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Dependency of mechanochemical reactions forming complex oxides on the crystal structures of starting oxides

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Mechanochemical reactions applicable to syntheses of perovskite-type compounds, $LaMO_3$, where M is trivalent metals, are taken as examples to investigate effects of crystal structures of starting materials, M_2O_3, on the reactions. The investigated oxides M_2O_3 are categorized into two groups: one is the corundum structure and the other the non-corundum structure. Under the experimental conditions, it has been found that the oxides with non-corundum structure react easily with La_2O_3 by their co-grinding at room temperature to form the corresponding compounds. On the contrary, none of such reactions can be occurred for the oxides with corundum structure. The difference has been discussed based on the grinding-induced phase transformation from loose packing of atoms to close packing of atoms. Based on the results, the extension to the synthesis of other compounds such as CrO_2 is presented.

1. Introduction

Ball mill has been used mainly to obtain size reduction of samples. Its use has recently been extended to a wide range such as stimulation of solid state reaction, so-called mechanochemical reaction, especially during high-energy dry milling. The reported mechanochemical reactions involve almost all the aspects of chemistry [1–6] and the interests in this research field tend to rise continuously, considering the increasing number of the related papers published annually. Unfortunately, there are, at present, no general rules that govern the various types of mechanochemical reactions and summarize the mass of details and rationalize the observations [7, 8]. There exists practical difficulty in summarizing all the experimental results from different researchers because various types of mills have been used and the energy level supplied may vary by cases. However, it seems to be interesting and necessary to make generalization beginning from a narrow range, if not possible covering all the ranges of mechanochemistry. It is believed that even such a generalization in narrow range will be of guiding effect for further research work. We have been attempting to summarize our experimental results on the mechanochemical synthesis of perovskite-type compounds. In this paper, we wish to report our findings that the reactivity of a starting sample depends closely on its crystal structure.

Perovskite-type compounds have been chosen as a research target, due to mainly the following two reasons. First, a large group of materials with perovskite structures exhibit various unique physico-chemical properties, depending on the constituent elements. Some, if not all, properties could be improved by mechanochemical synthesis, because this process produces very fine samples with active spots. Second, even only as La_2O_3 is concerned, with La in A-site, many trivalent metal oxides, M_2O_3, react with it to form various $LaMO_3$ with perovskite structure. This offers a large number of comparable studies that enhance reliability of the summarization on the entitled subject.

In this work, reactivity with La_2O_3 and phase transformation during grinding of oxides with cubic structure (Mn_2O_3, In_2O_3, Y_2O_3), oxides with both alpha and gamma structure (Al_2O_3, Fe_2O_3), Cr-oxide (α-Cr_2O_3) and Ga-oxide (both α- and β-Ga_2O_3) were investigated. Preparation of oxides with high reactivity instead of the corresponding crystalline ones and the application of the prepared samples to the syntheses of other functional materials as well as the perovskite sample are also discussed.

2. Experiment

Most of the samples used in the experiment were supplied from Wako Pure Chemicals Industry Co., Japan, except for the following specific indications. γ-Fe_2O_3 was obtained from High Purity Chemicals Laboratory, Japan. γ-Al_2O_3 was prepared by calcining $Al(OH)_3$ at 600°C for 2 h. α-Ga_2O_3 and β-Ga_2O_3 were prepared by calcining $Ga(OH)_3$ at 420 and 1000°C for 24 h,

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respectively. All the trivalent metal oxides were mixed with La_2O_3 in equimolar ratio as starting materials for grinding.

Grinding operation was conducted by using a planetary ball mill (P-7, Fritsch, Germany). 4 g of the oxide samples or mixed samples were put in a zirconia pot (45 cm^3) with 7 zirconia balls of 15 mm in diameter. The mill was run at approximately 600 rpm in air for 3 h. X-ray diffraction (XRD) analysis was performed to identify the phases in the samples before/after the grinding operation.

