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STRUCTURAL HOMOGENEITY IN ISOMORPHOUS MIXED CRYSTALS*

S. I. MORROW AND A. BRACUTI
Propellants Laboratory, Feltman Research Labs, Picatinny Arsenal, Dover, New Jersey 07801 (U. S. A.)
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ABSTRACT

Isomorphous mixed crystals of NH_4ClO_4 and $KClO_4$ have been prepared by phase rule techniques. They have been characterized by means of X-ray diffraction, DTA, and TGA procedures. At first there was some doubt as to their structural homogeneity. But we were unable to find any conclusive evidence to this effect. The possibility that traces of so-far, undetectable inhomogeneities might be present was not eliminated. It was concluded that indications of traces of free $KClO_4$ in the mixed crystals in DTA thermograms was due to loss of NH_4ClO_4 from them during heating. Defects so created should be of the Schottky type.

INTRODUCTION

The story of isomorphous mixed crystals is a time-honored one with origins in Rome De L'Isle's discovery in 1772 that cubic alums form mixed crystals or overgrowths of one crystal on another. In spite of the antiquity of the subject there are remarkably few reports in the literature of detailed investigations of the properties of ionic, isomorphous mixed crystals coprecipitated from a solvent such as water under rigorous, phase rule, equilibrium conditions. Although studies of mixed crystal or "alloy"systems in metallurgy have kept pace with a burgeoning metals technology, similar work in chemistry with inorganic salts has lagged. This is due in no small degree to the relatively greater structural complexity in most cases of systems composed of the latter type of salts.

Morrow[1] recently discussed the requirements for identifying an isomorphous relationship between inorganic salts. A relatively ideal case of an isomorphous pair, namely NH_4ClO_4 and $KClO_4$, has been of interest to us. The phase system leading to the formation of these mixed crystals, NH_4ClO_4–$KClO_4$–H_2O at 25.0°C, was investigated first by Karnaukhov[2] and, more recently, by Simanova and Shul'ts[3]. Both of these materials display isomorphic orthorhombic crystal structures at room temperature and isomorphic cubic structures at higher temperatures. These isomorphs

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closely resemble each other. The phase rule techniques used by these investigators seemed well-suited to making homogeneous microcrystalline samples of the mixed crystals in question. Consequently we undertook their preparation in this way and the characterization and determination of their homogeneity by means of differential thermal analysis in conjunction with X-ray diffraction techniques.

EXPERIMENTAL

Crystal synthesis

Reagent grade NH_4ClO_4 and $KClO_4$, which we recrystallized three times, was used to make our mixed crystals. We also used American Potash and Chemical Co. Trona Ultrapure NH_4ClO_4, which was equivalent to our triple recrystallized salt. Based upon calculations from Simanova and Shul'ts' phase diagram of the NH_4ClO_4–$KClO_4$–H_2O system at 25.0°C, we formulated initial synthesis mixtures from weighed quanties of the two salts and highly pure, distilled water. The systems were sealed in glass tubes containing several stainless steel balls. They were rocked gently in a water bath at 25.0°C so as to provide agitation by causing the steel balls and salt to slosh to and fro. At the end of a week the tubes were broken open at 25.0°C, liquor samples removed for analysis, and the solid phases immediately recovered by filtration on a fritted glass funnel attached to an evacuated flask. The crystals were dried in a vacuum oven for several hours at temperatures up to 40°C. They were pulverized and graded for particle size by sieving. Crystals were kept in desiccators over silica gel until used in characterization studies.

Thermal analysis

The DuPont 900 Differential Thermal Analyzer produced by the E. I. DuPont De Nemours and Co., Wilmington, Delaware was used in these studies. Thermal gravimetric data were obtained with the DuPont 950 Thermogravimetric Analyzer. All DTA measurements were carried out in the 2-mm microtube standard cell assembly with chromel–alumel thermocouples in direct contact with the samples. The latter were reduced to less than 44-micron particle size. Glass beads were used as reference standards. Sample and reference material depth in 2-mm OD capillary glass tubes was 3 mm. Heating rate was 20°C/min in air atmosphere. TGA runs were made in an atmosphere with 20°/min heating rate.

