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## Mechanochemical Synthesis of Double Tin and Alkaline Earth Metal Hydroxides

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### Abstract

An opportunity for direct mechanochemical synthesis of double tin and alkaline earth metal hydroxides *via* two procedures was demonstrated. The latter were based on reactions of chloride (IV) pentahydrate and alkaline earth metal hydroxides or salts (in the latter case, upon simultaneous action of NaOH). It was possible to synthesize Mg/Sn layered double hydroxide using only the first procedure. Calcium, strontium, and barium compounds were synthesised by both procedures. The X-ray diffraction patterns of double hydroxides  $M\text{Sn}(\text{OH})_6$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) are in good agreement with structural data acquired in early research works and presented in X-ray databases. The products contain trace carbonate impurities, which is related to their presence in the initial reagents.

**Key words:** double hydroxides  $M\text{Sn}(\text{OH})_6$  ( $M = \text{Ca}, \text{Sr}, \text{Mg}, \text{and Ba}$ ), mechanochemical synthesis, alkaline earth metal salts and hydroxides, impurities of alkaline earth metal carbonates

### INTRODUCTION

The Mg/Sn (IV) layered double hydroxides of general formula  $\text{MeSn}(\text{OH})_6$ , where Me is a doubly charged cation [1, 2], may be used as precursors for the synthesis of various single-phase and composite functional materials with the stoichiometric M/Sn ratio. In order to synthesise these materials, ultrasound assisted synthesis [3] or sol-gel synthesis methods using co-precipitation from solutions [4–7] were used. We have earlier carried out research on the synthesis of double hydroxide  $\text{MgSn}(\text{OH})_6$  by co-precipitation from solutions of salts with a view to further explore its thermal decomposition. It turned out that the thermolysis product of the resulting compound contained an excess of tin dioxide [6, 7], which might be explained by difficulty to attain precise stoichiometry when a co-precipitation reaction is carried out. Furthermore, attempts to synthesise

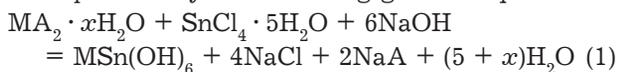
the barium analogue of this compound were not successful, as  $\text{BaSnO}(\text{OH})_4$  oxo-hydroxide instead of  $\text{BaSn}(\text{OH})_6$  was formed. In addition, the product contained a large amount of barium carbonate.

In the present work, a relatively facile hardware design method of solid-phase mechanochemical synthesis of double alkaline earth metal and tin hydroxides has been proposed. The procedure allows for more accurate controlling the quantitative composition of the initial reagents, decreasing the amount of solvents used (only for washing the product), and reducing synthesis time. Similar methods of soft mechanochemical synthesis are known and have been described earlier [8]. In particular, paper [9] described synthesis methods using reagents that were crystallohydrates of salts. A series of double hydroxides of  $M\text{Sn}(\text{OH})_6$  composition ( $M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) have been synthesised. The results are presented below.

## EXPERIMENTAL

Solid-phase synthesis of alkaline earth metal hydroxystannates was carried out in two ways.

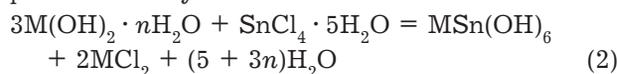
In the first case, a porcelain mortar was loaded with a mixture of solid reagents, such as  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (chemically pure grade) and alkaline earth metal salts  $\text{MA}_2 \cdot x\text{H}_2\text{O}$  taken in Sn/M atomic ratio of 1 : 1. Chemically pure  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2$  (anhydrous),  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ba}(\text{NO}_3)_2$ , were sampled as  $\text{MA}_2 \cdot x\text{H}_2\text{O}$  salts. The mixture was thoroughly mixed followed by adding granulated solid NaOH (chemically pure) in a Sn/Na atomic ratio of 1 to 6. The resulting reaction mixture (material mass of 2 g) was mechanically treated in a X 330H laboratory mill (at an acceleration of 40g, drum volume of 4 mL, grinding body made of tungsten carbide in the form of a hexagon with a mass of 20 g) for 3 min. As water was released during the reaction and the sample was transformed to a suspension, then the solid phase was filtered off on a paper filter using a water jet pump and repeatedly washed with distilled pre-boiled water to remove  $\text{CO}_2$ . The powders obtained on the filter were dried in a vacuum oven at 80 °C for 8 h. The reactions occurring may be expressed by the following general equation:



where M = Mg, Ca, Sr, Ba; A =  $\text{NO}_3^-$ , and  $\text{Cl}^-$ . As all reagents and products, except for  $\text{MSn}(\text{OH})_6$ , are freely soluble in water, then after washing-off on the filter, only the target product, *i.e.*, double tin and alkaline earth metal hydroxide, remains on the filter. The samples obtained in this way would be further indicated as M-A-Sn (M = Mg, Ca, Sr, Ba).