3. Results and discussion

The results indicate that oxides M_2O_3 with corundum structure (e.g., α-Al_2O_3, α-Fe_2O_3 and α-Cr_2O_3) do not react with La_2O_3 mechanochemically. On the other hand, as shown in Fig. 1, different phenomena are observed when oxides with cubic structures, e.g., Mn_2O_3, In_2O_3, Y_2O_3, γ-Al_2O_3, γ-Fe_2O_3, are used. The XRD patterns correspond to those of products, $LaMO_3$, accompanied by the complete disappearances of the starting oxides (La_2O_3 and M_2O_3). Solid state reactions induced by grinding occur to form $LaMO_3$ as follows:

$$La_2O_3 + M_2O_3 = 2LaMO_3 \qquad (1)$$

Further investigation has shown that besides oxides with cubic structure, the reaction occurs between oxides with different crystal structures, e.g. β-Ga_2O_3 with monoclinic structure reacts mechanochemically with La_2O_3 to form $LaGaO_3$. The diffraction patterns of the reaction products of the milling of the α-Ga_2O_3/La_2O_3 mixture and of the β-Ga_2O_3/La_2O_3 mixture are compared in Fig. 2. Although one small peak designated with circle mark can be attributed to that of $LaGaO_3$, a broadened peak corresponding to La_2O_3 is still observed when α-Ga_2O_3 is used, indicating that such solid state reaction in the α-Ga_2O_3/La_2O_3 system does not occur easily. In fact, both α-Ga_2O_3 and β-Ga_2O_3 are prepared by heating Ga-hydroxide. α-Ga_2O_3 is obtained at low temperature, while β-Ga_2O_3 is obtained at high temperature. Low temperature operation allows us to prepare α-Ga_2O_3 particles finer than that of β-Ga_2O_3. Generally, sample with smaller particle size is expected to exhibit high reactivity. The converse results between α-Ga_2O_3 and β-Ga_2O_3 indicate that the effect of crystal structure on the reactivity is superior to that of particle size.

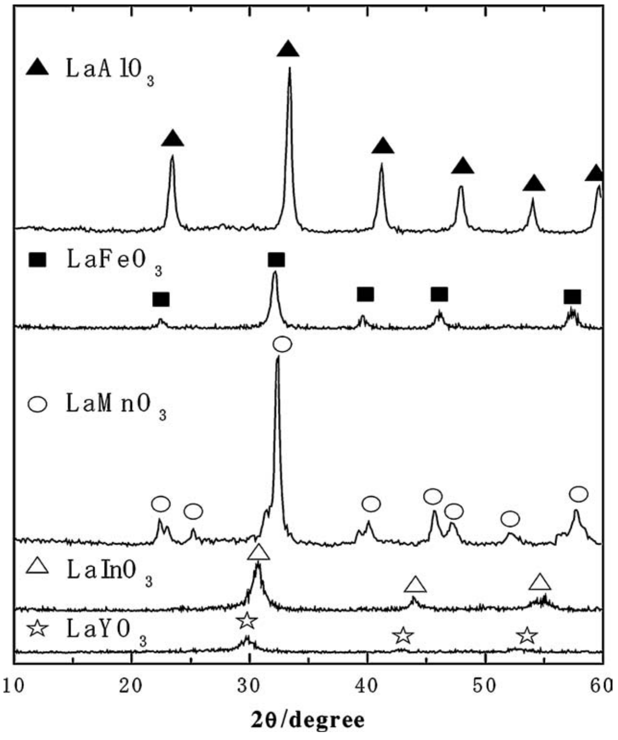

Figure 1 XRD patterns of the products of grinding of the mixture of La_2O_3 and M_2O_3 with cubic structure.

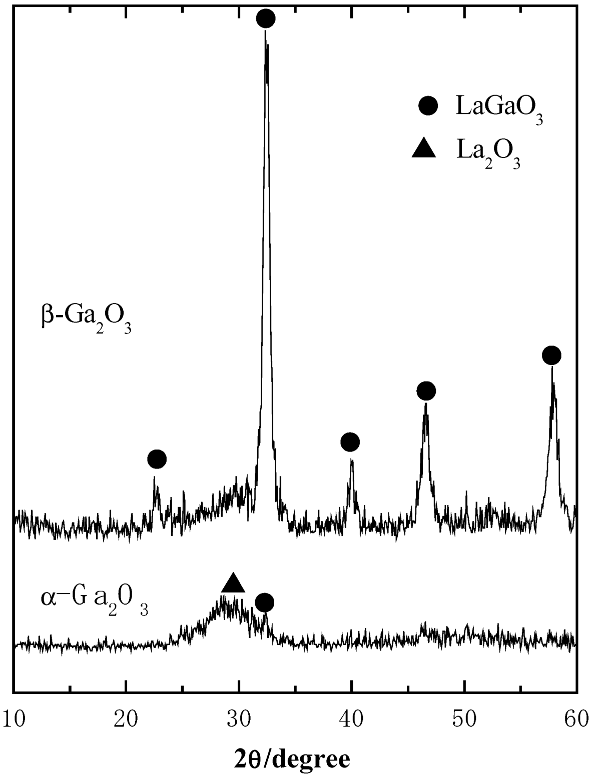

Figure 2 XRD patterns of reaction products of the milling of the α-Ga_2O_3/La_2O_3 mixture and of the β-Ga_2O_3/La_2O_3 mixture.

