Thermal behaviour of CuO doped phase-stabilised ammonium nitrate

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Abstract

Copper phase-stabilised ammonium nitrate (Cu-PSAN) was prepared by the incorporation of copper(II) oxide (CuO) into the ammonium nitrate (AN) crystal lattice by a melt process. We studied the phase transitions of ammonium nitrate and dimensional changes occurring during this phase stabilisation process. Crystallographic aspects of the solid-state reaction between AN and CuO and thermal behaviour of phase-stabilised ammonium nitrate (PSAN) are discussed. It was found that solid-state reaction occurred by an intermediate solid solution formation. Lattice parameters and unit cell volume are calculated as a function of temperature from XRD patterns. They show a non-linear and anisotropic behaviour with increasing temperature. Lattice expansion along *b*-axis and contraction along *a*- and *c*-axes are observed. Unit cell volume increases with temperature.
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1. Introduction

Solid propellants are extensively used in space and military missions. They consist of two major components, namely a gas producing solid oxidiser and an organic polymeric fuel, which also acts as a binder. Commonly used oxidisers are perchlorates and nitrates. Most solid rocket motors employ ammonium perchlorate (AP) as the main oxidiser [1,2]. It is characterised by high performance and good burning rate. However, propellants based on ammonium perchlorate have certain disadvantages. One of the preliminary products of combustion of ammonium perchlorate-based propellants is HCl, which in presence of water forms hydrochloric acid, which produces smoke and is highly toxic apart from corrosion problems of the launch pad. Another threat by the chlorine compounds emitted by AP is on the stratospheric ozone layer and consequent global warming. Moreover, these propellants do not meet the requirements of decreased sensitivity and disposal of AP after the life cycle of the propellants creates many problems. To overcome these environmental problems clean burning propellants, which eliminate chlorine as an ingredient, is put forward.

Ammonium nitrate is considered to be of interest as a potential replacement for ammonium perchlorate as a solid propellant oxidiser [3,4]. The substance is cheap, easily available and on firing no HCl is formed. No ecological problems arise, as the substance has been used as a fertiliser some more than half a century. The material offers the potential of developing insensitive, low signature and less polluting propellants. However, there are some drawbacks due to its polymorphism [5]. It has been reported that at normal pressure AN exists in five different polymorphic forms in the temperature range from zero to the melting point [6–9].

The structure of the low temperature phase V has been determined by neutron diffraction in two different studies [10,11]. It is an ordered structure with orthorhombic symmetry, with space group $Pccn$ and $Z = 8$. On heating, phase V transforms to phase IV with orthorhombic symmetry with space group $Pmmn$ with two NH_4NO_3, formula units per unit cell. In the presence of moisture, phase IV undergoes a room temperature transition to disordered phase III with orthorhombic unit cell belonging to the $Pnma$ space group. On heating, phase III undergoes a phase transition to a tetragonal phase II with space group $P\bar{4}2_1m$. Phase II, on heating transforms into a disordered cubic phase I, belonging to the $Pm3m$ space group with one molecule per unit cell. The phase I remains stable up to the melting point of ammonium nitrate.

The transition between different phases of AN have important consequences on practical applications. It is observed that AN composite propellant grain cracks on storage at room temperature due to IV → III transition [12]. Many approaches have been made to overcome the problem of IV → III phase transition and make the salt fit for reliable practical use. One of the approaches is phase stabilisation of ammonium nitrate [13–15]. Studies have shown that doping of AN with metal oxides influences significantly the phase transitions of AN and hence detected clues of a possible intermediate formation during the solid-state reaction [16]. Phase stabilisation of AN with metal oxides is beneficial with respect to burning rate, ignition and hygroscopicity [17–19].

This paper reports the effect of CuO on the phase stabilisation of AN and the aftermath of doping on the phase transition of ammonium nitrate. The investigation also study the dimensional change if any occurring during the transition along with the crystallographic aspects of the solid-state reaction and also the thermal behaviour of phase-stabilised ammonium nitrate (PSAN) using techniques of DSC, TR-XRD and IR-spectroscopy.

