

## Structural behaviour of $\text{AgNO}_3$ at low temperatures by neutron diffraction

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**Abstract.** Structural behaviour of silver nitrate ( $\text{AgNO}_3$ ) at low temperatures has been investigated by neutron powder diffraction and differential scanning calorimetry (DSC). Analysis showed abnormal changes in the rotations of nitrate ( $\text{NO}_3$ ) anions and thermal displacement parameters of the atoms near 220 K and 125 K. However, the basic lattice is compatible with the orthorhombic symmetry (space group  $\text{Pbca}$ ) till 12 K. The fine, small-scale structural anomalies probably originate from freezing of reorientation of  $\text{NO}_3$  ions from high-temperature disordered phase.

**Keywords.** Nitrate; neutron diffraction; crystal structure.

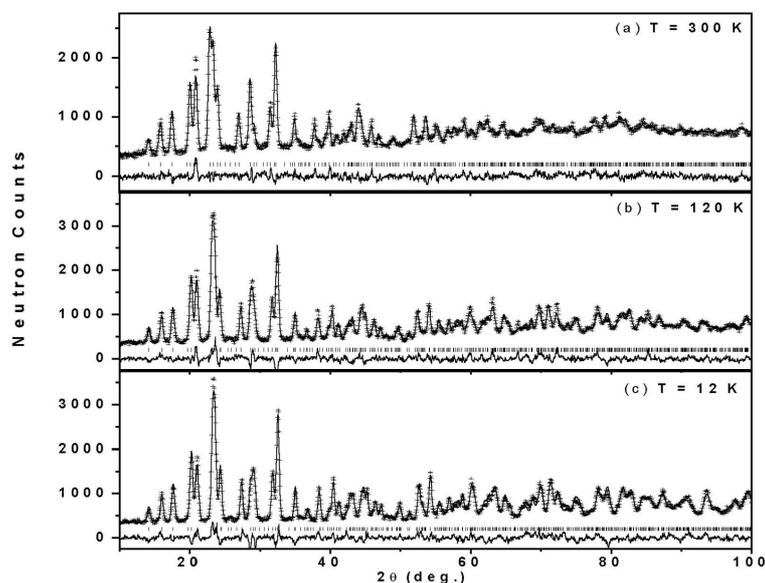
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### 1. Introduction

$\text{ANO}_3$  type of compounds exhibit a variety of phase transitions driven by reorientation or disordering of  $\text{NO}_3$  ions. Among them,  $\text{AgNO}_3$  has certain unique structural features. Its structure ( $\text{Pbca}$ ) [1] becomes orientationally disordered at a higher temperature [2] and exhibits slightly negative thermal expansion along the  $c$ -axis [3]. Interestingly, it also converts to a metastable ferroelectric phase only while cooling [4]. Below room temperature, spectroscopic study [5] reported some unusual changes in the intensities of spectra near 220 K and 140 K which were proposed to be of second-order transitions. In this report, we present the results of our structural study on  $\text{AgNO}_3$  by neutron powder diffraction in the range 300 K–12 K. Due to the sensitivity of neutrons to light atoms, a clear insight into the microscopic details on the motion of  $\text{NO}_3$  ions and associated subtle structural features may be obtained. In order to corroborate the results of neutron diffraction, DSC scans were performed below room temperature.

### 2. Experimental

Commercial  $\text{AgNO}_3$  powder (99.9% pure) was tightly sealed in a vanadium container and mounted on the PSD-based neutron powder diffractometer at Dhruva



