Fast synthesis of the polycrystalline materials on the base of $Zn_3V_2MoO_{11}$ and $Zn_{2.5}VMoO_8$[#]

Maya Markova-Velichkova[*], Reni Iordanova

Institute of General and Inorganic Chemistry, Department of Synthesis and Reactivity of Oxide Systems, Bulgarian Academy of Sciences, "Acad. G. Bonchev" str., bl. 11, 1113 Sofia, Bulgaria

Abstract

In our study we applied two different techniques for the preparation of $Zn_3V_2MoO_{11}$ and $Zn_{2.5}VMoO_8$ polycrystalline materials - melt quenching method (up-bottom) and mechanochemical synthesis (bottom- up). These compounds belong to the family of materials with general formula $M_{2.5}VMoO_8$ (M=Zn, Mg, Mn, Co). They are potential candidates as catalysts in processes of selective oxidation of hydrocarbons. Until now, these two compounds were obtained by conventional solid state reaction. Using infrared spectroscopy and X-ray diffraction we proved that the melt quenching technique is a quite appropriate method for the synthesis of bulk $Zn_3V_2MoO_{11}$ phase. Mechanochemical activation is more appropriated for the preparation of nonosized $Zn_{2.5}VMoO_8$ powder. It was established that the melt quenching technique and mechanochemical activation are faster in comparison with conventional ceramic methods for the given synthesis.

Keywords: zinc vanadates, mechanochemical synthesis, melt quenching method

I. Introduction

During the past decades, numerous investigations have been published about the compounds found in the ternary system MO-MoO_3-V_2O_5 (M = Zn, Mg, Mn, Co) [1–8]. For example, many compounds of the $M_{2.5}VMoO_8$ family were synthesized. This kind of materials adopt structures similar to molybdates such as $NaCo_{2.31}(MoO_4)_3$ [9] and $Cu_{3.85}(MoO_4)_3$ [10]. They are featured with one-dimensional columns built from face-sharing octahedra and isolated VO_4 and MoO_4 tetrahedra, which determine their promising catalytic properties (high selectivity and conversion) in the dehydrogenation of alkanes [11,12]. Because of the presence of two transition oxides in the composition, these compounds are also potential candidates for semiconductor applications.

The objects of our investigation are two compounds, which exist in the ZnO-MoO_3-V_2O_5 system - $Zn_{2.5}VMoO_8$ and $Zn_3V_2MoO_{11}$. Up to now they have been obtained by solid state reactions during long time heat treatment (20–100 hours) at different temperatures in the range 480–700°C [13].

The aim of this study is to check the possibility to prepare $Zn_{2.5}VMoO_8$ and $Zn_3V_2MoO_{11}$ for shorter time, using melt quenching and mechanochemical method of synthesis. The melt quenching method is well known for the preparation of glassy or metastable phases and also for the design of the so-called glass ceramics. Mechanical treatment in order to increase the reactivity of solids has been known in the ceramics industry for a long time, as a method for generating new surfaces and various defects. The advantages of mechanochemical activation are that the use of voluminous solutions and complicated operations as well as the sintering of the particles can be avoided.

II. Experimental

Melt quenching method

Stoichiometric mixtures of ZnO (Reachim, purity: 99.9%) and MoO_3 (Reachim, purity: 99.9%) and V_2O_5 (Merck, purity 99.9 %) were prepared in two different molar ratios: i) 60ZnO·20MoO₃·20V₂O₅ mol% (the sample with notation Z3V2M) for $Zn_3V_2MoO_{11}$, and ii)

62.5ZnO·25MoO$_3$·12.5V$_2$O$_5$ mol% (the sample with notation Z2.5VM) for Zn$_{2.5}$VMoO$_8$. The prepared mixtures were homogenized in agate mortar and melted for 20 min in air at 1280°C in a corundum crucible. The melts were quenched applying two different techniques: i) by pouring and pressing between two copper plates (cooling rate 10^2 K/s) and ii) roller technique (cooling rate 10^4–10^5 K/s).

