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Microwave Preparation of Oxide Bronzes

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Several vanadium, tungsten, and molybdenum oxide bronzes have been prepared using microwave irradiation. Metal oxides and alkali metal iodides were used as starting materials. Intermittent grinding and inert atmosphere were found to be necessary for the synthesis of most of the bronzes. The reaction temperatures are remarkably lower than those employed for conventional synthetic techniques and the microwave assisted reactions proceed at extremely fast rates. The microwave synthesized bronzes consist of particles having long, rectangular rod-like morphology. © 1999 Academic Press

Key Words: **microwave synthesis; oxide bronzes; intercalation.**

INTRODUCTION

Oxide bronzes are a class of compounds having the general formula A_xTO_n, where A is a metal atom which is incorporated into the largely covalently bonded transition metal (T)-oxide, TO_n network by intercalation. The A atoms are completely ionized in the structure and therefore the electron from the atom A is introduced into the d orbitals of the T atoms. Thus the T atoms are reduced to lower valence state. Also the electrons thus acquired by the T atoms are either localized, which results in making A_xTO_n a semiconductor, or are delocalised making them metallic conductors. It has been observed that the conductivities increase and activation energies decrease with an increasing level of metal intercalation into the host lattice of the semiconducting bronzes (1). Besides their fascinating electrical (2–8) and magnetic (9) properties, bronzes are interesting because of the variety of structures and the wide compositional ranges of stability exhibited by them. The compositional spread in bronzes is generally wider than even in nonstoichiometric binary compounds. Composition dependent structural changes are observed quite generally. There is thus the possibility of steep and sudden change in electrical properties when there is a composition dependent crossover from one phase to another. By virtue of the variety of their properties, bronzes find several applications such as in electrochromic displays (10–11), electrodes (12–14) and pH sensors (15–17). Other electrical properties of bronzes such as formation of charge density waves in them also possess the potential for interesting applications (18, 19).

The longest known and the best studied are the tungsten bronzes (20–22) of general formula A_xWO_3. The structure (23,24) consists of regular or distorted WO_6 octahedra, sharing common corners. The electron transport in cubic tungsten bronzes is attributed to the existence of an indirect overlap of tungsten t_{2g} orbitals with the oxygen p_π orbitals (4) in the W–O–W chains. Tungsten bronzes are very typical in that they exhibit both semiconducting (25) (low level of intercalation) and metallic (high level of intercalation) properties (2). For example, $Na_{0.025}WO_3$ shows a very small activation energy for the conductivity of 0.02 eV (26), while metallic conductivity has been reported in Na_xWO_3 for $0.58 < x < 0.9$ (2).

Molybdenum bronzes are less stable compared to tungsten bronzes. The octahedra in this case share both edges and corners. The vanadium bronzes possess more complex structures (26). The general structure is layered and consists of intercalated metal atoms which occupy voids and permit octahedral coordination. Due to its small size, the vanadium atom distorts the octahedra and in some cases the distortion leads to the formation of a nearly triangular bipyramid.

Several methods of synthesis of bronzes are known (27–35). Thermal (36, 37) and vapour phase preparations involve the use of reactive metals. Crystals of tungsten bronzes have been grown by chemical vapour transport using $HgCl_2$, $HgBr_2$ as transporting agents (38). Electrolytic reduction (8, 20, 39, 40) and electrochemical intercalation using fused salts have also been used in the preparation of bronzes (8, 20, 39–42). The formation of bronzes by decomposition of alkali iodide + metal oxide mixtures was reported by Ganguli *et al.* (43). A reductive intercalation method has been reported by Bhat and Gopalakrishnan for

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the preparation of tungsten, molybdenum, and vanadium bronzes where iodides of the intercalating metals have been used (44). A simple method to prepare bronzes has been demonstrated by Ayyappan and Rao, wherein the reaction of WO_3, MoO_3, and V_2O_5 with alcohols or glycols yields hydrogen bronzes (45). The synthesis of vanadium bronzes by sol-gel route has been described by Baffier *et al.* (46). Sol-gel synthesis has also been employed to synthesize tungsten bronzes (47). But these methods are quite tedious and take about 24 to 160 h for the completion of the reactions.