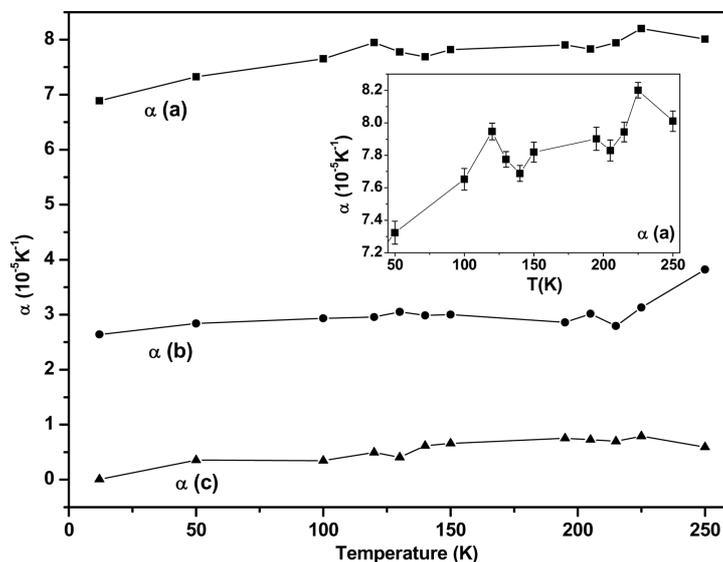
**Figure 1.** Rietveld refinement plot of  $\text{AgNO}_3$  at (a) 300 K, (b) 120 K and (c) 12 K with space group  $\text{Pbca}$ . Symbols (+): experimental data, solid line: fitted.

reactor, BARC. For low-temperature study, a close-cycle cryostat was used. Data were collected ( $2\theta$ ,  $4.5^\circ$ – $140^\circ$ ) at selected temperatures in the range 300 K to 12 K using neutrons of wavelength 1.249 Å. The stability of the temperature is  $\pm 1$  K. Diffraction data were analysed by Rietveld method with pseudo-Voigt peak-shape function using the program FULLPROF [6]. DSC scans were recorded using a Mettler-Toledo DSC 822 machine up to 125 K (lower limit of the machine) at a rate of 10 K/min.

### 3. Results and discussion

While analysing the room temperature data, both the reported models based on X-ray diffraction studies were considered. Refinements of the structural parameters with space group  $\text{Pbca}$  [1] lead to smooth convergence of the fits. Slight improvement in the agreement factor ( $R$ ) was obtained with anisotropic displacement parameters (Debye–Waller factors) of the atoms, but their values are found to be non-positive definite for most of the atoms. Hence, isotropic parameters were retained during the analysis. Final refinements resulted the  $R$ -value ( $R_p$ ) of 4.3%. Fitting of the data to  $\text{Pbca}$  structure is marginally better than the  $\text{P2}_1\text{2}_1\text{2}_1$  structure which was also proposed in literature. Hence, only the  $\text{Pbca}$  structure was considered for the analysis of the data at other temperatures.

Diffraction patterns recorded at low temperatures were similar to that at 300 K but have some changes in the intensities of the profiles were observed. At each



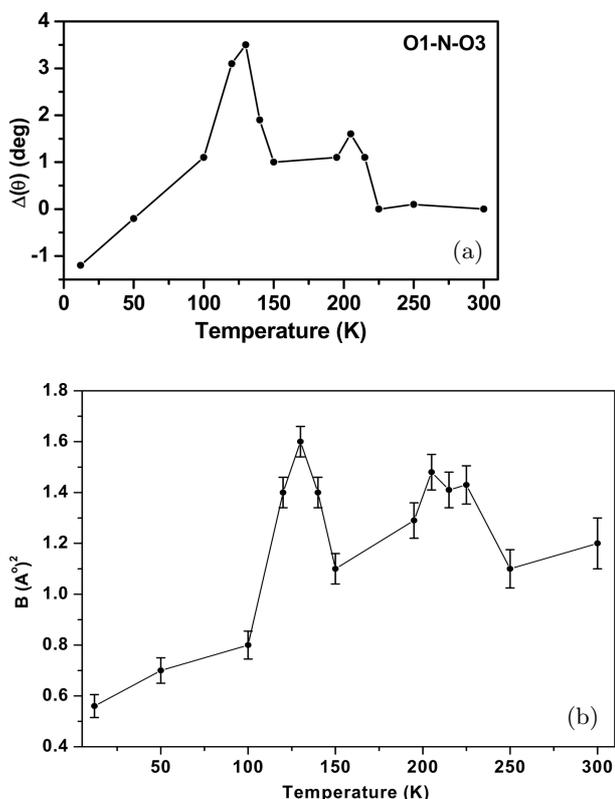
**Figure 2.** Thermal expansion coefficients ( $\alpha$ ) for the axis  $a$ ,  $b$  and  $c$  in  $\text{AgNO}_3$ . Inset: Enlarged picture for variation in  $\alpha$  ( $a$ ).

