J Therm Anal Calorim (2011) 105:123–127
DOI 10.1007/s10973-011-1412-1

A study of thermal and dielectric behavior of manganese malonate dihydrate single crystals

Varghese Mathew · Lizymol Xavier · C. K. Mahadevan · K. E. Abraham

Received: 13 November 2010 / Accepted: 14 February 2011 / Published online: 25 February 2011

Abstract Thermal decomposition of manganese malonate dihydrate single crystals grown by gel method has been studied using the TG-DTA and DSC techniques. The presence of water molecules and the dehydration stages are discussed. Dielectric constant, dielectric loss, and AC conductivity have been estimated as a function of temperature in the range of 40–120 °C for four different frequencies. Thermal studies reveal that the material is thermally stable up to123 °C. The dielectric measurements indicate that the dielectric parameters increase with the increase in temperature. Also, the dielectric constant and dielectric loss factor values decrease whereas the electrical conductivities increase with the increase in frequency of the AC applied.

Keywords Manganese malonate · Crystal growth · Thermal properties · Dielectric constant · Dielectric loss · AC conductivity

Introduction

Dicarboxylate ligands such as oxalate, malonate, and terephthalate are widely used in the construction of a variety of metal complexes with interesting compositions and topologies offering potential applications in electrical conductivity, magnetism, host–guest chemistry, ion exchange, catalysis, nonlinear optics, etc. Among these, malonate (the dianion of 1,3 propanedioic acid) can function as a versatile ligand with the simultaneous adoption of chelating bidentate and different carboxylate binding coordination modes like syn-syn, syn-anti, and anti-anti. Its ability to mediate ferromagnetic interactions between the metal ions that it bridges, is reported [1, 2]. Manganese complexes remain a center of interest because of a variety of their properties. As a dopant in crystalline matrix manganese influences the physical properties of the crystal. The Mn^{2+} d-electron states act as efficient luminescent centers. Manganese ions in organometallic compounds can be easily ordered into short- and long- order magnetic states [3, 4].

Synthesis and characterization of manganese malonate complexes were reported and the orthorhombic structure of manganese malonate dihydrate ($MnC_3H_2O_4{\cdot}2H_2O$) was confirmed [5, 6]. But reports on the crystallization of the material by gel method are scanty in literature. The gel growth technique is quite appealing on account of its unique advantages in terms of the quality of the crystals produced and the simplicity of the process [7]. In this investigation, manganese malonate dihydrate crystals have been grown in silica gel and characterized by thermal and dielectric studies. Herein the authors report the results obtained.

Materials and methods

Manganese malonate dihydrate crystals, $Mn(C_3H_2O_4)$ $2H_2O$ were grown by the hydrosilica gel method. The growth was accomplished by the controlled diffusion of

V. Mathew · L. Xavier
Department of Physics, St. Aloysius' College, Edathua 689573, India

C. K. Mahadevan
Physics Research Centre, S.T. Hindu College, Nagercoil 629002, India

K. E. Abraham (✉)
Department of Physics, S.B. College, Changanacherry 686101, India
e-mail: abrahamke@gmail.com

manganese ions through silica gel impregnated with malonic acid. The gel was prepared by mixing sodium metasilicate of density 1.033 g/cc with 1 M malonic acid. The gel was allowed to set and 0.3 M manganese chloride solution was carefully poured on the top of the gel. The outer electrolyte diffuses into the gel and manganese ions react with malonate ions, resulting in the crystallization of manganese malonate. Pink crystals of manganese malonate were grown after a period of 5 weeks. The growth and spectroscopic characterization of the crystal have been reported elsewhere [8].

The thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the title crystal were carried out using a Perkin Elmer Diamond TG/DTA instrument under nitrogen atmosphere from room temperature to 800 °C at a heating rate of 10 K/min. Differential scanning calorimetric (DSC) measurements were made using a Mettler Toledo DSC 822e instrument in the temperature range of 40–600 °C.

Dielectric (capacitance and dielectric loss, tanδ) measurements on manganese malonate dihydrate crystals were carried out by the parallel plate capacitor method as a function of temperature for four different frequencies (1, 10, 100 kHz and 1 MHz) using a precision LCR meter (AGILENT 4284 A model) [9, 10]. The sample crystals were powdered and pelletized into a dia 13 mm. The opposite flat faces of the pellet were coated with fine graphite powder. The sample was placed between the electrodes and heated from room temperature to 120 °C using a thermostat. The maximum temperature for the dielectric measurement was considered to be 120 °C as it was understood from the TG measurement that the crystal is thermally stable up to 123 °C. The observations were made while cooling the sample. The dielectric constant of the crystal was calculated using the relation. $\varepsilon_r = C_{crys}/C_{air}$, where C_{crys} is the capacitance of the crystal and C_{air} is the capacitance of the same dimension of air. From the dielectric constant ε_r and the loss factor (tanδ), the AC conductivity (σ_{ac}) of the sample can be evaluated using the relation. $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \tan\delta$ where f is the frequency of the applied field and ε_0 is the permittivity of free space.

