THE FORMATION KINETIC OF MECHANOCHEMICAL SYNTHESIZED PEROVSKITES

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Abstract

In this study, we aimed to achieve mechanochemical perovskite synthesis and to quantify the energy used during milling (E_b - impact energy and E_{cum} - cumulative energy) and to describe the relationship between them. For mechanochemical treatment a Fritsch Pulverisette-6 type planetary ball mill was used. As a model compound the widely used barium-titanate ($BaTiO_3$) was chosen, which was produced by the reaction of barium-oxide (BaO) and titanate-dioxide (TiO_2). The aim was to track the formation of $BaTiO_3$ and to determine the minimum milling energies required for its production. Three important parameters were considered for the calculation of energy values: the material of the milling vials and balls, the number of balls and the speed of rotation. The transformation was tracked by X-ray diffraction (XRD) measurement, and the applied energy was determined using the Burgio-Rojac energy model. Our goal was to draw conclusions that can be used to predetermine optimal milling parameters in the production of other perovskite structured materials. The hypothesis was verified by the mechanochemical synthesis of zinc-titanate ($ZnTiO_3$) which was produced by the reaction of zinc-oxide (ZnO) and TiO_2.

Introduction

Looking at the main three-component crystal structures, it found that of the thousands of complex structures, there are only a dozen ceramics that are significant in use. Among these, the A_2BX_4 spinel and ABX_3 perovskite structures stand out, and perovskite is the only structure, the chemical modification of which results in an extremely wide range of phases with completely different properties. Due to its unique electrical properties, the family of chemical compounds with a perovskite-type structure includes a wide range of electrotechnical materials: semiconductor dielectrics, superionic conductors, combined with ionic and electron conductivity for high-temperature superconductors. [1,2]

Mechanical activations and chemical reactions in planetary ball mills have long been known, but there are still challenges. There are many factors that influence the success of mechanochemical reactions: the material of the milling vial and balls; the rotational speed; the milling time; the number of balls and the filling ratio of the balls and reactants; the atmosphere and temperature in the vial, the physical and chemical properties of the reactants etc. These parameters are not independent of each other and play an important role in achieving optimal treatment, which results the best available yield. [3] For any combination of the factors above, the milling time in the given system must be determined separately. The intensity of milling energy affects the increase in the particle size of crystalline materials, and as the temperature changes, compounds of different compositions may be formed. [4] It should be considered that too long milling process can result in undesirable products, while insufficient treatment does not allow for proper conversion of starting materials.

Experimental

For mechanochemical treatment a Fritsch Pulverisette-6 type planetary ball mill was used. Each milling drum has a volume of 80 mL, the milling balls were 10 mm in diameter and 2.00 g BaO and 1.04 g TiO_2 were measured in the vial in each case. Based on the mass of the balls and the reactants weighed, the minimum and maximum ball-to-powder ratios can be determined in each milling drum. This number varied between 5.5-1 and 61.5-1. We were able to control this by milling vials made of different materials (silicon nitride Si_3N_4, hardened stainless steel FeNiCr, hard metal tungsten-carbide WC), we were able to change the milling energy within a wide spectrum. The transformation of starting materials was followed by XRD.

The Burgio-Rojac equation (1) can be used to determine two energy values: the E_b (1), which represents the total energy available during an impact event of a milling ball, and E_{cum} (2), which means the energy transferred to 1 gram of the powder during whole milling:

$$E_b = \frac{1}{2}\varphi_b K\left(\rho_b \frac{\pi d_b^3}{6}\right)\omega_p^2\left[\left(\frac{\omega_v}{\omega_d}\right)^2\left(\frac{d_v-d_b}{2}\right)^2\left(1-2\frac{\omega_v}{\omega_d}\right)-2r_p\left(\frac{\omega_v}{\omega_d}\right)\left(\frac{d_v-d_b}{2}\right)-\left(\frac{\omega_v}{\omega_d}\right)^2\left(\frac{d_v-d_b}{2}\right)^2\right] \quad (1)$$

where K is the geometric constant of the mill, φ_b is the obstruction factor, ρ_b is the density of the milling balls, d_b is the diameter of the balls, d_v is the diameter of the milling vial, ω_p and ω_v is the rotational speed of the disc and the crucible and r_p is the distance between the rotational axes of the disc and the crucible.

$$\boldsymbol{E_{cum} = \frac{E_b \times f \times t}{m_p}} \quad (2)$$

where f is the frequency of impacts, t is the milling time and m_p is the mass of the measured sample. [5]

In addition to $BaTiO_3$, we also produced $ZnTiO_3$ by mechanochemically. In these experiments, according to the stoichiometry of the reaction, 1.50 g of ZnO and 1.47 g of TiO_2 were measured in the vial in each case. This was necessary because the total weight had to be kept at around 3 grams, so that the ball-to-powder ratios previously used for $BaTiO_3$ could be interpreted in this case as well.

