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Invited review paper

A review on mechanochemical syntheses of functional materials

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ABSTRACT

This paper reviews mechanochemical (MC) syntheses of functional materials by means of dry grinding operation without heating. First of all, the authors have shown that the MC reaction is dependent on not only material function such as Gibbs free energy change of formation ($\Delta G < 0$) and structure type of the starting samples but also machine function enabling us to storage and accumulate the stress energy to the target materials. Then, they have concentrated the former one that the solid-phase reaction can be achieved by the necessary condition like $\Delta G < 0$ as well as the structure of the starting samples. The first example is MC synthesis of perovskite complex oxides, ABO_3, where A and B trivalent oxides, respectively. Then, another type of complex ones such as ABO_4 from A_2B_3 and B_2O_5, where B is pentavalent oxides, were shown. In these reactions, the structure of the starting samples are very important to determine the reaction completion or not. A reaction/non-reaction map has been introduced in this paper, and it is seen from the data that the radius (r_A, r_B and r_O) of the each metal elements in the reaction systems are crucial parameters in the reaction systems. The paper has extended to the synthesis of halides and sulfides conversion, and final example is a doping with non-ferrous metal element into oxide like TiO_2, attempting the improvement of its visible light photoreactivity. These information would be helpful to understand and estimate the MC solid-state reaction of the starting materials.

1. Introduction

Milling is known as one of the important unit operations and has been widely used in many processings of materials such as minerals, foods, medicine, chemicals and building materials. As an extended branch in milling operation, the field of mechanochemistry has attracted much attention and there have been increasing in research papers on this topic in recent years [1–5]. One of the unique phenomena in mechanochemistry is solid state reaction among two or more multi-components without heating, to produce a constituent compound. A potential application for this solid state reaction is not only material synthesis but also separation and recovery of chemical species and components from minerals and waste materials treated by the reaction through another chemical and/or physical operation.

This paper reviews mechanochemical syntheses of materials, focusing on recent researches in this field to understand the intrinsic nature of mechanochemistry.

2. Mechanochemical solid-state reactions

Milling induces mechanical activation of fine powder, which may affect interaction in a material itself as well as environmental phases when another material is present in a mill [6–12]. The interaction toward inside of a material appears as phase transformation including amorphization of crystalline phase [11], as shown in Table 1, and it extends solid state reaction when the activated solids are intimated each other with its boundary in a mill. The boundary of two or multicomponents of solid may be activated by following reasons: When the sample powders are trapped and crushed between two balls colliding inside a ball mill pot, they undergo deforming plastically, and are repeatedly flattened, cold-welded, fractured and rewelded. The force of the impact acts on the powder particles, leading to crystallographic bonds broken and new surface is produced. The new surfaces created enable the particles to weld together easily and this leads to an increase in the rate of dissolution of solid material. With continued mechanical deformation, new surface produced of the fragments created by this mechanism may reduce in particle size, and with the increase of surface energy of the material, other profound changes affecting the surface as well as the chemical, physico-chemical and structural properties may also take place. This is manifested by the presence of a variety of crystal defects such as increased number of grain boundaries, dislocations, vacancies and interstitial atoms, stacking faults, and deformed and ruptured chemical bonds. The presence of this defect structure enhances the diffusivity of solute elements. Consequently, grinding a mixture of two or more solids substances results in micro-homogenization of starting components, and sometimes, it induces formation and synthesis of new fine powders.

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