Mechanochemical synthesis

Stoichiometric mixtures of ZnO (Reachim, purity: 99.9%) and MoO$_3$ (Reachim, purity: 99.9 %) and V$_2$O$_5$ (Merck, purity 99.9 %) in molar ratio, which correspond to the two phases (62.5ZnO·25MoO$_3$·12.5V$_2$O$_5$ mol% and 60ZnO·20MoO$_3$·20V$_2$O$_5$ mol%) were subjected to intense mechanical treatment for different period of time (2h – 5h) in air using a planetary ball mill (Fritsch Premium Line 7). The balls to powder weight ratio was 10:1 at 850 rpm. Both container and balls were made of stainless steel.

Sample Characterization

Powder XRD patterns were obtained at room temperature with a Bruker D8 Advance diffractometer using Cu Kα radiation in the θ range 10< θ <60° in a step scan mode. Infrared spectra were performed on a Nicolet – 320 FTIR spectrometer using the KBr pellet technique in the range 400–1200 cm^{-1}. The morphology of the obtained samples was derived using scanning electron microscopy (JEOL JEM-200, CX).

III. Results

Fig. 1a,b represents the XRD patterns of the samples obtained by fast and slow cooling of the melts with nominal composition 60ZnO·20MoO$_3$·20V$_2$O$_5$ mol%.
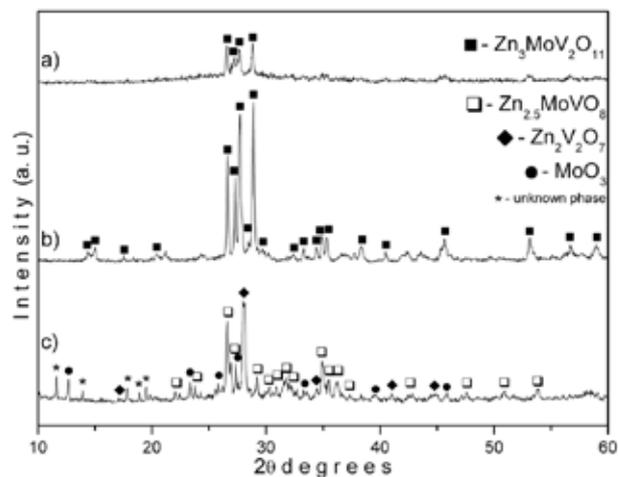

Figure 1. XRD patterns of the samples, obtained by melt quenching method: a) fast cooling sample Z3V2M, b) slow cooling sample Z3V2M and c) fast cooling sample Z2.5VM

In all cases Zn$_3$V$_2$MoO$_{11}$ phase was obtained, which correspond to XRD data obtained by Kurzawa et al. for the same phase [14]. The XRD pattern, which is presented on Fig. 1c, corresponds to the composition 62.5ZnO·25MoO$_3$·12.5V$_2$O$_5$ mol% It is shown that the obtained product is polyphased, i.e. it consists of several phases: Zn$_{2.5}$VMoO$_8$ (JCPS – 50-1894), Zn$_2$V$_2$O$_7$ (JCPS – 52-1893), MoO$_3$ (JCPS – 35-0609) and one unknown phase.

On Fig. 2a XRD pattern of stoichiometric mixture (62.5ZnO·25MoO$_3$·12.5V$_2$O$_5$ mol%) after 2 hours of milling is shown. Fig. 2b,c shows the XRD patterns
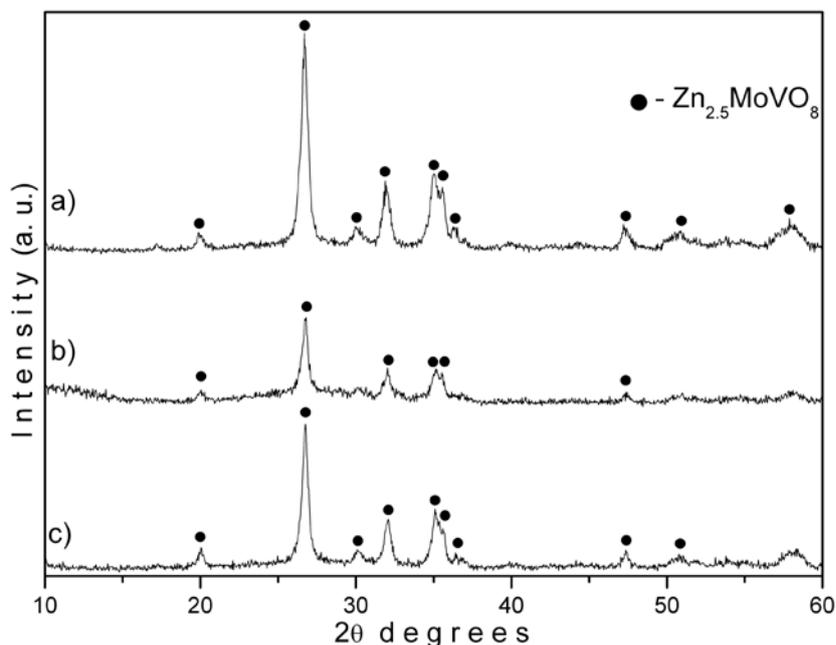