Results and discussion

Based on the Burgio-Rojac equation, E_b, E_{cum} values and the frequency of impact of the balls were calculated for each sample. By depicting these data, the so-called energy map of a milling series can be prepared. **Fig.1.** illustrates the relationship between E_b and the material of the applied vial and the frequency of impact. In case of Si_3N_4, only 300, 400 and 500 rpm, and for FeNiCr and WC vial data on samples milled at 200 rpm are also indicated. This can be explained by the fact that in samples milled at this value (Si_3N_4), the conversion of the starting materials was not occured at all, it started only at 300 rpm with the use of 25 milling balls.

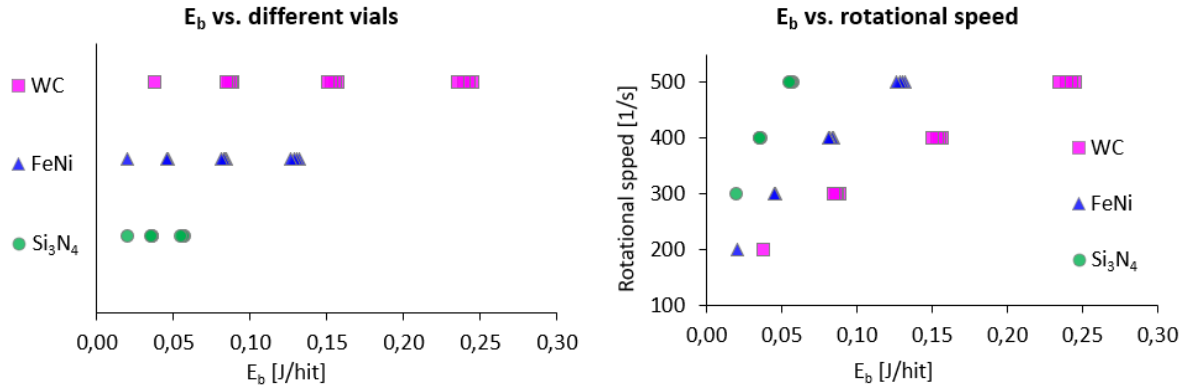

Figure 1: E_b points defined by the Burgio-Rojac equationas a function of the milling vials (left) and the frequency of impacts (right).

Fig.1. shows that in the case of higher density milling vials, increasing the speed has a much more significant impact on the dynamics of the growth of E_b. With the tungsten-carbide vial a much wider energy interval can be covered, but the minimum speed will determine its resolution, however in the case of the lower density Si_3N_4 vial this much more precisely controllable. [6]

During milling, an hourly sample was taken of, which was measured immediately with XRD. **Fig.2.** shows X-ray diffractograms of samples milled in different vials with the same setting (400 rpm, 20 balls). As expected, the formation of Ba/$ZnTiO_3$ differs significantly in the three vials.

