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Room temperature synthesis of zinc pyrovanadate $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$

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Zinc pyrovanadate was prepared at room temperature by using a new method, which consists of mixing zinc oxide powder, $ZnO{\cdot}0.3H_2O$, with a 1.5×10^{-3} M solution of vanadium oxide xerogel $V_2O_5{\cdot}2H_2O$. After a short time of stirring, the pH of the solution increases from 3.2 to 5.8 and a yellowish green precipitate was obtained. Although the reaction was not complete, the precipitate was composed mainly of zinc pyrovanadate. With prolonged stirring, a pure yellowish white zinc pyrovanadate was obtained while the pH of the solution, which stabilized around 5.6, was almost constant.

The requirement for new materials makes synthesis in materials chemistry an important area of research. New methods of preparation are needed especially for low cost new materials. Low temperature methods are attractive since they do not require any sophisticated apparatus and can lead to the preparation of metastable phases, which usually show good physical properties.

Recently a new zinc pyrovanadate $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$ was prepared under hydrothermal conditions at 438 K.[1] Here we report a new method that leads to the same material at room temperature.

Experimental

The method used in this work consists of two steps. The first is the preparation of zinc oxide by precipitation from a zinc chloride solution $ZnCl_2$ (BDH Ltd., Poole, England) by use of 10% aqueous ammonia as precipitating agent.[2] The zinc oxide obtained was washed with distilled water several times and dried at room temperature. Thermogravimetric analysis (TG 1000+ Rheometric Scientific) shows that the sample contains *ca.* 0.3 molecules H_2O per formula unit. The X-ray diffraction spectrum (Siemens D-5000 diffractometer), Fig. 1, indicates a crystalline phase with broadened peaks in comparison to that of commercial zinc oxide. It is found that $ZnO{\cdot}0.3H_2O$ is soluble in slightly acidic solution after several hours of stirring which probably is the consequence of small particle sizes. The second step consists of dissolving a vanadium oxide xerogel $V_2O_5{\cdot}2H_2O$, prepared by an ion-exchange method,[3] in distilled water. The xerogel of vanadium oxide has a low solubility in water at room temperature (*ca.* 340 mg l^{-1} for freshly prepared xerogel). Thus 255 mg of vanadium oxide xerogel, $V_2O_5{\cdot}2H_2O$, was dissolved in 750 ml of distilled water and a red solution was obtained after *ca.* 30 min of stirring. The measured pH (pH meter 6071 Jenco Electronics. LTD) of this solution was 3.2. Zinc pyrovanadate was prepared according to eqn. (1).

$$V_2O_5{\cdot}2H_2O\ (aq) + 3\ ZnO{\cdot}0.3H_2O\ (s) \xrightarrow[\text{stirring}]{\text{room temp.}} Zn_3(OH)_2V_2O_7{\cdot}2H_2O$$

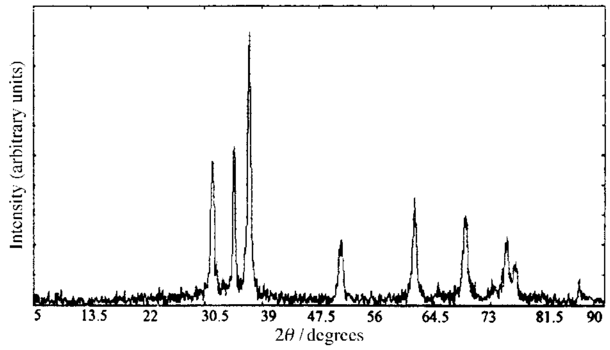

Fig. 1 X-Ray diffraction pattern of as-prepared $ZnO{\cdot}0.3H_2O$.

Results and discussion

No spectator ions are present with all the ions in solution (V^{5+}, Zn^{2+}, H^+, OH^-) participating to form the final product. Fig. 2 shows the change of the pH of the solution with stirring time. When zinc oxide was added to the vanadium oxide xerogel solution, after a short time of stirring (90 min), the pH of the solution increases from 3.2 to 5.8 (Fig. 2) accompanied by the formation of a yellowish green precipitate

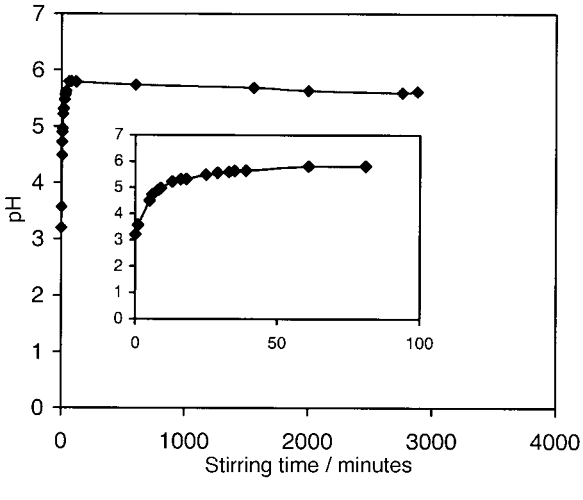

Fig. 2 Variation of pH with stirring time of the solution containing $ZnO{\cdot}0.3H_2O$ and $V_2O_5{\cdot}2H_2O$. To see the colour changes occurring as a function of stirring time see: http:/www.rsc.org/suppdata/jm/1999/1543.

