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Smart mechanochemistry—Charge transfer control for tailored solid-state reaction under minimum external energy

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Abstract

The present overview focuses on the process and its significance of charge transfer across the particulate boundary under mechanical stressing, by referring to examples of solid-state reactions in various systems. By utilizing charge transfer and related phenomena with and without additives, methods for smarter mechanochemical reaction are explored. Chemical interactions between organic species like amino acids and metals are understood under the concept of coordination, where charge transfer between the metal and the ligands play a principal role. Importance of forced symmetry breakage and intimate contact between dissimilar species under mechanical stressing is emphasized. Case studies are given on the role of amino-related organics added to the precursors to $BaTiO_3$.

Keywords: Charge transfer; Charge transfer complex; Glycine; Barium titanate; Organic solid-state reactions

1. Introduction

Nothing is more benign in materials synthesis than to use a cascade of natural changes. Some solid-state reactions proceed autogenously by instantaneous melting upon mixing [1]. This is basically the consequence of very rational charge transfer (CT). Apart from this kind of extreme case, rational incipient chemical bonds can be introduced in the starting mixture. This serves as a precursor to the subsequent reaction processes [2–5]. We note that most of the preliminary chemical interaction across the interparticulate boundary is the consequence of CT [6]. It is particularly important to recognize that charges can transfer across the interparticulate boundary at room temperature. Generally, smaller distance and stronger polarization favor CT. It is also important to notice that polarization is enhanced when the symmetry of the ligand field is broken. This happens under mechanical stress as a consequence of macroscopic and temporal deformation [7–10].

Control of charge transfer to tailor the solid-state reaction has not, however, been explored in a systematic manner. Major challenges in this respect are to elucidate the role of CT at the inter-particle boundary for subsequent reaction, and the tactics to bring CT under control for materials synthesis. The present overview focuses on the processes and significance of charge transfer across the particulate boundary under various conditions, by referring to examples of solid-state reactions in various systems. Case studies are introduced from the latest experimental results, including the role of proteins or amino acid additives to the precursors to $BaTiO_3$.

2. Consequences of milling a mixture with nylon balls

In the course of preparing ferroelectric materials like barium titanate ($BaTiO_3$, BT), the author's group has demonstrated the usefulness of mechanical activation [11–13]. Serious negative consequences of cationic contamination by prolonged and energy intensive milling by using milling media such as alumina, zirconia or corundum are well known. It is therefore important to use grinding media coated by some hard polymers like nylon.

When milling with nylon balls, it is fairly common to obtain mechanically activated products without serious agglomeration. Since surface of the products often changes to be hydrophobic, the surface of the milled product is more or less "coated" with nylon. A next question is, whether nylon could exert chemical effects on the milled products [13]. As we vibro-milled a stoichiometric mixture of $BaCO_3$ and TiO_2 for 10 h and subsequently calcined at temperatures between 950 and 1050 °C, we obtained very fine BT particles with their tetragonality very close to that of BT single crystal, as shown in Fig. 1 [11].

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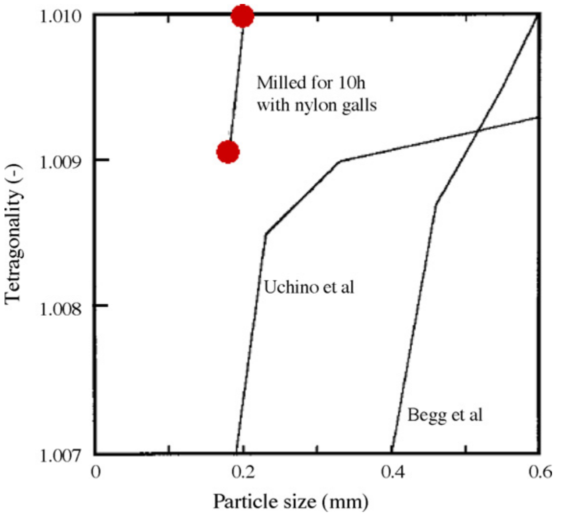

Fig. 1. Relationship between the tetragonality and the particle size for BT fired at 950 and 1050 °C after milling with nylon balls for 10 h without additives [18,19]. Two literature data referred: Uchino et al. [18] and Begg et al. [19].

