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Note

Microhardness, dilatometric and electrostriction studies on NaH_2PO_4-H_3BO_3 binary system

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The author reports the microhardness, electrostrictive and thermal expansive coefficients of NaH_2PO_4-H_3BO_3 binary system. Elastic stiffness coefficient of NaH_2PO_4-H_3BO_3 has been calculated from the microhardness data; further the electrostrictive results of this binary are observed to be supportive to the microhardness data. Thermal expansion coefficient and crystallographic data of NaH_2PO_4 and NaH_2PO_4-H_3O_3 binary are compared

NaH_2PO_4-H_3BO_3 binary system is reported earlier[1] to be tetragonal. In the present work, data on microhardness[2-4], electrostriction[5,6] and dilatometry[7] were carried out. From microhardness data elastic constants[8] and yield stress[9] were obtained. Comparison has been made on microhardness and electrostrictive data on the reported[10] $NH_4H_2PO_4$ and NaH_2PO_4-H_3BO_3 binary. Results on the thermal expansion coefficient of NaH_2PO_4 and its binary were discussed.

Experimental Procedure

NaH_2PO_4-H_3BO_3 crystals were grown from aqueous solution. The weight fraction of NaH_2PO_4 in the NaH_2PO_4-H_3BO_3 binary is 90.62%, the method of growth is reported earlier[1]. Microhardness of NaH_2PO_4-H_3BO_3 was determined using 160 mph microhardness tester fitted with Vickers diamond pyramid indentor and attached to a Carl-Zeiss [Jenavert] research microscope. For static indentation test, load p varying from 5 to 70 g were applied on the selected (100) face of the crystal over a fixed interval of time (10 s), and removed. The Vicker's hardness number (hereafter abbreviated as VHN) H_v was calculated using the relation H_v=1.8544 (p/d^2) kg mm^{-2} where p is the applied load in kg and d is the average diagonal length of the Vickers impression in mm after unloading. The elastic stiffness coefficient is calculated using the relation[8] $C_{ij}=H^{7/4}$. Electrostriction and thermal expansion coefficients were determined using an optical interference technique[11] described elsewhere. Electrostriction coefficient is obtained using the relation[12] R_{ijkl} = A/l where $A = (\lambda \times N \times C^2)/(2\times V^2)$.

Results and Discussion

Microhardness data—Fig.1 illustrate the variation of hardness with indentor load and Fig.2 gives the variation of the logarithm of applied load (p) with the logarithm of length of indentation (d), which is called log-log plot of Meyer. Microhardness is found to decrease with increase of indentor load (5-10 g) and remains unaffected beyond 10 g. The microhardness number H_v turns out to be 80±5 kg/mm^2 at 40 g load. Least square fit of the logarithm plot between length of indentation (d) and load (p) yielded a straight line (Fig.2). The slope of the this line gives the value of n, the work-hardening index. Onitsch[13] and Hanneman[14] have shown that the value of n comes out to be between 1 to 1.6 for hard materials and more than 1.6 for soft materials. The value of n for the NaH_2PO_4-H_3BO_3 is found to be close to 2, hence it is classified as a soft material. From the Wooster's relation[8] $(C_{ij}=H^{7/4})$ between elastic stiffness coefficient and hardness of a crystal, the value of C_{11} for the NaH_2PO_4-H_3BO_3 binary is calculated to be 12 ±1×10^{11} CGS units. The value of H_v for NaH_2PO_4-H_3BO_3 binary (80±5 kg/mm^2)

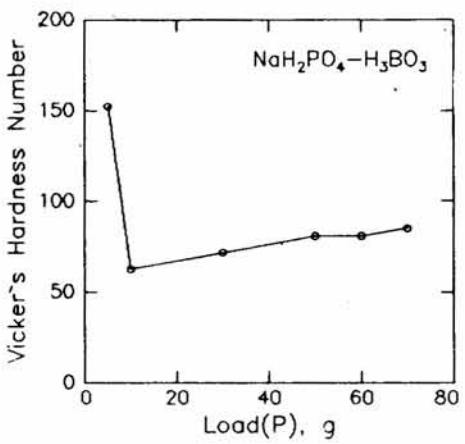

Fig.1—Variation of microhardness (H_v) with load (p)

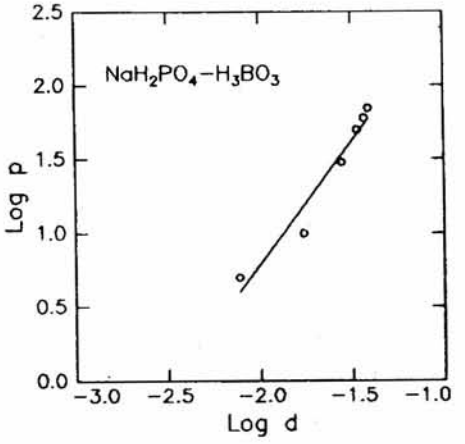

Fig.2—Log-log plot of Meyer for NaH_2PO_4-H_3BO_3 binary system

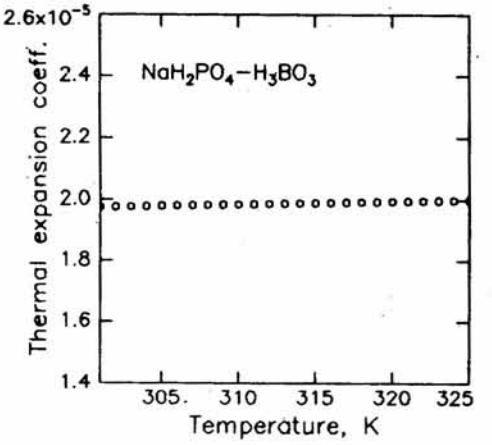

Fig.3—Temperature variation of thermal expansion coefficient of the binary (α_c)

