

Rapid synthesis and properties of FeVO_4 , AlVO_4 , YVO_4 and Eu^{3+} -doped YVO_4

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Abstract

Fine particle FeVO_4 , AlVO_4 , YVO_4 and $\text{Y}_{0.95}\text{Eu}_{0.05}\text{VO}_4$ have been prepared by the combustion of aqueous solutions containing corresponding metal nitrate, ammonium metavanadate, ammonium nitrate and 3-methyl-5-pyrazolone. The solutions containing the redox mixtures, when rapidly heated at 370 °C, ignite and undergo self-propagating, gas-producing, exothermic reactions to yield fine particle metal vanadates. Formation of crystalline vanadates was confirmed by powder X-ray diffraction patterns, ^{27}Al nuclear magnetic resonance, IR and fluorescence spectra.

Keywords: Rapid synthesis; Nuclear magnetic resonance; Fluorescence spectra; Infra red; X-ray diffraction

1. Introduction

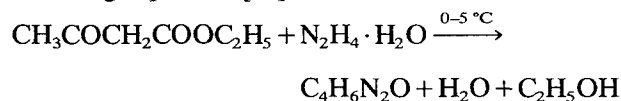
Metal vanadates, MVO_4 , where $\text{M} \equiv \text{Fe, Al, Y, Cr}$ etc., having triclinic or tetragonal crystal structure are of technological importance because of their use as laser hosts, masers and phosphors. Yttrium vanadate, YVO_4 , has several technological applications; when doped with europium, it forms a highly efficient red phosphor for colour television [1] and shows promise as a material for home lighting [2]. With certain rare earth oxide additions, YVO_4 forms optical maser materials [3]. The preparation of these materials is usually carried out by solid state reaction of the corresponding metal oxides such as Fe_2O_3 , Al_2O_3 , Y_2O_3 with V_2O_5 . The metal vanadate formation temperature varies from metal to metal, e.g. for Cr_2O_3 – V_2O_5 , 500 °C [4], Al_2O_3 – V_2O_5 , 650 °C [5], and Y_2O_3 – V_2O_5 , 1000 °C [6]. Further, doping of the metal vanadates with europium for the preparation of red-emitting Eu^{3+} – YVO_4 is critical and requires special methods such as wet chemical methods. Recently, the preparation of aluminum vanadate and yttrium vanadate was carried out by the alkoxide route [7,8]. This process although efficient requires expensive chemicals and special equipment. Here, we report the preparation of metal vanadates by the solution combustion process used earlier for the preparation of aluminas [9], ferrites [10], zirconia [11] and dielectric oxides [12].

2. Experimental details

Metal vanadates, MVO_4 , where $\text{M} \equiv \text{Fe, Al, and Y}$, and Eu^{3+} -doped YVO_4 were prepared by rapidly heating the aqueous solution containing stoichiometric amounts of metal nitrates (Fe, Al, Y and Eu), ammonium metavanadate, ammonium nitrate and 3-methylpyrazole-5-one (3MP5O) at 370 °C.

2.1. Preparation of fuel

3MP5O ($\text{C}_4\text{H}_6\text{N}_2\text{O}$) was prepared by the dropwise addition of 1 mol ethyl acetoacetate to 1 mol of hydrazine hydrate (99.9%) cooled in an ice bath according to the following equation [13]:



2.2. Calculation of stoichiometry of redox mixtures

The stoichiometric composition of the metal nitrate (oxidizer), ammonium metavanadate (fuel), ammonium nitrate (oxidizer) and 3MP5O (fuel) was calculated based on the total oxidizing and reducing valency of oxidizer and the fuel which serves as a numerical coefficient for stoichiometric balance such that the equivalence ratio ϕ_e is unity, i.e. $\text{O:F} = 1.0$ [14], and

the energy released is at a maximum. According to the concepts used in propellant chemistry, the elements H, C, V or any other metal are considered as reducing elements with the corresponding valencies +1, +4, +5 (or the valency of the metal ion in that compound) respectively. The element oxygen is considered as an oxidizing element with valency -2. The valency of nitrogen is considered to be zero. Accordingly, the valencies of ammonium metavanadate, $M(\text{NO}_3)_3$, ammonium nitrate and 3MP5O become +3, -15, -2 and +20 respectively. Therefore, the mole ratio of $\text{NH}_4\text{VO}_3:\text{NH}_4\text{NO}_3$ is 2:3 and of $M(\text{NO}_3)_3:3\text{MP5O}$ is 4:3.

