using a fully automatic combinatorial robot system in order to demonstrate the effective application of the combinatorial process. The following crystal structures were obtained by heat treating starting materials at temperatures between 1173 and 1373 K: ramsdellite, spinel, layer, rock salt, corundum, and rutile. The ramsdellite-type compounds in this pseudo-ternary system were obtained rapidly and within a wider composition range than previously reported.

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## 1. Introduction

Material explorations based on combinatorial chemistry began with the synthesis of peptides by Merrifield.<sup>1</sup> Recent progress in the field has led to the development of highly promising processes such as the thin film fabrication process using masking technology based on PLD, and the powder preparation process based on solid state reaction method and solution process.<sup>2–6</sup> Our group developed a combinatorial robot system that fully automates the preparation of ceramic powders based on the conventional solid state reaction process in air, from the weighing and mixing of the starting materials to the processing of the compounds in an electronic furnace. We also developed a combinatorial powder X-ray diffraction device that can prepare and identify about 200 compounds in 1 day. This combinatorial process can prepare compound groups with numerous composition ratios far more rapidly than the conventional preparation method.

One of the drawbacks to this combinatorial process is the staggering number of data generated when many elements are combined in the system without an adequate research plan. For example, in preparing compounds with three components changes in the composition ratio of each raw material at steps of 10, 5, and 2% leads to 66, 231 and 1326 combinations, respectively. When adding another component to prepare four-component compounds, changes in the composition ratio at the same steps lead to 506, 3311 and 45526 combinations. If the experimental results are to have optimal accuracy, the number of compounds that must be prepared grows exponentially. Under this condition, the use of combinatorial chemistry for detailed experiments requires a great deal of time.

In this study, we prepared a pseudo-ternary  $\text{LiO}_{0.5}\text{--CrO}_{1.5}\text{--TiO}_2$  system using the combinatorial robot system to illustrate the effective application of the combinatorial process. Safonov et al.<sup>7</sup> and Grey et al.<sup>8</sup> have already reported the  $\text{LiO}_{0.5}\text{--CrO}_{1.5}$  and  $\text{LiO}_{0.5}\text{--TiO}_2$  pseudo-binary systems, respectively. Further, Lee<sup>9</sup> and Pownceby et al.<sup>10</sup> and Somiya et al.<sup>11</sup> have described the phase diagrams of the  $\text{CrO}_{1.5}\text{--TiO}_2$  system at temperatures below 1673 K and in the range

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between 1673 and 2038 K, respectively. While the binary systems have been reported, the pseudo-ternary system between them still attracts greater interest due to its application to lithium batteries. Two different structures, i.e. ramsdellite and spinel structures have been reported in the pseudo-ternary system. Unlike the oxides with the spinel structure, those with the ramsdellite structure show reversible deintercalation and intercalation of lithium ions at a potential of 4 V versus  $\text{Li}/\text{Li}^+$ , a property that makes them suitable as cathode materials in lithium batteries.<sup>12</sup> If this ramsdellite structure is to be applied to batteries, it will be very important to first establish the conditions for synthesizing the structure.

## 2. Experimental

Pseudo-ternary Li–Cr–Ti oxides were prepared using the fully automatic combinatorial robot system developed in our laboratory. Starting materials included aqueous solutions of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{Cr}(\text{OCOCH}_3)_3$  and a slurry of  $\text{TiO}_2$  nanoparticles suspended in water. Solutions of this type are very useful for measuring and mixing starting materials in this combinatorial method. The materials were placed in vials at the starting position and pipetted into mixing vials at pre-determined mixing ratios using a micropipette attached to the robot hand. The liquids pipetted into each mixing vial were thoroughly mixed by repeatedly drawing them out of the vials and injecting them back in (50 repetitions). Next, solutions mixed at various component ratios were poured into hollows (36 hollows, 4 mm diameter  $\times$  1.5 mm depth) on a series of reaction pallets (35 mm  $\times$  35 mm  $\times$  5 mm each) and dried by heating at about 373 K on a hot plate. The pouring and drying processes were repeated until the hollows were filled with powders, whereupon the reaction pallet was automatically transferred to an electric furnace and baked for 5 h at a temperature of between 1173 and 1373 K. The

products obtained after baking were identified by a combinatorial powder X-ray diffractometer designed for the rapid and high-throughput characterization of products (jointly developed by our group and Rigaku Denki Corporation). The diffractometer is equipped with a slidable X–Y stage and a position-sensitive proportional counter (PSPC). Once the reaction pallet is placed on the X–Y stage, the incident X-ray enters one of the samples, the data is collected, and the X–Y stage slides to measure the next sample.

The present study was conducted in two steps which concept is shown in Fig. 1, the first to find the rough composition range where the ramsdellite phase can be observed, and the second to find the detailed composition range where ramsdellite-type structures are formed. So, in the first stage we combined the starting materials into 66 mixtures in order to synthesize 66 kinds of oxides with compositions adjusted at 10% steps. In the secondary stage, we prepared the oxides with compositions adjusted at 5% steps around the formation region of ramsdellite-type structure.