In recent years, a wide variety of inorganic solids have been prepared using microwave irradiation and the reactions have been found to require much shorter reaction times (48–51). Apart from saving reaction time, microwave synthesis is simple and clean. In this article, we report a novel method of synthesis of oxide bronzes using microwave irradiation.

EXPERIMENTAL

The reactants used in bronze preparation were all 99% to 99.8% pure and commercially available MERCK chemicals. Microwave synthesis was carried out in a domestic BPL–Sanyo microwave oven operating at 2.45 GHz frequency and a maximum output power of 750 Watts.

The method of synthesis requires the use of 5 g batches of a mixture of metal iodide and transition metal oxide. For example, for the preparation of $Li_{0.3}V_2O_5$, LiI, and V_2O_5 were the initial reactants and the reaction can be written as

$$0.3\mathrm{LiI} + V_2O_5 \rightarrow Li_{0.3}V_2O_5 + 0.15\ I_2\uparrow.$$

The mixtures are ground to a fine powder initially for about 20 to 25 minutes to ensure homogeneity. The mixture was placed in a silica crucible and microwave irradiated for about 5 to 10 minutes. Some preparations required intermittent grinding and reexposure to microwaves.

Temperatures at various stages of bronze formation were measured by inserting a Pt–Pt 13% Rh thermocouple into the reactants and a temperature versus time curve was plotted. Successive time–temperature readings were obtained by irradiating a fresh batch of the same composition and inserting the thermocouple at the end of the required interval and not by continued heating of the same sample.

The various bronzes prepared are listed in Table 1. The table also indicates the duration of microwave irradiation. Whenever the preparation required intermittent grindings, it is indicated as a sum of intervals. The phase purity of the bronzes was investigated using powder X-ray diffraction (Philips; Model PW 1050/70; Cu$K\alpha$ radiation).

It was observed from the XRD patterns of most tungstates that there was insufficient crystallization (broad peaks) and also impurity peaks. The bronzes were submitted to 20–35 minutes annealing in iodine atmosphere, which ensures avoidance of oxidation. The iodine atmosphere was created in the microwave oven by heating iodine crystals in a silica crucible kept beside the sample. The bronze was then placed in the crucible when the iodine vapours started evolving. The tungstate bronzes were microwave annealed for 20 to 35 minutes.

RESULTS AND DISCUSSION

Two typical XRD patterns of the bronzes prepared by microwave method are shown in Fig. 1 (a and b). The patterns due to $K_{0.51}V_2O_5$ and $Li_{0.1}V_2O_5$ compare very well with the literature reports [JCPDS files 39-0890 and in comparison with 19-0734, respectively] of XRD of samples of the same compositions obtained from conventional solid state synthesis. XRD peaks were sharp in the case of vanadates unlike in the case of tungstates and molybdates and hence did not require annealing. The better degree of crystallisation in the case of vanadates is possibly due to the higher temperature reached by these samples in microwaves because of better microwave coupling of vanadium oxide compared to MoO_3 or WO_3.

XRD studies also indicated that intermittent grinding (and inert atmosphere) was necessary in most cases to get single phase materials. A comparison of the X-ray patterns of $K_{0.25}V_2O_5$ illustrates this point (Fig. 2). Without intermittent grinding (and even when inert atmosphere of iodine was used), peaks due to unintercalated V_2O_5 are seen in the XRD. Also intermittent grinding was found to improve the kinetics of the reaction. This was evident in the case of tungsten bronzes in which the time required for the synthesis was reduced from more than 1/2 an hour to less than 10 minutes. The initial diffusion of Li^+ ions appears to block further diffusion of Li^+ ions. However, even with intermittent grinding impurity peaks were observed when the inert iodine atmosphere was not used (Fig. 3). These impurity peaks could be indexed to the oxidised product of LiV_3O_8 (JCPDS 18-754). The relative intensities of the impurity peaks increased with increasing concentration of lithium ions.

$Li_{0.042}MoO_3$ is isostructural with MoO_3 and gives X-ray pattern with relative intensities of peaks matching excellently with literature reports. But Li_xMoO_3 with $x = 0.3, 0.35$ and 0.38 gives rise to only broad peaks with low intensities. It was also found that annealing also does not improve the patterns (not shown) even after heating for half an hour in the microwave oven in an inert atmosphere. As noted earlier, the poor microwave coupling of MoO_3 and hence the relatively lower temperatures attained by the reactants may be responsible for the poor crystallinity of the resulting bronzes. It is known that good quality molybdate bronzes have been synthesized only by electrochemical and high pressure methods (52).