Figure 2. XRD patterns of the Zn$_{2.5}$VMoO$_8$ phase, obtained by mechanochemical activation: a) sample Z2.5VM after 2 hours of mechanochemical treatment, b) sample Z3V2M after 3 hours of mechanochemical treatment and c) sample Z3V2M after 5 hours of mechanochemical treatment
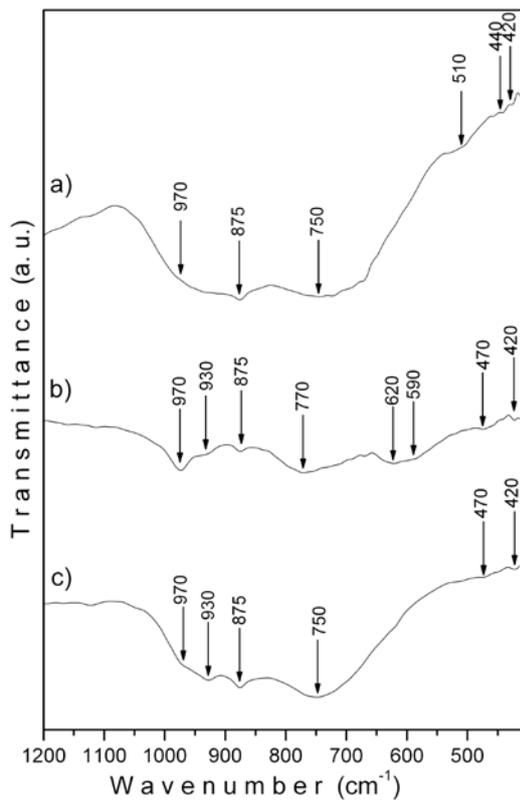
Figure 3. IR spectra of the samples, obtained by melt quenching method: a) fast cooling sample Z3V2M, b) slow cooling sample Z3V2M and c) fast cooling sample Z2.5VM
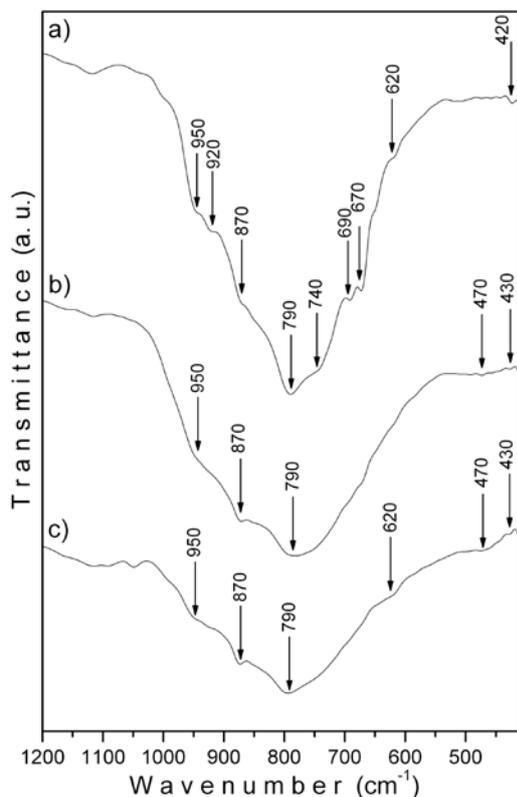

Figure 4. IR spectra of samples: a) Z2.5VM after 2 hours of mechanochemical treatment; b) Z3V2M after 3 hours of mechanochemical treatment and c) Z3V2M after 5 hours of mechanochemical treatment

of mechanically activated samples with composition $60ZnO \cdot 20MoO_3 \cdot 20V_2O_5$ mol% after 3 and 5 hours of mechanochemical activation. As it is seen on the Fig. 2, diffraction peaks of only orthorhombic $Zn_{2.5}VMoO_8$ phase are observed (JCPS – 50-1894) [15].