2.3. Product analysis

The solid combustion products, MVO_4 , were characterized by powder X-ray diffraction (XRD) patterns recorded using a Philips PW 1050/70 X-ray diffractometer with Cu $K\alpha$ radiation. IR spectra of the metal vanadates were recorded using a Perkin-Elmer model 781 IR spectrometer with KBr pellets. Average particle size and size distribution were measured using a micron photo sizer model SKC 2000 (Japan) which is based on Stoke's law of sedimentation and photoextinction phenomena. The specific surface areas of the powders were measured using a Micromettics Accusorb 2100E instrument by nitrogen adsorption, employing the Brunauer-Emmett-Teller equation. The powder densities were measured using a pycnometer with xylene as the liquid medium. The high resolution magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum of ^{27}Al was recorded at 7.05 T and an operating frequency of 78.206 MHz, using a Bruker MSL-300 spectrometer (Switzerland, Spectrospin AG) with respect to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

3. Results and discussion

The redox mixture containing metal nitrate, ammonium metal vanadate, ammonium nitrate and 3MP5O when rapidly heated at 370 °C ignites and yields voluminous powders. As-formed combustion products were X-ray amorphous which on calcining at 650 °C for 1 h show crystalline phases. The amorphous metal vanadates could be crystallized to single-phase material at 650 °C compared with 500–1000 °C required in the ceramic method. The low calcination temperature required to form the desired phases may be attributed to the formation of fine reactive M_2O_3 and V_2O_5 powders. The XRD pattern of the heat-treated (650 °C, 1 h) combustion products is shown in Fig. 1. The lattice constant calculated from the powder XRD pattern are summarized in Table 1 which are in agreement with those reported [15].

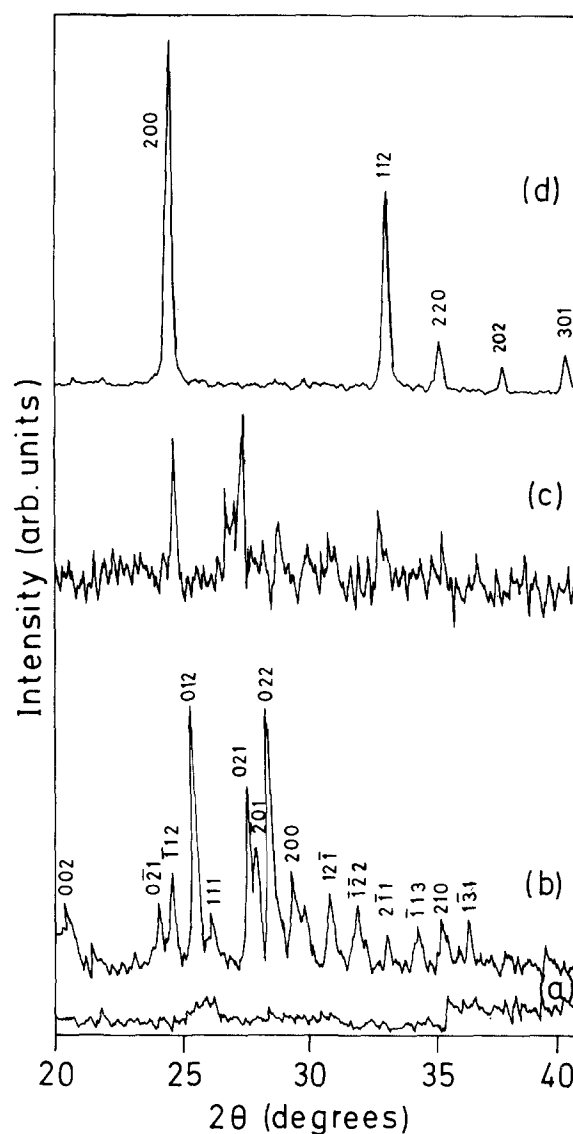
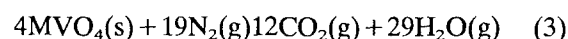
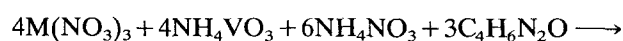
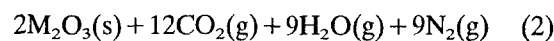
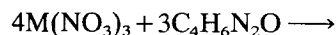
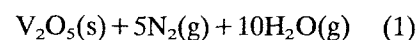
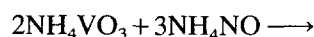


Fig. 1. Powder XRD patterns of as-prepared AlVO_4 (spectrum a), heat-treated (650 °C, 1 h) AlVO_4 (spectrum b), heat-treated (650 °C, 1 h) FeVO_4 (spectrum c), and heat-treated (650 °C, 1 h) YVO_4 (spectrum d).

