Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 406 (2003) 29–33

thermochimica acta

www.elsevier.com/locate/tca

A new method of $Fe_2(WO_4)_3$ preparation and its thermal stability

A.K. Sriraman, A.K. Tyagi*

Applied Chemistry Division, Bhabha Atomic Research Center, Mumbai 400085, India

Received 26 June 2002; received in revised form 14 February 2003; accepted 31 March 2003

Abstract

The title compound $Fe_2(WO_4)_3$, being a metastable phase, is very difficult to prepare by a solid state synthesis route starting from the corresponding oxides. It has been prepared by a newly developed solution route starting from aqueous solutions of ferrous ammonium sulfate and sodium tungstate. The various process parameters were optimized to get a suitable precursor, which upon calcination at 500 °C for 4 h gave a well crystalline product. The product was characterized by powder XRD to have a monoclinic unit cell of $Fe_2(WO_4)_3$. Its thermal stability was investigated by high-temperature XRD. It was found to decompose to $FeWO_4$ and WO_3 at 750 °C. The typical monoclinic to orthorhombic phase transition, and in turn negative thermal expansion, were not observed.

Keywords: Tungstates; XRD; Thermal stability; Solution route

1. Introduction

The compounds with general formula $A_2(MO_4)_3$ (A: trivalent cations and M: W^{6+}, Mo^{6+}, etc.) have gained a considerable importance in recent time, as many of them exhibit unusual properties like negative thermal expansion [1]. The detailed phase relations in $A_2(MO_4)_3$ (A: lanthanide and transition metal cations and M: W^{6+} and Mo^{6+}) have been reported by Nassau et al. [2] and Abrahams and Berstein [3]. Nassau et al. [2] have studied a wide range of tungstates and molybdates of all the lanthanides, and reported several kinds of structures viz., tetragonal, orthorhombic, monoclinic, in addition to a few unidentified phases. Abrahams and Berstein [3] reported that the counter-metal ions (A^{3+}) in these compounds exist in eight or six-fold coordination depending upon the radius ratio of the A^{3+} and O^{2-} ions. Thus, they proposed two broad classifications in this series, namely, an orthorhombic modification iso-strutctural to $Sc_2(WO_4)_3$, and a monoclinic $Eu_2(WO_4)_3$ structural type modification. It was also reported [3,4] that the molybdates of heavier rare-earths and transition elements crystallize with orthorhombic $Sc_2(WO_4)_3$ and monoclinic $Fe_2(WO_4)_3$ type modifications, respectively. However, it may be mentioned that these two structures are very closely related, and both have M^{6+} in the tetrahedral coordination. The low-temperature monoclinic modification has six distinguishable M^{6+} sites, whereas the high-temperature orthorhombic phase has only two distinguishable M^{6+} sites. In both the cases, the M^{6+} ions are connected to A^{3+} through an oxygen atom, i.e. by sharing the corners of MO_4 tetrahedra and AO_6 octahedra. Another surprising observation is that the corresponding molybdates in general have a better thermal stability than tungstates. It is difficult to prepare $A_2(WO_4)_3$ by a solid state route, as one usually ends up with more stable phases

---

* Corresponding author. Tel.: +91-22-2559-5330;
fax: +91-22-2550-5151/2551-9613.
E-mail address: aktyagi@magnum.barc.ernet.in (A.K. Tyagi).

0040-6031/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00201-6

like AWO_4. One such compound is $Fe_2(WO_4)_3$ for which several contradictory reports exist in literature. Nassau et al. [2] were first to report the preparation of $Fe_2(WO_4)_3$ by a solid state synthesis route. Pernicone and Fagherazzi [5] attempted to prepare this compound by Kerr et al.'s method [6] followed by a high-temperature annealing, but obtained a mixture of $Fe_2(WO_4)_3$ and WO_3. However, it is generally believed that none of these groups got an unequivocal single phasic product. Subsequently, Harrison et al. [7] prepared $Fe_2(WO_4)_3$ by a modified version of Kerr's ferric molybdate preparation starting with sodium tungstate hydrate and ferric nitrate hydrate. They used this oxide as a catalyst for methanol oxidation. Subsequent to this work, there were no attempts to develop new routes for preparation of $Fe_2(WO_4)_3$. Recently, this kind of open framework materials attracted a renewed interest due to negative thermal expansion behavior exhibited by them [8].