Since suppression of grain growth cannot always be explained by high homogeneity or well-dispersed state of the starting mixture, we suspected some chemical effect of nylon. In fact, simple addition of nylon 6 in hexafluoro-*iso*-propanol (HFIP) solution resulted in the decrease in the decomposition temperature of $BaCO_3$, as well as $CaCO_3$, as shown in Fig. 2. This is only explained by assuming that the carbonates became unstable by adsorption of nylon. Since nylon is very stable and HFIP is an unusual solvent, we further explored more convenient additives to elucidate the mechanisms of reaction promotion by additives.

3. Exploitation of further additives

When we substituted nylon in the previous experiment by a water-soluble protein, bovine serum albumin, BSA, which is an amide bonded polymer like nylon, we also obtained microparticles of BT. The average particle size of the BT obtained after calcining the mixture with 17 wt.% BSA was 180 nm. The tetragonality value was as high as 1.0085 [12]. The thermal decomposition behaviors of the reaction mixture and intact BSA are compared in Fig. 3. As shown in the right frame of Fig. 3, the observed thermal decomposition behavior in the temperature range between 300 and 600 °C significantly differs from the calculated one under the assumption of additivity. The apparent difference is due to the coexistence of TiO_2 in the sample containing BSA by 17% on the dry weight basis (sample B-17). According to the results of high temperature XRD, it is obvious

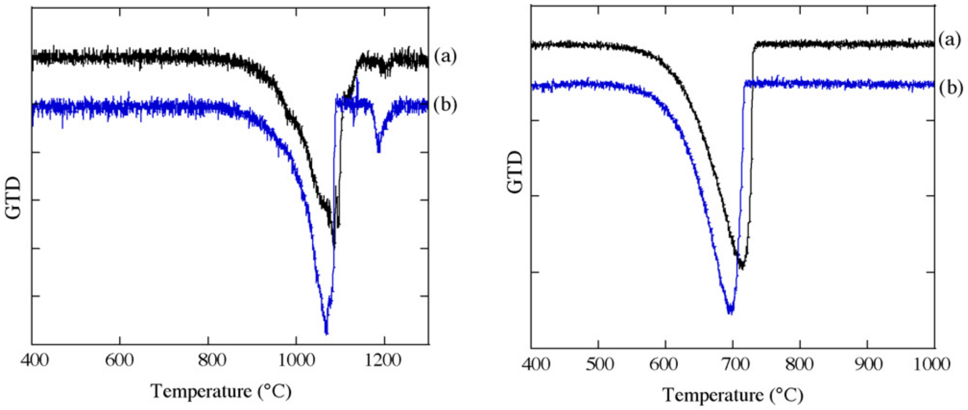

Fig. 2. Change in the decomposition temperature of $BaCO_3$ (left) and $CaCO_3$ (right) by adding 10 wt.% nylon 6 from HFIP solution. Decrease in the decomposition temperature by nylon addition is obvious.

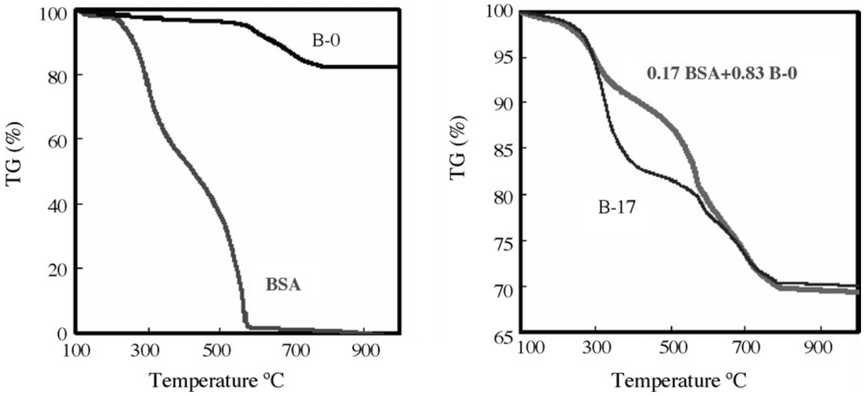

Fig. 3. Comparison of TG curves of the mixture for BT with and without BSA. The upper curve of the right side frame was calculated from the values of BSA and B-0 by assuming additivity [12].