Results and discussion

Thermal studies

Thermoanalytical studies are powerful tools with a wide range of applications from basic research to several industries in the development and characterization of a variety of products [11, 12]. Thermal studies of metal malonates have been reported by many authors [13–15]. But the investigations on gel-grown metal malonate crystals are very few [16–18]. The TG, DTA, DSC studies of the title compound were carried out and the corresponding plots are depicted in Fig. 1a–c, respectively.

The TG curve exhibits mass losses in two stages which indicate that the decomposition takes place continuously. It is seen that the TG curve shows a plateau up to 123 °C suggesting that the compound is thermally stable up to a

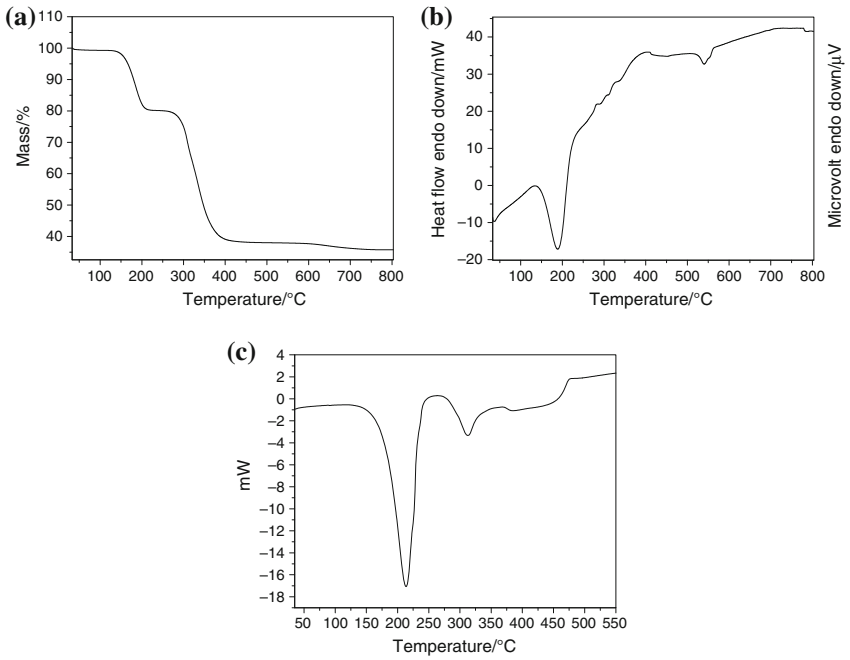

Fig. 1 TG, DTA, DSC patterns of manganese malonate crystals. **a** TG Pattern. **b** DTA Pattern. **c** DSC Pattern

temperature of 123 °C. After this temperature, the curve describes a mass loss of 19% in the temperature range of 123–209 °C. This mass loss is attributed to the dehydration of the sample by eliminating two water molecules from the structure of the compound. The calculated mass loss for the same is 18.67%.

The anhydrous malonate formed after dehydration remains stable up to 287 °C. In the temperature range of 287–398 °C, the TG curve shows a mass loss of 42%. This stage indicates the thermal decomposition of the anhydrous malonate to manganese oxide (MnO). The observed mass loss of 41% is in close agreement with the formation of MnO as the final product. The details are given below.

Molecular weight of the crystal $MnC_3H_2O_4{\cdot}2H_2O$ = 192.954
Molecular weight of $MnC_3H_2O_4$ = 156.922
Weight of 2 molecules of H_2O = 36.032
Amount of $MnC_3H_2O_4$ in the crystal = 81.33%
Water of crystallization = 18.67mass%
Weight loss observed in the first temperature region = 19%

The calculation shows that the molecular formula of the grown crystal can be written as $MnC_3H_2O_4$ $2H_2O$.

The DTA curve of the sample shows a smooth endotherm with a peak at 190.58 °C. Area under the peak is 6416.46 mJ and heat of transition ΔH = 0.73373 kJ/g. This reveals that two water molecules in the structure are eliminated in a single step. The curve shows multiple indistinguishable peaks between 280 and 385 °C. This indicates that the intermediate products undergo multiple oxidative decomposition process.