In this manuscript, we report a simple solution method for preparation of $Fe_2(WO_4)_3$, its thermal stability and thermal expansion behavior.

2. Experimental

AR grade ferrous ammonium sulfate, sodium tungstate, urea and hydrogen peroxide were used as the starting materials. Several processes were attempted to get the desired precipitates containing iron and tungsten. Each precipitate, obtained by different processes, was calcined at 500 °C for 4 h to obtain the crystalline phases. The phase identification was done by Philips Powder XRD, Model PW1710 control unit, coupled with PW1729 generator and PW 1820 vertical goniometer with monochromatized Cu Kα radiation. Thermal stability was in situ investigated using a Philips X'Pert Pro unit with an Anton Par high-temperature attachment. The bulk thermal expansion was measured in air from ambient temperature to 973 K as a function of temperature using an LKB 3185 fused quartz vertical thermo-dilatometer.

3. Results and discussion

The stock solution of the starting materials were prepared as follows: 70 g of AR grade ferrousammonium sulfate, $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ (0.18 M) was dissolved in one liter of distilled water to which a drop of dilute H_2SO_4 was added. The resulting solution had a pH of 1.8, strength 10 mg Fe^{2+} ml^{-1} (hereafter, it will be referred as solution-A). Similarly, 18 g of AR grade sodium tungstate, $Na_2WO_4{\cdot}2H_2O$ (0.45 M) was dissolved in one liter of distilled water (strength 0.055 M, pH 7.2, 10 mg W/ml, hereafter, it will be referred as solution-B). Four different mixtures were prepared from these solutions: each mixture was heated over a water bath at 60 °C, while maintaining the pH at ∼1.9. In the process-1, 50 ml of solution-A and 75 ml of solution-B were mixed. The product obtained from the process-1 consisted of small reddish brown flocs. This may be due to the hydrolyzed ferrous salt, which in turn is not available for the formation of iron tungstate. In process-2, urea (1 g per 50 ml of solution-B) was also added to the mixture of solutions-A and -B in the above mentioned ratio. The hydrolysis of urea resulted in a better control of pH, which facilitated in the formation of a coherent and course brown precipitate of iron tungstate. In process-3, no urea was added but H_2O_2 was added (1 ml per 50 ml of solution-B). Due to the addition of H_2O_2, the ferrous ions got instantly oxidized to ferric ions resulting in the non-availability of Fe^{2+} for the tungstate formation. The precipitate was found to be reddish green in color. Process-IV had both urea (1 g per 50 ml of solution-B) and H_2O_2 (1 ml per 50 ml of solution-B). The oxidation of Fe^{2+} to Fe^{3+} interfered with the tungstate formation despite the availability of urea. The precipitates from all the four processes were filtered through Whatman filter paper no. 542, washed with warm distilled water and dried at room temperature. Powder XRD revealed all the four precipitates to be amorphous in nature. In order to make them crystallize, all the four precipitates were heated at 500 °C for 4 h in static air in pellet form.

The XRD pattern of the product obtained by heating the precipitate obtained from the process-II, at 500 °C for 4 h, matched well with that of reported pattern of monoclinic $Fe_2(WO_4)_3$. The probable mechanism of $Fe_2(WO_4)_3$ formation is as follows:

$$Fe^{2+} + {WO_4}^{2-} = FeWO_4;$$

$${WO_4}^{2-} + 2FeWO_4 + [O] + 2H^+ = Fe_2(WO_4)_3 + H_2O$$

where [O] is the dissolved oxygen from solution.

The room temperature XRD pattern was refined using standard least square method and the monoclinic cell parameters obtained were as follows: $a = 15.86$, $b = 9.295$, $c = 18.42$ Å and $\beta = 125.1^\circ$, which are in a reasonably good agreement with the reported values [7].