is slightly higher compared to the reported[10] values of $NH_4H_2PO_4$ (70±2 kg/mm^2) but lower than that of KH_2PO_4 (160±2 kg/mm^2). This could be attributed to the difference in their molecular structure. The crystallographic structure of $NH_4H_2PO_4$, KH_2PO_4 and NaH_2PO_4-H_3BO_3 are similar in H_2PO_4 network and hence can be compared. In $NH_4H_2PO_4$ the N-H...O bond occurs between ammonium and phosphate groups where as KH_2PO_4 and NaH_2PO_4-H_3BO_3 are polar structures consisting of K^+ and $H_2PO_4^-$ and Na^+ and $H_2PO_4^-$ ions respectively. The size of cations, the magnitude of electron affinity, electronegativity values of NaH_2PO_4-H_3BO_3 are less in comparison with $NH_4H_2PO_4$ but more with KH_2PO_4. In the light of these facts it is proposed that the ionic bonding between Na^+ and $H_2PO_4^-$ ions is weaker than the bonding between K^+ and $H_2PO_4^-$ ions but stronger than that of N-H...O bond occurring between ammonium and phosphate groups justifying the value of H_v for NaH_2PO_4-H_3BO_3.

Electrostriction data—It is reported[1] that NaH_2PO_4-H_3BO_3 belong to tetragonal system at ambient temperature with C_{4h} or C_4 point group symmetry. These point groups evolve ten independent electrostrictive coefficientes[15] which are given below

$R_{1111} = R_{2222}$, $R_{1122} = R_{2211}$, $R_{1133} = R_{2233}$, $R_{1112} = -R_{2212}$, R_{3311}, R_{3333}, R_{2323}, $R_{2331} = -R_{3123}$, $R_{1211} = -R_{1222}$ and R_{1212}

The measured electrostrictive coefficients are $R_{1133} = R_{2233}$ and $R_{1111} = R_{2222}$ and their values are observed to be 50×10^{-18} m^2/V^2 and 23×10^{-18} m^2/V^2 respectively.

$NH_4H_2PO_4$ and NaH_2PO_4-H_3BO_3 are reported[16,17] to belong to same crystallographic system. Hence the literature data[10,11] of microhardness and electrostrictive coefficient on $NH_4H_2PO_4$ and NaH_2PO_4-H_3BO_3 can be compared. It is known that higher value of VHN indicates stronger bonding of atoms in the sample, which in turn are expected to possess lower values of electrostrictive coefficients. It may be pointed out that the VHN value of NaH_2PO_4-H_3BO_3 is greater than that of $NH_4H_2PO_4$. Thus the higher electrostrictive coefficient values of NaH_2PO_4-H_3BO_3 in comparison to that of $NH_4H_2PO_4$ is in concurrence with the microhardness studies.

Dilatometry data—Fig. 3 illustrates the thermal expansion coefficient measurement along c-axis (α_c) for a temperature range from 300 to 323 K and its value is found to vary from 19.75 to 20 × $10^{-6}K^{-1}$. NaH_2PO_4 is reported[17] to be orthorhombic with lattice parameters a = 6.606 Å, b = 7.275 Å and c = 11.384 Å. Thermal expansion coefficient of NaH_2PO_4 is reported[18] to be 38, 33 and 28.6 × $10^{-6}K^{-1}$ along a, b and c axes respectively. NaH_2PO_4-H_3BO_3 is reported[1] to be tetragonal, the weight fraction of NaH_2PO_4 and H_3BO_3 in the NaH_2PO_4-H_3BO_3 binary are 90.62 and 9.38% respectively. Further, the lattice parameters of the NaH_2PO_4-H_3BO_3 are a = 5.42 Å and c = 7.45 Å. The α_c for the binary may be compared with its pure sample at room temperature. Since there is a decrement in the value of the corresponding lattice parameter (c-

axis) the same trend is reflected in the value of α_c which is justified.

Conclusions

1. The Vicker's hardness number (H_v) of NaH_2PO_4-H_3BO_3 binary is 80±5 kg/mm^2 at 40 g load.

2. The microhardness data of NaH_2PO_4-H_3BO_3 binary is in concurrence with that of the electrostriction studies.

3. Thermal expansion coefficient (α_c) of NaH_2PO_4-H_3BO_3 binary is in accordance with its structural data obtained from X-ray diffraction technique

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