JOURNAL OF MATERIALS SCIENCE **31** (1996) 2683–2686

Characterization and thermal and electromagnetic behaviour of manganese tartrate crystals grown by the silica gel technique

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We report here on the dielectric properties (dielectric constant, ε' and dielectric losses ε''), magnetic properties (μ' and μ''), infrared spectroscopic, thermal studies (thermogravimetric analysis (TGA)), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) and X-ray diffraction (XRD) for the polycrystalline powdered samples of manganese tartrate $MnC_4H_4O_6{\cdot}2H_2O$ obtained by diffusion of manganese ions through silica gel impregnated with tartaric acid. The aforementioned properties are used as a probe for the detection and study of the different transitions that have been found in this salt. Energy dispersive analysis of X-rays (EDAX) confirmed the presence of manganese. X-ray diffraction data giving 2θ, intensity and *d*-values are reported for the first time. Infrared wavelengths in the range 500–4000 cm^{-1} and the description of peaks recorded for the material are given. Results of thermal analysis indicated that the material is thermally unstable. Dielectric and magnetic measurements were determined in the frequency range of 45 MHz to 2 GHz.

1. Introduction

This work is a part of our research programme concerning the investigation of the dielectric and magnetic properties of tartrates. Recently, considerable attention has been devoted to these molecules owing to their interesting properties [1–6]. Some tartrate molecules are ferroelectric, others possess structural phase changes. Of particular interest are sodium potassium tartrate (Rochelle salt), rubidium hydrogen tartrate (RHT) and ammonium hydrogen tartrate (AHT) crystals which are used for transducers and many linear and non-linear mechanical devices.

In this paper we report on the exact growth conditions of single manganese tartrate crystals, their electrical and magnetical properties and the results obtained their characterization by infrared spectroscopy, absorption spectroscopy, thermoanalytical techniques, such as thermogravimetric analysis (TGA), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC).

Single-crystal X-ray diffraction studies of manganese tartrate trihydrate have shown that it crystallizes in the monoclinic structure with unit-cell parameters of $a = 6.092$, $b = 12.285$, $c = 7.285$ nm [7].

2. Results and discussion

2.1. Growth procedure

Formation of manganese tartrate dihydrate was accomplished by the reaction between $MnCl_2$ and tartaric acid in sodium metasilicate gel. The experiments were carried out by the method of single test-tube diffusion, the gel itself containing one of the reacting components, i.e. tartaric acid. An aqueous solution of sodium metasilicate gel was added to another of tartaric acid L(+) until pH 4.5 was obtained, and set in test tubes 15 cm in length and 2.5 cm in diameter. An aqueous solution of $MnCl_2$ of the desired concentration was poured carefully over the set gel down the sides of the tube. The supernatant solution was allowed to diffuse into the gel medium. The experiments were carried out at 40 °C. Pure manganese tartrate crystals appeared within one week in the gel solution.

Some examples of crystals obtained are shown in Fig. 1. Fig. 2 shows a scanning electron microscope (SEM) enlargement of a part of the surface, in which the preferred direction of growth can be seen.

2.2. EDAX Results

Identification of manganese in the material was carried out by qualitative elemental analysis using energy dispersive analysis of X-rays (EDAX). Fig. 3 shows an EDAX curve of manganese tartrate. The peaks attributed to the presence of manganese at different energies are depicted.

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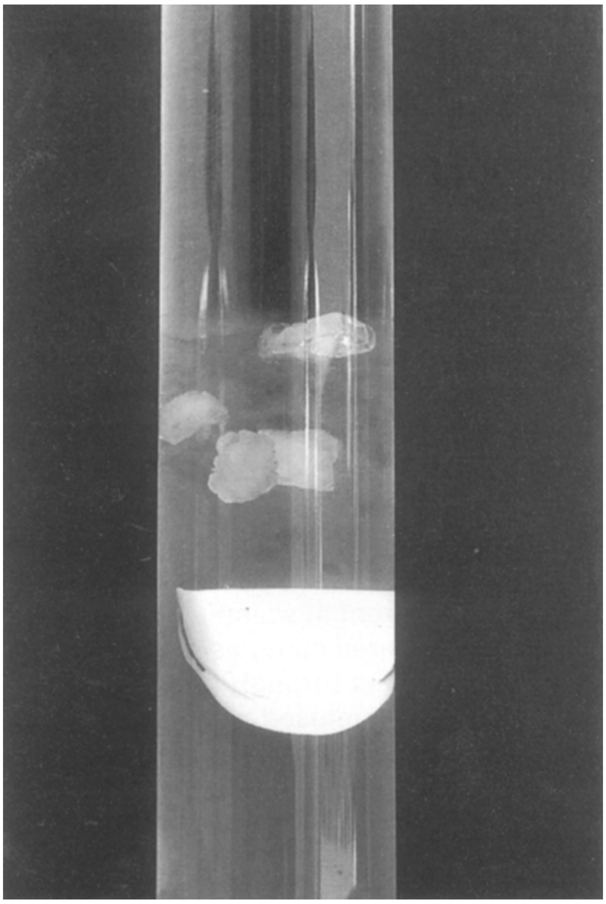

Figure 1 Manganese tartrate crystals grown in a glass tube.

