

## $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ proton conductor

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**Abstract.**  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ , a new proton conductor, has been synthesized by flux, melt and hydrothermal methods. The crystals were subjected to X-ray diffraction, differential thermal analysis, infrared spectroscopy and impedance measurements.

**Keywords.**  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ ; proton conductor.

### 1. Introduction

The growth and study of vanadates is not as popular as silicates, sulphates or phosphates, probably because of their limited use in modern technology. Vanadates have been synthesized only recently. The growth of vanadates by hydrothermal technique is also not known due to various reasons. An attempt was therefore made to synthesize some new vanadates with a device potential and various methods like flux, melt, solution and hydrothermal have been studied.

There has been a great interest in superionics including the fast proton conductors in recent years. The fast ionic and fast proton conductors are used in high temperature solid state batteries, fuel cells, hydrolysis cells, high energy density batteries and charge transport in complex biophysical systems. The features of proton conduction in solids are unique due to the missing electron cloud. There are very few anhydrous proton conductors reported so far like  $\text{NH}_4$   $\beta$ -alumina,  $\text{NH}_4$  zeolite,  $\text{LiN}_2\text{H}_5\text{SO}_4$ ,  $\text{LiH}_2\text{PO}_4$ ,  $\text{N}_2\text{H}_6\text{SO}_4$ ,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ,  $\text{NH}_4\text{Zr}_2\text{P}_3\text{O}_{12}$ ,  $\text{HZr}_2\text{P}_3\text{O}_{12}$  etc (Chandra 1984; Kreuer *et al* 1982; Clearfield *et al* 1984; Rudolf *et al* 1985; Subramanian *et al* 1984). An attempt has been made to find out new conductors with high proton conductivity. This paper reports the synthesis and characterization of a new proton conductor  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ .

### 2. Synthesis

Almost all the vanadates found in literature have been synthesized by the flux method. Here, an attempt has been made to develop  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$  by flux, melt and hydrothermal techniques. These methods have been critically evaluated and the advantages and disadvantages of each method have been discussed. Vanadates from solutions could not be synthesized due to lack of a suitable acid media. However,  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$  could be synthesized by using a saturated aqueous solution of  $(\text{NH}_3)_2\text{CO}_3$  and such studies are in progress.

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## 2.1 Flux method

Synthesis of vanadates by this method is not new and in most cases  $V_2O_5$  is used as a flux along with PbO and  $PbF_2$ . Wanklyn (1986) studied the growth of vanadate crystals by the flux method. Normally the starting components and the flux agents are taken in a platinum crucible and the mixture is heated up to  $850^\circ\text{C}$  followed by a slow cooling at 1 to  $5^\circ\text{C}$  per hour. The present authors have obtained well-developed crystals of  $NH_4Zr_2V_3O_{12}$  (figure 1a).

## 2.2 Melt technique

This technique is more suitable because of its simplicity and good results. The starting components such as  $NH_4VO_3$ ,  $ZrO_2$  were taken in the desired molar ratio in a platinum crucible kept inside the reactor whose temperature could be controlled with high accuracy. The crucible was initially heated up to  $600^\circ\text{C}$ , held overnight and subsequently the temperature of the crucible was raised up to  $950^\circ\text{C}$  and held for a few hours leading to the formation of a homogeneous melt which was slowly cooled to the room temperature in different phases. By this method the growth parameters like the temperature of the initial heating, temperature of the melt, cooling rate, molar ratio etc can be controlled. It is therefore necessary to consider these parameters otherwise and a slight change in any one of them could change the resulting product. The crystals obtained by this technique are superior in quality compared to those obtained from flux growth. They were steel grey in colour, small tabular and often flaky with metallic lustre and perfect basal cleavages (figure 1b).

## 2.3 Hydrothermal method

Hydrothermal synthesis of complex vanadates has not been reported so far. A series of experiments were therefore conducted by this method to obtain  $NH_4Zr_2V_3O_{12}$  crystals. Although, initial experiments with a varying molar ratio of the nutrient components yielded only a crystalline powder without any external morphology, we were able to finally synthesize small needle-like crystals of  $NH_4Zr_2V_3O_{12}$  under the following conditions: temperature  $250^\circ\text{C}$ , pressure 200 atm,  $NH_4VO_3$  5 g and  $HCOOH$  (2.0 M) 6 ml. The experiments were carried out for 8 days using teflon liners in Morey-type autoclaves of capacity 50 ml. Since crystallization occurred due to spontaneous nucleation, the furnace temperature was slowly increased to control the nucleation rate (nearly  $5^\circ\text{C}$  per hour). The main drawback of this method is the small size of the crystals (figure 1c).