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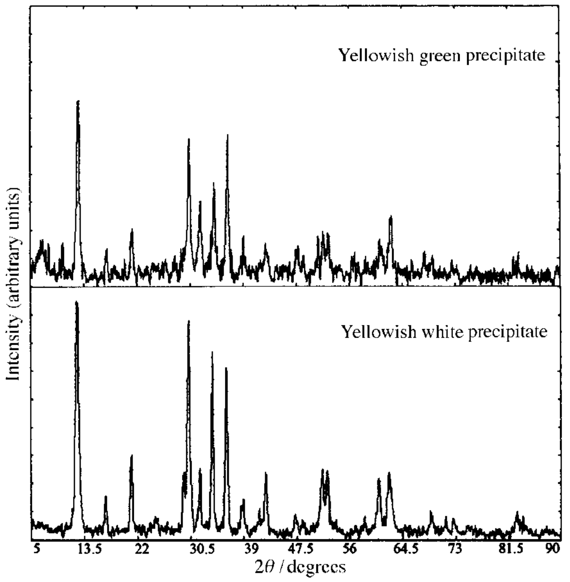

Fig. 3 X-Ray diffraction patterns of the yellowish green and yellowish white precipitates.

mixed with a white powder, seen at the bottom of the glass beaker. The white powder was analyzed by X-ray diffraction and found to be zinc oxide. With longer stirring time, the remaining zinc oxide is progressively dissolved in solution and the color of the solution, after 2 days of stirring, became yellowish white while the pH, which stabilized around 5.6, was almost constant (Fig. 2). The yellowish green and the yellowish white precipitates obtained after 90 min and 48 h of stirring, respectively, were dried at room temperature and analyzed by X-ray diffraction (Fig. 3). The X-ray diffractogram of the yellowish white precipitate shows a crystalline phase whose diffraction peaks are in good agreement with the published X-ray diffractogram of zinc pyrovanadate.[1] The X-ray diffractogram of the yellowish green precipitate is composed of zinc pyrovanadate diffraction peaks but mixed with other low intensity unidentified peaks and also shows lower crystallinity than the yellowish white precipitate. A thermal analysis study was conducted on the yellowish white precipitate (Fig. 4). The TGA curve shows two breaks at *ca.* 250 and 350 °C in good agreement with a recent study[4,5] which reported that zinc pyrovanadate shows two weight loss steps: removal of water of hydration which is reversible and removal of hydroxy groups which is irreversible. Therefore, the first loss corresponds to removal of water of hydration and the remainder of the weight loss corresponds to loss of hydroxy groups. The DSC curve (DSC LN+ Rheometric Scientific) as shown in Fig. 5, recorded the thermal characteristics only between room temperature and 500 °C owing to the limited operating temperature range of the instrument. Two peaks are observed: a sharp endothermic peak with a maximum at 211 °C, and a weak exothermic peak around 400 °C. The endothermic peak at 211 °C corresponds to removal of two molecules of water of hydration per formula unit. To establish the nature of the exothermic peak, the as prepared zinc pyrovanadate was annealed in air at 250, 500 and 800 °C for 5 h. Fig. 6 shows the evolution of the X-ray diffraction patterns as a function of the annealing temperature. At 250 °C, the X-ray diffraction pattern still shows only the X-ray diffraction peaks of zinc pyrovanadate but with low intensity and broad background. It appears that disorder has been introduced in one plane and is probably a consequence of loss of hydroxy groups from the

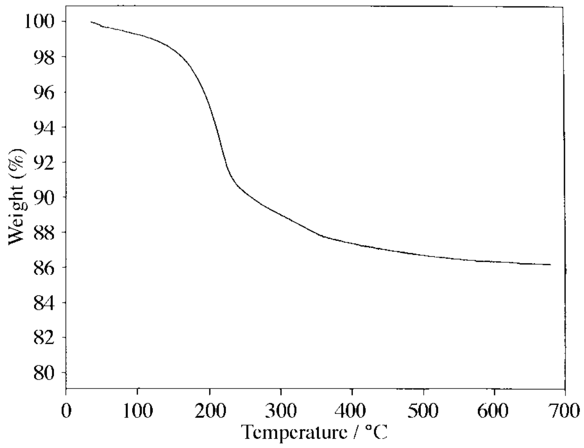

Fig. 4 TG curve of $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$.

