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Molten salt synthesis of barium molybdate and tungstate microcrystals

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Abstract

Pure microcrystalline barium molybdate $BaMoO_4$ and barium tungstate $BaWO_4$ materials were prepared by molten flux reaction using alkali metal nitrates as reaction media. The obtained crystals have rhombic shape and expose mostly (111) crystallographic planes. Their mean size depends on the flux temperature and the nature of the alkali metal cation. Monomeric molybdate and tungstate used as precursors yield target products already at 673 K whereas if polymerized ammonium oxosalts were used, then higher temperatures were necessary to obtain barium salts. The optimal temperature for the preparation of pure crystals with well defined shape was found to be near 773 K. UV–visible spectra have been measured to precise energy gaps in these important d^0 transition metal compounds. The values of Eg for these two mixed oxides are 4.3 eV for $BaMoO_4$ and 3.8 eV for $BaWO_4$. Such values contradict to what can be expected from the known data on their structure and the relative electronegativity of W and Mo ions. The possible explanations of this observation are commented.

Keywords: Molten salt; Molybdate; Tungstate; Scheelites; Band gap

1. Introduction

$BaWO_4$ and $BaMoO_4$ with a tetragonal Scheelite structure are important materials in the electrooptical industry due to emission of blue luminescence [1]. They also proposed as low nuclear spin optical hole burning hosts [2]. Moreover, these compounds have been tried as materials for Stimulated Raman Scattering (applied to obtain laser frequency shift) and the $BaWO_4$ material appeared to be the most efficient known Raman active crystal for picosecond pump pulses [3]. Belonging to the d^0 compounds with average wide gaps, the compounds of this type can be envisaged as photocatalysts, either pure or doped. The preparation methods of $BaWO_4$ are high temperature flux crystallization [4,5], solid state reaction [6,7], and hydrothermal–electrochemical method [8] was previously described.

For some applications, microcrystalline powders with well defined morphology would be preferable. Therefore several works recently dealt with the morphology control of barium molybdate and tungstate. Thus, $BaWO_4$ crystals with different morphology, such as olive-like, flake-like, and whisker-like structures have been successfully prepared through a hydrothermal process in the presence of different surfactants [9]. Dendrite-like, hollow and various ordered structures were prepared by the solution methods, applying organic template and soft hydrothermal conditions, use of polymer or microemulsion [10–14].

Molten nitrates can be considered as relatively low temperature ionic solvents, which possess considerable basicity and can precipitate oxidic species. Earlier, different classes of compounds were synthesized in molten nitrate fluxes, such as simple and mixed oxides [15–17], niobate of lithium $LiNbO_3$ [18], and mixed phosphates [19]. The nature of alkali metal cation was found to influence the melts reactivity in the expected sequence Li > Na > K [20]. It was found that molten nitrates are convenient ionic solvents providing simple and well reproducible preparation ways to many inorganic materials with original morphology. In this work barium molybdate and tungstate were prepared using molten nitrates as reaction medium. The influence of the reaction conditions on the products composition and properties was studied.

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2. Experimental

Barium chloride, alkali metal tungstate or molybdate and Na or K nitrate in a 12-fold molar excess (all from Aldrich) were thoroughly mixed and placed in a Pyrex reactor. The mixtures were heated to a target temperature 673–823 K for 12 h. After cooling, the solidified melt was washed with distilled water at room temperature then the product was dried overnight in air at 373 K.

X-ray diffraction patterns were recorded on a BRUKER diffractometer by using CuKα radiation. Identification of phases was made using standard JCPDS files. Chemical analyses were carried out by using the atomic emission method. Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 device, at the center of electronic microscopy of Claude Bernard University (Lyon).

Reflectance UV–visible spectra were collected and converted to absorbance using a Perkin-Elmer Lambda 9 scanning spectrometer equipped with an integrating sphere over the spectral range 200–2500 nm (6.2–0.5 eV). The band gap energies quoted in this study are based on Shapiro's method [21].

3. Results and discussion

Table 1 summarizes the conditions of preparations and their results. Monomeric molybdate and tungstate used as the precursors lead to the target barium salts already at 673 K whereas at these temperatures the polymeric heptamolybdate and metatungstate ammonium salts produced large amounts of Mo and W trioxides impurities.

