



Correlation between mechanochemical reactivity forming ABO_4 -type complex oxides and the structures of product materials

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ABSTRACT

Through the experiments for syntheses of ABO_4 (A : Al, Fe, Cr, In, La, Bi; B : P, V, Nb, Sb), investigations on the relation between mechanochemical reactivity and (I): the crystal structure of starting materials or (II): the crystal structure of product materials has been conducted. It has been found that it is a necessary condition to use structurally active substances against milling operation for the occurrence of a mechanochemical reaction. In addition, it is easier to facilitate a mechanochemical reaction to form ABO_4 -type oxide which is of larger size of cation and in denser structural state.

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1. Introduction

Mechanical milling has been used in a wide range even up to solid-state reaction, so-called mechanochemical reaction, especially during high-energy dry milling. The reported mechanochemical reactions cover almost all the aspects of chemistry [1–15] and the interests in this field tend to rise continuously, considering the increasing number of the related papers published annually. However, there exists the need for further understanding the nature of mechanochemical reaction and more effort to summarize the experimental results, considering the current situation, of which the mechanochemical synthesis is conducted mostly based on researchers' experience because there are no general rules that govern the various types of mechanochemical reactions and rationalize the observations. In our past investigations [16,17], it has been found that the mechanochemical reactions depend on the crystal structures of starting materials and the starting materials which easily undergo polymorphous transformation from loose packing to close one of atoms seem to have high reactivity. For example, γ - Al_2O_3 rather than α - Al_2O_3 reacts with La_2O_3 to form $LaAlO_3$ mechanochemically [18]. This does not mean that γ -alumina can react mechanochemically with any other active samples by grinding operation. Recently we have published several reports on the syntheses of ABO_4 -type oxides based on mechanochemical reactions between trivalent oxides (A_2O_3) and pentavalent oxides (B_2O_5) [19–21]. We have found that γ - Al_2O_3 does

not react even with phosphorus pentoxide (P_2O_5), although both compounds are active and react with other compounds easily. Clearly there is a need to develop general rules to realize a wide range of understanding on mechanochemical reactions. This may allow further improvement and application for designing new materials or other research fields.

As one effort for the aim, the purpose of this work is to clarify the mechanism of the involved mechanochemical reactions to form ABO_4 -type oxides, of which the variety of the crystal structures [22,23] allows a reasonable approach toward the correlation between the occurrence of a mechanochemical reaction and the crystal structures of starting and product samples. Since many factors including both mechanical operation and chemical natures of the used compounds may influence the occurrence of mechanochemical reaction, the data obtained at the same conditions of milling operation are used. And the focus is put on the effects of physicochemical properties of chemical compounds involved.

2. Experimental

In_2O_3 , La_2O_3 , Bi_2O_3 , P_2O_5 , V_2O_5 and Nb_2O_5 (Wako Pure Chemical Industries Ltd., Japan), $FeOOH$ (goethite phase, Kojundo Chemical Lab. Co., Ltd., Japan) and Sb_2O_5 (Sigma-Aldrich, USA). $Cr_2O_3 \cdot nH_2O$ (amorphous phase) prepared by calcining $Cr(OH)_3 \cdot nH_2O$ at 300 °C for 2 h, were used in this experiment. $AlOOH$ (boehmite phase) was prepared by calcining $Al(OH)_3$ at 400 °C for 2 h. For prevention of water absorption, P_2O_5 was handled under dry air through all experiment. Trivalent oxide or oxy-hydroxide (A_2O_3 or $AOOH$) and pentoxide (B_2O_5) were mixed with equal A/B atomic ratio, and 2 g of the mixture were put into a zirconia pot of 45 cm³ inner volume with 7

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zirconia balls of 15.7 mm diameter. Grinding operation was conducted in air by using a planetary ball mill (P-7, Fritsch, Germany). The milling was operated normally at 700 rpm for 2 h, through the experiment. In case of no observation of reaction product, extension up to 8 h of grinding operation was performed for confirmation. X-ray diffraction (XRD) analysis was performed to identify the phases in the samples. Other detailed experimental conditions are referred to from the published reports [19–21], of which remaining amount of V_2O_5 in the synthesis reaction of $CrVO_4$ has been quantitatively evaluated [20].