Temperatures shown in the figures require correction for chromel–alumel thermocouples according to charts supplied by DuPont. The usual correction is not more than 3°C. Temperatures cited in the text are corrected ones.

X-ray analysis

X-ray diffraction measurements were made with a Norelco diffractometer with CuKα radiation. The instrument was manufactured by the Phillips Electronic Instrument Co., Mount Vernon, New York.

DISCUSSION

We sought to prove by direct means whether or not NH_4ClO_4–$KClO_4$ mixed crystals made by phase rule methods are truly homogeneous. Direct proof to this effect is generally lacking in phase rule studies. The composition of the solid phase is determined customarily by the method of Schreinmaker's wet residues. In some cases the crystals are examined microscopically to see if they are of uniform crystal type. Also they are sometimes analyzed by means of X-ray diffraction. In most instances, though, there is insufficient interest in the solid phases themselves to justify extensive characterization studies and absolute proof of their homogeneity. We utilized differential thermal analysis extensively along with X-ray diffraction techniques to examine the NH_4ClO_4–$KClO_4$ mixed crystals and to demonstrate their homogeneity.

Phase rule procedures utilizing the data of Simanova and Shul'ts were used in coprecipitating the mixed crystals isothermally under equilibrium conditions. A report of the synthesis aspects of our work will be made in the future elsewhere. It was necessary to recover the solid phase under non-equilibrium conditions inasmuch as equilibrium is necessarily disrupted in so doing. It should be emphasized too that it is impossible to recover a solid phase in contact with a liquid phase uncontaminated by it. This is to say that no separation technique in such cases is 100% efficient. Consequently, when the crystals are dried they can be expected to be contaminated with minor amounts of mixed crystals with compositions differing from the bulk of the crystals formed at chemical equilibrium. Our products were dried in a vacuum oven for several hours at about 40°C. It is possible that in this way minor inhomogeneities in the crystals may have been removed by low-temperature annealing.

The compositions of the NH_4ClO_4–$KClO_4$ mixed crystals that we made and characterized are shown in Table I. X-ray diffraction patterns in each case indicated that within the limit of detection each mixed crystal system was composed of a single phase and component. We compared the major lines observed in the case of two samples of mixed crystals, where $KClO_4$ is the minor component, with the diffraction

TABLE I

COMPOSITION OF MIXED CRYSTALS MADE BY AN EQUILIBRIUM ISOTHERMAL COPRECIPITATION PROCESS

Target composition (% by weight) NH_4ClO_4–$KClO_4$
94.8– 5.2
89.7–10.3
83.8–16.2
79.4–20.6
74.2–25.8
34.2–65.8
51.2–48.8
50.2–49.8
25.9–74.1
9.6–90.4
1.4–98.6

patterns of physical mixtures having comparable compositions. In Table II the mixed crystals contain 5.2% $KClO_4$ and 94.8% NH_4ClO_4 and the physical mixture 8.0% $KClO_4$ and 92.0% NH_4ClO_4 by weight. The diffraction pattern of the physical mixture shows the principle lines of the two components, NH_4ClO_4 and $KClO_4$. It will be noticed that at the 8.0% by weight concentration level of $KClO_4$ in the mixture, only the two strongest lines in the pattern are detected. On the other hand, the mixed crystals display a pattern that closely resembles that of NH_4ClO_4 and can be indexed on the basis of a single component. Thus, as expected there is no evidence of the presence of either free component in the mixed crystals.

TABLE II

INTERPLANAR SPACINGS OF MIXED CRYSTALS AND PHYSICAL MIXTURES CONTAINING $KClO_4$ AS A MINOR COMPONENT

Mixed crystal, 5.2% $KClO_4$	*Physical mixture, 8.0% $KClO_4$*	*NH_4ClO_4, d (Å)*	*$KClO_4$ d (Å)*	*hkl*	*I/I_0*
4.58	4.58	4.58	—	011	100
—	—	—	4.47	011	—
3.918	3.922	3.922	—	201	—
3.610	3.611	3.611	—	210	60
—	3.484	—	3.487	210	100
3.243	3.251	3.249	—	211	60
—	3.139	—	3.145	211	78
2.964	2.969	2.970	—	112	—
—	—	—	2.831	020	67