## 3. Characterization

$NH_4Zr_2V_3O_{12}$  crystals were characterized through various techniques like XRD, DTA, IR-spectroscopy and complex impedance measurements.

X-ray powder diffraction patterns were recorded using X-ray diffractometer (JEOL, model JDX 8P) with a monochromatic  $FeK_\alpha$  ( $\lambda = 1.934 \text{ \AA}$ ) as the source. The structure was found to be monoclinic with cell parameters  $a = 12.19$ ,  $b = 11.81$ ,  $c = 15.15 \text{ \AA}$ ,  $\beta = 101.96^\circ$  and  $V = 2133.71 \text{ \AA}^3$ . Table 1 gives the powder diffraction pattern for  $NH_4Zr_2V_3O_{12}$  crystals.

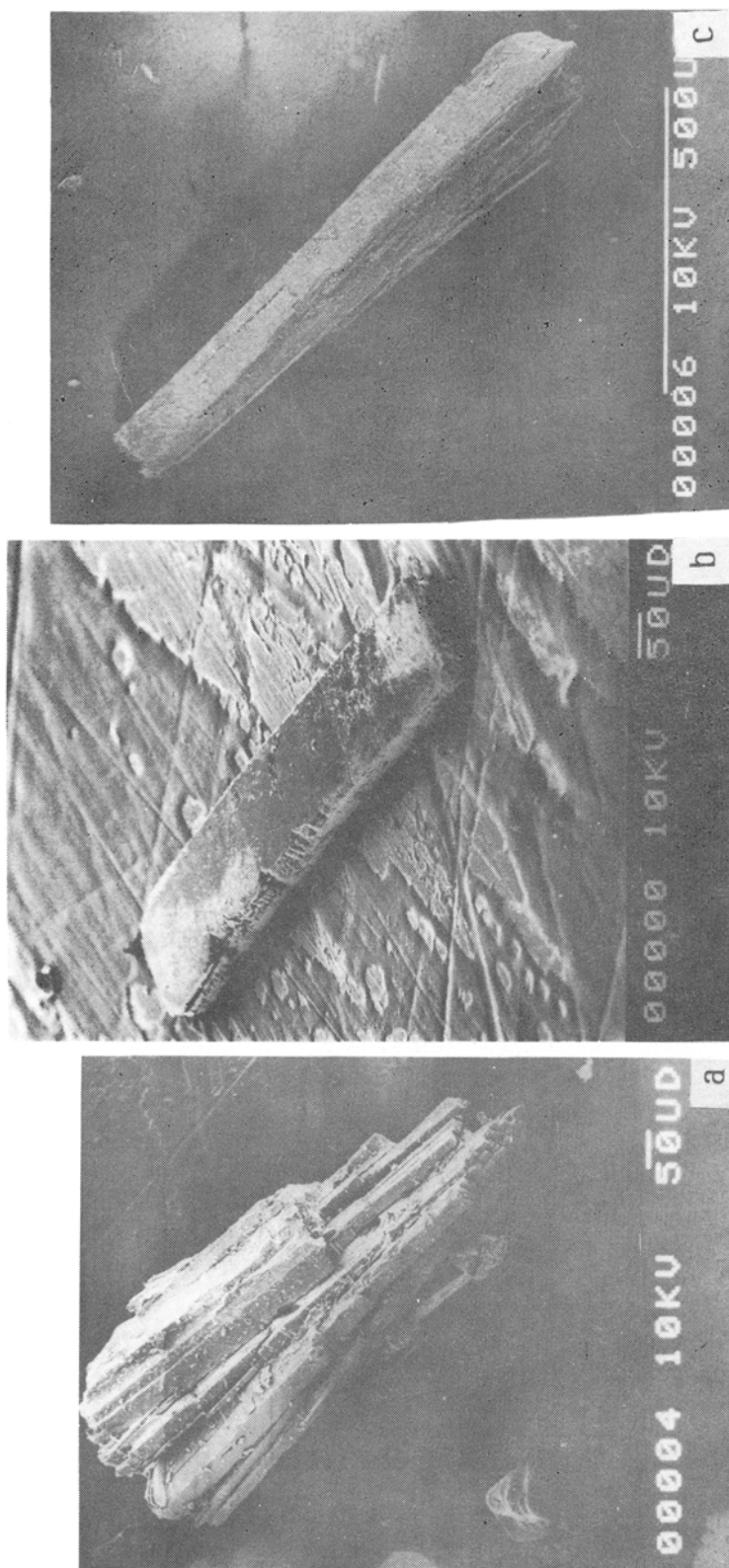
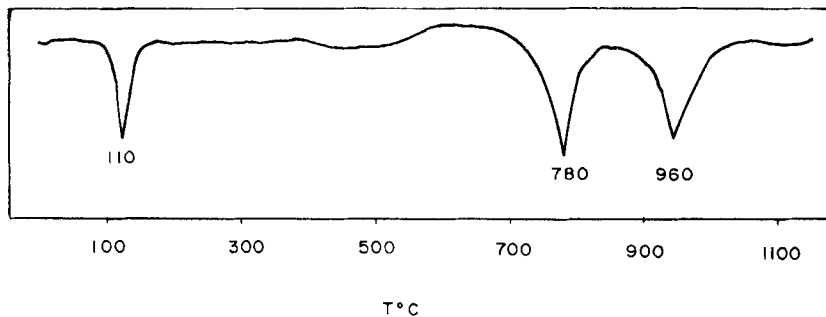


