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Ultra fast elemental synthesis of high yield copper Chevrel phase with high electrochemical performance

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ABSTRACT

Self-propagating High-temperature Synthesis (SHS) was applied for the first time to prepare Chevrel phases, $M_xMo_6T_8$ (M=metal, T=S, Se). Combined electron microscopy and X-ray powder diffraction were used to clarify the chemical reactions in the Cu–Mo–S system. It was shown that the replacement of the frontal combustion by thermal explosion increased the $Cu_2Mo_6S_8$ yield from 86 to 96%, while the synthesis remained ultra-fast: 10–20 min in a hot furnace (1000 °C), as compared to at least 17 h of heating for the conventional solid state technique. The synthesized material conformed to the requirements of cathode precursors for Mg batteries, and its electrochemically activity was similar to that of the conventional product.

1. Introduction

The molybdenum chalcogenides, $M_xMo_6T_8$ (M=metal, T=S, Se, Te), also known as Chevrel phases, are an important class of inorganic compounds with remarkable superconductive, magnetic, thermoelectric, and catalytic properties [1–4]. Their crystal structure is based on the Mo_6-clusters, octahedral groups of molybdenum atoms with metal–metal bonds [1, 2]. Our interest in Chevrel phases is related to their unusually high cation mobility at ambient temperatures [5], which allows using the sulfides and selenides as unique cathodes in "green" Mg rechargeable batteries [6, 7], or as ceramic membranes for selective cation extraction from liquid wastes [8].

Two major ways to produce Chevrel phases were proposed. The first method is a high-temperature solid state synthesis, first reported by Chevrel et al. [9], where a stoichiometric mixture of the elements or chalcogenides is sealed under vacuum in a quartz ampoule, and heated over several days at temperatures reaching 1100–1200 °C. Although it was shown that Chevrel phases can be prepared at much lower temperatures [10], the long annealing at ~1100 °C is necessary to reduce the amount of undesirable impurity, layered MoT_2 [11]. In the second approach reported by Rabiller-Baudry et al. [12], Chevrel phases were synthesized from soluble sulfide precursors, such as polythiomolybdates and metal salts, by multi-step heating up to 800 °C. This method generated particles with high surface area, crucial for catalysis, but presented two major disadvantages: (1) the polythiomolybdates themselves had to be pre-synthesized and (2) the hydrogen flow used as a reducing agent in the reaction had to be strictly controlled.

In order to reduce the duration and the temperature of the solid-state synthesis, in our previous work we proposed using stainless-steel Swagelok tube fittings [13] instead of the quartz ampoule, or performing the synthesis in a molten salt media (KCl) [14]. A great advantage of the last method is its suitability for mass-production of Chevrel phases (Table 1), but still the synthesis takes days and requires special equipment with high-energy consumption. These drawbacks can be overcome by using self-propagating high-temperature synthesis (SHS), a relatively novel and simple technique [15–19]. The main principle of SHS is to initiate a self-sustaining highly exothermic reaction in the form of a combustion wave or thermal explosion. The temperatures reached are extremely high (up to 4000 K) and the burning front propagates at high speed (between 0.1 and 20 cm/s) [19]. The synthesis is extremely fast and the overall reaction process takes only a few seconds or minutes. The material obtained with SHS usually presents high porosity, which may be regarded as an advantage for electrochemical and catalytic applications.

A selection of reactions suitable for SHS is commonly based on thermodynamic calculations, in particular on the adiabatic flame

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Table 1
Comparison of the energy consumption parameters for different methods of the solid-state synthesis of Chevrel phase, $Cu_2Mo_6S_8$.

Method	Temprature of synthesis T_s,°C	Time		Potencial of larga scaling	Ref.
		Heating from RT to T_s (h)	Dwelling at T_s		
Cinventional solid state synthesis in quartz tube	1050	48	48 h	No	[27]
Cinventional solid state synthesis in Swagelock	900	8	16 h	Yes	[13]
Synthesis in molten salt	850	6	60 h	Already industrial	[14]
Thermal explosion or bulk mode of SHS	1000	–	10–20 min	Yes	This work

temperature T_{ad} that should be higher than 1800 K. The calculations by Goroshin et al. [20] showed that the combustion should be sufficient to synthesize most of the binary metal–sulfur mixtures. Based on the known high release of heat for the metal–chalcogen reactions, it is expected that the SHS method should be convenient for the Chevrel phase production. Two additional points appear to favor the combustion synthesis of $M_xMo_6T_8$:

- The high thermal conductivity of the starting ternary mixtures, which is related to the large metal/chalcogenide ratio in its composition, should lead to fast heat transmission from the hot to the cold layers.
- The low thermal conductivity of Chevrel phases [3] should result in the slow heat loss in the after-burning zone, thus leading to a more complete reaction.