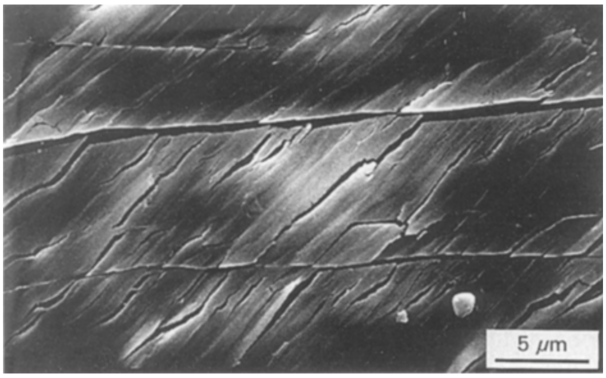

Figure 2 SEM illustrating a part of the surface at a high magnification.

2.3. X-ray diffraction

The computed XRD data of manganese tartrate are given in Table I. The characteristic X-ray data for this material are reported for the first time.

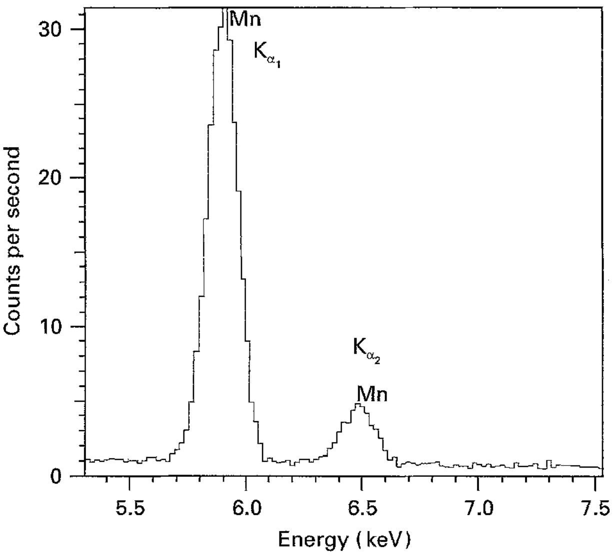

Figure 3 EDAX curve of manganese tartrate showing the presence of Mn.

TABLE I X-ray diffractometric studies of $MnC_4H_4O_6{\cdot}2H_2O$

I/I_0	2θ	d values (nm)
100.00	16.50	0.623795
27.27	18.40	0.559853
23.86	18.90	0.545171
34.09	19.45	0.529897
26.14	24.80	0.416838
52.27	26.70	0.387659
27.27	29.80	0.348108
27.27	30.45	0.340847
22.72	40.60	0.258001
27.27	42.45	0.247243
27.27	43.85	0.239721
95.45	44.85	0.234642
43.18	52.30	0.203098

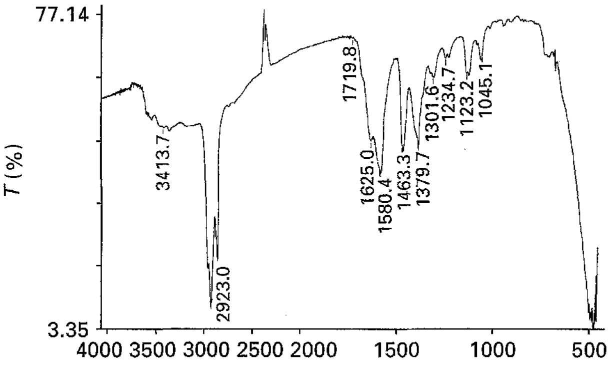

Figure 4 Infrared spectrum of manganese tartrate crystals.