Taking the above results into account, it can be concluded that trivalent metal oxides with cubic or monoclinic structure react easily with La_2O_3 to generate corresponding $LaMO_3$ compounds. None of such reaction is observed in the cases of oxides with corundum structure.

In order to examine this phenomenon, these starting trivalent metal oxides are also ground individually at the same grinding conditions. In fact, researches on the phase transformations in oxides have been reported [9–12]. Although not shown here, it is found that after grinding, the oxides (α-Al_2O_3, α-Fe_2O_3 and α-Cr_2O_3) with corundum structure still maintain the crystalline structure unchanged, except for the decrease in the peak intensity with the increase in the grinding time. When other oxides (γ-Fe_2O_3, β-Ga_2O_3, C-Y_2O_3) with non-corundum structure are ground, polymorphic transformations take place from the cubic and monoclinic phases to the rhombohedral phase (corundum structure). As shown in Fig. 3, γ-Fe_2O_3 and

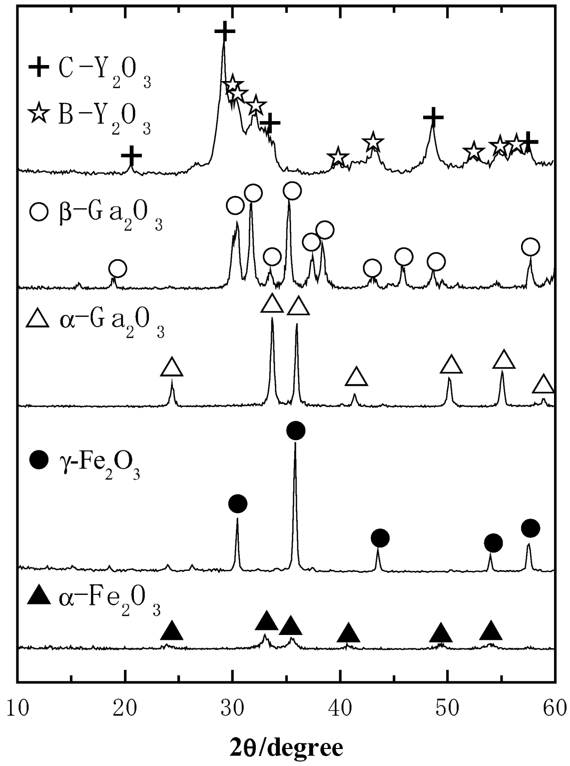

Figure 3 Phase transformations in the ground simple oxides (see text for details).

β-Ga_2O_3 transform into α-Fe_2O_3 and α-Ga_2O_3, respectively, both with corundum structure. C-Y_2O_3 transforms to B-Y_2O_3, with a sort of approximate corundum structure. Table I illustrates the change of density and crystal structure of oxides induced by grinding. Through the increase of density and change of structure, it can be concluded that grinding makes the crystal lattice of these oxides distorted and changes the relative distribution between atoms. These varieties induce the phase transformation from loose packing to close packing of atoms, accompanied by the increase in density. When these oxides are ground with other compounds, e.g., La_2O_3, the changes do not stay at the phase transformation, but new compounds with other compositions are formed, i.e., mechanochemical reaction takes place. The co-existence of La_2O_3 prevents the phase transformation of these oxides. The rearrangement of the heterogeneous constituents results in a new compound. On the other hand, the oxides with the stable corundum structure remain unchanged during grinding. It is difficult to expect a new combination with other compound without the destruction of the original structure.

TABLE I Changes of density and crystal structure of oxides caused by mechanochemical treatment

	C-Y_2O_3 → B-Y_2O_3	
Crystal structure	cubic	monoclinic
Density (g/cm^3)	5.03	
	β-Ga_2O_3 → α-Ga_2O_3	
Crystal structure	monoclinic	rhombphedral
Density (g/cm^3)	5.9	6.44
	γ-Fe_2O_3 → α-Fe_2O_3	
Crystal structure	cubic	rhombphedral
Density (g/cm^3)	5.07	5.29

The above results are very helpful for choosing starting samples for designing a specific reaction. Since the oxide with corundum structure can not be used for the mechanochemical preparation of complex oxide (due to the reason mentioned above), the preparation of a suitable sample (as a precursor) is needed to overcome the barrier. Several successful cases have been reported [13–15]. Taking the synthesis of $LaCrO_3$ as an example, instead of the use of crystalline Cr_2O_3, we prepared an amorphous hydrated oxide, $Cr_2O_3 \cdot nH_2O$, with similar composition to CrOOH, by calcining available reagent of $Cr(OH)_3 \cdot nH_2O$ at a relatively low temperature. $LaCrO_3$ can be easily obtained by grinding the prepared sample with La_2O_3 [14].