2. Experimental

Samples of ammonium nitrate and copper oxide in the molar ratio 8:1 were used for the investigation. Copper phase-stabilised ammonium nitrate (Cu-PSAN) has been prepared by incorporating copper oxide into the ammonium nitrate crystal lattice by a melt process.

DSC measurements were carried out by using Shimadzu, TA-60WS Thermal Analysis System in nitrogen atmosphere, with a heating rate of $10\,^{\circ}C\,min^{-1}$. Samples were loaded in encapsulated aluminum pans. IR spectra were recorded using Shimadzu IR spectrometer in the range $4000–400\,cm^{-1}$ using KBr pellet technique. X-ray diffraction patterns were measured with a Siemens D 5000 Bragg–Brentano diffractometer equipped with a sealed chromium tube using a Braun OED-50M position sensitive proportional counter for fast recording. The measurements were performed by placing the sample on a flat sample holder, while the samples were heated by a temperature device, together with a programmable temperature controller. Non-isothermal series were measured with stepwise heating from 55 to $275\,^{\circ}C$ with a temperature interval of $10\,^{\circ}C$. The diffraction patterns were recorded in the angular range $10–60°\,2\theta$.

3. Results and discussion

The DSC curve of pure ammonium nitrate is shown in Fig. 1. As can be seen pure ammonium nitrate shows five endothermic transitions corresponding to three enantiotropic changes followed by melting and decomposition. First endothermic peak at $49.8\,^{\circ}C$ shows IV → III transition of pure ammonium nitrate. Second endotherm at $86.5\,^{\circ}C$ shows III → II transition and the peak at $126.1\,^{\circ}C$ shows II → I transition. Peak at $167.7\,^{\circ}C$ is due to melting of ammonium nitrate. Endothermic peak at $243.3\,^{\circ}C$ indicates complete decomposition of ammonium nitrate.

The dimensional changes with temperature for the phase transitions of pure ammonium nitrate is shown in Fig. 2. The graph
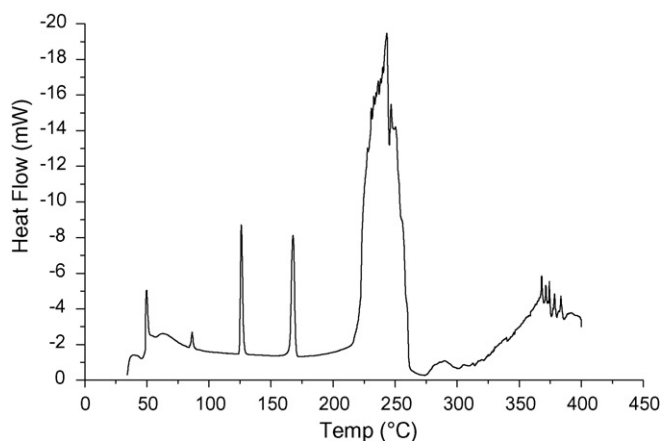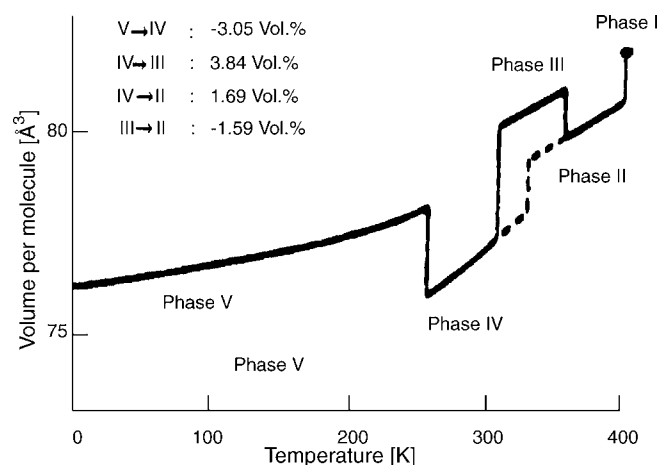

Fig. 1. DSC curve of pure AN.