3. Results and discussion

3.1. Milled products

Besides the published results [19–21], other new data are presented before performing a full discussion. Fig. 1 shows XRD patterns of a Bi_2O_3 and B_2O_5 mixture milled for 2 h. The XRD analysis has confirmed that Bi_2O_3 reacts with every pentavalent oxide of P_2O_5 , V_2O_5 , Nb_2O_5 and Sb_2O_5 powders to form $BiPO_4$ (JCPDS No. 80-0209), $BiVO_4$ (JCPDS No. 83-1700), $BiNbO_4$ (JCPDS No. 71-1518) and $BiSbO_4$ (JCPDS No. 82-1805). Together with the published data, it becomes known that mechanochemical reactions can be carried out between La_2O_3 , In_2O_3 or Bi_2O_3 with the four pentavalent oxides to synthesize the corresponding compounds.

On the other hand, as to other trivalent oxides of Fe_2O_3 , Cr_2O_3 , Al_2O_3 , there exist various crystal states. It has been known that the crystal structures of starting samples play an important role in stimulating a mechanochemical reaction. Furthermore, it has been found that the starting materials which easily undergo the polymorphic transformation from looser packing of atoms to closer packing of atoms have the higher reactivity [16–18]. Based on such knowledge, gamma-type oxides with cubic structure or oxyhydroxides are used as starting materials. In the case of chromium oxide, for example, amorphous hydrated $Cr_2O_3 \cdot nH_2O$ with similar composition with $CrOOH$ rather than the crystalline Cr_2O_3 with corundum-type structure, has been found to react with V_2O_5 , Nb_2O_5 , Sb_2O_5 to form $CrVO_4$, $CrNbO_4$ and $CrSbO_4$, respectively, as shown in Fig. 2. In addition, $CrVO_4$ generated by milling has rutile-type structure, being a high-pressure phase [21]. However, it has been found that no reaction to form $CrPO_4$ has occurred even with the use of amorphous oxide, particularly considering P_2O_5 is very active sample and has high tendency to react with other sample.

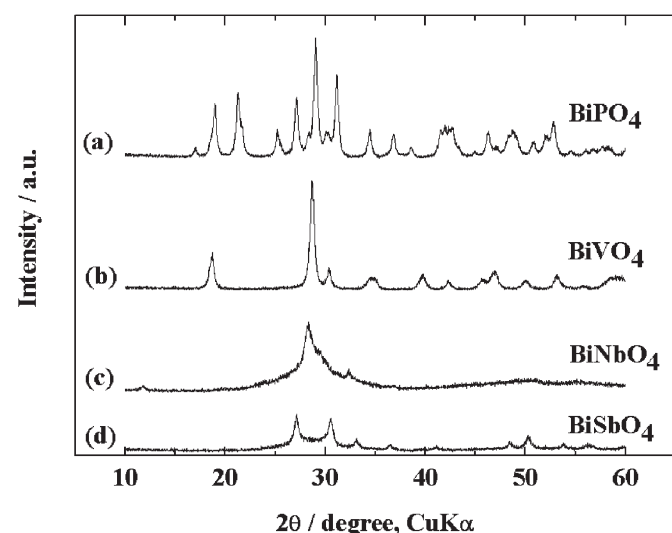


Fig. 1. XRD patterns of four kinds of a mixture of Bi_2O_3 and B_2O_5 ($B = P, V, Nb, Sb$) milled for 2 h, (a): Bi_2O_3 - P_2O_5 , (b): Bi_2O_3 - V_2O_5 , (c): Bi_2O_3 - Nb_2O_5 , (d): Bi_2O_3 - Sb_2O_5 .

