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Growth and Characterization of a New Double Sulfate, $AgNH_4SO_4$

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The double sulfate compound, silver ammonium sulfate ($AgNH_4SO_4$) has been synthesized and characterized. Powder X-ray diffraction has shown it as a monoclinic system with unit cell dimensions a = 6.49(4), b = 8.47(2), c = 8.71(2) Å, and β = 91.913°. A single crystal rotational X-ray photograph also gave the same unit cell dimensions. The infrared spectra exhibit typical NH_4^+ and SO_4^{2-} vibrational modes. Thermal study using differential scanning calorimetry has shown the existence of a phase transition at 79°C followed by another thermal anomaly at 211°C. The $AgNH_4SO_4$ crystals also exhibit aging effects, transforming after long storage into Ag_2SO_4. Results are discussed in detail.

Introduction

After Mathias and Remeika (*1*) discovered ferroelectricity in $(NH_4)_2SO_4$ (T_c = −50°C), many of the double sulfates containing ammonium sulfate as one of the constituents were found to be ferroelectric and attracted the attention of many researchers. Among these compounds, $LiNH_4SO_4$, $NaNH_4SO_4 \cdot 2H_2O$, and $(NH_4)_2Cd_2(SO_4)_3$ were studied very widely (*2–4*). To date there has been no information concerning the possibility of synthesizing a compound with ammonium sulfate and silver sulfate in the molar ratio 1 : 1. We were successful in realizing the compound $AgNH_4SO_4$ (SAS). It exhibits a phase transition around 79°C before undergoing another thermal anomaly at 211°C. The orientation of the ammonium ion appears to possess so compact an arrangement in the unit cell that even prolonged X-irradiation could not generate a paramagnetic NH_3^+ center.

In this communication we report crystal growth and characterization of $AgNH_4SO_4$, which on prolonged storage transforms into Ag_2SO_4 as a major phase and SAS and $(NH_4)_2SO_4$ as minor phases.

Experimental

Single crystals of $AgNH_4SO_4$(SAS) were obtained by slow evaporation, at 300 K, of a solution containing the sulfates Ag_2SO_4 (99.99%, Alfa) and $(NH_4)_2SO_4$ (99%, E. Merck, India) in a 1 : 1 ratio. Both sulfates were dissolved in ammonia solution (specific gravity 0.91, about 25% NH_3) and the resulting solution was kept in a dark place for crystal growth. The crystals of SAS grew to an approximate size of 1 × 1 × 5 mm within a period of about 3 months. The crystals collected were perfectly transparent with a rectangular bar-like morphology. After a month's standing or on exposure to ambient light, the transparent crystals were found to slowly turn brownish and opaque but still nonhygroscopic. This colored material was checked and identified as Ag_2SO_4 by powder XRD. Hence, the experiments were always performed on fresh and transparent crystals.

The structural studies were conducted with the help of powder X-ray diffraction

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(XRD) (Siefert) with Cu$K\alpha$, $\lambda = 1.5418$ Å radiation. A rotational X-ray photograph of the single crystal was taken on a Siemens single crystal XRD OR 3M/V. The infrared (IR) spectrum of $AgNH_4SO_4$ was recorded on a Perkin–Elmer double beam spectrometer using the KBr disc technique, where the sample was uniformly dispersed in a KBr medium. All these studies were done at room temperature.

The thermal analysis of the sample was performed with the DUPONT model 910 Differential Scanning Calorimeter (DSC) over a temperature range of −150 to +300°C with different heating rates varying from 1°C per min to 80°C per min.

Results and Discussion

Structural aspects. The analysis of the single crystal rotational X-ray photograph of a small transparent crystal of SAS has given the lattice parameters $a = 6.49(4)$, $b = 8.47(2)$, $c = 8.72(2)$ Å, and $\beta = 91.913°$, which suggests a monoclinic unit cell for the compound. The present data available from an X-ray rotational photograph would not allow one to identify the space group, which requires Weissenberg photographs of the compound. The powder X-ray diffraction (XRD) pattern obtained for the fine powder crushed from the crystals of SAS with its well resolved 28 reflections was fitted to this monoclinic unit cell. The corresponding (hkl) indices, d_{obs} and d_{calc}, are presented in Table I. To determine the value of Z (the number of formula units per unit cell), we have determined the bulk density of the sample as 2.42 g/cc. With the resulting cell volume, we calculated Z as equal to 4, using $\rho_{x\text{-ray}} = 3.27$ g/cm^3, which agrees with the average value of bulk densities of Ag_2SO_4 ($\rho = 5.45$ g/cm^3) and $(NH_4)_2SO_4$ ($\rho = 1.769$), i.e., 3.6 g/cm^3.