TABLE 1
Bronzes Prepared by Microwave Assisted Synthesis[a]

Composition	Cubic	Hexagonal	Tetragonal	Orthorhombic	Monoclinic	Triclinic
K_xWO_3		$K_{0.33}WO_3$ (3 + 4) $K_{0.2}WO_3$ (3 + 4)	$K_{0.57}WO_3$ (2.5 + 3.5 + 3)			
Cu_xWO_3				$Cu_{0.26}WO_3$ (2 + 3)		$Cu_{0.77}WO_3$ (2 + 3)
Li_xWO_3	$Li_{0.35}WO_3$ (2 + 1.5 + 3) $Li_{0.5}WO_3$ (2 + 2.5 + 3 + 3)		$Li_{0.1}WO_3$ (45) $Li_{0.25}WO_3$ (2 + 2)			
Li_xMoO_3				$Li_{0.042}MoO_3$ (2 + 3)	$Li_{0.35}MoO_3$ (1 + 3) $Li_{0.38}MoO_3$ (2 + 2)	
K_xMoO_3					$K_{0.3}MoO_3$ (5)	
$Li_xV_2O_5$				$Li_{0.04}V_2O_5$ (10 + 3) $Li_{0.1}V_2O_5$ (2.5 + 4) $Li_{0.95}V_2O_5$ (3 + 6.5) LiV_2O_5 (3 + 6.5)	$Li_{0.3}V_2O_5$ (2.5 + 3) $Li_{0.4}V_2O_5$ (4 + 6)	
$Cu_xV_2O_5$					$Cu_{0.4}V_2O_5$ (2 + 3) $Cu_{0.95}V_2O_5$ (2 + 6)	
$K_xV_2O_5$					$K_{0.25}V_2O_5$ (2 + 2.5) $K_{0.33}V_2O_5$ (2 + 2) $K_{0.375}V_2O_5$ (2 + 2.5) $K_{0.51}V_2O_5$ (2 + 3)	

[a] Listed according to their structures. Numbers in parantheses indicate the period of exposure to microwaves (in minutes); '+' indicates intermittent grinding. The compositions listed are nominal compositions.

In tungsten bronzes which were synthesized with intermittent grinding it was observed that X-ray patterns compared fairly well with those reported in the literature. However, the peaks were not sharp. On heat treatment, the peaks were found to become sharp in some of the bronzes like $K_{0.25}WO_3$ and $K_{0.33}WO_3$ (Fig. 4). There was not much improvement in other compositions like $K_{0.57}WO_3$ and lithium tungstates, even after annealing for 10 to 20 minutes in the microwave oven. The lack of sharpness of the XRD peaks in the case of lithium bronzes may arise from random site distortions produced in the lattice due to the small size of the intercalated lithium ion.

Temperatures of heat treatment were measured by inserting a Pt–Pt 13% Rh thermocouple into the reaction mixture by interrupting the irradiation briefly. The temperature at the end of heat treatment was found to be in the same range of 443 to 473 K for most tungsten bronzes. It is therefore evident that tungsten bronzes of potassium and lithium are poor susceptors of microwaves.

The temperature–time profile during the synthesis of a typical bronze $K_{0.33}V_2O_5$ is presented in Fig. 5. The maximum temperature during microwave irradiation was only 803 K (with a possible error of about $+30$ K caused by the limited speed with which measurements could be made in the interruption method). It may be noted here that conventional methods of preparation of bronzes involve heating to much higher temperatures. The somewhat sudden drop in the temperature after about 1.5 minutes