The concentration of $KClO_4$ is slightly higher, 10.3%, in the mixed crystal and physical mixture samples shown in Table III than in those in Table II. Again, the pattern of the mixed crystals resembles NH_4ClO_4 and can be indexed as a single component. In this case, the concentration of $KClO_4$ is sufficiently high so that more principle lines appear in the pattern of the physical mixture. There is no indication

TABLE III

INTERPLANAR SPACINGS OF MIXED CRYSTALS AND PHYSICAL MIXTURES CONTAINING $KClO_4$ AS A MINOR COMPONENT

Mixed crystal, 10.3% $KClO_4$	*Physical mixture, 10.3% $KClO_4$*	*NH_4ClO_4, d (Å)*	*$KClO_4$ d (Å)*	*hkl*	*I/I_0*
4.57	4.59	4.58	—	011	100
—	4.48	—	4.47	011	—
3.907	3.930	3.922	—	201	—
3.601	3.611	3.611	—	210	60
—	3.426	—	3.487	210	100
3.273	3.273	3.249	—	211	60
—	3.150	—	3.145	211	78
2.954	2.975	2.970	—	112	—
—	2.837	—	2.831	020	67

from X-ray studies of a second component in these mixed crystals. Neither salt component affected the interplanar distance (*d*-spacing) of the other in the case of the two physical mixtures. However, as can be seen from the data in the two tables, the interplanar distances in the host lattice contracted as $KClO_4$ was isomorphously introduced into NH_4ClO_4. This is to be expected since K^+ ion has a smaller radius than that NH_4^+, 1.33Å *vs.* 1.43Å. Of course dimensional changes in the crystal lattice can be measured with great accuracy by means of refined X-ray diffraction measurements. These studies are in progress and results will be reported in the future.

In the case of our particular mixed crystal systems it was possible to detect by means of DTA one-half of one percent or less of each constituent present as a physical impurity in the other isomorph. Thus, this analytical method served as an effective means for determining if traces of unassimilated phases of either component were present in the mixed crystals. Fig. 1 shows DTA thermograms for two physical mixtures. The one contains 1.9% NH_4ClO_4 and 98.1% $KClO_4$. The other contains 99.52% NH_4ClO_4 and 0.48% $KClO_4$. Utilizing maximum ΔT scale sensitivity, 0.1°/in, it is possible to get strong polymorphic transition endotherms, capable of revealing fractions of a percent impurity. As can be seen in Fig. 1 even with 0.5 and 1.0°C/in settings respectively, it is possible to detect 0.48% levels of the one component present as an unassimilated impurity in the other.

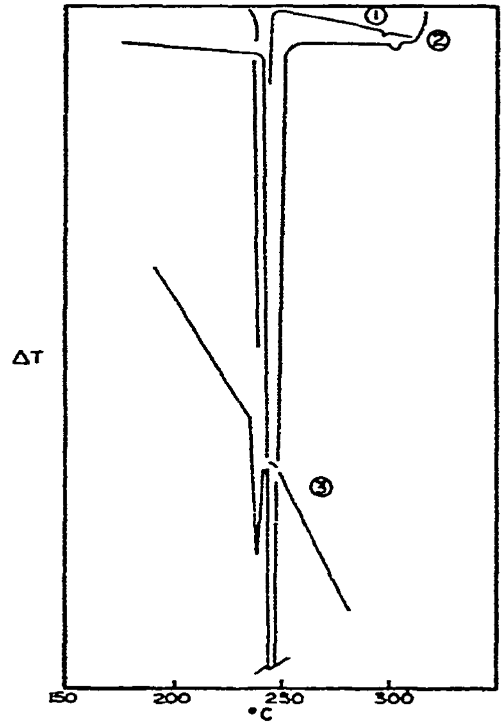

Fig. 1. DTA of physical mixtures showing sensitivity of method to detection of minor component by means of transition endotherm; curves 1 and 2, physical mixtures with 99.52% NH_4ClO_4, 0.48% $KClO_4$ and ΔT 1 °C/in and 0.5 °C/in, respectively; curve 3, physical mixture with 1.90% NH_4ClO_4, 98.1% $KClO_4$ and ΔT 0.1 °C/in.