Figure 1. a c.  $NH_4Zr_2V_3O_{12}$  crystals. a. Flux grown b. Melt grown c. Hydrothermally grown.

**Table 1.** X-ray powder diffraction pattern for  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$ .

<i>l</i>	$d_o$	$d_c$	<i>hkl</i>
6	14.817	14.434	100
8	12.190	—	010
8	11.556	—	001
8	8.882	9.017	101
10	8.382	—	011
10	7.935	—	—
11	7.058	7.217	111/200
8	6.842	—	—
5	6.542	—	—
15	6.016	6.108	020
6	5.068	5.057	121
3	4.979	4.909	112
8	4.794	4.8112	300
100	4.381	4.4280	301
15	4.105	4.0723	030
11	3.862	3.8490	003
8	3.676	3.6711	013
15	3.562	3.5578	113
24	3.405	3.3962	203
8	3.148	3.1766	023
8	2.970	2.9683	223
27	2.880	2.8868	004
10	2.761	2.7576	114
8	2.638	2.6325	403
6	2.609	2.6090	024
8	2.527	2.5286	242
11	2.480	2.4754	304
5	2.382	2.3925	043
13	2.278	2.2710	243
6	2.234	2.2389	254
16	2.186	2.2086	342

**Figure 2.** DTA curve for  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$  crystals.

The DTA curve (figure 2) was recorded using an apparatus (Stanton Redcroft, model DTA 673-4) with a temperature programmer and a potentiometric recorder (model RE-571-20). The sample holder was platinum and  $\text{Al}_2\text{O}_3$  was used as a standard. The heating rate was  $5^\circ\text{C}$  per min.  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$  crystals show multiple

phase transitions at temperatures 110°, 780° and melts at 960°C. The phase transition at 110°C was also confirmed through impedance measurements. Efforts are being made to shift the first phase transition temperature at 110°C to a much higher temperature to make the material more suitable for battery applications by introducing some selective dopants into the composition of NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub>.

The infrared spectrum of NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> (figure 3) was recorded in the range 4000 to 400 cm<sup>-1</sup> using a spectrophotometer (Specord 75 IR, GDR) with liquid paraffin. It is well known that orthovanadates with a *T<sub>d</sub>* symmetry have four fundamental vibrations namely  $\nu_1(A_1)$ , 870 cm<sup>-1</sup>,  $\nu_2(E)$ , 345 cm<sup>-1</sup>,  $\nu_3(F_2)$ , 825 cm<sup>-1</sup> and  $\nu_4(F_2)$ , 480 cm<sup>-1</sup> (Nakamoto 1966). NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> crystals show a characteristic strong absorption for (NH<sub>4</sub>)<sup>+</sup> at 3250 cm<sup>-1</sup>. On the whole the absorption bands are not sharp for this compound and this happens in most of the vanadates.

