X-ray data for the substitutional solid solution of the binary system ammonium dihydrogen phosphate with boric acid

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Abstract. X-ray powder diffraction data for the binary system ammonium dihydrogen phosphate with boric acid is studied and it is inferred that the binary belongs to tetragonal system and forms a substitutional solid phase. On the basis of the space group the binary is predicted to exhibit electrooptic property along with piezoelectric and electrostriction properties. It is proposed that the phosphorus atom of ammonium dihydrogen phosphate is substituted by the boron atom of boric acid.

Keywords. X-ray diffraction; substitutional solid solution; tetragonal system.

1. Introduction

Ammonium dihydrogen phosphate ($NH_4H_2PO_4$, ADP) belongs to the family XH_2PO_4. The other members of the family are KH_2PO_4 and NaH_2PO_4; $NH_4H_2PO_4$ and KH_2PO_4 belong to tetragonal system (Hellwege 1975). It has been reported that KH_2PO_4 and NaH_2PO_4 form a solid solution with amorphous boric acid (H_3BO_3) (William 1958). We have studied the powder X-ray diffraction patterns of these tetragonal systems (Haranadh *et al* 1992). It was found that ADP formed a solid solution when mixed with boric acid. We have investigated the crystal system of this binary compound.

2. Experimental

Pure crystals of ADP and amorphous boric acid were weighed in equimolar proportions and the mixture was dissolved in triple distilled water. The weight fraction of ADP in the ADP/boric acid binary compound was 56·54%. Crystals obtained were about 1 mm in dimensions and were colourless. For recording the X-ray powder diffraction patterns a Seifert diffractometer was used with Cu-K_α radiation ($\lambda = 1·542$ Å). The density of the sample was determined by the flotation method. Birefringence was determined by the Babinet compensator technique using a He–Ne laser.

3. Results and discussion

The X-ray data for the binary compound are presented in table 1. Table 2 gives unit cell dimensions, unit cell volume, observed density, calculated density and the possible space groups of both pure ADP and the binary system of ADP/boric acid. From table 1 it is seen that for all reflections the observed values of d (interplanar spacing) are in good agreement with those calculated. The maximum difference between d_{obs} and d_{cal} values was 0·73%. It is inferred from the X-ray data that the binary system

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Table 1. X-ray powder data.

2θ (deg)	hkl	d(obs) (Å)	d(cal) (Å)	2θ (deg)	hkl	d(obs) (Å)	d(cal) (Å)
28·45	002	3·105	3·100	69·00	413	1·361	1·371
33·30	121	2·674	2·672	70·30	422	1·335	1·336
37·30	122	2·398	2·404	76·30	008	1·245	1·246
38·51	104	2·317	2·317	78·45	510	1·215	1·215
44·52	301	2·019	2·020	80·45	227	1·190	1·196
57·15	226	1·609	1·609	87·45	416	1·112	1·116
62·45	411	1·480	1·487	88·00	504	1·109	1·111
67·30	315	1·387	1·387				

Table 2. Lattice parameters and crystal data.

	ADP + Boric	ADP
Crystal system	Tetragonal	Tetragonal
Cell dimensions (Å)		
a	6·202	7·500
b	6·202	7·500
c	10·000	7·549
Molecular weight	88·415	115·03
Number of molecules in unit cell (z)	4	4
Observed density (g/cm³)	1·510	1·803
Calculated density from X-ray data (g/cm³)	1·526	1·798
Volume of unit cell (Å³)	384·648	424·699
Possible space group	$P4_2 2$	$I\bar{4}2d$

of ADP/boric acid belongs to tetragonal system. The systematic absence of 00l for l odd uniquely determines the space group to be $P4_2 2$. The unit cell volume of the binary compound (384·648 Å³) is less than that of the pure sample (424·699 Å³).

