Journal of Thermal Analysis, Vol. 8 (1975) 387–392

INVESTIGATION OF THERMAL DECOMPOSITION REACTIONS BY MEANS OF THERMAL ANALYSIS AND DIELECTRIC CONSTANT MEASUREMENT*

I. R. Bonilla, P. da R. Andrade and A. Bristoti

Instituto de Fisica, UFRGS, Porto Alegre, Brasil

(Received October 17, 1974)

Dielectric constant measurements as a function of temperature and thermal analysis were performed in copper sulphate pentahydrate and sodium nitrite to study the nature of the decomposition reactions. The application of these combined techniques to the study of several possible mechanisms of thermal decomposition is advanced.

Usually materials undergoing a phase transition show anomalous behavior of thermal characteristic curves and of the dielectric constant at the transition temperature. It is interesting, then, to correlate both behaviors by performing thermal analysis and by measuring the temperature dependence of the dielectric constant in the same sample. In this note we shall discuss information obtained on two compounds, i.e. copper sulphate pentahydrate and sodium nitrite using this combined experimental approach. Particularly, copper sulphate pentahydrate is of interest for this kind of measurement since it contains water molecules of crystallization which are lost step-wise on heating. Sodium nitrite is also of interest since it exhibits a crystal transition of the order-disorder type. It has been shown that nitrogen ions can assume two equivalent positions along the b-axis of the crystal [4]. These random particles show a typical dielectric relaxation behavior after the transition temperature. Both behaviors may be compared in terms of a change in the crystalline structure and the relaxation mechanism and their respective contributions.

Thermal analyses were carried out using a Paulik–Paulik–Erdey-type "Derivatograph" model 1969 manufactured by MOM, Budapest. This equipment gives simultaneously: the mass loss as a function of temperature (TG); the first derivative of the mass as a function of temperature (DTG); differential thermal analysis (DTA) curve, and the temperature inside the sample (T). A change in the DTA curve indicates a crystallographic modification that may or may not be accompanied by a mass change. In the first case changes in TG and DTG curves occur, whereas in the second case only DTA and T curves show variation.

Measurements of the dielectric constant as function of the temperature were carried on by using a wide range linear capacitor meter described elsewhere [1].

---

* Work supported in part by the Conselho Nacional de Pesquisas and the Banco Nacional de Desenvolvimento Econômico (Brasil).

This equipment has been proven useful for locating phase transitions in ferroelectric materials and is sufficiently sensitive to detect other types of transitions.

The TG, DTG, DTA and dielectric constant measurements were performed at a heating rate of 0.5 °C/min. Copper sulphate pentahydrate is known to decompose on heating [2] in three steps: copper sulphate tri-hydrate, copper sulphate monohydrate and anhydrous copper sulphate. The tri-hydrate compound is stable over only a very small temperature range (see figure 3). In order to obtain the

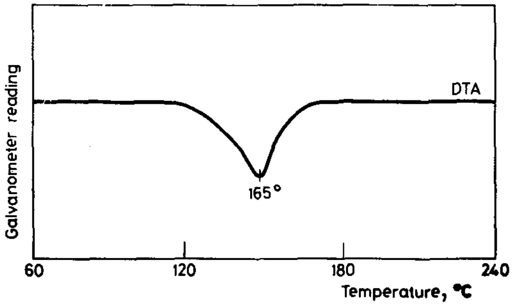

Fig. 1. DTA curve for $NaNO_2$; temperature range 25°—225°

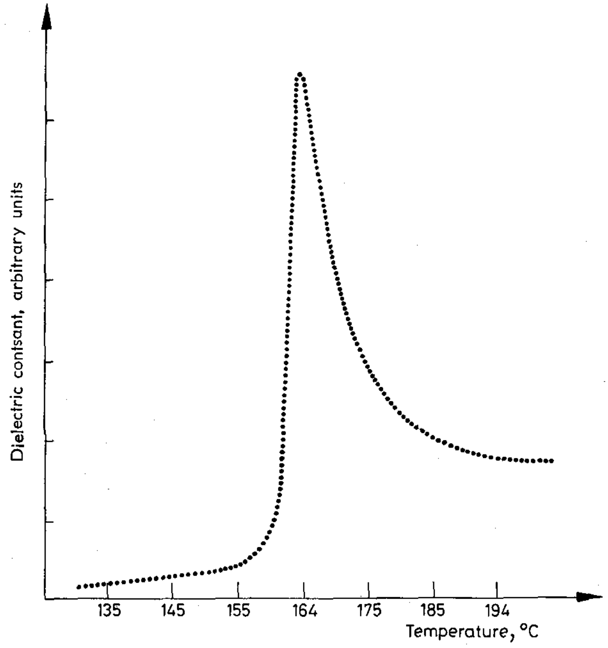

Fig. 2. Dielectric constant vs. temperature for $NaNO_2$ for a frequency of 1 kHz and temperature range 120°—200°

largest range of stability of this compound various heating rates and grain sizes were tried. The best resolution was obtained with a heating rate of 0.5 °C/min and grain size having diameter between 0.10 mm and 0.20 mm. For this situation the compound is stable over a temperature range of 5°. The formation of tri-hydrate was confirmed by X-ray diffraction analysis [3]. The sample for this analysis was prepared by quench cooling of the furnace of the Derivatograph at 85° to room temperature (see figure 3). The monohydrate copper sulphate and the anhydrous copper sulphate are stable over very large ranges of temperature and are not too sensitive to either heating rate or grain size.