The impedance was measured for NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> crystals taken in the form of pellets (10 mm dia., 2 to 3 mm thickness, 85 to 90% compactness and pressure 5 ton sq. cm<sup>-1</sup>). The pellets were sintered in a vacuum chamber at 300°C. A capacitance bridge (General Radio model 160B) was used. The conductivity was measured at varying a.c. internal frequency range and the proton conductivity measured as a function of temperature. The Arrhenius plot in figure 3 shows a high proton conductivity of the order of 10<sup>-3</sup> and 10<sup>-1</sup> per ohm/cm at 100°C. Beyond this temperature the proton conductivity falls down sharply due to the phase transition at 110°C and raises again steadily above 220°C. The proton conductivity value obtained for NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> is much higher than the proton conductivity values reported for NH<sub>4</sub>-zeolites, NH<sub>4</sub> β"-alumina and other related compounds. The conduction mechanism is (NH<sub>4</sub>)<sup>+</sup> migration as in NH<sub>4</sub>-zeolites and NH<sub>4</sub> β"-alumina. As seen in figure 4, there is a discontinuity in the Arrhenius plot of NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> and similar discontinuities in the Arrhenius plots have been reported earlier in various proton conductors (Chandra 1984; Subramanian *et al* 1984). However, such factors were earlier explained in terms of the loss of water in the compound. In the present case, there is no such loss of water (normally occurring above 100°C) and also the loss of ammonia (occurring above 500°C). The corresponding activation energy values were calculated from the slopes of the Arrhenius plots (0.3 eV and 0.75 eV respectively for the low temperature and high temperature regions).

The complex admittance plots (conductance *G* vs susceptance *B*) were obtained over a wide range of frequency for a number of samples of NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> crystals and a plot is given in figure 5 which shows a semi-circle whose centre is slightly below the *G* axis. The angle between the diameter of the semi-circle and the *G* axis is around 35° which can be explained on the basis of the dispersion of the relaxation time that occurs in the polycrystalline material (Bayard and Barna 1978; Almond *et al* 1984). This also shows that the intergranular impedance or the grain boundary effects are negligible compared to the bulk impedance of the sample.

#### 4. Conclusions

A new proton conductor, NH<sub>4</sub>Zr<sub>2</sub>V<sub>3</sub>O<sub>12</sub> has been synthesized by various methods. The melt grown crystals are quite superior in quality with metallic lustre and flaky to massive in habit. It crystallizes in the monoclinic system and shows multiple phase transitions at 110°C and 780°C. Its high proton conductivity makes it a prospective material for fuel cells.

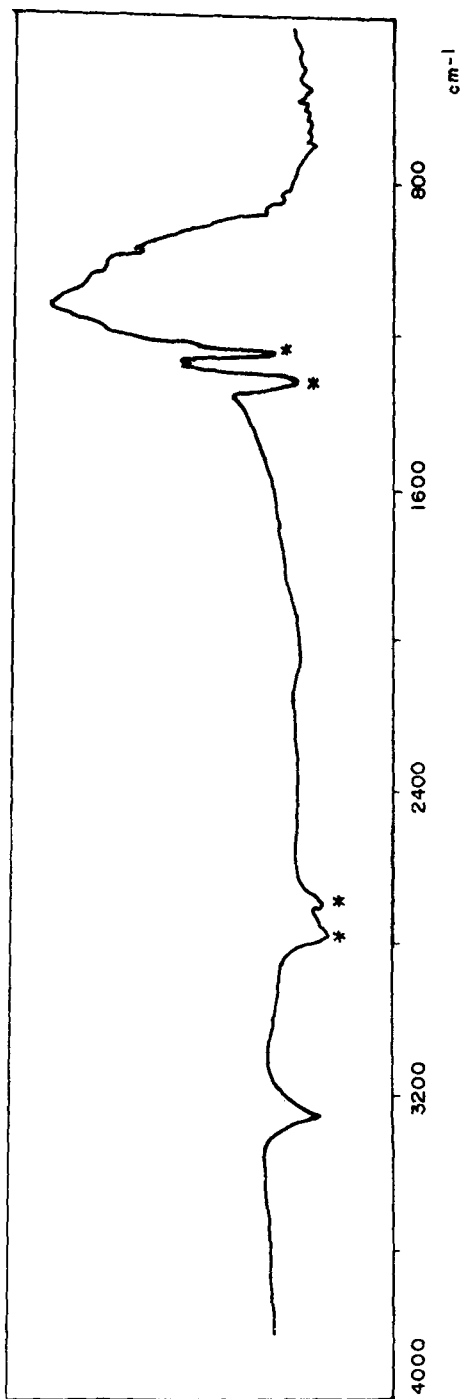


Figure 3. IR-spectrum for  $\text{NH}_4\text{Zr}_2\text{V}_3\text{O}_{12}$  crystals.