## 3. Results and discussion

Fig. 2 shows reaction phase diagrams of the samples heated at temperatures between 1173 and 1373 K. The products prepared from starting materials with large contents of  $\text{LiOH}\cdot\text{H}_2\text{O}$  did not yield clear XRD patterns due to the hygroscopic property of  $\text{Li}_2\text{O}$  and the sublimation of  $\text{Li}_2\text{O}$  at high temperature. For this reason, the reaction phases in the  $\text{LiO}_{0.5}\text{–CrO}_{1.5}\text{–TiO}_2$  system were identified only in the composition range of  $\text{Li}/(\text{Li} + \text{Cr} + \text{Ti}) \leq 0.3$ . The colored regions in Fig. 2(a)–(c) indicate the compositions of the layer-type  $\text{LiCrO}_2$  structure, spinel-type structures such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and rock salt-type  $\text{Li}_2\text{TiO}_3$  structure, respectively. Fig. 2(d) and (e) indicate the composition ranges where the other structures based on corundum ( $\text{Cr}_2\text{O}_3$ )- and rutile ( $\text{TiO}_2$ )-

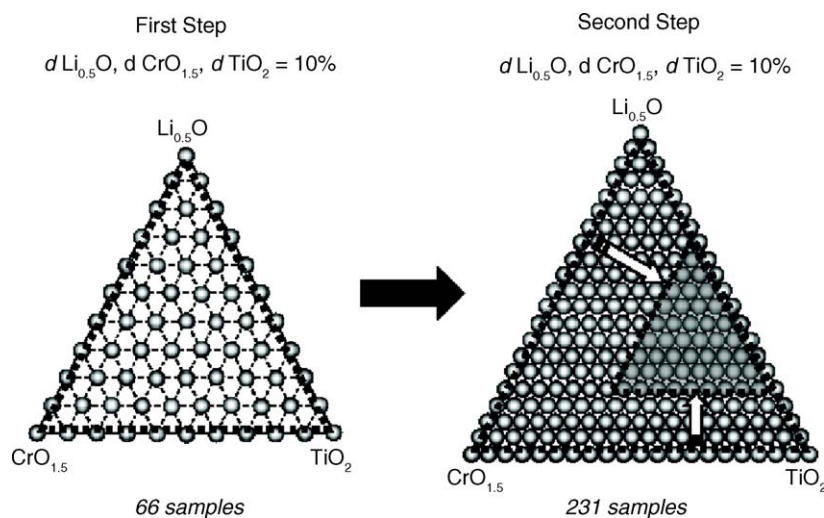


Fig. 1. Effective process in the combinatorial material exploration. Aim of the first step experiment is to find composition range of various crystal structures in rough. The second step finds the detailed composition range where the searching structure is formed.