Fig. 2. Change in volume of AN phases with temperature.

shows an abrupt volume expansion (3.84%) during IV → III phase transition. This causes crack formation in the propellant grain, which leads to catastrophic burning behaviour. This dimensional change has to be suppressed to get phase-stabilised ammonium nitrate (PSAN).

The DSC curve of Cu-PSAN is shown in Fig. 3. The first two DSC endothermic peaks near 86.7 and $125.3\,^{\circ}C$ are due to phase
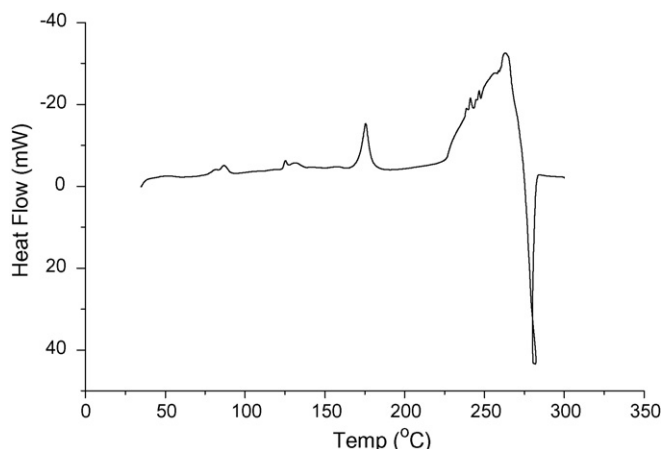

Fig. 3. DSC curve of Cu-PSAN.

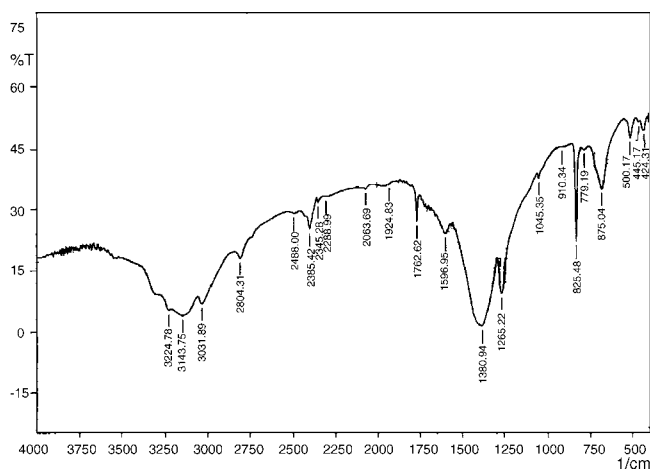Fig. 4. IR spectra of Cu-PSAN.

Fig. 5. TR-XRD pattern of Cu-PSAN.

transitions III → II and II → I, respectively. From the curve it is clear that the room temperature transition, viz., IV → III is completely absent in Cu-PSAN. This shows that Cu-PSAN is well phase stabilised. The endothermic peak corresponding to the melting occurs near 175.5 °C after which an endothermic decomposition of PSAN occurs with T_{max}, 262.9 °C. Further decomposition is an in situ oxidation by the nitrate groups of PSAN as seen from the exotherm with T_{max}, 280 °C.