The application of the specifically prepared sample has been extended to the synthesis of CrO_2, a metastable compound with ferromagnetic properties at room temperature. CrO_2 is usually prepared by heating CrO_3 under high pressure of oxygen in order to prevent the formation of Cr_2O_3, a more stable compound. The mechanochemical process offers a simple way to synthesize CrO_2 based on the following reaction formula:

$$2CrOOH + CrO_3 = 3CrO_2 + H_2O \qquad (2)$$

It is expected that CrO_2 can be prepared by solid state reaction between hexavalent oxide (CrO_3) and trivalent oxide (CrOOH). Similar to the results of synthesis of perovskite compounds, CrO_2 can be obtained by grinding CrO_3 with the prepared $Cr_2O_3 \cdot nH_2O$, and not such reaction was observed in the case of the use of crystalline Cr_2O_3 sample. 120 min grinding allows a nearly completeness of the reaction. Since CrO_2 is metastable compared to the crystalline Cr_2O_3, small peaks of Cr_2O_3 appeared in the pattern of the ground sample (see Fig. 4). It has been found that a little excess addition of CrO_3 is beneficial to the prevention of formation of Cr_2O_3, shown in Fig. 4. Magnetic evaluation of the prepared samples indicated that it does not match the commercially available sample. The main

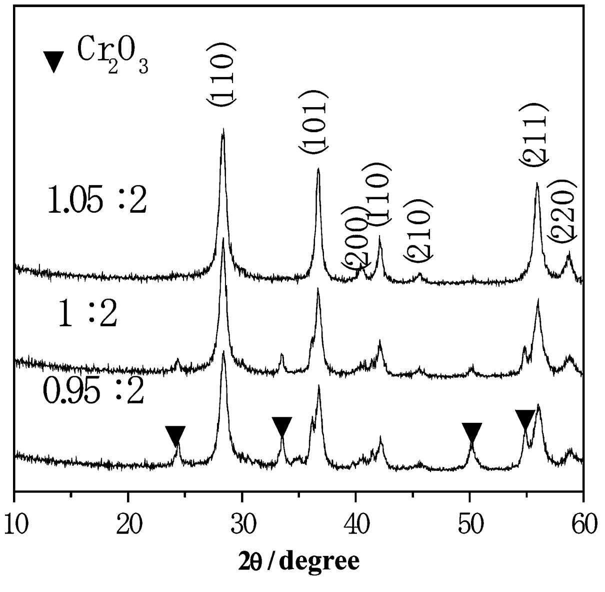

Figure 4 XRD patterns of reaction products of the milling of the CrO_3/CrOOH mixture with different adding molar ratio of CrO_3.

reason may come from the morphology. SEM observations have revealed that different from the needle-like morphology of the commercial one, the ground sample exhibits agglomeration state of fine particles, disadvantage for the magnetic output.

Further researches on the use of the synthesis reaction have been conducted as an easy doping method. By substituting hexavalent CrO_3 by other hexavalent oxides such as MoO_3 and WO_3 and pentavalent oxides such as V_2O_5, a doped CrO_2 can be easily obtained by mechanochemical route. Another doping method is to use trivalent and/or tetravalent oxides to replace CrOOH. The combination of elements with different valences is promising also in doping the basic CrO_2 material. This offers an easy method to regulate the magnetic resistance of the prepared sample by doping various elements in different molar ratio. The detailed characterizations of the vanadium and iron doped CrO_2 samples are under investigation.

4. Conclusion

The dependency of mechanochemical reaction on the crystalline structure of starting sample, with the examples of the syntheses of perovskite-type compounds and metastable CrO_2, has been presented in this paper. The revealed results exhibit a guiding effect in choosing the starting compounds to achieve the mechanochemical stimulation of specific solid state reaction. It is expected that the choice of the starting materials with high reactivity by regulating the crystalline states allows us to take versatile applications of the mechanochemical process in the syntheses of various types of functional materials.

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