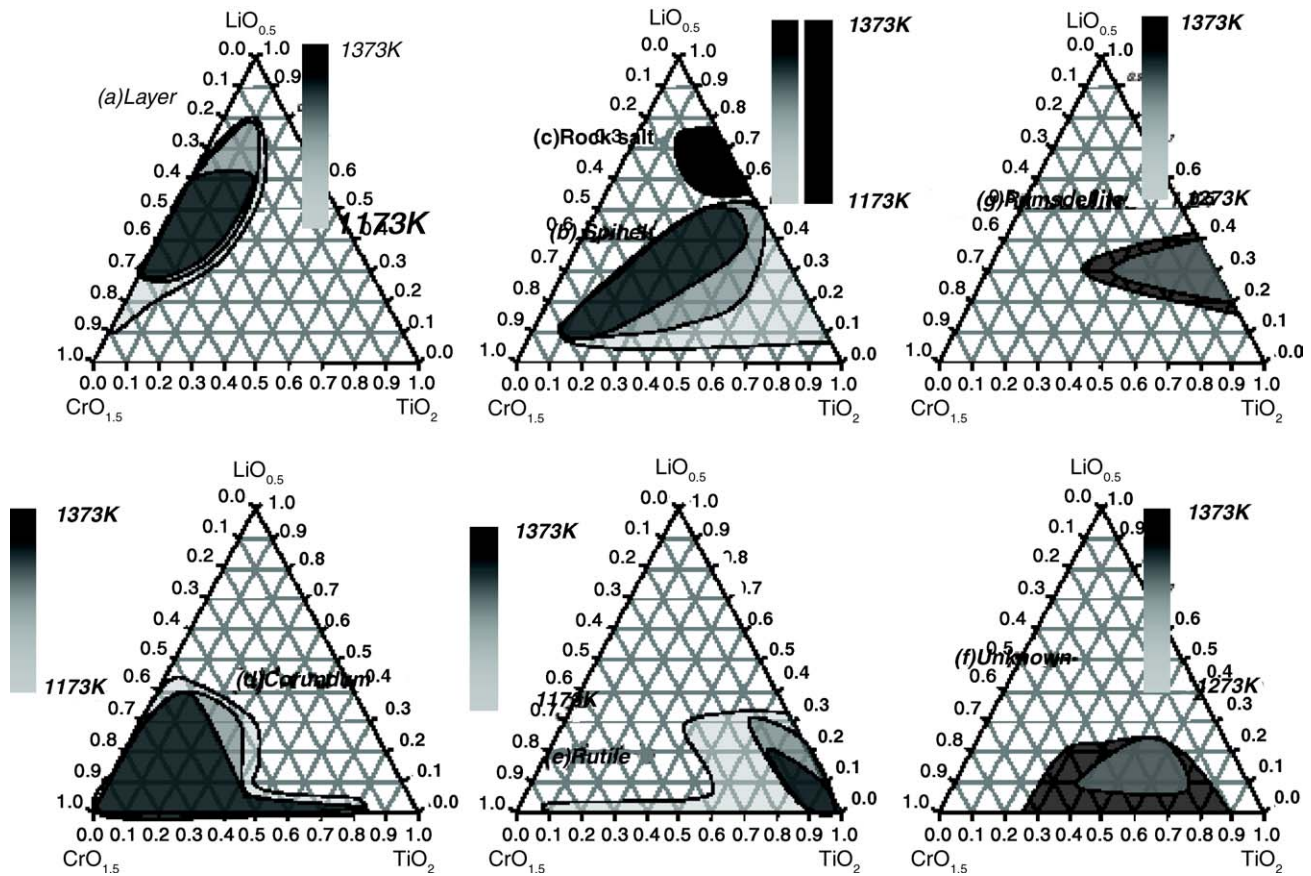


Fig. 2. Reaction phase diagrams of  $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{TiO}_2$  ternary compounds. The samples were heated at temperatures between 1173 and 1373 K for 5 h: (a) layer structure based on  $\text{LiCrO}_2$ ; (b) spinel structure such as  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ; (c)  $\text{Li}_2\text{TiO}_3$ ; (d) not determined structure; (e) corundum structure; (f) rutile structure; (g) ramsdellite structure based on  $\text{Li}_2\text{Ti}_3\text{O}_7$ .

type structures, were observed, respectively. The structures of the products in the composition range indicated in Fig. 2(f) have not been identified. At a heating temperature of 1273 K, ternary oxides with a ramsdellite structure, partly coexisting with other phases, were obtained at Li:Cr:Ti compositions of 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 Fig. 2(g). At a heating temperature of 1373 K, the ramsdellite phase was obtained in the samples prepared at the above compositions, as well as the Li:Cr:Ti compositions of 4:1:5 and 3:4:3.

Fig. 3 shows the finally obtained ternary phase diagrams of the Li–Cr–Ti oxides heated at temperatures between 1273 and 1473 K for 5 h. The closed and open circles indicate the compositions at which the single phase of the ramsdellite-type structure and the multi phase with the ramsdellite phase were obtained, respectively. In a previous study we investigated the formation of the ramsdellite structure from 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 with a cation-to-anion ratio of 5 to 7. The use of the combinatorial method in the present study allowed us to investigate the formation region of the ramsdellite phase in the whole composition range in order to establish the phase diagrams within a period of only 2 days.

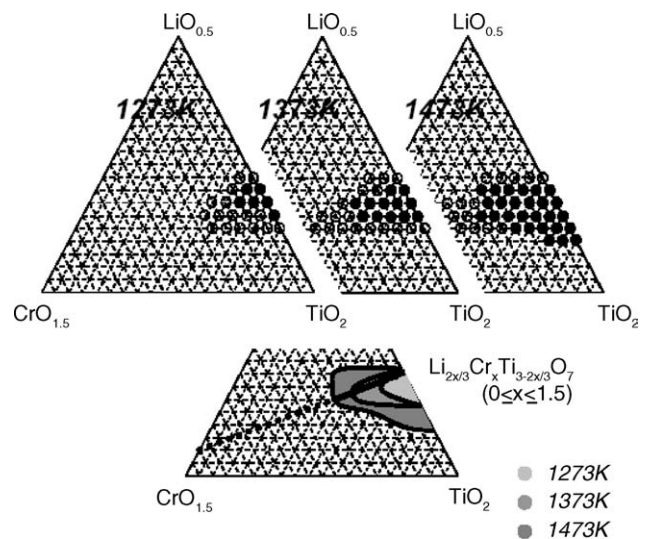


Fig. 3. Phase diagrams of  $\text{Li}_2\text{O}-\text{Cr}_2\text{O}_3-\text{TiO}_2$  pseudo-ternary system. The samples were heated at temperatures from 1173 to 1373 K for 5 h: (a) 1273 K; (b) 1373 K; (c) 1473 K; (○) ramsdellite and other structure, (●) ramsdellite structure.

#### 4. Conclusion

We investigated the phase relation of the pseudoternary  $\text{Li}_2\text{O}-\text{CrO}_{1.5}-\text{TiO}_2$  system using a fully automatic combinatorial process in order to explore the composition range in which the ramsdellite structure is formed. The ramsdellite-type compounds prepared using this system were obtained within a wider composition range than has been previously achieved. Furthermore, the two-step approach used in the study was effective for high-throughput screening for the determination of composition ranges and the detailed exploration of structures.

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