ADP when mixed with boric acid forms a substitutional solid solution. Phosphorus in ADP is supposed to be replaced by boron. The atomic radii of phosphorus (1·11 Å) and boron (0·88 Å) are nearly equal and this allows formation of a substitutional solid solution. Since an atom of higher atomic radius is being replaced by an atom of slightly lower atomic radius the volume of the unit cell of the binary compound is smaller compared to that of pure ADP. Similar behaviour has been reported earlier for the binary compound of KH_2PO_4 (KDP) with boric acid (Haranadh *et al* 1992).

The decrease in unit cell volume should be more for the ADP/boric acid binary compound compared to the KDP/boric acid binary (287·5 Å³) compound, since the weight fraction of boric acid is higher by 10% in ADP/boric acid (56·54% boric acid) than in KDP/boric acid (36% boric acid). This large difference in the unit cell volumes can be attributed to the radii of ammonium radical and potassium atom. The radius of ammonium (2·184 Å) is larger than that of the potassium atom (2·025 Å). Thus the decrease in the unit cell volumes of binaries has been to some extent compensated by their respective radii of ammonium and potassium.

Similar behaviour is also expected in the case of NaH_2PO_4/boric acid binary

compound unit cell, since the atomic radius of sodium (1·570 Å) is much smaller compared to that of ammonium and potassium.

From knowledge of the tetragonal space groups we predict that the ADP/boric acid binary compound should exhibit electrooptic property (Kaminov 1974) along with electrostriction and piezoelectric properties (Narasimhamurty 1981). The number of independent electrostrictive coefficients is seven while the number of independent piezoelectric coefficients is one. The density of the binary ADP/boric acid compound, calculated by the flotation method as well as from the X-ray data are in good agreement.

Packing index is defined (Fairbairn 1943) as $PI = (V_a/V_c) \times 10$, where V_a is the volume of the individual atoms in the unit cell and V_c is the volume of the unit cell of the crystal. Packing index of the ADP/boric acid binary compound is 2·103. This may be compared with that of pure ADP which is 1·235. Thus it is concluded that the atoms in the binary are less compactly packed and loosely bound when compared to its pure sample. A similar decrease is observed in the case of KDP/boric acid binary compound, whose packing index is 6·416 whereas the packing index is 4·753 for the pure sample.

Birefringence of the ADP/boric acid binary compound has been measured in *ab* plane using a Babinet compensator (Chavan and Patil 1985). The value of Δn for ADP/boric acid at room temperature is measured to be 0·0152 while the value for pure ADP (Zernike Jr 1964) is 0·041. This decrease in birefringence supports the X-ray data in which *a* and *b* values of the unit cell are smaller for ADP/boric acid compared to pure ADP, since birefringence is a bulk property.

4. Conclusions

(i) ADP/boric acid binary compound belongs to tetragonal system.
(ii) ADP/boric acid binary compound forms a substitutional solid solution.
(iii) In the binary compound of ADP/boric acid, phosphorus atom in ADP is substituted by boron atom of boric acid.
(iv) The volume of the unit cell is decreased because of the substitution of an atom with lower atomic radius (boron) by that of higher atomic radius (phosphorus).

Acknowledgements

References

Chavan S H and Patil R N 1985 *Indian J. Pure Appl. Phys.* **23** 101
Fairbairn H W 1943 *Bull. Geol. Soc. Am.* **54** 1305
Haranadh C and Madhu Mohan M L N 1992 *Bull. Mater. Sci.* **14** 385
Hellwege K H 1975 *Numerical data and functional relationships in technology* (New York: Springer) p S135
Kaminov I V 1974 *An introduction to electrooptic devices* (New York: Academic Press) p 111
Narasimhamurty T S 1981 *Photoelastic and electrooptic properties of crystals* (New York: Plenum Press) pp 342, 662
William F L 1958 *Solubilities* (New Jersey: Van Nostrand) p 276
Zernike Jr 1964 *J. Opt. Soc. Am.* **54** 121