Pressure Induced Water Insertion in the Defect Pyrochlore NH_4NbWO_6

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A sudden and reversible increase of about 5% in the unit cell volume of ammonium tungstoniobate at pressures around 2.5 GPa was observed with pressure transmitting media containing water. This behavior was attributed to high pressure water insertion from the pressure media into the host structure of NH_4NbWO_6. The effects of different water contents of the pressure transmitting medium on the high pressure behavior of NH_4NbWO_6 were studied by high pressure energy dispersive x-ray diffraction and by Raman spectroscopy of the ammonium ν_2 bending mode. The water insertion occurs with no apparent change in the pyrochlore framework, and a preliminary analysis indicates a partial occupation of the site $16e$ ($F\bar{4}3m$) by the oxygen of the water molecules. [S0031-9007(97)02887-1]

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Since the early work of Byströn on $CaNaNb_2O_6F$ [1] and the discovery of ferroelectricity in $Cd_2Nb_2O_7$ by Cook and Jaffe [2], a wide range of compounds of general formula $A_2B_2X_6X'$ with the pyrochlore structure have been prepared. Because of their relatively open structures, pyrochlore compounds should exhibit interesting behavior under high pressure. This was little explored, however, as pointed out by Jayaraman [3]. More recently, the pressure dependence of the ionic conduction mechanism in the defect pyrochlore NH_4NbWO_6 was studied in the pressure range up to 3 GPa and at temperatures between 25 and 400 °C [4,5].

The crystal structure of NH_4NbWO_6 can be described as a rigid framework of corner-sharing oxygen octahedra with randomly distributed niobium or tungsten lying near the center of the octahedron. The large $NH_4{}^+$ cations are only weakly bonded to the rest of the framework and partially fill the cavities produced by the interconnected octahedra. They form a sublattice that is responsible for the ionic conductivity in this compound.

In order to investigate the structural changes induced by high pressure in ammonium tungstoniobate, a series of high pressure energy dispersive x-ray diffraction spectra was obtained in the pressure range up to 8 GPa using a diamond anvil cell. The samples were prepared at the Institut für Werstoffwissenschaften, Universität Erlangen-Nürnberg, following the procedure described by Brunner [6], and were characterized, at ambient pressure and temperature, by angle-dispersive x-ray diffraction. Rietveld refinement of the powder diffraction pattern revealed that the correct space group is noncentrosymmetric, $F\bar{4}3m$, rather than $Fd3m$, as had been proposed in the literature [7,8]. A more detailed discussion of the structure of this compound at ambient pressure and temperature is given elsewhere [9].

The samples of NH_4NbWO_6 were contained in a 300 μm diameter hole drilled in a Waspalloy gasket, along with a small ruby chip as pressure gauge [10]. The individual peak width of the ruby fluorescence doublet also enabled us to verify the degree of hidrostaticity during the experiments, especially when using liquid pressure media. Energy dispersive x-ray diffraction (EDXRD) experiments were performed with an intrinsic germanium detector and a conventional tungsten x-ray tube operating at 45 kV and 20 mA. Peak positions in the EDXRD spectra were determined by fitting the peaks to Gaussian profiles using the program XRDA [11]. Raman spectra were obtained using a micro-Raman instrument consisting of a Jobin-Yvon HR320 monochromator equipped with a 1800 grooves/mm holographic grating, followed by a Notch filter and a EG&G Princeton Applied Research nitrogen cooled CCD detector, with a nominal 30 mW HeNe laser (632.8 nm) as excitation source.

Different pressure transmitting media were used in the course of high pressure experiments, including NaCl, methanol-ethanol (4:1), methanol-ethanol-water (16:3:1), and silicone oil. Energy dispersive x-ray diffraction experiments performed using NaCl as pressure medium showed that the compound NH_4NbWO_6 undergoes a second-order phase transition at about 4.5 GPa, followed by a first-order phase transition above 7 GPa [12].