In the DSC study, two endothermic stages are observed. But at 474.8 °C, an exothermic phase transition process is noticed. The thermal effect is 0.00516 kJ/g. The result of DSC measurements is presented in Table 1.

The DSC curve comprises of three steps:-

Step 1 The initiation temperature is 179.93 °C and equilibrium temperature is 233.11 °C. At 179.93 °C, initiation of phase change starts and completed at the peak endotherm temperature of 213.76 °C. The temperature at which the sample and reference come to equilibrium by thermal diffusion appears to be at 233.11 °C. (i) Area under the curve is 3646.145 mJ and (ii) heat of transition, i.e., enthalpy change of transition is 589.61 J/g.

Step 2 At 287.67 °C initiation of phase change starts and the phase change ends at peak endo-down temperature of 311.96 °C. The temperature at which the sample and reference come to thermal equilibrium by thermal diffusion appears to be at 331.34 °C. (i) Area under the curve is 511.5 mJ and (ii) heat of transition ΔH, i.e., enthalpy change of transition is 82.71 J/g.

Step 3 At 463.98 °C, initiation of phase change starts and the transition ends at the peak exo-up temperature of 474.80 °C. The temperature at which the sample and reference come to thermal equilibrium by thermal diffusion appears to be at 475.48 °C. (i) Area under the curve is −31.89 mJ and (ii) heat of transition ΔH, i.e., enthalpy change of transition is −5.16 J/g.

Table 1 Values of ΔH and T_i (Transition temperature) from DSC measurements

Sample	Mass of sample	ΔH (kJ/g)	T_i (°C)
$MnC_3H_2O_4{\cdot}2H_2O$	6.184 g	0.58961	213.76
		0.08271	311.96
		0.00516	474.8

The TG/DTA/DSC results obtained are fairly in agreement with those in the literature [19–21].

Dielectric studies

The dielectric properties of solid give us a good insight into the electric field distribution within them. By the study of dielectric constant ε_r, dielectric loss (tanδ) and AC conductivity (σ_{ac}) as a function of frequency and temperature, the various polarization mechanisms in the material can be understood. Figure 2 shows the variation of dielectric properties of manganese malonate dihydrate crystals with temperature at four different frequencies, viz. 1, 10, 100 kHz and 1 MHz. The dielectric parameters—ε_r, tanδ, and σ_{ac} are observed to increase with rise in temperature. The variation with temperature of dielectric parameters is more pronounced at lower frequencies than at higher frequencies. Moreover, when the frequency is 1 MHz, no significant variation of dielectric constant, dielectric loss and AC electrical conductivity versus temperature could be observed. The values of ε_r and tanδ decrease with the increase in frequency. The σ_{ac} value increases with the increase in frequency. This is considered to be a normal dielectric behavior.

The results indicate that the ε_r values observed at lower temperatures are significantly less (<4.0 up to 80 °C for 1 kHz frequency) (see Fig. 2a). The microelectronics industry needs to replace the dielectric materials in multilevel interconnect structures with low dielectric constant materials as an inter layer dielectric (ILD) which surrounds and insulates interconnect wiring. Silica has the ε_r value $\approx$4.0, in part as a result of Si–O bonds. Several innovative developments have been made for the development of new low ε_r value materials to replace silica. However, there is still a need for new ε_r value dielectric materials [22]. In addition, materials in the single crystal form would be very