We were led early in the DTA investigation of our mixed crystals to speculate whether small amounts of free $KClO_4$ might be present in them. This came about as the result of observation in some cases of what appeared to be small secondary endotherms at slightly over 300 °C. These occur at the same temperature as the $KClO_4$ orthorhombic-to-cubic, phase-transition endotherm. The secondary "$KClO_4$" endotherms can be seen in Fig. 2. Although such endotherms could be due to the orthorhombic-to-cubic transition of free, unassimilated $KClO_4$ impurities in the mixed crystals (seed crystal residues, in fact) another possible cause was discovered in the

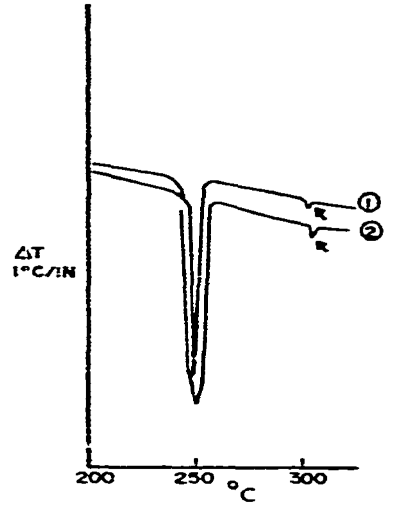

Fig. 2. DTA of mixed crystals showing weak secondary endotherms; curve 1, 89.74% NH_4ClO_4 and 10.26% $KClO_4$; curve 2, 83.76% NH_4ClO_4 and 16.24% $KClO_4$.

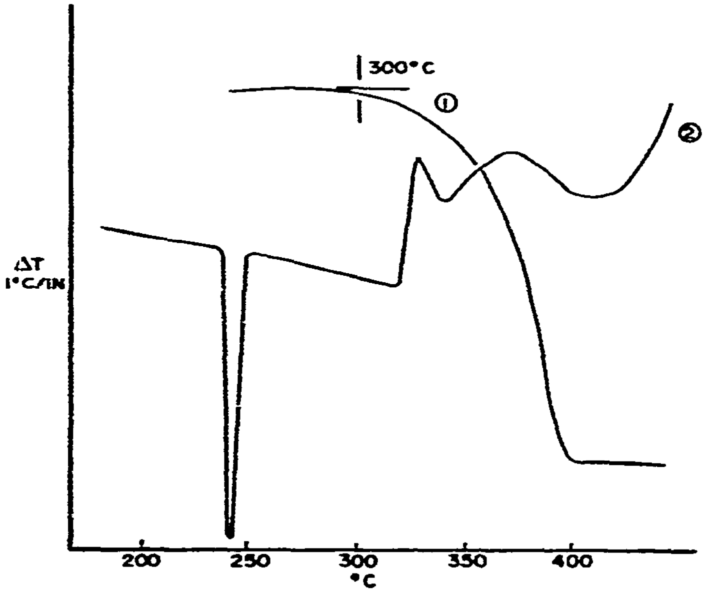

Fig. 3. Thermograms of pure NH_4ClO_4; curve 1, TGA, and curve 2, DTA.

course of our thermal studies. Ammonium perchlorate begins to undergo rapid weight loss at about 300°C as is shown in the combined DTA and TGA curves in Fig. 3. Being the more volatile component, NH_4ClO_4 leaves the mixed crystal at temperatures above 300°C. Thus, the possibility arises that defect mixed crystals might be produced at temperatures above 300°C. These should have vacant NH_4^+ and ClO_4^- lattice sites or Schottky defects, the existence of which could be expected to be revealed by density measurements of mixed crystals heat treated at or above 300°C.