The structural parameters of $AgNH_4SO_4$ are compared with those of related double sulfates in Table II.

The other interesting aspect of $AgNH_4SO_4$ is that after about a month's storage the compound transforms into Ag_2SO_4. We have confirmed this by recording the XRD pattern of the powder of the crystals which have been stored for 30 days. This XRD pattern, along with that of SAS, is given in Fig. 1 and this pattern coincides perfectly with that of the standard Ag_2SO_4 (5), confirming the transformation of SAS into Ag_2SO_4, which is possible only with the release of NH_4^+ & SO_4^{2-} ions from $AgNH_4SO_4$. But as could be seen from Fig. 1, there are no strong reflections other than those of Ag_2SO_4 representing either of the SAS/$(NH_4)_2SO_4$ phases. Some of the unidentified weak reflections do come from $(NH_4)_2SO_4$ hinting its presence as a minor phase.

TABLE I

d_{obs} (Å)	d_{calc} (Å)	I/I_0	hkl
6.0056	6.0712	20	011
5.1405	5.1490	7	110
4.3575	4.3548	3	002
4.2302	4.2338	56	020
3.8667	3.8726	24	012
3.2503	3.2429	10	200
3.0593	3.0728	3	$\bar{2}01$
2.9853	3.0065	9	201
2.8847	2.8885	3	211
2.8182	2.8225	17	030
2.6749	2.6834	12	$\bar{1}03$
2.5636	2.5604	18	202
2.1789	2.1774	26	004
2.1151	2.1149	9	$\bar{3}01$
2.0273	2.0248	7	114
1.9529	1.9521	100	$\bar{2}23$
1.8861	1.8919	4	$\bar{3}21$
1.7585	1.7624	11	$\bar{3}03$
1.6261	1.6271	4	323
1.5477	1.5522	1	125
1.4968	1.4962	2	$\bar{3}41$
1.4727	1.4703	2	144
1.4116	1.4113	2	060
1.3719	1.3731	2	026
1.3419	1.3419	4	$\bar{2}53$
1.2316	1.2313	2	245
1.2213	1.2211	2	$\bar{3}53$

Infrared spectroscopy. The typical IR spectrum at RT of SAS is shown in Fig. 2. NH_4^+ and SO_4^{2-} ions are the only IR-active molecular groups in the compound. At first

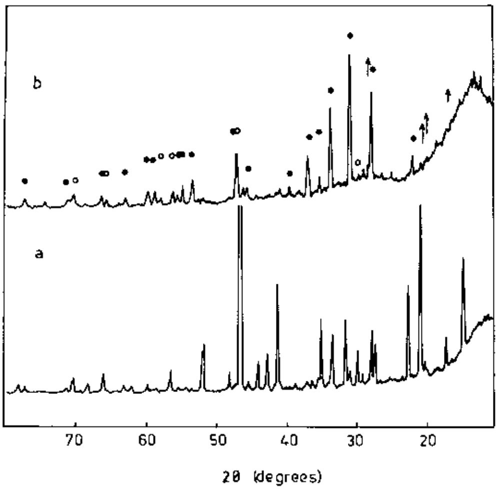

FIG. 1. The XRD patterns of (a) $AgNH_4SO_4$ and (b) $AgNH_4SO_4$ after 30 days storage. The transformation of $AgNH_4SO_4$ into Ag_2SO_4 is very clearly seen in (b). The full circles show the reflections corresponding to Ag_2SO_4 and the empty circles show the unindexable lines (few of which can be identified as weak reflections of $(NH_4)_2SO_4$). The arrows locate the positions where the maxima of $(NH_4)_2SO_4$ should have occured if it were to be a major phase after the transformation.

glance, one finds a general coincidence with the spectra of NH_4^+ vibrations coupled with SO_4^{2-} vibrations—for example, in $LiNH_4SO_4$, $NaNH_4SO_4 \cdot 2H_2O$ and $(NH_4)_2SO_4$.