Table 1
Preparation conditions and properties of the $BaMo(W)O_4$ solids issued from molten nitrate fluxes

Reaction mixture components[a]	Reaction T, K[b]	Product composition, DRX	Mean crystal size (μm) of $BaMo(W)O_4$
KNO_3 Na_2MoO_4	673	$BaMoO_4$	1.5, agglomerated
$NaNO_3$ Na_2MoO_4	673	$BaMoO_4$	2
KNO_3 Na_2WO_4	673	$BaWO_4$	12
$NaNO_3$ Na_2WO_4	673	$BaWO_4$	14
$NaNO_3$ $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	673	$BaMoO_4$, MoO_3	ND
$NaNO_3$ $(NH_4)_4W_{12}O_{40}\cdot 2H_2O$	673	$BaWO_4$, WO_3	ND
KNO_3 Na_2MoO_4	773	$BaMoO_4$	5.4, agglomerated
$NaNO_3$ Na_2MoO_4	773	$BaMoO_4$	6.2, well shaped
KNO_3 Na_2WO_4	773	$BaWO_4$	34
$NaNO_3$ Na_2WO_4	773	$BaWO_4$	41
$NaNO_3$ $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	773	$BaMoO_4$	3.2, agglomerated
$NaNO_3$ $(NH_4)_4W_{12}O_{40}\cdot 2H_2O$	773	$BaWO_4$, WO_3	ND
KNO_3 Na_2MoO_4	823	$BaMoO_4$	16, particles cracking
$NaNO_3$ Na_2MoO_4	823	$BaMoO_4$	19, particles cracking
KNO_3 Na_2WO_4	823	$BaWO_4$	32, particles cracking
$NaNO_3$ Na_2WO_4	823	$BaWO_4$	45, particles cracking
$NaNO_3$ $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	823	$BaMoO_4$	14, particles cracking
$NaNO_3$ $(NH_4)_4W_{12}O_{40}\cdot 2H_2O$	823	$BaWO_4$	27, particles cracking

[a] $BaCl_2$ was always used as barium parent salt; molar excess of VI group metal to Ba was 1.5; that of alkali metal nitrate to Ba was 12.
[b] Reaction time was 12 h.

This can be easily understood considering that in order to give $BaMoO_4$ and $BaWO_4$, the polymeric precursors should be first depolymerized by the nitrate melts. Indeed, if alkali metal monomolybdate or monotungstate are taken as the precursors then the reaction occurs analogously to aqueous precipitation:

$$Ba^{2+} + MoO_4^{2} = BaMoO_4 \tag{1}$$

In the case when polyoxosalts precursors were used such as heptamolybdate or metatungstate of ammonium, then formation of nitrogen oxides was observed during the reaction, due to Lux–Flood interaction of polyoxospecies with the melt. As shown in earlier studies [15], first the ammonium salts decompose to the corresponding oxides, and then the oxides undergo the sequences of Lux–Flood reactions as exemplified for molybdenum:

$$3MoO_3 + 2KNO_3 \rightarrow K_2Mo_3O_{10} + 2NO_2 + 1/2O_2 \tag{2}$$

$$2K_2Mo_3O_{10} + 2KNO_3 \rightarrow 3K_2Mo_2O_7 + 2NO_2 + 1/2O_2 \tag{3}$$

$$K_2Mo_2O_7 + 2KNO_3 \rightarrow K_2MoO_4 + 2NO_2 + 1/2O_2 \tag{4}$$

The final products of such reactions are the corresponding monomer ions salts, but the reactivity of the corresponding oxides is such that at least 773 K temperature is necessary to depomymerize them. Moreover, being less reactive, tungsten oxide requires higher temperatures to be transformed into the monomer tungstate.

X-Ray diffraction confirms purity of materials at various preparation temperatures. Only the peaks of target phases were observed as exemplified by $BaMoO_4$ prepared using Na_2MoO_4 precursor (Fig. 1). The peaks are narrow and have similar intensity whatever preparation temperature, beside the solid obtained from KNO_3 at 673 K, represented by agglomerates of small crystals, in which case the XRD lines are broadened and their intensity decreased. Chemical analysis shows nearly perfect stoichiometry and the absence of alkali metal impurities (sometimes expected in this type of preparations, especially when the specific surface areas of the materials obtained are high).

As follows from the data of Table 1, $BaMoO_4$ gives systematically much smaller crystals than $BaWO_4$. At the same time slight increase of crystals size observed from KNO_3 to $NaNO_3$ melt and from polymeric to monomeric M(VI) precursor. The best results were obtained in $NaNO_3$ melt at 773 K.

At these conditions, statistical crystals shape analysis showed that 70% of the $BaMoO_4$ facets are those of (111) crystallographic planes, whereas the remaining 30% are distributed between (110) and (001) faces (Fig. 2). As with $BaWO_4$, almost the totality of facets exposed were the (111) planes (Fig. 2, f).

Increasing temperature from 773 to 823 K leads instead of the expected increase of mean crystals size to their breaking. The crystals lost regular shape and many smaller particles appeared issued from the broken larger particles, as observed in Fig. 2, d for the $BaMoO_4$ case.

The analysis of the crystals properties as a function of preparation conditions shows that the optimal route which leads to pure and well shaped crystals is using $NaNO_3$ melt at 773 K and monomer molybdate or tungstate salts as precursors. Otherwise, if highly dispersed materials are desired, then KNO_3 flux at 673 K should be used.

Since the target applications of the materials prepared are related to their optical properties, the optical diffuse reflectance spectra were measured and compared. The spectra are represented in Fig. 3; the band