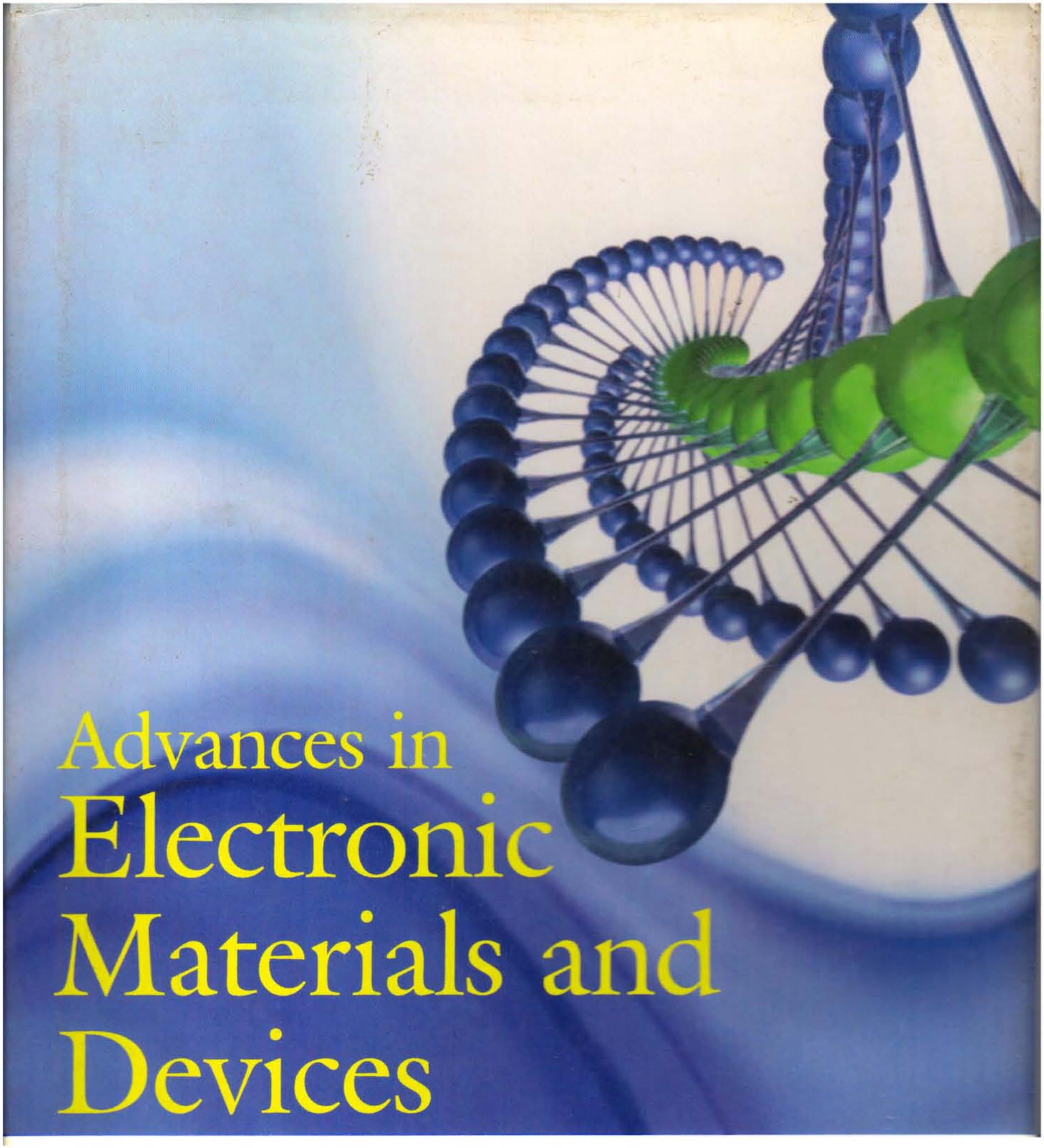

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X-ray Diffraction Structure Analyses of $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$ Mixed Crystals: Nature of H-bonds

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Abstract: Structural analyses of $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$ for $x = 0.14$, 0.33 and 0.50 (TRAHS) single crystals are performed by X-ray diffraction experiments in order to investigate the hydrogen bond (H-bond) connection in $(SO_4 \cdot H \cdots SO_4'')$ dimers. The H-bond length R_{o-o} is determined from the model for H-bond attached to oxygen atoms. In the study, hydrogen bonding is realised with R_{o-o} distance being 2.549 Å in $(NH_4)_3H(SO_4)_2$ and 2.492 Å in $Rb_3H(SO_4)_2$. The H-bond length R_{o-o} of TRAHS varies with x and is less than that obtained for pure crystals. The values with $x = 0.14$, 0.33 and 0.50 are 2.449, 2.522 and 2.515 Å, respectively. These are close to but still longer than the so-called critical bond length R_c. The observed lattice parameters vary systematically with x showing that the mixed crystals are solid solution of two analogues. All these crystals are monoclinic with the space group C2/c and Z = 4.