Fig. 4 shows that in physical mixtures of NH_4ClO_4 and $KClO_4$ the normal polymorphic transition temperature of each component is observed and gives a gross

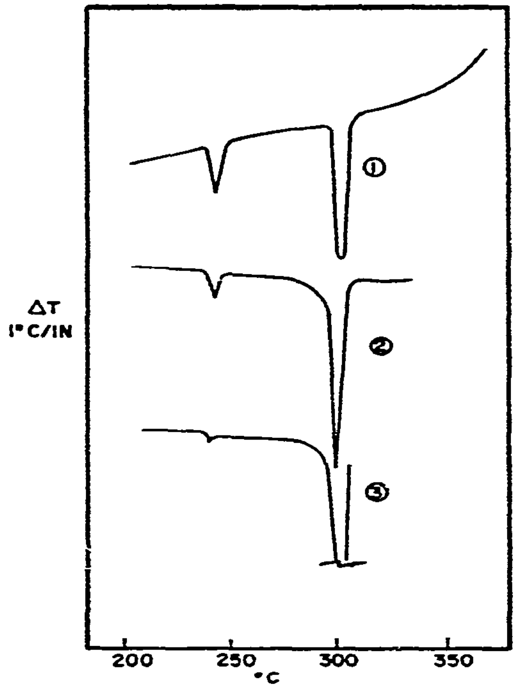

Fig. 4. Thermograms showing sensitivity of DTA method to concentration of each componen NH_4ClO_4 and $KClO_4$ in physical mixtures; curve 1, 1:1 by weight mixture; curve 2, 9.99% NH_4ClC_4 90.01% $KClO_4$; curve 3, 1.9% NH_4ClO_4, 98.1% $KClO_4$.

indication of the sensitivity of the method to concentration. The relative areas of the NH_4ClO_4 and $KClO_4$ endotherms are indicative of their respective concentrations in the mixture. This behavior is in contrast to that in mixed crystals, where a modified, phase-transition temperature is observed. Fig. 5 shows the DTA curve of a 1:1 ratio by-weight, mixed crystal compared to a physical mixture of the same composition. The transition temperature of the mixed crystal is about half way between those of the pure components. This corroborates the findings by X-ray diffraction that the mixed crystal was homogeneous. Also, it shows that as a first approximation the properties were intermediate between those of the pure components and a function of the concentration. We are in the process of examining the exact nature of the latter dependency and will report on it and other properties of our mixed crystals in the future. We concluded that for all practical purposes our mixed crystals are chemically and structurally homogeneous. This is not to rule out the possibility that relatively insignificant, at least concentration-wise, inhomogeneities and defects may be discovered by means of the application of other highly sensitive analytical techniques. It remains clear, though, that the phase rule method, as is to be expected, is a remarkably good one for preparing water soluble homogeneous mixed crystals. Also the value of DTA techniques in characterizing heat sensitive mixed crystals is clearly indicated.

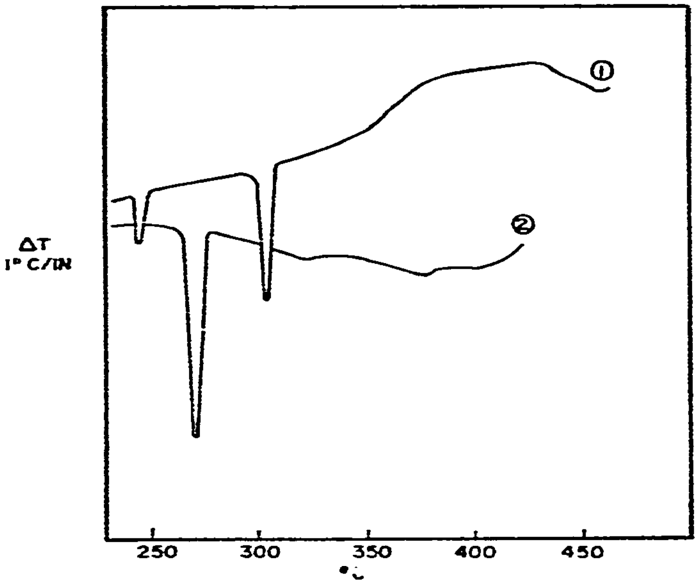

Fig. 5. Thermograms showing difference in behavior between physical and chemical mixtures; curve 1, 1:1 weight ratio NH_4ClO_4 and $KClO_4$, physical mixture; curve 2, 1:1 weight ratio NH_4ClO_4 and $KClO_4$ mixed crystal.

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