In order to study the phase transition from monoclinic to orthorhombic modification, the XRD pattern

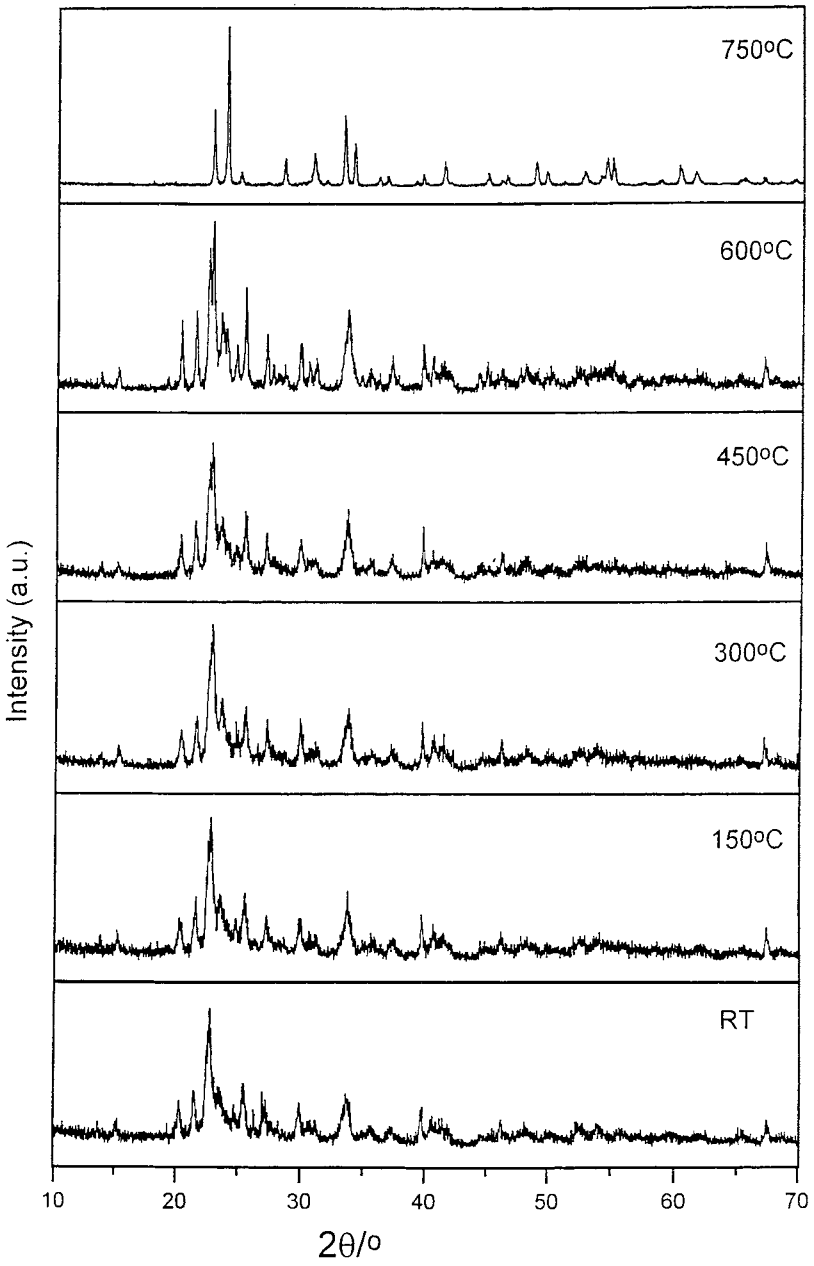

Fig. 1. XRD patterns of monoclinic $Fe_2(WO_4)_3$ at different temperatures.