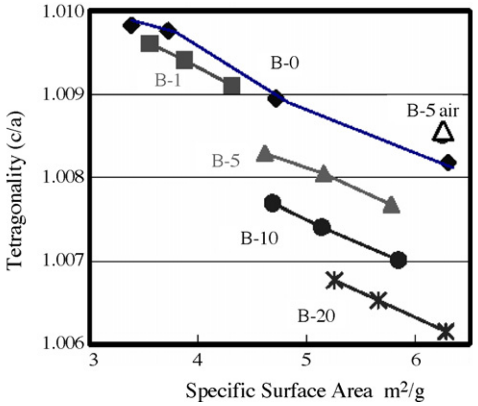

Fig. 4. Relationship between tetragonality and BET surface area of BT with varying amount of BSA [12].

that the weight loss between 500 and 600 °C is attributed to the decomposition of $BaCO_3$, which occurs at lower temperatures by adding BSA to the mixture of $BaCO_3$ and TiO_2.

We also note that the total weight loss of B-17 at 1000 °C, where the formation of BT is completed, was smaller by approximately 2% than that of the hypothetical value calculated from the simple additivity assumption of BSA, i.e. from samples B-17 and B-0 (without BSA). This is explained by the calcination residuals of BSA, most probably as free carbon. This simultaneously indicates the interaction between BSA and the mixture of $BaCO_3$ and TiO_2.

Suppression of grain growth was also observed and is presumably associated with the calcination residue. We therefore calcined the reaction mixture with BSA in air flow, instead of stagnant air, to eliminate free carbon. This significantly increased the value of tetragonality, as shown in Fig. 4 by an open triangle, upper right, and implies that residual carbon plays two opposite roles, i.e. to suppress grain growth and, simultaneously, to introduce defects. Calcination in air flow eliminates the negative effects.

4. Effect of glycine on the synthesis of fine grained BT

Principal role of BSA, as we suspected, was the coordination of the protein species to Ba, easing the decomposition of $BaCO_3$, one of the starting materials for BT. We then replaced protein with amino acids which is more beneficial with its smaller molecular size, easier handling and lower price as compared to proteins. Addition of glycine, (NH_2CH_2COOH, Gly) being one of the most popular amino acids, to the equimolar mixture of $BaCO_3$ and TiO_2, led to results similar to or better than those with nylon and BSA.

Upon calcining the mixture for BT, we always observe a two-step weight loss process. The first step is mainly attributed to the initial stage chemical interaction between the two reactant species. The second step is found to be affected by physical factors such as the states of dispersion [13]. While the first step initiates at 548 °C for sample W without Gly, 1, 2, and 20 wt.% of Gly addition (four curves from top to bottom in Fig. 5) decreases the initiation temperature to 537, 523 and 509 °C, respectively.

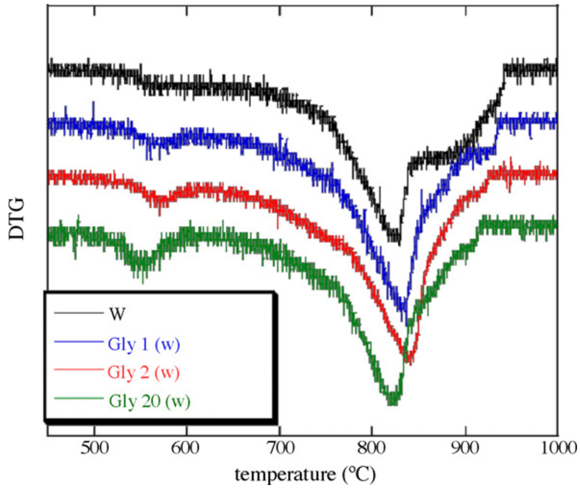

Fig. 5. Differential thermogravimetric profiles for the mixtures with varying amount of glycine. Sample W, without additives; Gly *n* (w), with glycine added by *n* wt.% from aqueous solution, and dried.

