Mechanochemically assisted room temperature solid state metathesis reaction for the synthesis of MMoO_4 ($\text{M} = \text{Ca}, \text{Sr}$ and Ba)

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Abstract. This communication reports a novel mechanochemically assisted room temperature solid state metathesis reaction for the synthesis of submicron-size alkaline-earth molybdates crystallizing in a tetragonal Scheelite structure. The solids were characterized by powder XRD, FTIR, TGA, DTA, SEM, EDAX and TEM to ascertain their composition, phase homogeneity and morphology.

Keywords. Molybdate; mechanochemical; solid state metathesis; Scheelite.

1. Introduction

Metathesis (double exchange) reactions taking place in solid state are not quite common. However, these extremely fast, self-energetic reactions yield crystalline materials in very short time intervals with unusual microstructures (Gillan and Kaner 1996). Generally, solid state metathesis (SSM) reactions involve the exchange of reacting partners and are largely driven by the lattice energy of a co-produced salt (Wiley *et al* 1992). SSM reactions have been reported to form metal pnictides, chalcogenides, carbides, silicides and borides as well as ternary phases (Parkin 1996). Recently, Gopalakrishnan and his group synthesized several complex metal oxides through solid state metathesis route taking place at higher temperatures (Gopalakrishnan *et al* 2000; Mandal and Gopalakrishnan 2004, 2005). In all these reactions metal halides have been used in conjunction with alkali and alkaline earth salts of main group anions; this has the advantage of making the reaction extremely exothermic and easy removal of the co-produced salt by water (Panda *et al* 2003). Recently, we communicated a preliminary report on the formation of calcium hydroxyapatite through a SSM route and realized that microwave medium can further accelerate to produce the products in short duration (Parhi *et al* 2004). Later, we extended this method to strontium and barium hydroxyapatites (Parhi *et al* 2006a). We also demonstrated that such a metathetic reaction occurs in solution leading to the formation of nano-sized alkaline-earth hydroxyapatites under hydrothermal condition (Parhi *et al* 2006b). In addition to microwave medium, mechanochemical synthesis (ball-milling) are also known to induce nucleation leading to new products

(Stojanovic *et al* 2005). However, solid state reactions occurring under mechanochemical influence taking place at room temperature are rare (Xian *et al* 1991). In this communication, we report the formation of divalent molybdates through mechanochemically assisted solid state metathesis route at room temperature.

2. Experimental

2.1 Synthesis

Pure $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, CaCl_2 , SrCl_2 and BaCl_2 obtained from CDH, India were employed for the preparation of the title compounds. An equimolar mixture of ACl_2 ($\text{A} = \text{Ca}, \text{Sr}$ and Ba) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were well-ground in an agate mortar in the molar ratio 1 : 1 at room temperature for 30 min. The solids were washed with water to remove sodium chloride that is a by-product of the reaction and dried at 100°C . The solids were characterized using powder X-ray diffraction (PXRD), FTIR, TGA/DTA, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX). Room-temperature powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer using Ni-filtered CuK_α radiation.

3. Results and discussion

Figures 1(a) and (b) show PXRD patterns of a mixture of CaCl_2 and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ before and after grinding. Figure 2(a) shows the presence of single phasic CaMoO_4 after washing off the byproduct, NaCl and drying it in air. We repeated the procedure several times and the results obtained clearly show that the following SSM reaction is initiated by mechanochemical means.

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Figure 1. PXRD patterns of a mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and CaCl_2 : (a) before grinding (*corresponds to peaks of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and corresponds to peaks of CaCl_2), (b) after grinding (*corresponds to the byproduct NaCl) and (c) single phasic calcium molybdate after washing.

PXRD patterns of the other two divalent molybdates, synthesized by room temperature SSM reaction are shown in

figures 2(b) and (c). In all the cases, intensities of the peaks and cell parameters clearly confirm that the phases belong to tetragonal Scheelite (table 1). The X-ray patterns of all the phases reported here match very well with the phases reported in the powder diffraction database

Figure 2. PXRD patterns of (a) CaMoO_4 , (b) SrMoO_4 and (c) BaMoO_4 .

Figure 3. Scanning electron micrographs of (a) CaMoO_4 , (b) SrMoO_4 and (c) BaMoO_4 .

Table 1. Cell parameters of AMoO_4 ($A = \text{Ca, Sr and Ba}$).

Product	a (Å)	c (Å)	Ionic radius for A(Å)*
CaMoO_4	5.199	11.365	1.00
SrMoO_4	5.394	12.020	1.18
BaMoO_4	5.580	12.821	1.35

*Ionic radius (Shannon and Prewitt 1969) for alkaline-earth metal is in coordination number VIII.

(JCPDS 2000). Cell parameters of the molybdates show a strong correlation with radius of alkaline-earth ion suggesting the composition of the phases are close to AMoO_4 ($A = \text{Ca, Sr and Ba}$). TGA showed insignificant weight loss below 600°C and FTIR spectra of all the solids showed bands characteristic of molybdates in the region $830\text{--}890\text{ cm}^{-1}$ due to $\nu(\text{Mo--O})$ stretching and the band at 650 cm^{-1} is attributed to the $\nu(\text{Mo--O--Mo})$. Figure 3 shows SEM images of the divalent molybdates prepared by mechanochemically assisted SSM method. Calcium and strontium molybdates show ill-defined morphologies with extensive agglomeration while barium molybdates show acicular shaped crystals; the particles are in the submicron size. Recently, Thangadurai *et al* (2004) have observed the formation of these Scheelite phases by a metathetic reaction occurring in aqueous solution between alkaline chlorides and sodium molybdates.

4. Conclusion

An ambient temperature synthesis of divalent molybdates reported here suggests that mechanochemically assisted solid state metathesis route can be exploited to prepare

known and probably new oxides by this convenient and economical route.

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