The reaction *via* the second procedure was carried out between chemically pure solid  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and metal hydroxides, such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . These hydroxides were obtained immediately before synthesis by sodium hydroxide precipitation from solutions of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{BaCl}_2$  salts prepared using pre-boiled water due to the high tendency of strontium and especially barium hydroxides to absorb atmospheric  $\text{CO}_2$  to form carbonates. The precipitate was filtered on a paper filter using a water pump, rinsed with  $\text{H}_2\text{O}$  several times, vacuum dried at 50 °C for 8 h. The resulting alkaline earth metal hydroxides were mixed with milled  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  in Sn/M atomic ratio of 1 : 3 (the total mass of the reaction mixture was 2 g) and the mixture was mechanically treated under

the same conditions as in the first procedure. The resulting product was repeatedly rinsed with distilled water on paper filter using a water pump followed by drying in a vacuum oven at 80 °C for 8 h. In general terms, a reaction equation for this procedure may be written as



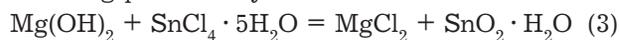
The samples obtained in this way would be further indicated as M-OH-Sn (M = Mg, Ca, Sr, Ba).

The X-ray diffraction patterns of the resulting samples were recorded on the D8 Advance diffractometer using  $\text{CuK}\alpha$  radiation and a Lynx-Eye one-dimensional detector with a nickel filter, shooting range  $2\theta = 8\text{--}70^\circ$  with a step of  $0.02^\circ$  and an accumulation time of 35.4 s.

## RESULTS AND DISCUSSION

Figure 1 presents powder X-ray diffraction patterns of synthesis products,  $\text{MSn}(\text{OH})_6$  compounds based on alkaline earth metal salts and hydroxides using the two procedures described above.

Upon synthesis of  $\text{MgSn}(\text{OH})_6$  using the first procedure when magnesium chloride was taken as the initial salt, a monophasic well-crystallised product is generated. The latter corresponds to  $\text{MgSn}(\text{OH})_6$  compound described earlier with cubic structure (*Pn-3* symmetry group,  $a = 0.777$  nm). It is impossible to carry out the reaction *via* the second procedure using the mechanical treatment of a mixture of  $\text{Mg}(\text{OH})_2$  and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . The interaction begins after adding water to the reaction mixture, however, magnesium chloride is formed resulting presumably from the reaction:



The resulting magnesium chloride remains in the solution and is removed upon rinsing, whereas the precipitate after washing and vacuum drying turns into nanocrystalline  $\text{SnO}_2$ , very broad reflexes of which are recorded in X-ray diffraction patterns.

Furthermore, Fig. 1 gives XRD patterns of synthesis products of  $\text{MSn}(\text{OH})_6$  compounds based on calcium, strontium, and barium salts or hydroxides. It has turned out that regardless of the synthesis procedure, almost monophasic mixed hydroxides of  $\text{MSn}(\text{OH})_6$  composition are generated where M = Ca, Sr, and Ba. The samples contain carbonate impurities, which is due to their presence in the initial hydroxides used for synthesis.