Formation of metal vanadates by the combustion may be represented by the following reaction sequence:



(15 mol of gases per MVO_4 unit) where $\text{M} \equiv \text{Al}$, Fe and Y .

The metathetically formed V_2O_5 (Eq. (1)) and M_2O_3 (Eq. (2)) further react to give MVO_4 . The overall

Table 1
Powder X-ray data of metal vanadates

Compound	Crystal system	Lattice parameters (nm)
FeVO ₄	Triclinic	$a = 0.806\ 72$, $b = 0.934\ 72$, $c = 0.672\ 38$
AlVO ₄	Triclinic	$a = 0.647\ 11$, $b = 0.775\ 21$, $c = 0.908\ 51$
YVO ₄	Tetragonal	$a = b = 0.711\ 92$, $c = 0.628\ 98$

reaction is given by Eq. (3). The large amount of gases evolved during the combustion yield foamy, voluminous, fine particle metal vanadates.

Formation of aluminium vanadate was further confirmed from MAS ²⁷Al NMR. Aluminium vanadate has double-bent chains of edge-sharing aluminate polyhedra which are joined by VO₄ tetrahedra [16]. The most important structural feature influencing the chemical shift position is the local coordination, with octahedral AlO₆ resonating between +15 and -30 ppm and the much less common AlO₅ group resonating between +40 and +25 ppm, while the tetrahedral AlO₄ group typically resonates between +80 and +50 ppm, all relative to [Al(H₂O)₆]³⁺ [17]. The MAS ²⁷Al NMR of AlVO₄ shown in Fig. 2 exhibits only one peak at -13 ppm. The resonant peak at -13 ppm can be assigned to the AlO₆ octahedra of AlVO₄.

Formation of metal vanadates was also confirmed by IR data. IR spectra show absorptions due to vanadium–oxygen stretching from tetrahedral and due to metal–oxygen stretching from octahedral sites in the regions 800–1050 cm⁻¹ and 500–650 cm⁻¹ respectively [18].

Combustion-synthesized Eu³⁺ (5 mol.%) doped yttrium vanadate showed XRD patterns similar to that of the parent compound, yttrium vanadate. The presence of dopant ions in the host lattice was confirmed by its fluorescence spectra. Doping of yttrium vanadate with Eu³⁺ ions involves atomic level substitution of the Y³⁺ ions present in these lattices by Eu³⁺ ions. Such substitutions invariably require high temperature and long processing periods. The solution combustion process allows uniform homogeneous doping of Eu³⁺ in YVO₄. The room temperature fluorescence spectrum of Eu³⁺-doped YVO₄ is shown in Fig. 3. It shows four absorptions at 611, 615, 619 and 595 nm. The bands at 611, 615 and 619 nm result from the ⁵D₀ → ⁷F₂ transition of the Eu³⁺ ion when excited by 253 nm light. The crystal field splitting of the ⁷F₂ level can lead to five distinguishable states, and the transitions at 611, 615 and 619 nm differ in regard to the particular ⁷F₂ state on which they terminate. The emissions at 595 nm are due to ⁵D₀ → ⁷F₁ as reported [1].

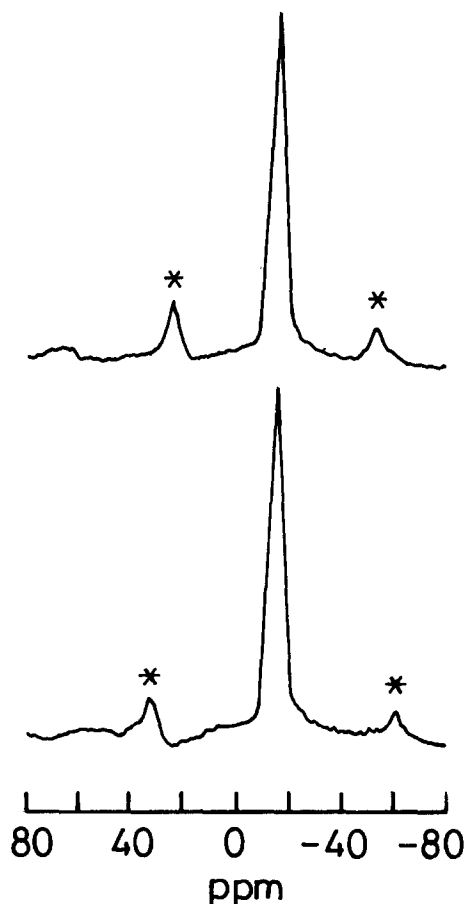


Fig. 2. ²⁷Al MAS NMR of heat-treated (650 °C, 1 h) AlVO₄. (*, spinning side band).