A tetrahedral molecule like NH_4^+ can rotate about three principal axes besides undergoing vibrations (υ_1, υ_2, υ_3 and υ_4) in four different ways (7). The rotational mode (υ_6) can have three values corresponding to the three components of the moment of inertia ellipsoid. Also, it is possible to generate combination bands of υ_6 with υ_2 (1080 cm^{-1}) and υ_4 (1400 cm^{-1}) resulting in ($\upsilon_2 + \upsilon_6$) and ($\upsilon_4 + \upsilon_6$) in the region 1700 cm^{-1} to 2000 cm^{-1} (8). Figure 2 shows the presence of υ_2, ($\upsilon_4 + \upsilon_6$) and the absence of ($\upsilon_2 + \upsilon_6$) mode where υ_5 and υ_6 are rotatory lattice modes. The υ_6 mode of NH_4^+ occurs at ca. 225 cm^{-1}. In the same way, the other IR absorption bands of $AgNH_4SO_4$ can be assigned as follows:

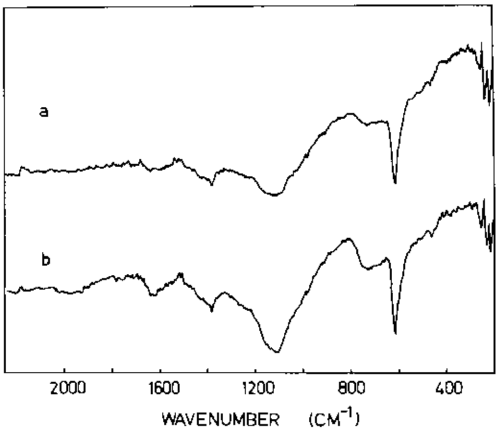

FIG. 2. The room temperature Infrared spectra of (a) X-irradiated and (b) unirradiated $AgNH_4SO_4$. The intensity rise in the SO_4^{2-} absorption bands upon X-irradiation is clearly seen at 1104 and 613 cm^{-1}.

225	465	615	730	888	982/1040	1105
$\nu_6(NH_4^+)$	$\nu_2(SO_4^{2-})$	$\nu_6(SO_4^{2-})$	?	?	$\nu_1(SO_4^{2-})$	$\nu_3(SO_4^{2-})$

1400/1620	1760	2000	3140 (cm^{-1})
$\nu_4(NH_4^+)$	$\nu_4(NH_4^+) + \nu_6(NH_4^+)$	$\nu_2(NH_4^+) + \nu_6(NH_4^+)$	NH (stretching)

TABLE II

Compound	a (Å)	b (Å)	c (Å)	β (°)	Z	Vol (Å^3)	Ref.
$AgNH_4SO_4$	6.4895	8.4676	8.7144	91.91	4	478.86	This work
Ag_2SO_4	5.817	12.704	10.269		8	758.87	(5)
$(NH_4)_2SO_4$	7.782	5.993	10.636		4	496.03	(5)
$LiNH_4SO_4$	8.74	9.16	5.13		4	410.69	(6)
$NaNH_4SO_4 \cdot 2H_2O$	8.216	12.854	6.252		4	660.26	(3)

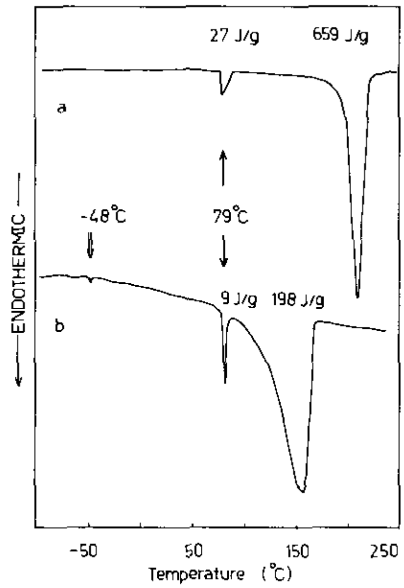

FIG. 3. The DSC scan of $AgNH_4SO_4$ with a heating rate of 10°C/min (a) for a fresh transparent and colorless SAS sample and (b) for a 10-month-old (opaque) SAS.