Keywords: $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$, Zero-dimensional hydrogen-bonded crystal, Single crystal X-ray diffraction, Structure analysis.

Introduction

X-ray structural analyses of $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$ (TRAHS with $x = 0.14$, 0.33 and 0.50) are carried out on P4 four circle diffractometer at room temperature using $\lambda = 0.71073$ Å to investigate the H-bond connection in $(SO_4 \cdot H \cdots SO_4'')$ dimers. The H-atoms positions could not be located directly from the structural refinements of the crystals. The H-bond length R_{o-o} is determined from the model for H-bond attached to oxygen atoms [1]. The nature of H-bond and the dynamics of ammonium ions in these crystals is still not unambiguously understood in spite of several efforts. We, therefore, undertook the structural analyses of

$(NH_4)_3H(SO_4)_2$ (TAHS) [2] and $Rb_3H(SO_4)_2$ (TRHS) [4] along with their mixed crystals TRAHS ($x = 0.14$, 0.33 and 0.50). The lattice parameters obtained in the recent structure analyses of TAHS and TRHS match well with the earlier reports [3, 5]. In this article, we report the crystal structure analyses of the mixed single crystals TRAHS ($x = 0.14$, 0.33 and 0.50) and also suggest the possible H-bond nature from these data. The Fourier map is used to obtain distortion in the electron density distribution around O_1 atom that supports the H-bond formation. The H-bond is more evident in Fourier map in mixed crystals and the H-atoms positions are localised. This indicates that the H-atom disorder is less in mixed crystals than in pure crystals. The importance of study in relation to tetrahedral orientation dynamics and ordering in low temperature phase is discussed.

Experiment and Structure Refinements of the Mixed Crystals $[Rb_x(NH_4)_{1-x}]_3H(SO_4)_2$

Single crystals of TRAHS with $x = 0.14$, 0.33 and 0.50 were grown by slow evaporation method from aqueous solutions of Rb_2SO_4 (5.25 wt%) and $(NH_4)_2SO_4$ (15.75 wt%) with H_2SO_4 (7.0 wt%); Rb_2SO_4 (10.5 wt%) and $(NH_4)_2SO_4$ (10.5 wt%) with H_2SO_4 (7.0 wt%); and Rb_2SO_4 (15.0 wt%) and $(NH_4)_2SO_4$ (5.0 wt%) with H_2SO_4 (7.0 wt%), respectively. A spherically-shaped crystal of diameter 0.35 mm with a single domain was used. Intensity datum were collected on Siemens P4 automatic four-circle X-ray diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The measuring time varied from 0.5 to 2.0 s step^{-1} in the ranges $2 < 2\theta < 50°$ for $-18 \le h \le 1$, $-6 \le k \le 1$, $-11 \le 1 \le 12$ (max $\sin\theta/\lambda = 0.8069$ Å^{-1}) using $\lambda = 0.71073$ Å in TRAHS with $x = 0.14$. In case of TRAHS ($x = 0.33$), $2 < 2\theta < 50°$ for $-1 \le h \le 18$, $-1 \le k \le 6$, $-12 \le 1 \le 11$ and in TRAHS ($x = 0.50$), $2 < 2\theta < 50°$ for $-18 \le h \le 1$, $-6 \le k \le 1$, $-11 \le 1 \le 12$. After processing the raw data, Lorentz and polarisation corrections are made. 992 measured reflections were averaged to 654 unique observed reflections [$F_0 > 4\sigma(F_0)$]; $R(\text{int}) = 0.1157$; $R(\sigma) = 0.0445$ in TRAHS ($x = 0.14$) and 1141 measured reflections were averaged to 775 unique observed reflections; $R(\text{int}) = 0.1544$; $R(\sigma) = 0.0465$ in TRAHS ($x = 0.33$). Also 1116 measured reflections were averaged to 762 unique observed reflections; $R(\text{int}) = 0.1455$; $R(\sigma) = 0.0510$ in TRAHS ($x = 0.50$). Three standard reflections were monitored every hundred reflections. An examination of the diffraction symmetry and systematic absences confirmed the same space group C2/c as most of the $M_3H(XO_4)_2$ type crystals. The unit cell parameters were determined by least-squares fit of the θ values of 25 reflections in the range $10.0° < \theta < 30.0°$. The function minimised was $\Sigma w(|F_0| - |F_c|)^2$, $w = 1/\sigma^2(|F_0|)$.

The model summaries concerning unit cell information for mixed crystals TRAHS ($x = 0.14$, 0.33 and 0.50) are given in Table 1. The final R-factor and the weighted R-factor are 0.161 and 0.221 in TRAHS ($x = 0.14$), 0.112 and 0.258 in TRAHS ($x = 0.30$) and 0.167 and 0.281 in TRAHS ($x = 0.50$), respectively, where these two discrepancy factors are defined as $R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$ and $R_w = \{\Sigma w(|F_0| - |F_c|)^2/\Sigma w(|F_0|)^2\}^{1/2}$. No correction was made for absorption in the present structures.