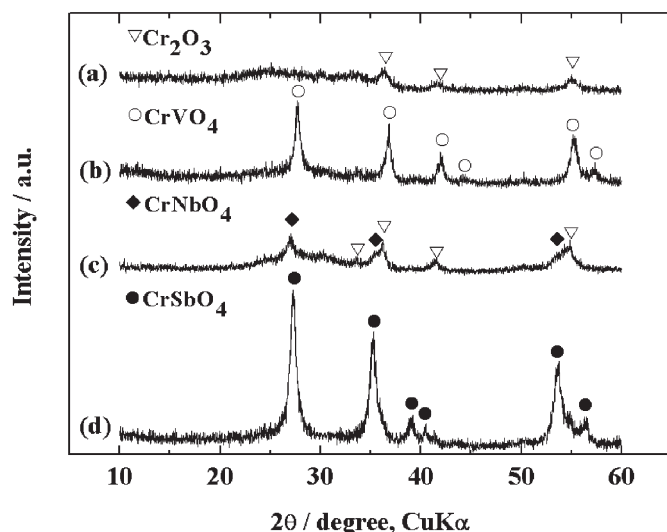


Fig. 2. XRD patterns of four kinds of a mixture of $Cr_2O_3 \cdot nH_2O$ and B_2O_5 ($B = P, V, Nb, Sb$) milled for 2 h, (a): $Cr_2O_3 \cdot nH_2O$ - P_2O_5 , (b): $Cr_2O_3 \cdot nH_2O$ - V_2O_5 , (c): $Cr_2O_3 \cdot nH_2O$ - Nb_2O_5 , (d): $Cr_2O_3 \cdot nH_2O$ - Sb_2O_5 .

Similarly, for syntheses of $FeBO_4$ and $AlBO_4$ ($B = P, V, Nb, Sb$), $FeOOH$ and $AlOOH$ were used as starting materials, respectively, instead of α - Fe_2O_3 and α - Al_2O_3 . Figs. 3 and 4 shows XRD patterns of $FeOOH$ - B_2O_5 or $AlOOH$ - B_2O_5 mixtures milled for 2 h, respectively. In Fig. 3, formations of $FeSbO_4$ and $FeNbO_4$ have been observed. However, it is seen that the starting sample $FeOOH$ has remained in the ground samples when P_2O_5 and V_2O_5 are used. There exists a clear difference in the reactivity toward $FeOOH$ between the four pentoxides. In Fig. 4, similar phenomena have been observed. Resulting from the difference in the reactivity of the four pentoxides toward $AlOOH$, only the formation of $AlSbO_4$ without $AlPO_4$, $AlVO_4$ and $AlNbO_4$, has been confirmed. Even with prolonged milling time to 8 h, no change in the phases of these non-reacted systems has been observed. These results indicate that, although it is necessary to use structurally active substances for stimulating mechanochemical reactions, it is not a sufficient condition. Since no reaction occurs between two active substances of, for example, $FeOOH$ and P_2O_5 , it seems that there exist other factors to influence the occurrence of a

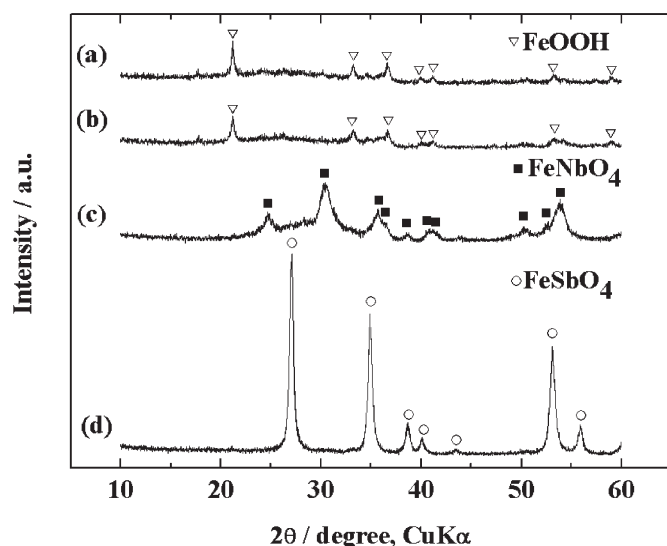


Fig. 3. XRD patterns of four kinds of mixture of $FeOOH$ and B_2O_5 ($B = P, V, Nb, Sb$) milled for 2 h, (a): $FeOOH$ - P_2O_5 , (b): $FeOOH$ - V_2O_5 , (c): $FeOOH$ - Nb_2O_5 , (d): $FeOOH$ - Sb_2O_5 .

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