Based on this, the band at ca. 730 cm^{-1} could be assigned to Ag–O stretching vibrations. In general, the IR spectrum of $AgNH_4SO_4$ is in line with those of similar double sulfate compounds such as $Cu(NH_4)_2SO_4 \cdot xH_2O$, and $NaNH_4SO_4 \cdot 2H_2O$. Upon X-irradiation for 3h (Fig. 2b), SAS shows a different response for IR radiation with the main difference being the absence of $\{v_4(NH_4^+) + v_6(NH_4^+)\}$, $\{v_2(NH_4^+) + v_6(NH_4^+)\}$ vibrations and the NH stretching mode at 3140 cm^{-1} (not shown in Fig. 2). Furthermore, there is also a decrease in the intensity of $v_4(NH_4^+)$ and the sharpenness of the SO_4^{2-} modes (v_3(1104 cm^{-1}) and v_4(613 cm^{-1})). Hence, upon X-irradiation, we observe a rise in the intensity of SO_4^{2-} modes in these crystals. This observation also explains the absence of any EPR response even after prolonged X-irradiation.

Thermal analysis. Fig. 3a illustrates the DSC scan of SAS from −100 to 250°C. It has two endotherms. The one at lower temperature probably represents a phase transition involving NH_4^+/SO_4^{2-} disordering, analogous to what might happen in $(NH_4)_2SO_4$ and $LiNH_4SO_4$, whereas we believe that other one at ca. 211°C represents the beginning of the decomposition of the compound.[1] As shown in Fig. 3a, the large amount of energy (635 J/g) involved in the completion of the thermal event at 211°C also suggests the possibility of its being a decomposition reaction. At this point it is interesting to note that the enthalpy involved with the 79°C transition is 29.87 J/g whereas the ferroelectric- to paraelectric phase transition at 185.6°C in $LiNH_4SO_4$ involved only 2.27 J/g (*9*). Now, whether the thermal anomaly at 79°C involves any structural change can be checked by comparing the molar entropy change of this transition with that calculated from Boltzmann's statistical equation (*10*),

$$\Delta S = k \ln(W_2/W_1), \qquad (1)$$

where k is the Boltzmann constant and W_2/W_1 is the ratio of the numbers of two different arrangements of two systems. In the present case we consider this as the probability of having NH_4^+/SO_4^{2-} in different orientations before and after the 79°C transition. So, if NH_4^+/SO_4^{2-} underwent any kind of structural reorientation, then that would result in an increase in W_2/W_1 ratio and thus an increase in the transition entropy.

Hence, expressed in molar terms, Eq. (1) becomes

$$\Delta S_t = Ak \ln(W_2/W_1), \qquad (2)$$

where A is Avogadro's number and $\Delta S_t = \Delta H_t/T_t$ (from experiment). Therefore by substituting the experimental values of ΔH_t and T_t (namely, 29.87 J/g and 352.55 K) in Eq. (2) we get ΔS_t = 4.50 cal mol^{-1} K^{-1}. This value of ΔS_t is of the same order as for the ferroelectric-to-paraelectric phase transition in $(NH_4)_2SO_4$ (4.2 cal mol^{-1} K^{-1}) (*11*) and much larger than 1.1 cal mol^{-1} K^{-1} for

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[1] Apparently SAS, like $LiNH_4SO_4$, does not melt before decomposition. Our attempts to prepare SAS by fusion of $(NH_4)_2SO_4$ and Ag_2SO_4 resulted in the melting and volatilization of the latter around 240°C.

TABLE III

Compound	ΔS_t (cal mol^{-1} K^{-1})	T_c (K)	W_2/W_1	Ref.
$AgNH_4SO_4$	4.5	352.5	9.5	This work
$(NH_4)_2SO_4$	4.2	223	8.2	(*11*)
$LiKSO_4$	1.76	706	2.4	(*9*)
$NaNH_4SO_4 \cdot 2H_2O$	0.79	99	1.5	(*13*)
$LiNH_4SO_4$	0.15	459	1.1	(*9*)

the antiferroelectric-to-paraelectric transition in ADP and for the structural transition in NH_4Cl (viz., 1.11 cal mole^{-1} K^{-1}) (*10*). It is pertinent to note that for displacive phase transitions such as the cubic-to-tetragonal transition in $BaTiO_3$ and the commensurate-to-incommensurate transition in K_2SeO_4 at 127 K, ΔS_t values are much smaller, being 0.12 and 0.21 cal mole^{-1} K^{-1} respectively (*12*). Now the ratio W_2/W_1 for SAS is