Calcination at 850 °C revealed that addition of Gly by 0.5% followed by 3 h milling brought about the pure BT phase equivalent to those obtained from the mixture after milling 7–10 h with nylon balls without Gly. As shown in Fig. 6, grain growth was suppressed drastically by Gly addition. It is decisively important that the addition of Gly gives higher tetragonality with smaller grains, as shown in Fig. 7, to obtain BT particles less than 0.2 μm with their lattice tetragonality as high as 1.0098.

5. Rational coordination of additives through charge transfer

Coordination chemistry with alkaline earth metals has been explored in the interests of biochemical and metabolic issues, particularly for Mg and Ca [14]. With very different motivation, interaction of amino acids like glycine with inorganic materials or alkaline earth metals was extensively studied. Gonzales-McQuire et al. [15] reported the role of several amino

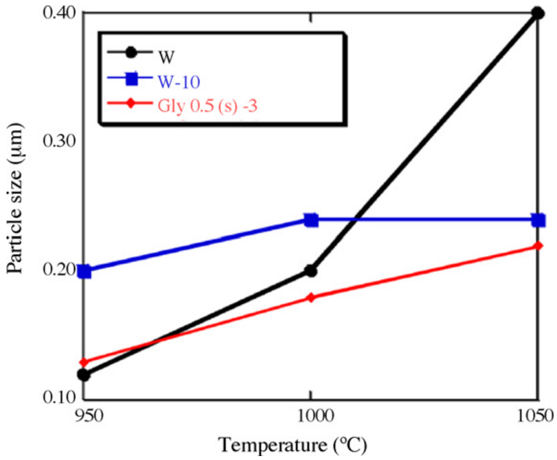

Fig. 6. Relationship between particle size and calcination temperature. Sample W, without additives; W-10, without additives and milled by nylon ball for 10 h; Gly 0.5 (s) −3, with glycine added by 0.5 wt.% as powders and subsequently vibro-milled for 3 h.

Table 1
Change in the FT-IR spectra by Gly addition and subsequent milling

Sample	δ_{oop}BaCO$_3$	ν C–N (G)	ν_S C=O (B)	ν_{as} C=O, CO$_3^{2-}$ (B)	ν_{as} C=O$_2$ (G)	$\nu_s + \delta_{ip}$ BaCO$_3$	$\nu_{as} + \nu_s$ BaCO$_3$	ν NH	ν CH
W	856.7	–	1059.9	1452.7	–	1751.2	2452.2	–	–
Gly	–	1127.6	–	–	1596.1	–	–	2593.0	2959.2
Gly 5 (w)	857.1	1129.3	1060.1	1449.9	1597.2	1751.4	2452.9	2609.1	2923.7
Gly 5 (w)-3	857.6	1134.7	1060.0	1450.2	1602.7	1751.2	2452.3	2607.1	2924.0
(A)[a]	0.9	7.1	0.1	−2.5	4.6	0.2	0.1	14.1	−35.2
(B)[b]	0.5	5.4	−0.1	0.3	5.5	−0.2	−0.6	−2	0.3

[a] Gly 5 (w)—Gly or W.

[b] Gly 5 (w) 3—Gly 5 (w).

acids including glycine on the crystal growth of hydroxyapatite. They emphasized the preferential binding of the amino acid α-carboxylate group for control of crystal growth. Murugavel et al. reported the preferential complex formation of alkaline earth metals in the interests of biochemistry of living organisms [14]. In the field of thin film science and technology, orientation of the organic species forming thin films with respect to their substrates is of main interest. Tzvetkov et al. studied the orientation of glycine adsorbed on the Al_2O_3/NiAl (1 1 0) substrate [16]. A finer study using STM, reported on the atomic orientation of an amino acid [17].

In spite of entirely different nature of these research works, we find several common aspects of the coordination of amino acids to the metallic species. Amino acids have bonding of two atomic species, oxygen and nitrogen with their lone pair electrons. We might generally expect the preferential coordination of oxygen in the carboxylic group to metals, where the high electron density of oxygen in COO^- may interact ionically with the metallic cations.

Solid-state ligand exchange reactions under mechanical stressing have been studied in author's laboratory [7–10]. One of the main results was the enhanced reactivity of coordination with the symmetry loss of the ligand field [7,9]. We recall that the ligand field is always subjected to distortion during mechanochemical processing. Importance of forced symmetry breakage and intimate contact between dissimilar species under mechanical stressing should be kept in mind.