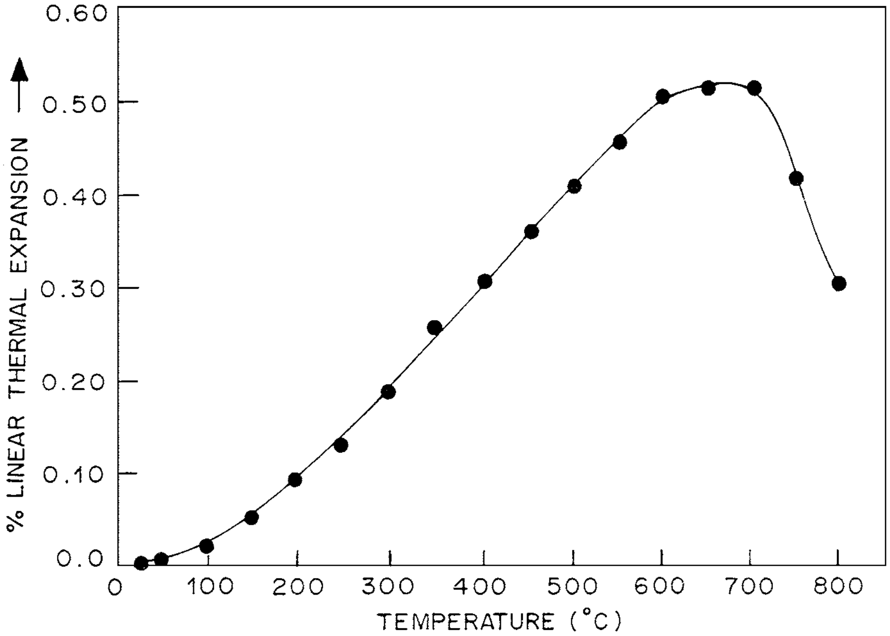

Fig. 2. Linear thermal expansion (%) vs. temperature for $Fe_2(WO_4)_3$.

of the heated product (500 °C for 4 h) was recorded from ambient temperature to 750 °C at a regular interval of 150 °C. Typical XRD patterns at different temperatures are shown in Fig. 1. The XRD pattern at room temperature matched well with that of monoclinic $Fe_2(WO_4)_3$, which remained unchanged till 600 °C. However, the resolution of the multiplet at about 23° increase in the XRD pattern at 600 °C but without additional peaks, which indicates that the $Fe_2(WO_4)_3$ is stable up to 600 °C. The characteristic phase transition from monoclinic to orthorhombic modification was not observed. Strikingly the XRD pattern completely changed at 750 °C. The analysis of the XRD pattern recorded at 750 °C revealed the presence of $FeWO_4$ and high-temperature tetragonal modification of WO_3, which is reported to exist at 725 °C (JCPDS 5-388). Hence, this compound is not expected to show negative thermal expansion as in the $A_2(WO_4)_3$ class of materials, where A is trivalent cation, the monoclinic modification shows positive thermal expansion whereas the orthorhombic modification exhibits negative thermal expansion [1]. In order to study the bulk thermal expansion of $Fe_2(WO_4)_3$ a pellet of diameter 10 mm and height about 8 mm was made. It was sintered at 500 °C for 6 h. The linear expansion (%) versus temperature curve is shown in Fig. 2. A linear positive thermal expansion was observed up to about 600 °C, which is a characteristic of the monoclinic modification of this class of materials. Subsequently, a contraction was observed which should not be taken as negative thermal expansion as the pellet was sintered at 500 °C. It is easy to comprehend that the contraction above 600 °C is due to sintering effect.

4. Conclusion

A new solution route to prepare $Fe_2(WO_4)_3$ has been developed, which could be used to prepare up to 5 g level also in a single batch. This compound has a poor thermal stability, revealed by high-temperature XRD as it showed a thermal decomposition instead of phase transition. This compound is expected to show an interesting response under high pressure. The high pressure studies are in progress and will be reported elsewhere.

Acknowledgements

We thank Dr. N.M. Gupta, Head, Applied Chemistry Division, BARC, for his keen interest in this work. Dr. M.D. Mathews and Shri B.R. Ambekar of Applied Chemistry Division are thanked for providing the dilatometry support and other assistance.

References

[1] A.K. Tyagi, S.N. Achary, M.D. Mathews, J. Alloys Comp. 339 (2002) 207.

[2] K. Nassau, H.J. Levindtein, G.M. Loiacono, J. Phys. Chem. Solids 26 (1965) 1805.

[3] S.C. Abrahams, J.L. Berstein, J. Chem. Phys. 45 1966 2475.

[4] H.Y. Chen, Mater. Res. Bull. 14 (1979) 1583.

[5] N. Pernicone, G. Fagherazzi, J. Inorg. Nucl. Chem. 31 (1969) 3323.

[6] P.F. Kerr, A.W. Thomas, A.M. Langer, Am. Miner. 48 (1963) 14.

[7] W.T.A. Harrison, U. Chowdhry, C.J. Machiels, A.W. Sleight, A.K. Cheetham, J. Solid State Chem. 60 (1985) 101.

[8] T.A. Mary, J.S.O. Evans, A.W. Sleight, T. Vogt, Science 272 (1996) 90.