Aside from these transitions, a sudden increase of the lattice parameter of NH_4NbWO_6 was observed at pressures between 2 and 3 GPa when using water containing pressure transmitting media. This effect is dependent on the water content in the pressure transmitting medium and is not observed when the pressure medium is anhydrous. This can be seen in Fig. 1, where the change in the unit cell volume is plotted against pressure for various pressure transmitting media. The effect is more pronounced when the pressure medium is a methanol-ethanol-water mixture (16:3:1 in volume). A further increase in the water content of the pressure medium (in this case, methanol-ethanol-water, 16:3:2 in volume) does not induce a greater increase in the unit cell volume.

It is well known that any small departure from hydrostatic conditions inside the gasket leads to a broadening of the characteristic doublet in the ruby fluorescence

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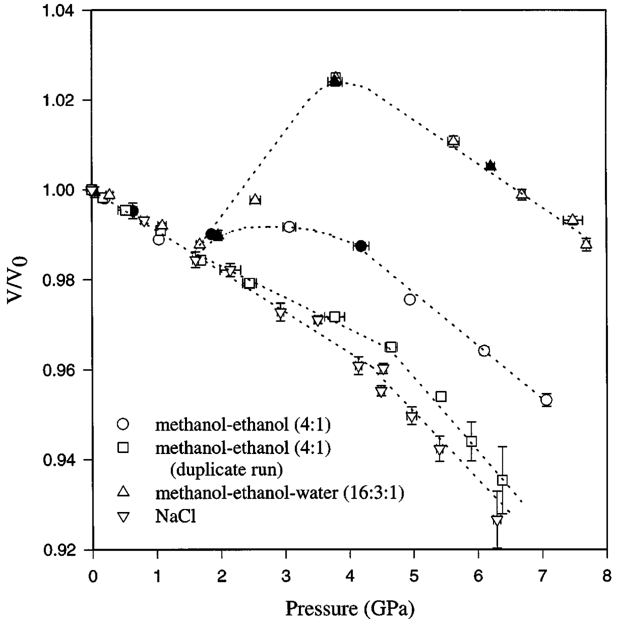

FIG. 1. Effect of different pressure media on the variation of NH_4NbWO_6 unit cell volume with pressure. Pressure media are methanol-ethanol (4:1)—(∘) and (□), methanol-ethanol-water (16:3:1)—(△), and NaCl— (▽). Open and solid symbols refer to increasing and decreasing pressure, respectively. Dotted lines are plotted to guide the eye. Some residual water is expected in the methanol-ethanol (4:1) medium.

spectra [13]. Since in our experiments such broadening of the ruby doublet was not observed (except for the case of NaCl as pressure medium, which is a soft solid), there is no evidence that the sample had been submitted to stress induced by nonhydrostatic conditions inside the gasket during the measurements. No departure from cubic symmetry was found, regardless of the different pressure medium utilized, at least up to 7 GPa. In all of our experiments, the upper limit for the deviation from one for the c/a ratio of a possible tetragonal lattice was about 0.2%.

There are two data sets in Fig. 1 in which the pressure medium is a mixture of methanol-ethanol (4:1). The difference between them is the ratio of pressure medium:powder sample in the gasket. The NH_4NbWO_6 cell volume increased in the run with the greater amount of methanol-ethanol mixture, which can be explained in terms of the residual water content in the analytical grade ethanol.

Consequently, we interpreted these results as the effect of high pressure water insertion in the ammonium tungstoniobate compound. This insertion reaction is fully reversible, with any hysteresis being less than ~0.3 GPa. No appreciable change was observed in the EDXRD spectra of the hydrated sample under high pressure, indicating that the framework of the host structure probably remains unchanged. After complete pressure release, the lattice parameter assumes its original value.