**Table 1.** Inter-atomic distances ( $\text{\AA}$ ) and bond angles (deg.) of the nitrate groups in  $\text{AgNO}_3$ .

	300 K		12 K
N-O1	$1.233 \pm 0.009$	N-O1	$1.186 \pm 0.006$
N-O2	$1.228 \pm 0.009$	N-O2	$1.259 \pm 0.005$
N-O3	$1.214 \pm 0.009$	N-O3	$1.245 \pm 0.006$
O1-N-O2	$128.4 \pm 0.7$	O3-N-O1	$121.6 \pm 0.4$
O2-N-O3	$111.3 \pm 0.7$	O3-N-O2	$115.5 \pm 0.4$
O3-N-O1	$120.2 \pm 0.7$	O1-N-O2	$122.8 \pm 0.4$

temperature, refinement was carried out by starting with room temperature parameters. The data were fitted smoothly to the orthorhombic  $Pbca$  structure with isotropic thermal displacement parameters for all the atoms. Typical Rietveld fits for the data at 300 K, 120 K and 12 K ( $R_p = 5.3\%$ ) are displayed in figure 1 and bond parameters are listed in table 1.

Results showed weak anomalies near 220 K and 125 K in mean thermal expansion coefficients estimated from the refined lattice constants (figure 2). The O-N-O angles changed significantly i.e., the O1-N-O2 angle decreases whereas O2-N-O3 angle increases non-linearly with temperature. The maximum variation in the bond angles is about  $5.6^\circ$  from 300 K. Likewise, maximum tilt of nitrate plane normal is about  $2.8^\circ$ . Interestingly, the angles ( $\Delta\theta$ ) of the tilt of O1-N-O3 and O2-N-O3 angles from 300 K values undergo abnormal variations at around 220 K and 125 K (figure 3). The error in the estimation of angles is about  $\pm 0.45^\circ$ . Similarly,



**Figure 3.** Temperature variation of (a) tilt in the angle of O1–N–O3 with respect to 300 K position and (b) isotropic thermal displacement parameter of the oxygen atom O1.

thermal displacement parameters ( $B$ ) of atoms (as obtained from the refinements) also undergo anomalous variations with temperature (figure 3). These variations are the result of thermal motion of the constituting atoms, which contribute to the changes in the intensities of diffraction profiles with temperature.

DSC showed a weak endothermic peak (corresponding enthalpy of 0.014 kJ/mol) around 225 K and another weak but broad hump (enthalpy of 0.02 kJ/mol) around 140 K. It may be noticed that the structural anomalies and the abnormal intensity changes of the bending mode of Raman and IR spectra, involving anion motions, reported in previous studies [5] occur nearly at the same temperature regions. However, as indicated by diffraction patterns, it is unlikely that the abnormal structural changes are associated with any significant change in the symmetry of the structure at the specified low temperatures. Thus, the observed anomalies are associated with very fine structural rearrangements involving small orientations of the nitrates. Such anomalies of smaller magnitude were not manifested, to the best of our knowledge by any of the basic nitrates so far. Though the exact origin of the structural features cannot be inferred from diffraction data alone, similar low temperature behaviour manifested by  $\text{Tl}(\text{Cs})\text{NO}_2$  [7] suggests that, the anomalies in  $\text{AgNO}_3$  may

be a result of freezing of orientational disorder of nitrates from high-temperature phase. Additional supportive information, like dielectric studies, may give a clear picture of the possible origin of the low-temperature anomalies. Anisotropic thermal parameters obtained from a single crystal or powder diffraction with better resolution data, enable anisotropy in the disorder.

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