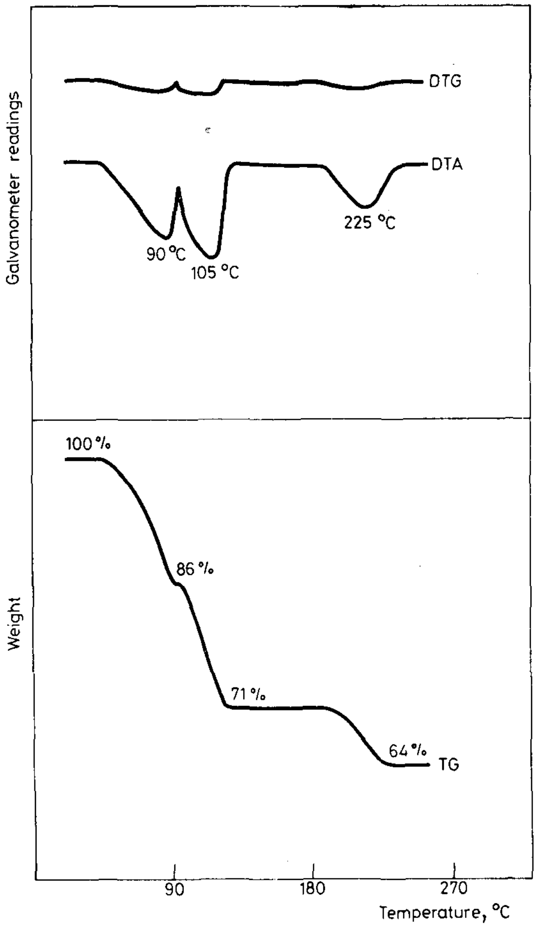

Fig. 3. TG, DTG and DTA curves for $CuSO_4 \cdot 5H_2O$ from 25° to 240°. Heating rate 0.5 °C/min

For measurement in sodium nitrite it was unnecessary to vary the grain size or the heating rates, since this compound undergoes only ferroelectric transition in the range of temperature studied in this note.

The results obtained with sodium nitrite are shown in Fig. 1 and Fig. 2. The results obtained with copper sulphate pentahydrate are shown in Fig. 3 and Fig. 4. In Fig. 1 one sees the DTA heating curve for sodium nitrite in the temperature range from 25° to 225°. The TG and DTG are not presented because both were determined to be constant in this range of temperature. In the DTA curve a sharp change occurs at 165°, a known transition temperature in sodium nitrite. This change could be interpreted as a possible structure phase transition, since there is no variation of mass and a downward peak indicates an endothermic reaction. However Fig. 2 clearly shows a well-defined Debye relaxation behavior for the dielectric constant of sodium nitrite as a function of temperature. This relaxation behavior has been well confirmed by many experiments [4]. Further it is generally accepted that this relaxation is due to a diffusion process of the nitrogen ions along the b-axis in this crystal [5]. Recently [6 – 9] it was assumed that the phonon associated with this disorder mechanism is in the liberation mode B_1. This implies also that the frequency of this mode is related to the activation energy of this disorder mechanism. This viewpoint leads to the important conclusion that the "ferroelectric" phonon does not go to zero at the critical temperature.

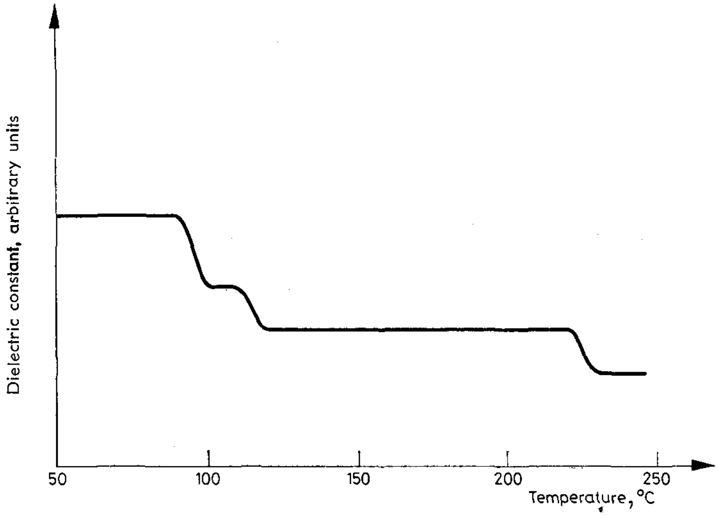

Fig. 4. Dielectric constant vs. temperature curve for $CuSO_4 \cdot 5H_2O$ for a frequency of 1 kHz. Temperature range 50° – 240°. $CuSO_4 \cdot 3H_2O$ is formed at 90°, $CuSO_4 \cdot H_2O$ at 110° and $CuSO_4$ at 220°