The particulate properties of the combustion-derived metal vanadates are summarized in Table 2. The powder densities of the combustion products are 65%–75% of the theoretical values, which indicates the porous nature of the combustion residues. The surface area values are in the range 2–14 m² g⁻¹. The high surface area value of the metal vanadate obtained by the combustion process could be attributed to the large amount of cold gases evolved during the combustion which dissipate the heat, thereby inhibiting sintering of the combustion product. The particle size distribution of YVO₄ prepared by the combustion process is shown in Fig. 4. It can be seen that 50% of the particles lie below 3.13 μm.

4. Conclusions

3MP50 appears to be an ideal fuel for the combustion synthesis of metal vanadates AlVO₄, FeVO₄, YVO₄ and Eu³⁺-doped YVO₄. The novel combustion process yields voluminous oxides with specific surface areas from 2 to 14 m² g⁻¹. The main advantages of the process are improvement in processing time and a saving in energy. The novelty of the combustion solution

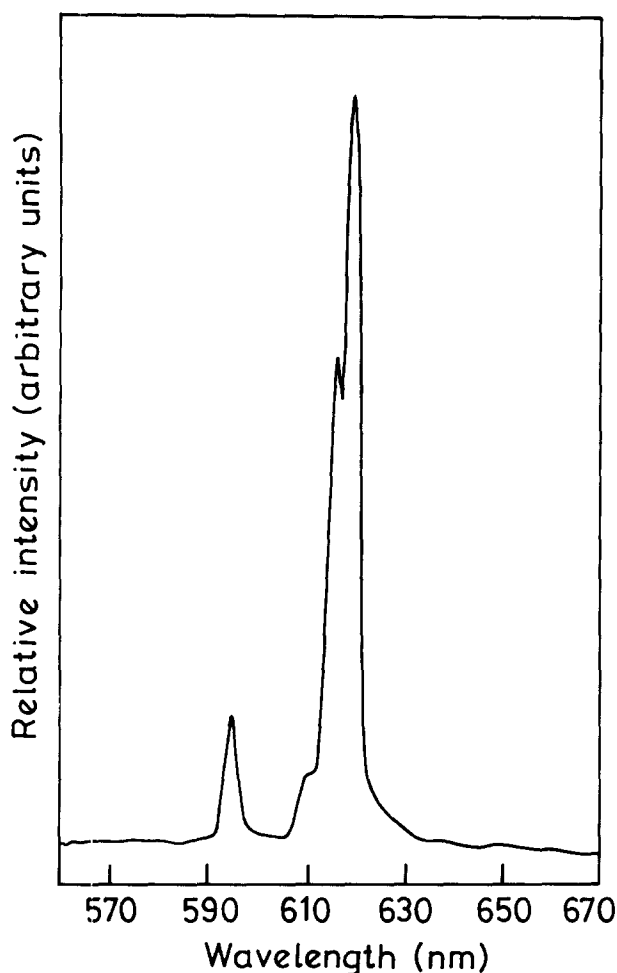


Fig. 3. Room temperature emission spectrum of heat-treated (650 °C, 1 h) Eu^{3+} -doped YVO_4 .

Table 2
Properties of vanadates

Vanadates	Powder density (g cm^{-3})	Surface area ($\text{m}^2 \text{g}^{-1}$)	Particle size from surface area (μm)	Average agglomerate size (μm)
FeVO_4	2.370	2.0	0.9118	4.59
AlVO_4	2.561	7.0	0.3346	4.82
YVO_4	2.979	14.0	0.1436	3.13

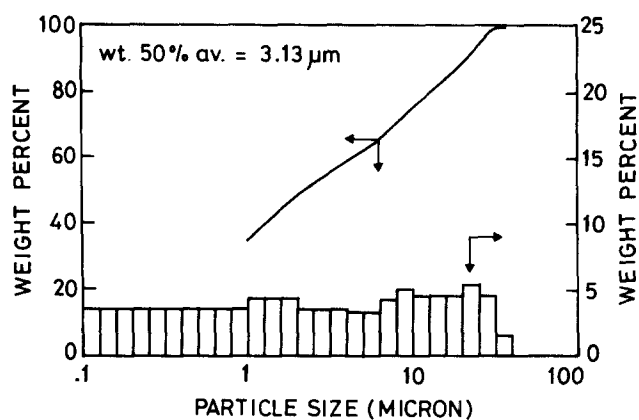


Fig. 4. Particle size distribution of as-prepared YVO_4 .

route is that the desired impurity ion can be doped as demonstrated in the case of Eu^{3+} -doped YVO_4 .

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