The lack of hysteresis in the water insertion process, at least within the sensitivity of our x-ray diffraction and Raman measurements, and the similarity to other hydrated pyrochlores [14,15] constitute a good indication that the water intercalated in ammonium tungstoniobate occupies a well defined site in the cavities of the framework structure. A preliminary analysis based on electrostatic calculations suggested the site $16e$ (x, x, x), with $x \approx 5/8$, as the probable crystallographic site occupied by the oxygen of the water molecule. Based on this model, powder pattern simulations showed that water insertion, without any other change in the ammonium tungstoniobate structure, is accompanied by a increase of the relative integrated intensity of the 222 Bragg peak and a decrease in the intensity of the 311 Bragg peak. Other less intense peaks also change after water insertion. Actually, as can be seen in Fig. 2, a remarkable change in the relative intensity of the 311 and 222 reflections is observed in the EDXRD spectra at the pressure of water insertion with methanol-ethanol-water (16:3:1) pressure medium. However, no significant change is observed when the pressure medium is sodium chloride, indicating that this effect is not a simple result of rearrangement of the NH_4NbWO_6 structure at high pressures. No change in the 222 peak intensity is expected if water inserts in the unoccupied sites $4a$ $(0, 0, 0)$ or $4d$ $(3/4, 3/4, 3/4)$ of space group $F\bar{4}3m$.

Because of the water molecule proximity, the normal mode frequencies of the ammonium ion should be altered after water insertion. A study of the pressure dependence of the ammonium ν_2 Raman peak frequency was performed in order to check this hypothesis, and the results are summarized in Fig. 3, with methanol-ethanol-water (16:3:1), methanol-ethanol (4:1), and silicone oil as pressure transmitting media.

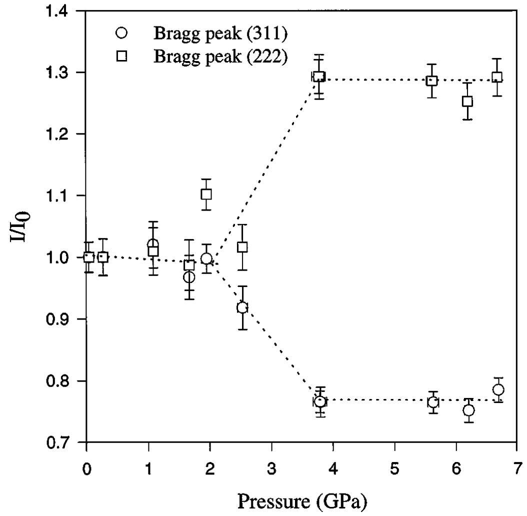

FIG. 2. Pressure dependence of the relative intensity of 311 and 222 Bragg peaks as determined by EDXRD measurements. Open circles and squares refer to the 311 and 222 reflections, respectively. Pressure medium methanol-ethanol-water (16:3:1). Dotted lines are plotted to guide the eye.

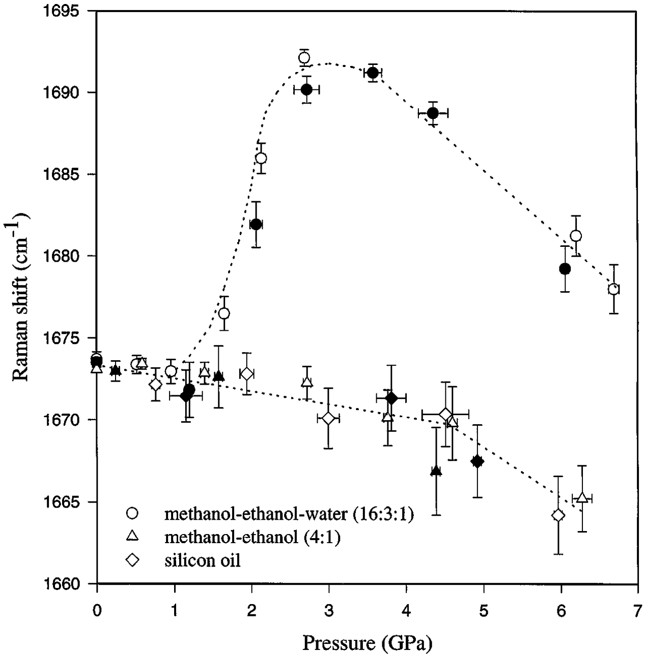

FIG. 3. Pressure dependence of the Raman shift of the ν_2 bending mode of the ammonium ion for different pressure transmitting media, methanol-ethanol-water (16:3:1)—(○), methanol-ethanol (4:1)—(△), and silicone oil—(◇). Open and solid symbols correspond to increasing and decreasing pressure, respectively. Dotted lines are plotted to guide the eye.