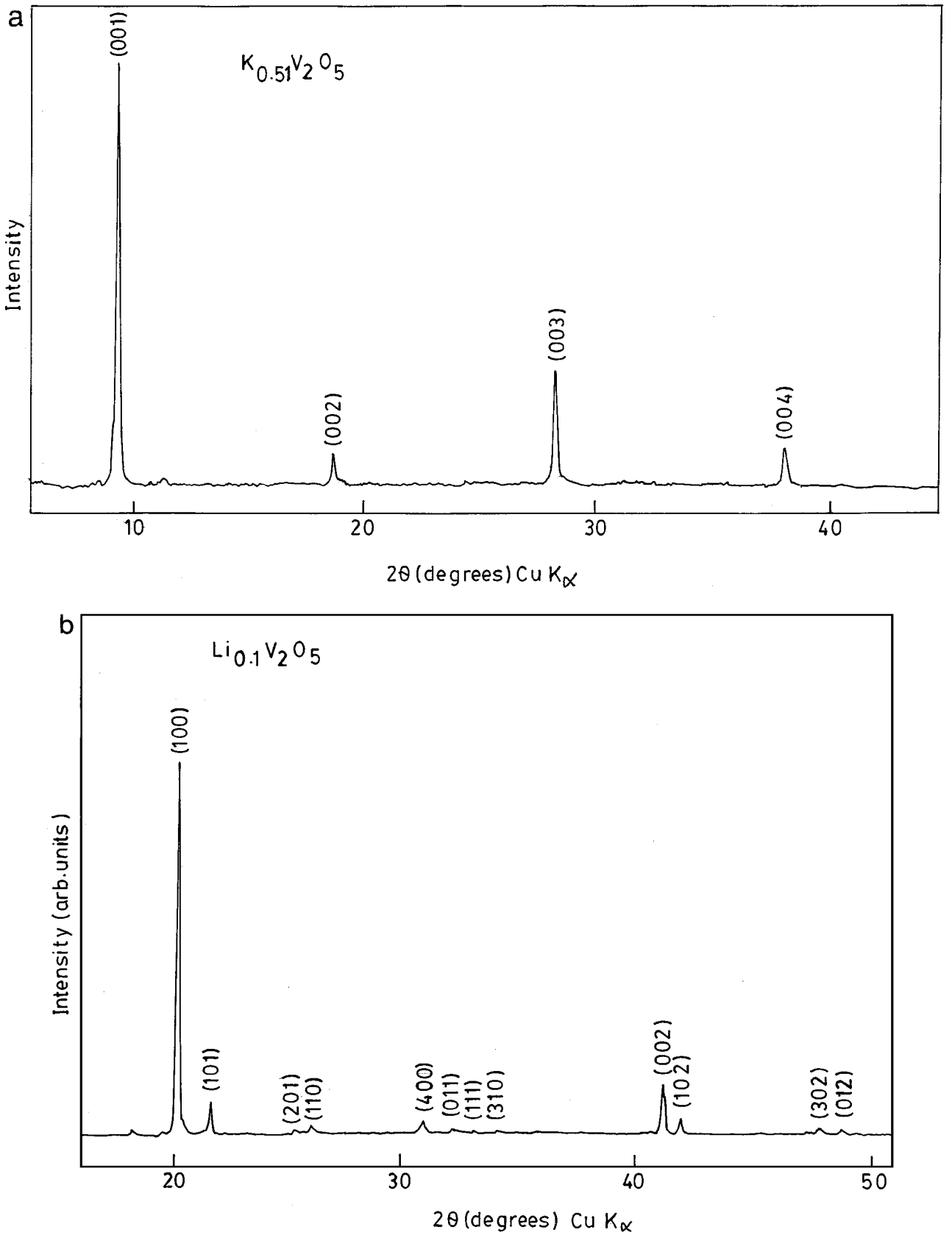

FIG. 1. X-ray diffraction patterns of two typical bronzes (a) $K_{0.51}V_2O_5$ and (b) $Li_{0.1}V_2O_5$ prepared by microwave assisted reaction.