On comparing, the DSC pattern of pure AN (Fig. 1), with that of Cu-PSAN (Fig. 3), it is clear that Cu-PSAN is well stabilised. As can be seen from the DSC trace of Cu-PSAN there is no endothermic peak below 50 °C. It is to be noted that first endothermic peak occurs only at 86.7 °C. This drastic shift of the phase transition temperature to higher side, from room temperature regime to 86.7 °C, clearly indicates that CuO doping is effective for the phase stabilisation of AN phase IV. Copper oxide significantly influences the transition temperature of AN by the formation of a solid solution of copper(II) diamine dinitrate in the AN crystal lattice. The reaction proceeds by the equation [20]:

$$2NH_4NO_3 + CuO \xrightarrow{\Delta} [Cu(NH_3)_2](NO_3)_2 + H_2O$$

The infrared spectrum of Cu-PSAN is shown in Fig. 4. Peaks at 3224.76 and 3143.75 cm^{-1} are due to N–H stretching frequencies. These peaks indicate the presence of coordinated ammonia in the compound. A strong band at 1380.94 cm^{-1} confirms the presence of uncoordinated nitrate ion. This band is due to asymmetric stretching of NO_3^- ion. Another band at 825.48 cm^{-1} indicates out of plane deformation of NO_3^- ion. A band at 509.17 cm^{-1} is due to M–N stretching vibration. Thus, from IR spectra it is clear that Cu-PSAN contains coordinated ammonia molecules and uncoordinated nitrate ion.

The temperature resolved X-ray diffraction patterns (TR-XRD) of Cu-PSAN recorded from 55 to 275 °C is shown in Fig. 5. The pattern recorded at 55 °C (pattern no. 1) shows five peaks corresponding to ammonium nitrate (0 1 2), (2 0 0), (1 1 1), (3 1 0) and (2 1 2) planes. The first pattern also shows peak corresponding to copper oxide (3 0 3) plane and copper diamine dinitrate peaks in accordance with the JCPDS file
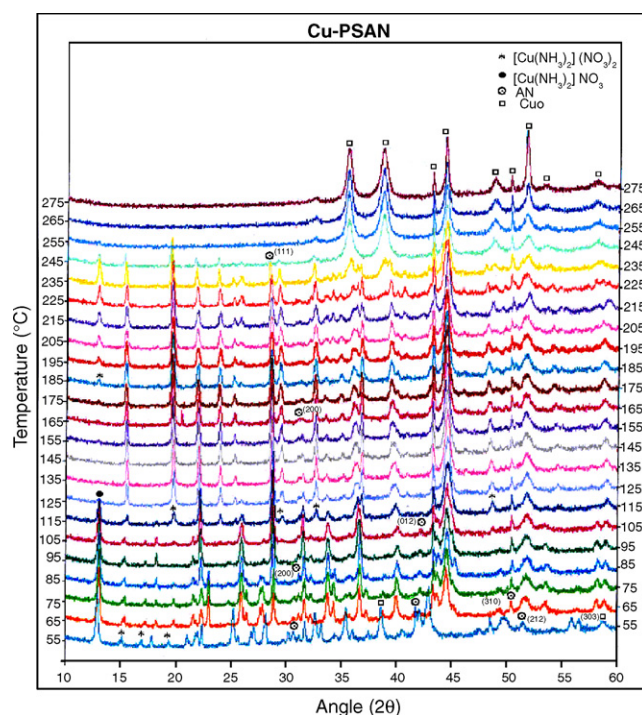
[21]. Appearance of AN(IV) peaks and CuO peaks at 55 °C indicate the presence of unreacted reactants. On heating the sample stepwise from 55 to 275 °C, the unreacted CuO and AN undergo solid-state reaction resulting in the formation of Cu-PSAN, i.e. diamine copper(II) dinitrate solid solution. During heating, in addition to solid solution formation, simultaneous phase transition of AN and decomposition of PSAN is taking place.

A close perusal of the first pattern (55 °C) reveals the existence of peaks at 15.24°, 17.2° and 19.54° 2θ. These peaks are identified as the peaks of $[Cu(NH_3)_2](NO_3)_2$ initially present in the sample. It can be seen that intensity of (0 1 2) planes of AN and (3 0 3) planes of CuO decreases with increase of temperature and gradually vanishes at 105 °C. After an interval new peaks appear at 29.6° and 48.4° 2θ at 115 °C. These are the peaks of Cu-PSAN. Simultaneous disappearance of (0 1 2) planes of AN and (3 0 3) planes of CuO at 105 °C and the appearance of product peaks at 115 °C, after a time gap indicates the formation of solid solution of diamine copper(II) dinitrate.