Above 4.5 GPa, independent of the pressure medium used, a splitting of the ν_2 peak was observed. Because of the poor statistics, it was not possible to decompose the broad peak into its components and the results showed in Fig. 3 correspond to the shift with pressure of the position of maximum intensity in the peak profile. This splitting of the doubly degenerate ν_2 peak occurs at the same pressure in which the compound undergoes a second order phase transition [12] and corresponds to a lowering of the local site symmetry of the ammonium ion.

In the case of aqueous pressure media, there is a reversible increase of the ν_2 frequency over the same pressure range that the lattice expansion was observed. This frequency increase is the expected effect of hydrogen bonding on bending modes, and seems to be a direct consequence of the interaction between ammonium ions and the inserted water molecules. No similar effect is observed when the pressure medium is silicone oil, as can be seen in Fig. 3.

Based on the total water content inside the gasket, it is possible to roughly estimate that the high pressure water insertion leads to a hydrated form $NH_4NbWO_6 \cdot xH_2O$ with $x \leq 0.4$, resulting in a partial occupation of the $16e$ site. Powder pattern simulations with variable occupation factor of the $16e$ site suggest an equimolar water stoichiometry in order to account for the intensity variation of the 311 and 222 reflections. The disagreement with the estimated molar ratio of 0.4 is possibly a consequence of the crudeness of the structural model, which does not take into account minor rearrangements of the structure after water insertion. Also water displacement from the position corresponding to the minimum electrostatic potential would modify the dependence of the Bragg peaks intensities on the water content in NH_4NbWO_6.

Other drastic effects due to the interaction between the sample submitted to high pressure and the pressure medium were observed, for example, in the case of zeolites [16] and solid C_{60} [17]. In the latter, irreversible inclusion of pentane molecules into interstitial sites of the C_{60} lattice was observed above 1.4 GPa and 475 K, with a mixture of pentane-isopentane (50/50, by volume) as the pressure medium. However, due to its irreversible character, this reaction cannot be considered as a kind of intercalation, at least in the sense given by Murphy and Christian [18].

In a recent Letter [19], Jayaraman *et al.* reported a high pressure phase transition in $CuGeO_3$ induced by methanol intercalation from the pressure medium. However, this claim is not conclusive [20].

Considering the open structure of the pyrochlore compounds, it is not surprising that some of them exhibit a variety of intercalation reactions. Indeed, water and alkali metal ion intercalation in defect pyrochlore compounds has already been reported. Darriet *et al.* [21] showed that $KNbWO_6$ and $KTaWO_6$ are hygroscopic at ambient conditions. No significant change in the x-ray diffraction patterns of these compounds was observed after hydration, but the lattice parameter increased about 1.5%.

Alkali metal ion insertion, by ion exchange, was reported by Murphy, Dye, and Zahurak [22] in defect pyrochlores $A\text{NbWO}_6$, yielding compounds with stoichiometry $A_2\text{NbWO}_6$ $(A = \text{Na, K, Rb})$. Lithiation reactions in some tungsten bronzes and WO_3 with pyrochlore structure were also reported [23].

In conclusion, we observed an increase in the unit cell volume of NH_4NbWO_6 at pressures of about 2.5 GPa, which was interpreted as the resulting effect of a high pressure insertion reaction between water from the pressure transmitting medium and the sample of ammonium tungstoniobate. Aside from the volume increase of the host pyrochlore, other effects of such water insertion are the change in the relative intensity of 311 and 222 Bragg peaks, and the positive shift of the ammonium ν_2 bending mode frequency. To the best of our knowledge, this is the first observed fully reversible high pressure water insertion reaction with a volume increase and no great change in the host structure. It must be stressed that Le Chatelier's principle is not violated by the increase of the pyrochlore unit cell volume with pressure, since by our estimates, after complete insertion of the water from the pressure medium into the pyrochlore cavities, the correspondent volume reduction of the pressure transmitting medium would be sufficient to compensate for the volume increase of the host structure.

It is our intention now to perform a systematic study of this kind of effect in other defect pyrochlores, as well as a detailed study of the microscopic mechanism and the kinetics of this insertion reaction.

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