2.4. Infrared spectroscopy

The infrared spectrum of manganese tartrate in the wavenumber range 500–4000 cm^{-1} is presented in Fig. 4. A broad band appearing in the 3000–3600 cm^{-1} region is due to OH stretching mode and to water. The strong peaks at 1580 and 1625 cm^{-1} are attributed to the C=O stretch of the carbonyl group. The strong peak at 1463 cm^{-1} is assigned to C=O symmetric and δ(O–C=O) modes. The peaks at 1220, 1234, 1301 and 1379 cm^{-1} can be attributed to the OH plane bending mode. The peaks at 1045, 1110 and 1123 cm^{-1} are due to various types of C–H vibrational modes. The bands below 600 cm^{-1} are due to metal oxygen bonds.

2.5. Thermal behaviour

The TG and DTG thermograms of manganese tartrate are shown in Fig. 5. As indicated, the material started decomposing at about 90 °C and the process continued up to about 500 °C, after which the material was reduced to its oxide. The first stage of the decomposition (90–150 °C) resulted in the elimination of two water molecules. The measured weight loss in the first stage was about 14.87% of the total weight. In the second stage (300–500 °C) the material was reduced to manganese oxide; the weight loss in this stage was about 54.40%.

Fig. 6 shows the DSC curve recorded for manganese tartrate. An endothermal peak observed at 111.4 °C, is due to the decomposition of water. The exothermal peak at 326 °C represents the reduction of manganese tartrate to its oxide. Examination of the TG, DTG and DSC curves indicates that the transformations are associated with mass changes and there is no physical (crystallographic) transformation independent of mass change or decomposition of the material.

2.6. Electromagnetic studies

The permittivity and permeability of the manganese tartrate were measured at room temperature using the HP 8510B network analyser in coaxial sample holder (10 cm APC-7 Beadless Air Line). The length of the sample is 10 mm.

The results of measuring the complex ε and μ of this material are shown in Figs 7 and 8.

Fig. 8 indicates that the material is not electrically lossy ($\varepsilon'' \approx 0.2$) and has a relatively low dielectric constant ε' varying from about 4.2 to 3.5 over the band.

The fact that the material is not magnetically lossy is confirmed by Fig. 8, which indicates a value of μ'' about zero. The real part of permeability μ' attains a constant value of 1.0 beyond 870 MHz.

However, because of the large errors in small ε'' and μ'', the measurements of low-loss samples are difficult to carry out with this technique. In order to obtain reasonable accuracy ε'' and μ'' should be greater than 0.1.

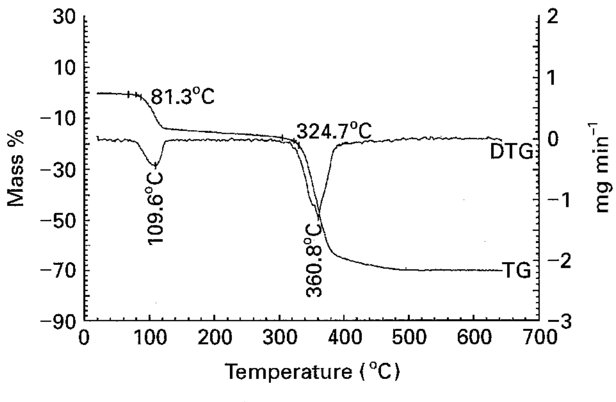

Figure 5 TG and DTG curves of manganese tartrate single crystals.

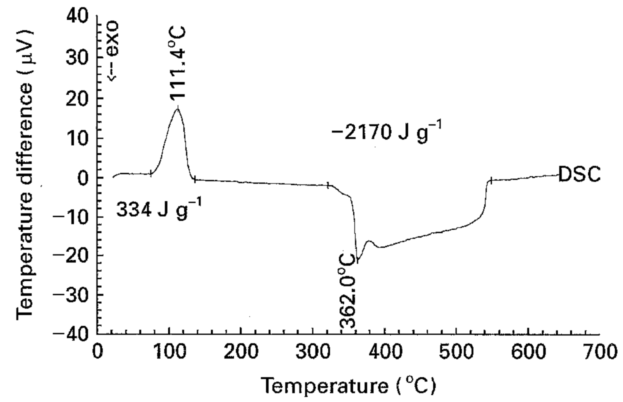

Figure 6 DSC curve of manganese tartrate crystals.