Additional information on the phase formation and structural features of $Zn_{2.5}VMoO_8$ and $Zn_3V_2MoO_{11}$ phases could be obtained by IR spectroscopy (Figs. 3 and 4). As one can see from the Fig. 3, the vibrational spectra of the samples prepared by melt quenching method are very similar, corresponding to the phase $Zn_3V_2MoO_{11}$ (XRD diffraction Fig. 1). The main absorption band is situated at 750–770 cm^{-1}. Three other bands - 870–970 cm^{-1} are also recognized. All bands in the range 750–970 cm^{-1} can be assigned to the vibrations of isolated strongly deformed MO_4 polyhedra. The absorption between 550–650 cm^{-1} is probably due to the formation of edge-shared polyhedra (Fig. 3b – slow cooled sample) [16,17]. The spectra of fast quenched samples (Fig. 3a,c) are not well resolved because of their partial amorphization. The bands in all spectra below 500 cm^{-1} should be connected with vibrations of ZnO_6 units [18,19].

Fig. 4a demonstrates infrared spectra of the sample $62.5ZnO \cdot 25MoO_3 \cdot 12.5V_2O_5$ mol% after 2 hours of mechanochemical treatment. On Fig. 4b,c are presented vibrational spectra of the mechanically activated sample with initial composition $60ZnO \cdot 20MoO_3 \cdot 20V_2O_5$ mol% after 3 and 5 hours milling time. The spectra of mechanochemical treated samples are characterized with very strong absorption near 790 cm^{-1} and not well resolved shoulders in the range 870–970 cm^{-1}. The band at 790 cm^{-1} is due to asymmetrical stretching vibrations of isolated MO_4 tetrahedra.

Fig. 5 represents SEM image of $Zn_3V_2MoO_{11}$ phase, obtained by melt quenching method of fast cooling sample with composition $60ZnO \cdot 20MoO_3 \cdot 20V_2O_5$ mol%. It is seen the formation of small crystals (5–10 μm) immersed into the amorphous matrix. The SEM micrograph of $Zn_{2.5}VMoO_8$ phase, obtained by mechanochemicaly activated precursors shows the formation of spherical-like aggregates with size dimension of the crystallites below 1 μm (Fig. 6).

IV. Discussion

In order to understand the features of the applied techniques we take into account the crystallographic structure of $Zn_{2.5}VMoO_8$ and the connectivity of the different polyhedra. $Zn_3V_2MoO_{11}$ phase crystallizes in the monoclinic system, but there is no data for the structural polyhedra in the unit cell [13,14]. This compound melts incongruently at 800±5°C with a deposition of $Zn_{2.5}VMoO_8$ crystals. Crystallographic data of the other compound - $Zn_{2.5}VMoO_8$ are summarized by Wang et al. [12]. According to them, this compound crystallizes in the orthorhombic system. In the structure, $Zn(3)O_6$
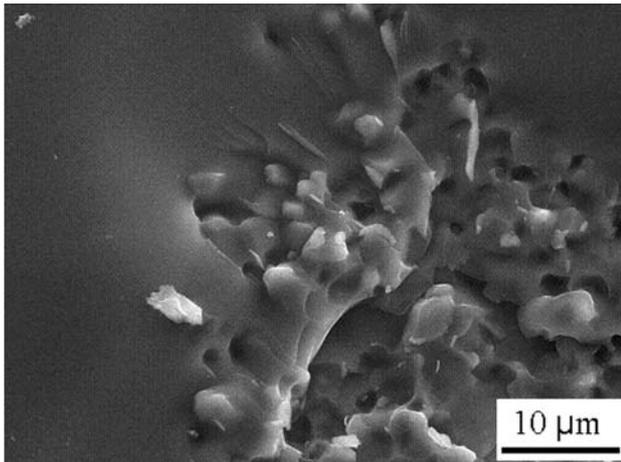
Figure 5. SEM micrograph of fast cooling sample Z3V2M, containing $Zn_3V_2MoO_{11}$ crystals, according to X-ray data