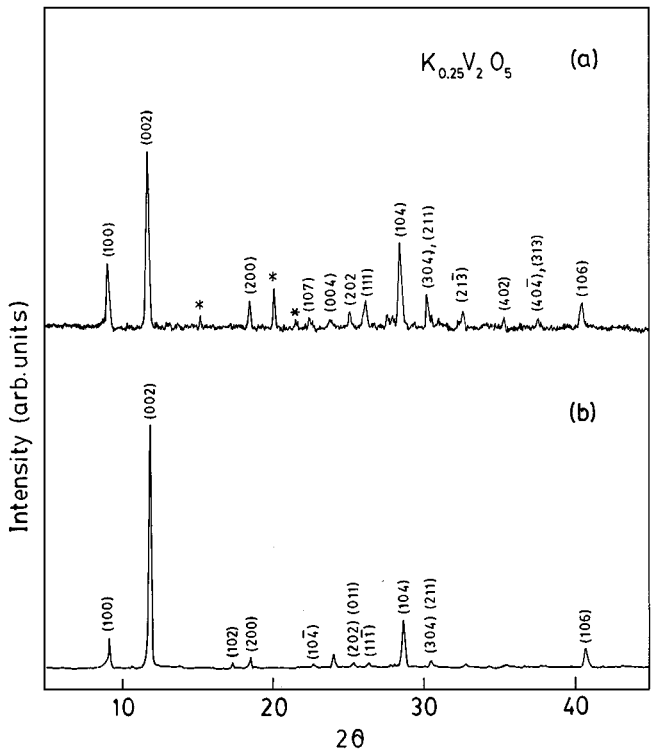

FIG. 2. XRD patterns of $K_{0.25}V_2O_5$ synthesized (a) without intermittent grinding and (b) with intermittent grinding. *indicates reflections due to unreacted V_2O_5 impurity.

may be attributed to the possibility that bronze couples less efficiently with microwaves. The temperatures were essentially constant after about 5 minutes of irradiation.

The various reaction steps involved in the formation of bronzes and the nature of reaction enthalpies may be visualized as follows. (The reactions are all assumed to be in solid state).

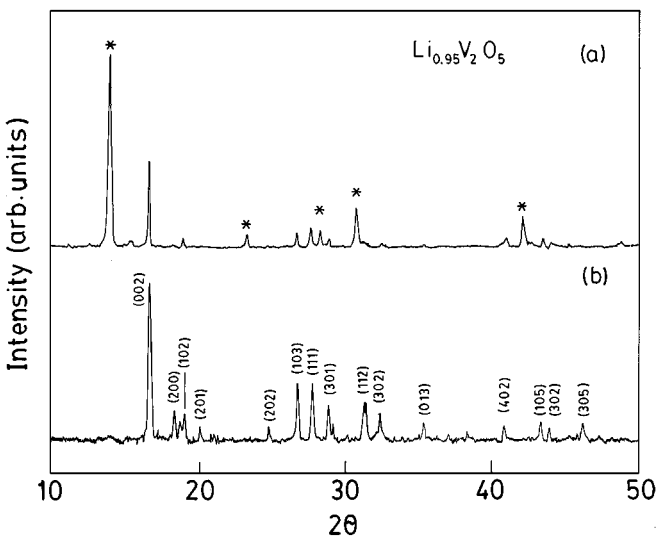

FIG. 3. XRD patterns of $Li_{0.95}V_2O_5$ (a) synthesized in air and (b) synthesized in iodine atmosphere. *indicates reflections due to oxidized impurity, LiV_3O_8.

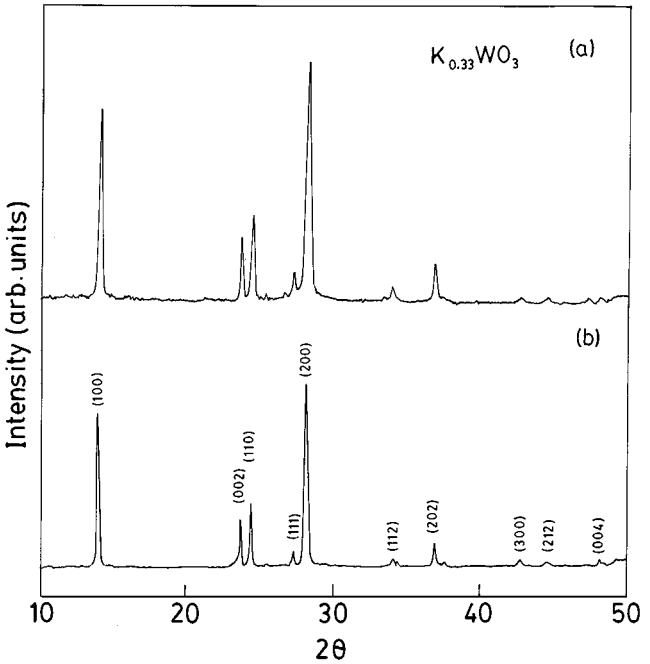

FIG. 4. XRD patterns illustrating the effect of annealing. (a) $K_{0.33}WO_3$, as synthesized (b) annealed for 20 minutes in iodine atmosphere.