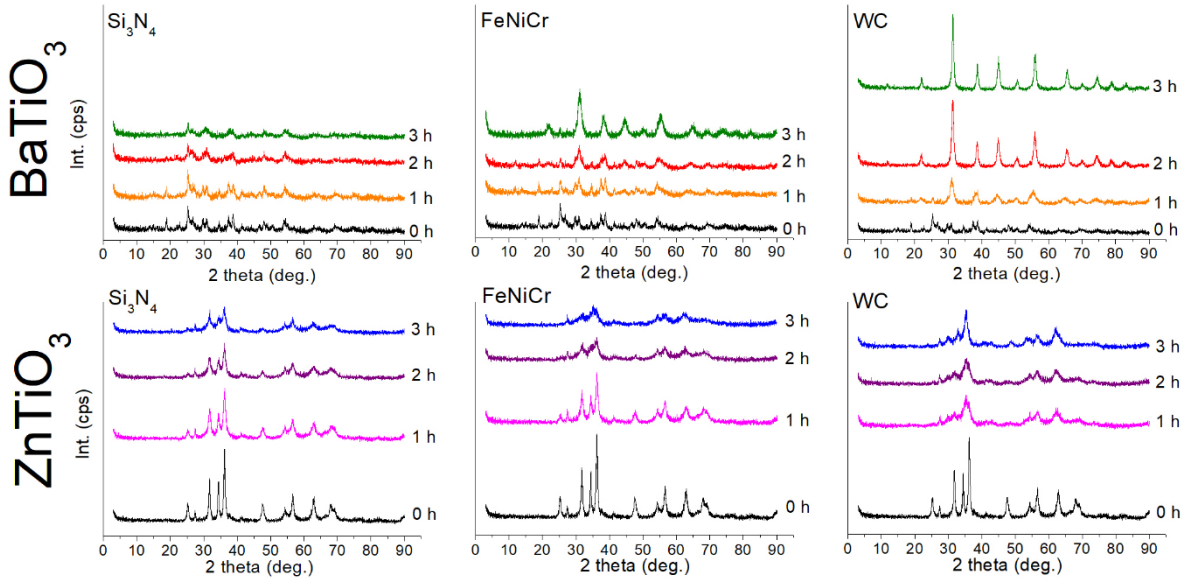

Figure 2: XRD of samples milled with the same parameters (400 rpm, 20 balls). The 0-hour sample is made of the BaO/ZnO-TiO_2 starting materials mixture.

The E_b are almost doubling in the case of milling vials treated with the same parameters but having different material. This is reflected in the XRD recordings, where a fundamental difference can be found that the production of $BaTiO_3$ is already sufficient for a lower E_b value, resulting in 35.5 J/hit. Typical reflections appear already during treatment in the FeNiCr vial after 1 hour. In the case of $ZnTiO_3$, the transformation of the starting materials in the Si_3N_4 vial

does not take place at this E_b value, and the reflections characteristic of crystalline $ZnTiO_3$ appear in the FeNiCr drum only after 2 hours.

To better represent the measured results, diffractograms were read and used to track the formation of reactants at the intensity of most intense $BaTiO_3$ peaks (2θ 31.4°), i.e. based on the fact that the intensity of this peak shows the increasing appearance of the product in the vial. The same was done for $ZnTiO_3$ based on reflection of 2θ 36.3°. The results are presented in **Fig.3.**

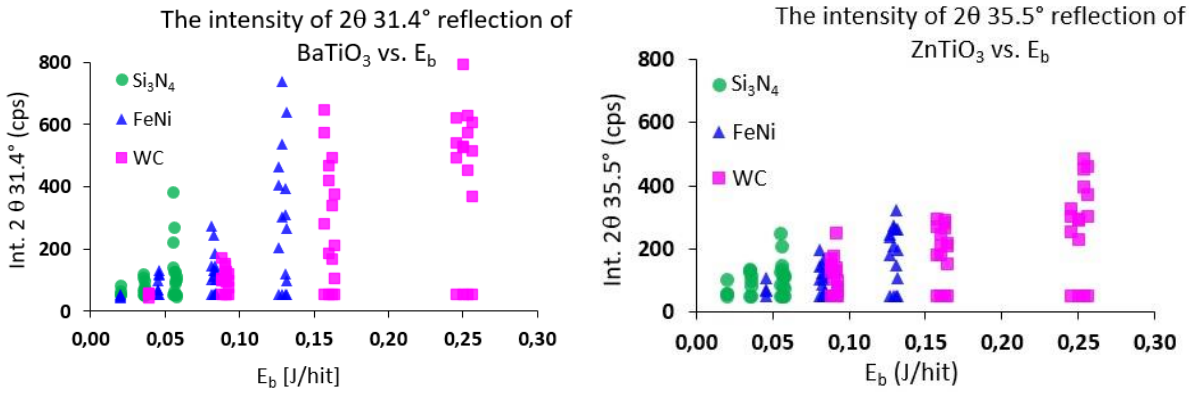

Figure 3: XRD measurement-based formations of $BaTiO_3$ and $ZnTiO_3$ of the samples in different milling vial.

Good correlation between the performed E_b and the conversion rate is observed in the case of $BaTiO_3$ and $ZnTiO_3$ also. E_b which is necessary to produce the perovskite structure, begins at a nearly similar value, however, $BaTiO_3$ is already formed at ball-impact energy of 0.12 J/hit, while the same is only done at 0.25 J/hit in the case of $ZnTiO_3$. By this way, it can be stated that the thresholds E_b to produce the $BaTiO_3$ perovskite is correspond to the above values.

Conclusion

By increasing the milling time, we could increase the E_{cum}, which is able to correct the low E_b to a certain extent, but it should be noted that in this case the perovskite crystal structure may be damaged. For both perovskites, the formation of the structure can be achieved mechanochemically in a similar energy range. From this we can conclude that the experience gained during the research can already be used to produce perovskites from the components of metal oxide. As a result, it can be a general mechanochemical perovskite synthesis model.

Acknowledgements

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