NH₄Zr₂V₃O₁₂ proton conductor

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Abstract. NH₄Zr₂V₃O₁₂, 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. NH₄Zr₂V₃O₁₂; 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 NH₄β-alumina, NH₄ zeolite, LiN₂H₆SO₄, LiH₂PO₄, N₂H₆SO₄, (NH₄)₃H(SO₄)₂, NH₄Zr₂P₃O₁₂, HZr₂P₃O₁₂ 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 NH₄Zr₂V₃O₁₂.

2. Synthesis

Almost all the vanadates found in literature have been synthesized by the flux method. Here, an attempt has been made to develop NH₄Zr₂V₃O₁₂ 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, NH₄Zr₂V₃O₁₂ could be synthesized by using a saturated aqueous solution of (NH₃)₂CO₃ 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°C followed by a slow cooling at 1 to 5°C per hour. The present authors have obtained well-developed crystals of NH$_4$Zr$_2$V$_3$O$_{12}$ (figure 1a).

2.2 Melt technique

This technique is more suitable because of its simplicity and good results. The starting components such as NH$_4$VO$_3$, 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°C, held overnight and subsequently the temperature of the crucible was raised up to 950°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$_4$Zr$_2$V$_3$O$_{12}$ 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$_4$Zr$_2$V$_3$O$_{12}$ under the following conditions: temperature 250°C, pressure 200 atm, NH$_4$VO$_3$ 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°C per hour). The main drawback of this method is the small size of the crystals (figure 1c).

3. Characterization

NH$_4$Zr$_2$V$_3$O$_{12}$ 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$_{α}$ ($λ=1.934$ Å) as the source. The structure was found to be monoclinic with cell parameters $a=12.19$, $b=11.81$, $c=15.15$ Å, $β=101.96°$ and $V=2133.71$ Å$^3$. Table I gives the powder diffraction pattern for NH$_4$Zr$_2$V$_3$O$_{12}$ crystals.