$$A^+I^- \rightarrow A^+ + I^- + \Delta E_1 \quad [1]$$

$$I^- \rightarrow I + e^- + \Delta E_2 \quad [2]$$

$$I \rightarrow \tfrac{1}{2}I_2 - \Delta E_3 \quad [3]$$

$$e^- + M^{6+} \rightarrow M^{5+} - \Delta E_4 \quad [4]$$

$$A^+ + \text{oxide} \rightarrow \text{bronze} - \Delta E_5 \quad [5]$$

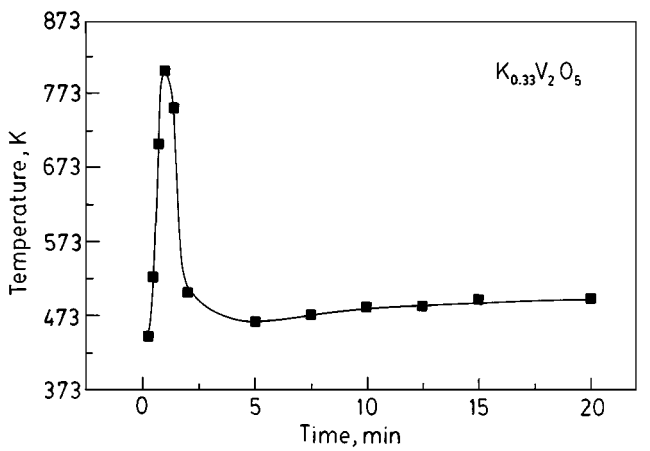

FIG. 5. Temperature–time profile during the synthesis of $K_{0.33}V_2O_5$. Note that the maximum temperature attained by the reaction mixture is less than 820 K, which is far less than the temperatures employed in conventional preparations.