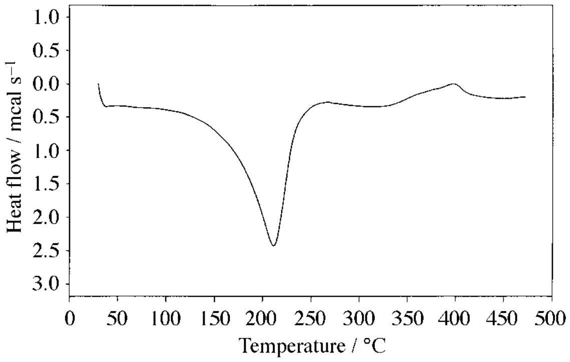

Fig. 5 DSC curve of $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$.

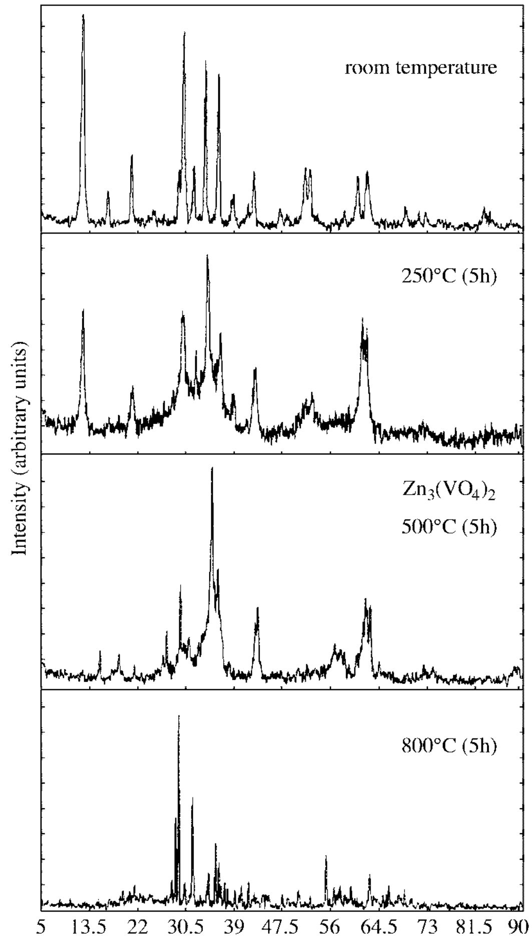

Fig. 6 Evolution of the X-ray diffraction pattern of $Zn_3(OH)_2V_2O_7{\cdot}2H_2O$ annealed at different temperatures.

material. At 500 °C, the pattern of zinc orthovanadate $Zn_3(VO_4)_2$ (JCPDS 34-0378) is evident, while at 800 °C, the X-ray diffraction pattern shows new diffraction peaks that do not correspond to the previous phases. Upon heating zinc pyrovanadate above 250 °C, hydroxyl groups are removed and a structural transformation occurs. The exothermic peak seen at 400 °C in the DSC curve can be attributed to the structural transformation of zinc pyrovanadate to zinc orthovanadate.

Zinc pyrovanadate thus has been prepared at room temperature by using a solution of vanadium oxide xerogel. In previous studies,[6,7] also by using the same solution, it has been possible to prepare new metastable phases of indium and chromium vanadates. This indicates that a solution of vanadium oxide xerogel is a reactive starting material for preparing new vanadates at low temperature. Using such a method, according to previous studies[6,7] and also the present work, the stirring time, besides other experimental parameters, is an important parameter which affects the final product. In the present case, a long stirring time is required since (a) zinc oxide requires time to dissolve in solution, and (b) the small unidentified diffraction peaks, observed in the diffractogram of the yellowish green precipitate (Fig. 3) disappear with a longer stirring time to give zinc pyrovanadate as a pure phase with better crystallinity. A detailed study of the species formed as a function of stirring time, especially during the interval when the pH increases rapidly, is necessary to understand the mechanism involved in this reaction and therefore to attempt to reduce the required preparation time.

Finally, it is of interest that zinc pyrovanadate was prepared at the same pH as for the hydrothermal synthesis[1] (pH 5.6), although the two methods used different starting materials and different experimental conditions.

References

1 P. Y. Zavalij, F. Zhang and M. S. Whittingham, *Acta Crystallogr., Sect. C*, 1997, **53**, 1738.
2 K. Melghit, B. Belloui and A. H. Yahya, *Malays. J. Anal. Sci.*, in press.
3 P. Adebert, N. Baffier, N. Gharbi and J. Livage, *Mater. Res. Bull.*, 1981, **16**, 669.
4 F. Zhang, P. Y. Zavalij and M. S. Whittingham, *Mater. Res. Soc. Symp. Proc.*, 1998, **496**, 367.
5 T. Chirayil, P. Y. Zavalij and M. S. Whittingham, *Chem. Mater.*, 1998, **10**, 2629.
6 M. Touboul, K. Melghit and P. Benard, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 151.
7 M. Touboul and K. Melghit, *J. Mater. Chem.*, 1995, **5**, 147.

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