However, the technical simplicity of SHS is associated with a complexity of physico–chemical processes, which take place upon combustion and subsequent crystallization of the synthetic products. In addition, the extreme character of the combustion reactions results in the intrinsic difficulties of their studies. As a result, practical use of this method for chalcogenides was mostly restricted to binary systems [20–23]. Since little is known about the mechanism of the ternary reactions, the ability of any three-component mixture to produce a stable combustion wave should be verified in practice.

Thus, the aim of this work is to study the potential of SHS for synthesizing Chevrel phases. It is shown that five interesting compounds (Mo_6Se_8, $MnMo_6S_8$, $Cu_2Mo_6S_8$, $PbMo_6S_8$ and $PbMo_6Se_8$) can be obtained by combustion (to our knowledge, we are the first to present the SHS of cluster compounds). However, from the relatively low product yields obtained in these preliminary experiments, it was clear that each M–Mo–T system requires individual optimization of synthetic parameters like particle size of reactants, composition of the green mixture, combustion atmosphere and pressure, initial temperature and so on. We focus herein on the formation mechanism for $Cu_2Mo_6S_8$, as the best precursor for the Mo_6S_8-based cathodes in rechargeable Mg batteries. The phase relations in the Cu–Mo–S system were studied by combined X-ray powder diffraction, electron microscopy and thermal analysis. Based on this study, the bulk mode of SHS (thermal explosion) is further proposed. The electrochemistry of the material with high yield of $Cu_2Mo_6S_8$ obtained by combustion is compared with that of Chevrel phase produced by conventional long-term solid-state synthesis.

2. Experimental

2.1. Materials

The combustion products were obtained from the elemental high-purity powders (Aldrich: 99.95% for Mo $<10\ \mu m$; 99.9% for Mo $<5\ \mu m$; 99.98% for S; 99.7% for Cu $<10\ \mu m$; 99.5% for Cu $<20\ \mu m$; 99.99% for Mn; 99.95% for Pb; Acros: 99.7% for Se) mixed in stoichiometric proportions. The green mixture was ground in a mortar and pestle for ~2 min, pressed into a pellet (pressure of 0.134 GPa) and then ground again. This procedure was repeated twice. For the Mn–Mo–S system, in addition to elements, a mixture of MnS (99.9%, Aldrich), molybdenum and sulfur was tested. For the Cu–Mo–S system we also used composition of $Cu_2Mo_6S_{8.5}$ with extra sulfur amount. The morphology of the Cu and Mo precursors can be seen from the SEM images in Fig. 1. The particle size for other precursors was 2–15 μm for Pb, 8–35 μm for Mn and 1–2 μm for MnS.

2.2. Synthetic methods

We initiated the combustion reaction using two distinctive techniques:

- Frontal combustion (for all the M–Mo–T systems under study): The combustion was performed in quartz tubes under Ar (Fig. 2) or vacuum (for the Mn–Mo–S system). The ratio between reactants (about 10 g) and total reactor volume was 1 to 10. The reactions were initiated at the bottom part of the tube by temperature controlled furnace heated up to 800 °C, which can be considered as the onset temperature for initiation of the reaction, or by applying propane–oxygen Bunsen burner at 1500 °C to the reaction tube for a period of less than a second.
- Thermal explosion or bulk combustion (for the Cu–Mo–S system): The elemental mixture (2 or 5 g) with extra sulfur ($Cu_2Mo_6S_{8.5}$ stoichiometry) was loaded into a Swagelok stainless steel vessel under argon atmosphere, and introduced in the hot furnace (1000 °C) for 2 and 10 min for 2 g samples or for 10 and 20 min for 5 g samples. The ratio between reactant and total reactor volumes was 1 to 2.

Each experiment was repeated at least twice with similar results.

For the X-ray diffraction analysis (XRD) the Cu–Mo–S elemental mixture was loaded into stainless steel Swagelok under argon atmosphere and heated at a rate 1 °C/min in a furnace to different temperatures, without annealing and for 24 h of annealing. For comparative purposes, $Cu_2Mo_6S_8$ was prepared also by a known [13] solid-state technique: a mixture of binary sulfides (MoS_2, CuS) and elemental Mo loaded in Swagelok was heated at a rate 0.75 °C/min in a furnace to 900 °C, for 17 h annealing.

2.3. Electron microscopy, X-ray diffraction and thermal analysis

Scanning electron microscopy of the materials was carried out with a FEI Inspect-S SEM operating at 15 kV. Surface area measurements were calculated according to the B.E.T model.

High-resolution transmission electron microscopy was carried out with a JEOL JEM-2100 LaB_6 at 200 kV. Transmission Electron