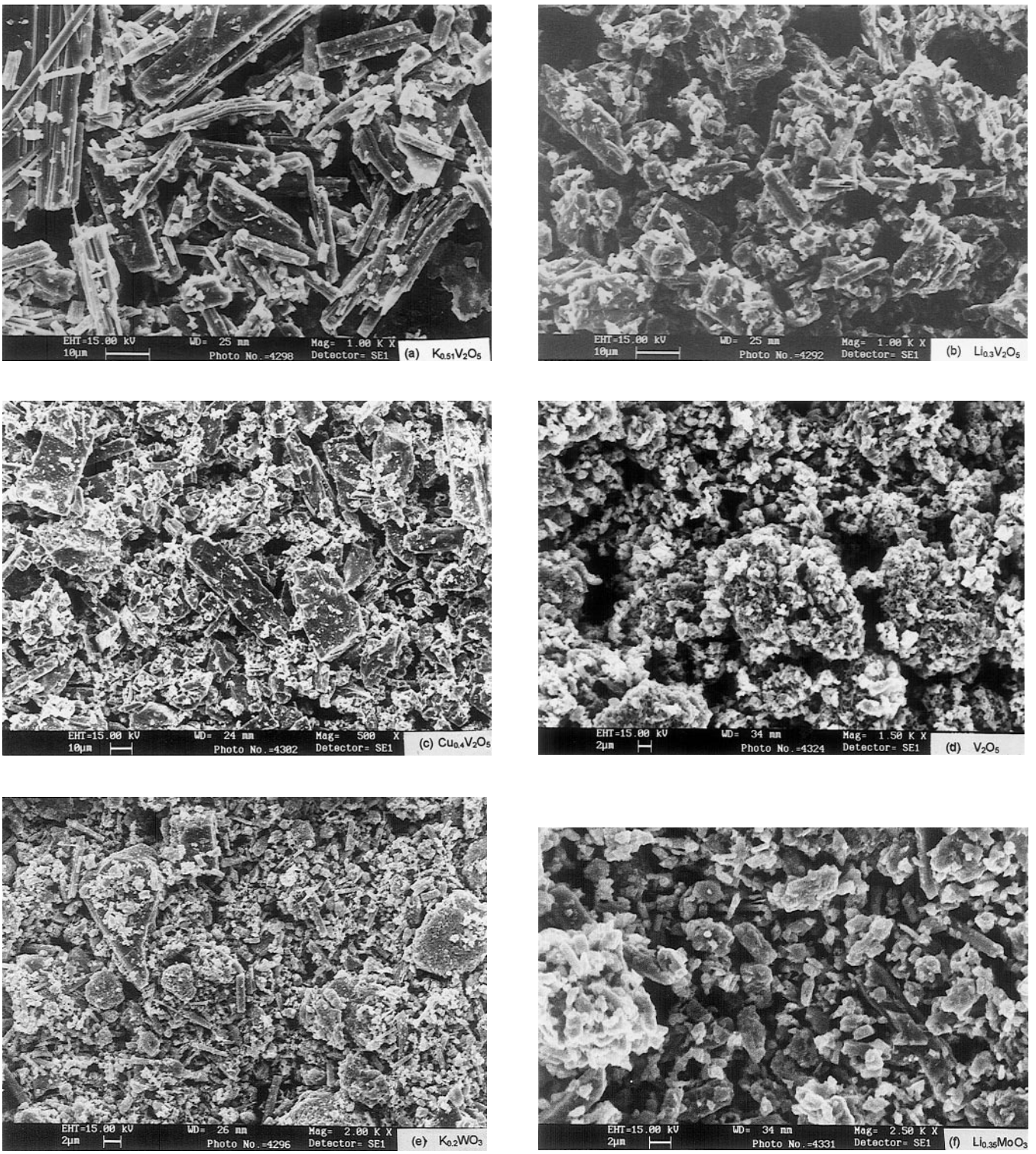

FIG. 6. SEM micrographs of: (a) $K_{0.51}V_2O_5$, (b) $Li_{0.3}V_2O_5$, (c) $Cu_{0.4}V_2O_5$, (d) V_2O_5, (e) $K_{0.2}WO_3$, and (f) $Li_{0.35}MoO_3$ (see text for details).

The energy terms ΔE_2, ΔE_3, and ΔE_5 are presumably small compared to ΔE_1 and ΔE_4. The initial rise in the temperature can be due to the dominance of the exothermic ΔE_4. Once the bronze is formed, microwave coupling is greatly reduced resulting in a temperature drop and reduction in the rate of formation of bronze. Regrinding exposes

fresh V_2O_5 and reestablishes the fast rate. The rapidity of the microwave reaction compared to the conventional reactions can be understood by the fact that ionic diffusion is greatly enhanced in the presence of microwave field as demonstrated by Freeman *et al.* (53). Thus there appears to be a genuine microwave effect apart from the mere heating effect assisting the formation of bronzes.

The maximum temperatures attained by the reaction mixtures having been very low, it would be interesting to examine the morphology of the products which have all been in the form of powders. The scanning electron micrographs of K-, Li-, and Cu- vanadates are shown in Figs. 6a, 6b, and 6c, respectively. The ordering of these micrographs has been on the basis of the decreasing definition of the crystallite facets. $K_{0.51}V_2O_5$ is seen to give rise to long rectangular crystallites with sharp features. The same trend is evident to decreasing extents in $Li_{0.3}V_2O_5$ and $Cu_{0.4}V_2O_5$. The observed crystallite morphology appears to have no relation to that of V_2O_5 particles (Fig. 6d) in the reactants. The tendency towards formation of long faceted rectangular crystallites seems to be an inherent feature of even tungstates (Fig. 6e) and molybdates (Fig. 6f) although to much lower extent.

It would appear therefore that there is a pronounced tendency towards recrystallization in all the bronzes. Since the measured apparent temperature is not very high, it tempts us to speculate that (i) the recrystallization step does not involve any molten phases and (ii) the exothermic steps ([3], [4], and [5] in the intercalation reaction visualized earlier) involved in reactions are rapidly and effectively utilized in bringing about recrystallization. Since microwave heating is known to assist ionic diffusion, the biased directional diffusion of alkali ions into the transition metal oxide lattice may produce a structure-directing influence which may be partly responsible for the observed morphologies.

CONCLUSION

Several oxide bronzes have been synthesized using microwave irradiation. Intermittent grinding and inert atmosphere were necessary for getting a monophasic product. The temperatures of microwave reactions are found to be much lower than in conventional processes. The reactions appear to be remarkably fast. The product bronze particles possess rectangular crystallite morphologies and are particularly well defined in vanadates.

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