and $Zn(4)O_6$ octahedra form the zigzag sheets by sharing edges and corners, face-sharing $Zn(1)O_6$ octahedra form one-dimensional chains passing through the center of hexagonal tunnels, and the very unusual $Zn(2)O_6$ trigonal prisms form columns parallel to the *a* axis. Disordered $(V/Mo)O_4$ tetrahedra are linked to ZnO_6 octahedra and/or trigonal prisms by sharing corners to form the three dimensional framework. The peritectic temperature of this incongruently melting compound is 845°C, depositing a solid phase of $ZnMoO_4$ [15].

Applying melt quenching technique at nonequilibrium conditions during the cooling of the melts with nominal composition $60ZnO·20MoO_3·20V_2O_5$ mol%, we obtained the low temperature compound $Zn_3V_2MoO_{11}$. At the same conditions, from the melt with nominal composition $62.5ZnO·25MoO_3·12.5V_2O_5$ mol%, mixture of $Zn_{2.5}VMoO_8$, $Zn_2V_2O_7$, MoO_3 and one unknown phase was obtained. More over, part of the melts is possible to be supercooled in solid amorphous state. This is seen from the presence of amorphous halo together with diffraction peaks.
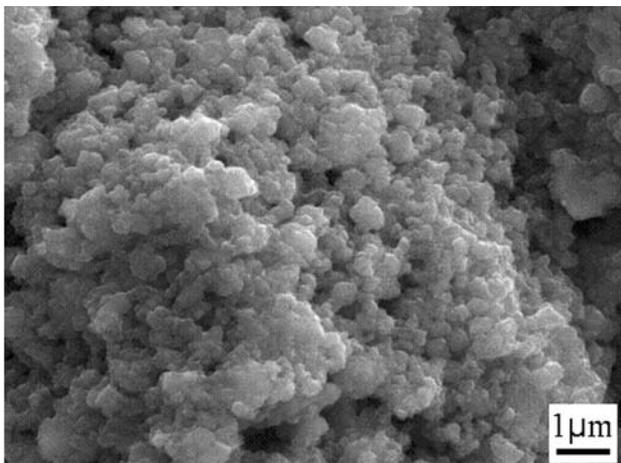

Figure 6. SEM micrograph of sample with nominal composition Z2.5VM after 2 hours of mechochemical treatment, containing $Zn_{2.5}VMoO_8$ crystals, according to X-ray data

Applying mechanochemical reaction (bottom-up), irrespective to the initial compositions, the only crystalline phase is $Zn_{2.5}VMoO_8$. As it is shown above, its crystal structure contains different types of associated ZnO_6 units connected with isolated V/MoO_4 tetrahedra. According to the presented IR spectra, the isolated tetrahedra of this compound are more symmetrical, because the bands in the range 870-950 cm^{-1} are not well resolved. In the spectrum of compound $Zn_3V_2MoO_{11}$ these bands are more intensive, which resulted from the removal of the degeneracy and the activation of the symmetrical vibrations. This kind of spectra is typical for the vibration of more deformed polyhedra. In the spectrum of $Zn_3V_2MoO_{11}$, bands in the range 620–590 cm^{-1} also appear which may be connected with the formation of edge-sharing units Mo_2O_2 [16]. This is why, from kinetic point of view, during mechanochemical treatment we suggest that it is easier to obtain $Zn_{2.5}VMoO_8$ in which weak bonds of ZnO_6 units with corner-shared tetrahedra are realized.

IV. Conclusions

In this study we proved that the melt quenching is a very appropriate method for the synthesis of bulk $Zn_3V_2MoO_{11}$ phase for a short time. By mechanochemical reaction, $Zn_{2.5}VMoO_8$ phase was obtained at room temperature after two hours, which is several time faster than classical solid state reaction.

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