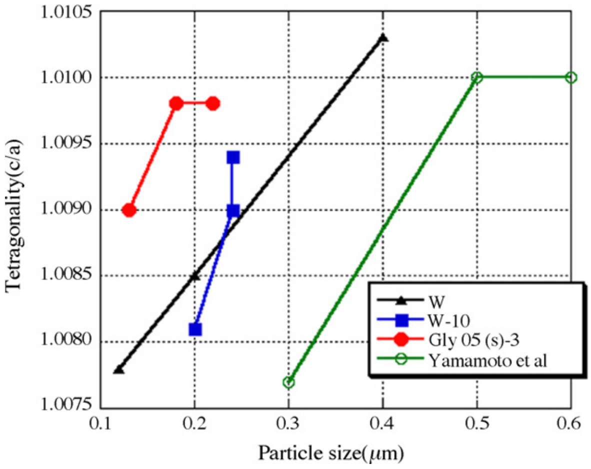

Fig. 7. Relationship between tetragonality and particle size. Sample names are the same as those in Fig. 6. A literature cited is: Yamamoto et al. [20].

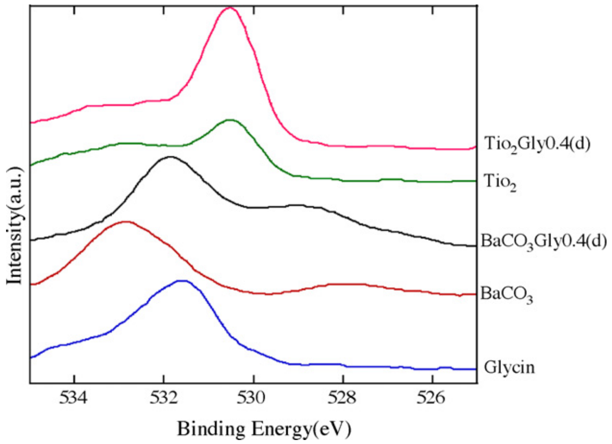

Fig. 8. X-ray photoelectron spectrograms for O_{1s}. Gly 0.4 (d) denotes samples with glycine added by 10 wt.%.

We have studied in more detail the case of coordination of Gly with Ba. Fig. 8 demonstrates the change in the O_{1s} and Ba_{3d} binding energies by adding Gly. Apparent O_{1s} signal on $BaCO_3$ after Gly addition is close to that of intact Gly, i.e. a large positive shift by 0.9 eV. In contrast, Gly addition did not bring about appreciable chemical shift of O_{1s} binding energy of TiO_2 [13]. Though not shown in the figure, Ba_{3d} exhibits a positive shift as well. In case of Ti_{2p}, the chemical shift was less than 0.2 eV and hence, insignificant. All these results suggest that Gly exerts chemical interaction more preferentially on Ba than on Ti.

As shown in Table 1, ν_{as} C=O of $BaCO_3$ exhibits a red shift after Gly addition, implying the weakening of the chemical bonds within the CO_3-triangle. The stretching bands of COOH and NH in Gly exhibit blue-shifts, indicating the increase in the C=O and N–H bond strengths. This can be explained by assuming the coordination by oxygen of COO^-, although the coordination by nitrogen of NH to the ligand field of Ba cannot be excluded. In addition, a remarkable blue shift of COO in Gly might imply the intensified coordination by COO^- due to the increasing symmetry loss around CO_3-triangle by milling.

6. Conclusions

Charge transfer during mechanical stressing on the reactive mixture was considered particularly in view of coordination bonding between organic additives like glycine and metallic species like Ba included in the starting materials for inorganic syntheses, e.g. of micro particulate and well crystallized $BaTiO_3$. Conditions indispensable for rational charge transfer toward coordination are sufficient polarization at the solid surface and the small enough distance between the dissimilar species in order for the charge transfer to occur across the interparticulate boundary. Appropriate mechanical stressing automatically fulfills these conditions as a consequence of local plastic deformation at the contact points with sufficient symmetry loss of the ligand field, enabling charge transfer through the enhanced polarization and forced contact or decreasing distance small enough for charge transfer.

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