The above happens because the activation energy does not go to zero. The crystal would not necessarily need to undergo a structure or phase transition at the critical temperature. Following this viewpoint we may give a different interpretation for the variation of the DTA curve shown in Fig. 1. A diffusion process of the nitrogen ions produces a dielectric relaxation. The variation of the DTA curve could also be due to this diffusion process. More specifically, the absorbed energy would be due to the variation of the activation energy. This would be consistent with the endothermic character shown in Fig. 1. This assumption permits both the behaviors of the DTA curve and the dielectric constant as a function of temperature to be interpreted in a consistent way.

Fig. 3 shows the TG, DTG, and the DTA curves for copper sulphate pentahydrate. Both TG and DTA clearly show that there are several transitions. At 90° there is a transition from penta-hydrate to the tri-hydrate. At 105° the tri-hydrate goes to the mono-hydrate and finally at 225° a transition from the mono-hydrate to anhydrous sulphate occurs. The variation of mass shows clearly that there is a release of water molecules. A change of crystalline structure must necessarily occur.

The dielectric behavior of copper sulphate pentahydrate as a function of temperature is shown in Fig. 4. Although the DTA curves are similar in shape for copper sulphate pentahydrate and sodium nitrite, the dielectric constants vs. temperature curves are completely different for the two compounds. It is clear that the dielectric constant does not show any significant Debye relaxation behavior. The variation for the dielectric constant is small in all three transitions. If one takes the dielectric behavior of sodium nitrite as a framework we can analyze this small variation as due only to a very fast diffusion process of the water molecules, i.e. the release of the water molecules is very fast. If the water molecule required an appreciable time to leave the crystal a dipole dielectric relaxation would be expected. It is clear that if both measurements are combined it is possible to obtain some valuable information about the decomposition reaction. The dielectric behavior would indicate the "velocity" of this reaction. It is interesting to mention that similar conclusions concerning this aspect of the decomposition reaction has been made by Paulik and Paulik in a different way [10]. Those authors have also described the possibility of slow decomposition reactions.

The above has demonstrated the usefulness of combined DTA and careful dielectric measurements. Strictly speaking a relation between decomposition and dielectric relaxation times must exist. Presently we are guiding our research efforts on this direction.

References

1. H. N. Rutt and I. R. Bonilla, submitted to publication in J. Sc. Instr.
2. J. I. Taylor and H. P. Klug, J. Chem. Phys., 4 (1936) 601.
3. R, F. Zahrobsky and W. H. Baur, Acta Cryst., 24B (1968) 508.
4. I. Hatta, J. Phys. Soc. Japan, 24 (1968) 1043; S. Nomura, J. Phys. Soc. Japan, 16 (1961) 2440; Y. Takagi and K. Gesi, J. Phys. Soc. Japan, 22 (1967) 979.
5. Y. Yamada, Y. Fujii and I. Hatta, J. Phys. Soc. Japan, 24 (1968) 1053.
6. P. da R. Andrade, A. D. Prasad Rao, R. S. Katiyar and S. P. S. Porto, Solid State Comm., 12 (1973) 847.

7. P. da R. Andrade and S. P. S. Porto, Solid State Comm., 13 (1973) 1249.
8. A. D. Prasad Rao, P. da R. Andrade and S. P. S. Porto, Phys. Status Solidi, (b) 61 (1974) K71.
9. L. Merten and P. da R. Andrade, Phys. Stat. Solidi, (b) 62 (1974) 641.
10. F. Paulik and J. Paulik, J. Thermal Anal., 5 (1973) 253.

Résumé — On a étudié la nature des réactions de décomposition du sulfate de cuivre pentahydraté et du nitrite de sodium par analyse thermique et en mesurant la constante diélectrique en fonction de la température. On propose d'appliquer ces techniques combinées à l'étude des mécanismes possibles de plusieurs décompositions thermiques.

Zusammenfassung — Messungen der Dielektrizitätskonstante als Funktion der Temperatur sowie die Thermoanalyse wurde an Kupfersulfat-Pentahydrat und Natriumnitrit zur Untersuchung der Zersetzungsreaktionen durchgeführt. Die Anwendung dieser kombinierten Techniken zum Studium verschiedener möglicher Mechanismen der thermischen Zersetzung wird gezeigt.

Резюме — Измерения диэлектрической постоянной, как функции температуры, и термический анализ были применены при изучении природы реакций разложения пентагидрата сульфата меди и нитрита натрия. Предложено использовать эти комбинированные методы для изучения нескольких возможных механизмов термического разложения.