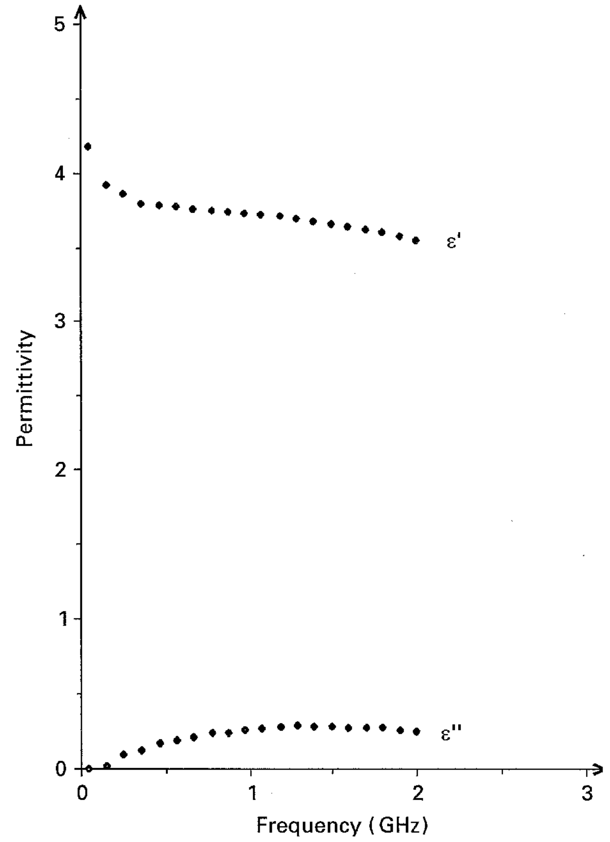

Figure 7 Complex permittivity at room temperature (≈25 °C) as a function of frequency for manganese tartrate crystals.

3. Conclusions

1. Growth of manganese tartrate crystals is accomplished by allowing diffusion of manganese chloride through silica gel impregnated with tartaric acid in a single-gel tube system.
2. EDAX confirms the presence of Mn as a constituent of the grown material. Infrared spectra establish the presence of carbon, oxygen and water of crystallization in the material.
3. The thermogravimetric analysis suggest that the gel-grown manganese tartrate is associated with two molecules of water of hydration.
4. The results of thermal analysis suggest that the gel-grown manganese tartrate is thermally unstable

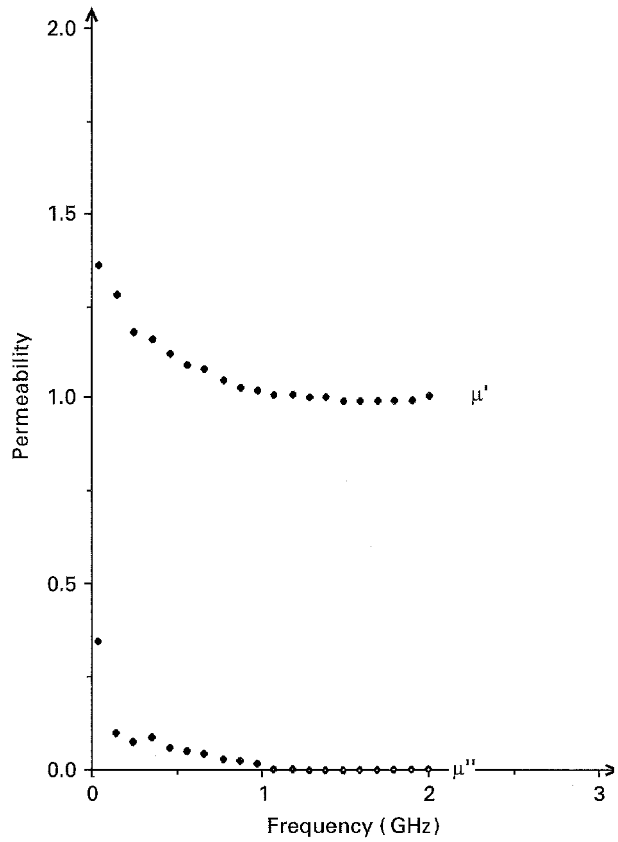

Figure 8 Complex permeability measured at room temperature (≈25 °C) as a function of frequency for manganese tartrate crystals.

even at low energies. Decomposition starts at about 90 °C and the process continues up to 500 °C, after which it reduces to its oxide.

Comparison of the TG and DSC curves suggests that the transformations are associated with mass changes and there is no physical (crystallographic) transformation independent of mass change.

5. The complex permittivity and permeability of manganese tartrate crystals are determined at fixed temperature of 25 °C in the frequency range of 45 MHz to 2 GHZ.
6. SEM studies indicate the preferred direction of growth.

Acknowledgements

The authors are grateful to Professor J. P. Parneix for the use of network analyser facilities in the École Nationale Supérieure de Chimie et Physique de Bordeaux and to Professor P. Martín, University of La Laguna, for the DSC measurements.

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Received 1 December 1994
and accepted 25 October 1995