It is observed that intensity of (1 1 1) planes of AN increases up to 165 °C and then decreases. With AN, the most intense peaks (1 1 1), (3 1 0) and (2 1 2) remain throughout the reaction with a gradual intensity decrease, while the (2 0 0) peaks disappear with time. This implies that AN planes are becoming the part of the product lattice. The peak corresponding to (0 1 2) planes of AN show a small shift towards lower angle side. This indicates the solid solution formation of diamine copper(II) dinitrate.

The lattice parameters are calculated for AN phase IV at different temperatures from the d spacing of XRD pattern. Variations of lattice parameter with temperature are shown in Figs. 6–8.
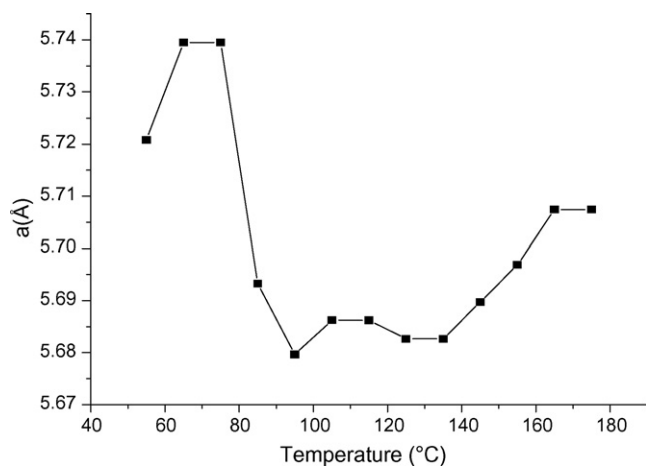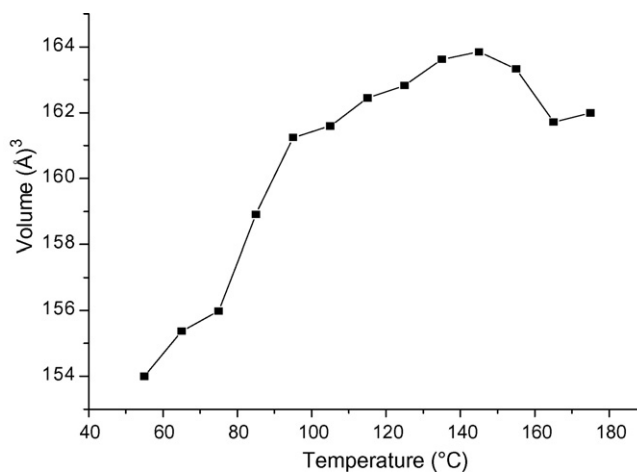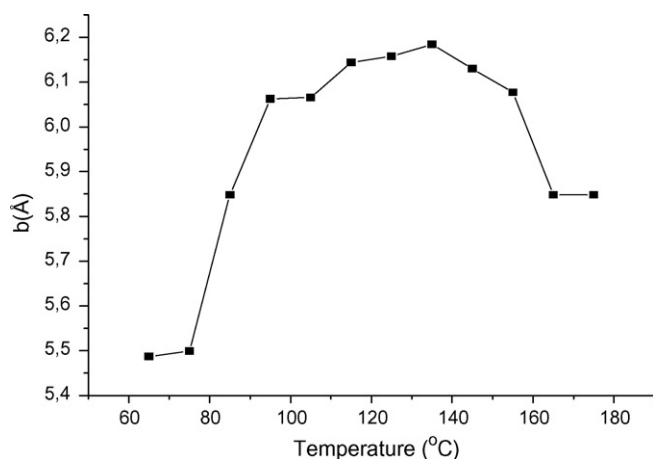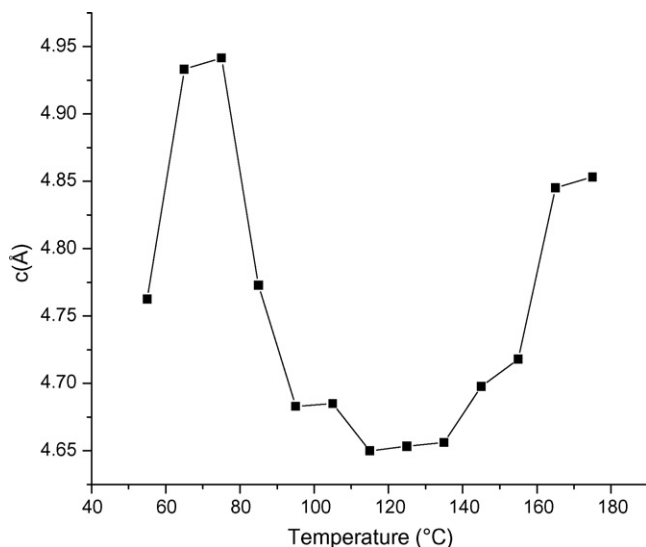
Fig. 6. Lattice parameter *a* vs. temperature.