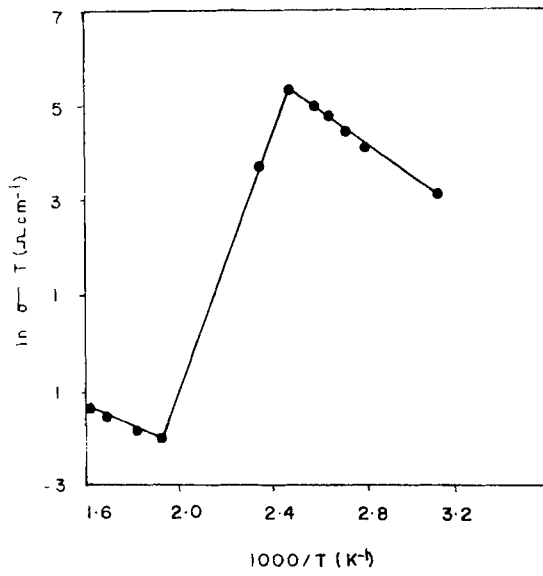


Figure 4. Arrhenius plot for  $NH_4Zr_2V_3O_{12}$ .

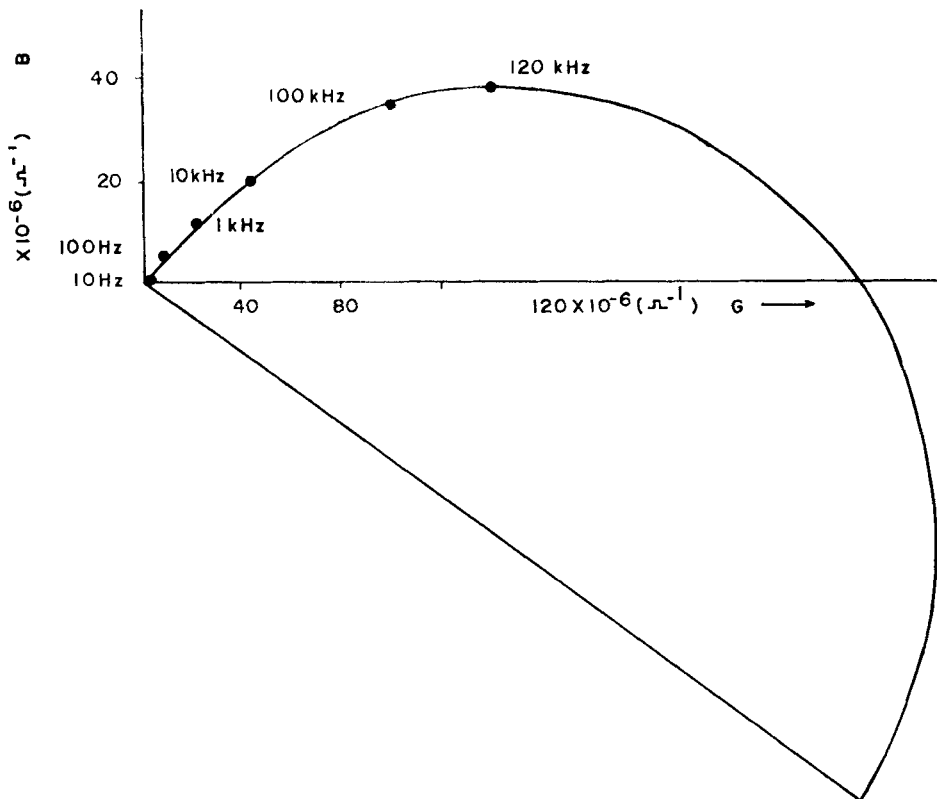


Figure 5. Complex admittance plot for  $NH_4Zr_2V_3O_{12}$  at 100°C.

### Acknowledgements

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