$$W_2/W_1 = 9.5,$$

which when compared with W_2/W_1 ratios of similar double sulfates undergoing phase transition (see Table III) indicates the possibility of having more orientations for NH_4^+ and SO_4^{2-} ions after transition. This could also be an indication of a possible structural transition. From Table III, it is clear that only $(NH_4)_2SO_4$ and $AgNH_4SO_4$ have large W_2/W_1 ratios. In the case of the former, there are two chemically inequivalent NH_4^+ and SO_4^{2-} in both the paraelectric and ferroelectric phases and both the ions are distorted from perfect tetrahedral arrangements. The change in the distortion of the ions with temperature, together with dynamic interaction between these ions through the hydrogen bonding network is mainly responsible for the phase transition (*14*). But in the case of $AgNH_4SO_4$, the intensity rise in SO_4^{2-} modes in IR spectra (Fig. 2) upon X-irradiation, as already discussed, coupled with higher a W_2/W_1 ratio of $\simeq 9.5$, suggests that distortions and the reorientations that the SO_4^{2-} ion might undergo appear to play a major role in the phase transition. By contrast, the SO_4^{2-} ion in both $NaNH_4SO_4 \cdot 2H_2O$ and $LiNH_4SO_4$ do not seem to undergo any such distortion/reorientation through the phase transition.

Although the XRD data are insufficient to confirm the formation of $(NH_4)_2SO_4$ from SAS after either storage or X-irradiation, the DSC experiment performed on a 10-month-old single crystal of SAS gave evidence for the presence of $(NH_4)_2SO_4$ as one of the products. The sample was opaque (brownish) unlike the fresh SAS crystal which is colorless and transparent. The DSC scan over a temperature range −100 to +250°C is shown in Fig. 3b. A very weak endotherm at −48°C indicates the existence of $(NH_4)_2SO_4$. However, the anomaly at 79°C, a characteristic of SAS, persists even after such a long time when the XRD of (Fig. 1b) the stored SAS shows it to consist Ag_2SO_4 as a major component. In comparison with Fig. 3a, the 79°C anomaly is immediately followed by a huge endotherm at 95°C till 156°C, with decreased enthalpies of 9 J/g and 198 J/g, respectively, suggesting the minor nature of the SAS phase. The presence of both the thermal anomalies (characteristic of $(NH_4)_2SO_4$ and SAS) and the XRD evidence for Ag_2SO_4 suggest that the decomposition[2] of SAS upon prolonged storage (and irradiation) is not complete and the products of this incomplete decomposition are $(NH_4)_2SO_4$ and Ag_2SO_4. However,

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[2] This aspect, however, deserves a separate, detailed investigation.

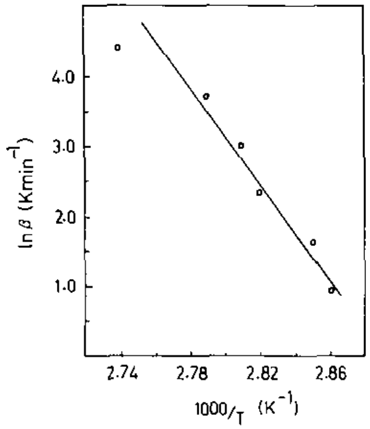

FIG. 4. Kissinger plot of $AgNH_4SO_4$ for nonisothermal kinetics.

SAS still persists—probably as a minor phase. So the equation for the decomposition could be

$$2AgNH_4SO_4 \rightarrow xAg_2SO_4 + yAgNH_4SO_4 + z(NH_4)_2SO_4$$

with $(y, z) \ll x$.

With a view of studying the kinetics of the transition at 79°C, the endotherm was monitored as a function of heating rate, employing the nonisothermal technique. The simplified Kissinger's equation which makes possible the determination of the activation energy (E) for a simple reaction regardless of the order of the reaction by making differential thermal analysis patterns at a number of heating rates is (*15*)

$$\frac{d(\ln \beta)}{d(1/T)} = -E/R,$$

where β is the heating rate, T is the transition temperature, E is the activation energy, and R is the universal gas constant. The Kissinger plot thus obtained is given in Fig. 4. Here ln β plotted against $1000/T$ is linear. The slope of the curve gives the activation energy as 69.63 cal $mole^{-1}$ K^{-1} for the thermal anomaly at 79°C.

Conclusions

In analogy with $LiNH_4SO_4$, $NaNH_4SO_4 \cdot 2H_2O$, and related sulfates, we succeeded in synthesizing $AgNH_4SO_4$, which has not been reported up to now. $AgNH_4SO_4$ has been characterized for the first time as a monoclinic phase with $Z = 4$ and found to possess a phase transition at 79°C followed by the decomposition of its constituents at 211°C. The detailed crystal structure and the nature and mechanism of the phase transition are under investigation.

Acknowledgments

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