Fig. 9. Cell volume vs. temperature curve.

Fig. 7. Lattice parameter *b* vs. temperature.

parameters with temperature represent the non-homogeneous compositional change of the solid solution in the AN lattice. Anisotropic expansion along the *b*-axis is due to the preferential diffusion of Cu^{2+} ions. Cell volumes of AN(IV) at different temperatures are plotted in Fig. 9. From the plot it can be seen that unit cell volume increases with temperature. The increase in unit cell volume is because of the expansion of the ammonium nitrate lattice by the formation of solid solution inside it. The reaction between AN and CuO takes place by the interdiffusion of Cu^{2+} and H^+ ions into and out of the AN lattice, resulting in the formation of diammine copper(II) dinitrate solid solution.

When temperature of the sample reaches 245 °C (pattern no. 20) all Cu-PSAN peaks disappear indicating complete decomposition of PSAN resulting in CuO as the end product. Existence of peaks at $2\theta = 32.62°$, $35.45°$, $38.58°$, $44.26°$ and $50.3°$ correspond to that of CuO as reported in the JCPDS file [23]. DSC decomposition pattern at the temperature range 245–280 °C (Fig. 3), surmise the observation of the decomposition of Cu-PSAN to CuO.

4. Conclusions

Incorporation of CuO into the ammonium nitrate lattice resulted in the formation of phase-stabilised ammonium nitrate. The thermal behaviour of phase-stabilised ammonium nitrate is totally different from that of pure ammonium nitrate. Solid-state reactions take place between CuO and ammonium nitrate, thereby shifting the temperature regime corresponding to phase transitions. The reaction proceeds by an intermediate solid solution formation. The IV → III transition, which is responsible for the restricted use of ammonium nitrate as a solid propellant oxidiser is completely absent in the case of copper phase-stabilised ammonium nitrate. Thus, CuO is a very effective phase stabilising agent. X-ray diffraction and IR spectral studies revealed the existence of solid solution formation. Temperature resolved X-ray diffraction pattern shows that decomposition product of copper phase-stabilised ammonium nitrate (Cu-PSAN) is CuO. This study gives an insight into the solid-state thermal decomposition of phase-stabilised ammonium nitrate.

Lattice parameter plots show that there is an expansion of the lattice along *b*-axis and contraction along *a*- and *c*-axes. According to Vegard's law unit cell parameters should change linearly with composition [22]. The non-linear change of unit cell

Fig. 8. Lattice parameter *c* vs. temperature.

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