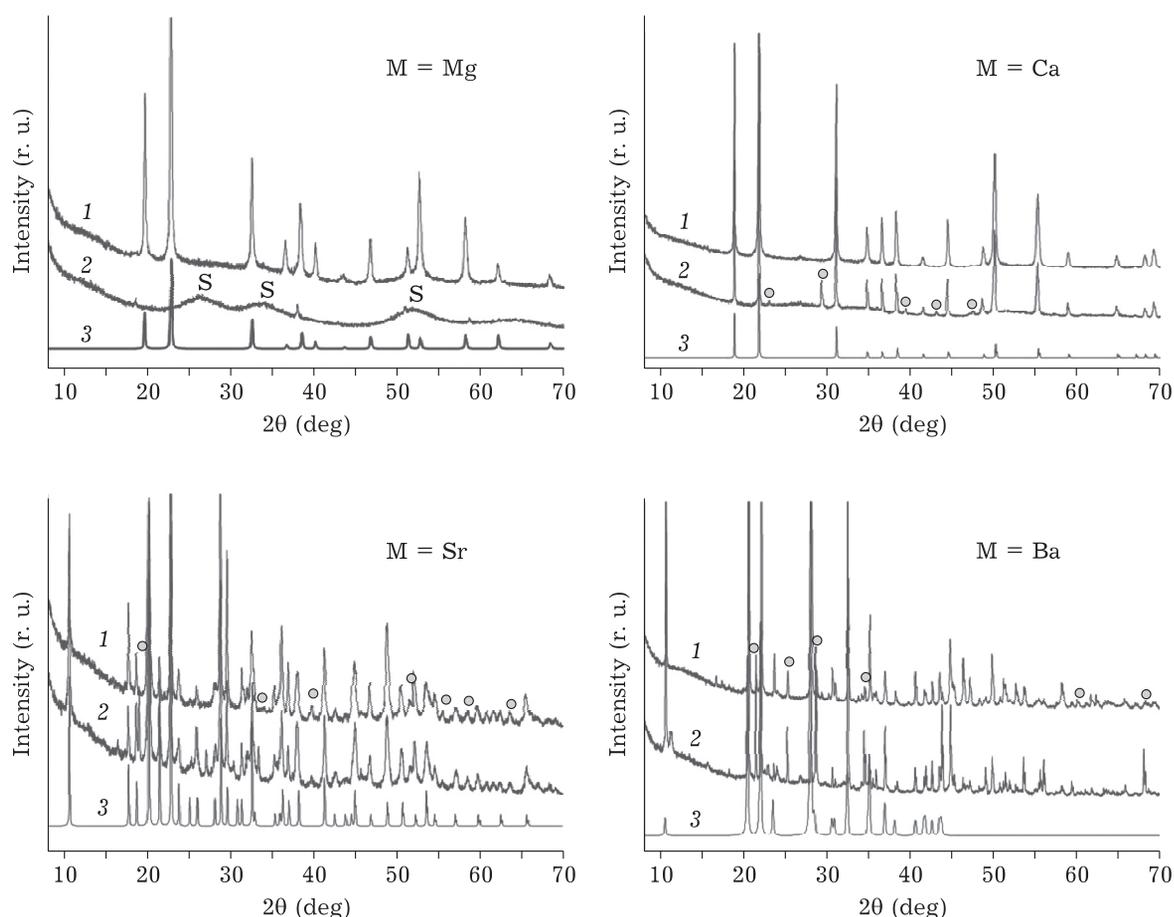


Fig. 1. Powder X-ray diffraction patterns of samples of M-A-Sn (1) and M-OH-Sn (2) obtained from various alkaline earth metal salts and hydroxides compared to diffractograms of  $\text{MSn}(\text{OH})_6$  compounds plotted according to data of files from the PDF2 database: No. 74-366 (M = Mg), No. 73-2383 (M = Ca), No. 9-86 (M = Sr), and No. 9-53 (M = Ba) (3). S and gray symbols indicate reflexes referred to cassiterite phase and impurities of corresponding metal carbonates, respectively.

## CONCLUSION

Thus, this research paper has demonstrated an opportunity for direct mechanochemical synthesis of double tin and alkaline earth metal hydroxides,  $\text{MSn}(\text{OH})_6$  (M = Mg, Ca, Sr, Ba) starting with tin chloride (IV) pentahydrate *via* two procedures:

1) using alkaline metal (M = Mg, Ca, Sr, Ba) salts when adding sodium hydroxide according to reaction (1);

2) based on alkaline earth metal (M = Ca, Sr, Ba) hydroxides *via* reaction (2).

The X-ray diffraction patterns are in good agreement with the structural data obtained in the early research and presented in the PDF2 crystallographic database. The products contain trace carbonate impurities, which is related to their presence in the initial reagents.

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