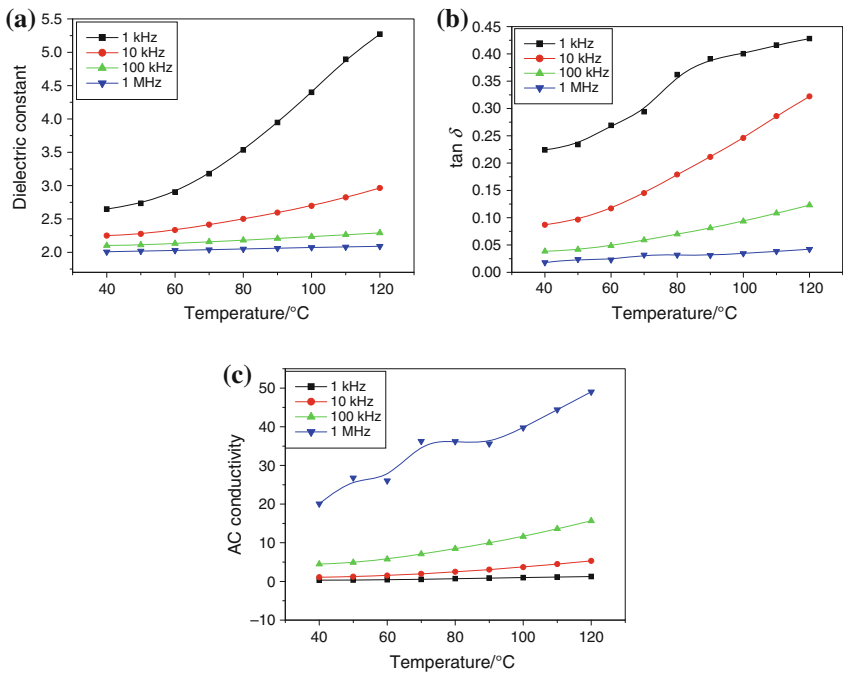

Fig. 2 Dielectric properties of manganese malonate crystals. **a** Variation of dielectric constant with temperature. **b** Variation of dielectric loss with temperature. **c** Variation of AC conductivity with temperature

much interesting. Meena and Mahadevan [22] have found that L-arginine acetate and L-arginine oxalate are promising low ε_r value dielectric materials. Also, Mahadevan and his co-workers have observed significant reduction in ε_r value of potassium dihydrogen orthophosphate (KDP) single crystal when doped with urea [23] and with L-arginine [24] which makes KDP as a low ε_r value dielectric material. Considering the above factor, the title compound crystal can also be considered as a promising low ε_r value dielectric material.

The dielectric behavior of the title compound crystal can be understood on the basis that the mechanism of polarization is similar to the conduction process. For this type of single crystals, the electrical conductivity can be determined by the proton transport within the frame work of hydrogen bonds because of the presence of water molecules [24]. Also, the conductivity observed in this study increases smoothly through the temperature range (40–120 °C) considered; there is no sharp increase that would be characteristic of a superprotonic phase transition [24]. So, two mechanisms can be considered. The first mechanism is identical to the conductivity mechanism in ice also containing hydrogen bonds. According to the second mechanism, conductivity is associated with the incorporation in the crystal lattice of impurities having different valences and the formation of corresponding defects in ionic crystals. The conductivity of ice is determined by the simultaneous presence of positive and negative ions and orientational defects-vacant hydrogen bonds (L-defects) and doubly occupied hydrogen bonds (D-defects). Other possible defects are vacancies and defect associates. The temperature dependence of conductivity observed in this study for the title compound allows us to mention that the conductivity of manganese malonate dihydrate crystal is determined by both thermally generated L-defects and the foreign (natural) impurities incorporated with the lattice and generating L-defects there. So, the proton transport in the crystal depends on the generation of L-defects. Hence, the increase of conductivity with the increase in temperature observed for the manganese malonate dihydrate crystal can be explained as due to the temperature dependence of the proton transport.

Conclusions

The growth of manganese malonate dihydrate single crystals was achieved using gel technique by the process of diffusion. The TG/DTA/DSC thermograms reveal the different stages of decomposition for the grown crystals and the presence of two water molecules in the title compound. The sample reduces to the metal oxide at around 370 °C as in the case of many metal organic compounds. The low ε_r values observed (<4.0) at low temperatures indicate that the title compound crystal is a promising low ε_r value dielectric material useful in microelectronics industry. The conductivity behavior could be understood as because of the proton transport within the framework of hydrogen bonds.

References

1. Zhang Q-Z, Yang W-B, Chen S-M, Lu C-Z. Synthesis and crystal structures of two metal complexes incorporating malonate and organodiamine ligands. Bull Korean Chem Soc. 2005;26:1631–4.
2. Delgado FS, Kerbellec N, Ruiz-Perez C, Cano J, Lloret F, Julve M. Malonate–containing manganese (III) complexes; synthesis, crystal structure and magnetic properties of As Ph4 [Mn (mal)2 (H2O)2]. Inorg Chem. 2006;45:1012–20.
3. Bhagavannarayana G, Kushwaha SK, Parthiban S, Meenakshisundaram S. The influence of Mn-doping on the non-linear optical properties and crystalline perfection of tris (thiourea) zinc (II) sulphate crystals. J Cryst Growth. 2009;311:960–5.
4. Marczynski S, Guskos N, Typek J, Grech E, Kolodziej B. Magnetic ordering process in manganese (II) di (hydrogen malonate) monohydrate complex studied by ESR spectroscopy. Mater Sci Poland. 2006;24:1139–44.
5. Gupta MP, Chand P. The crystal structure of manganese malonate dihydrate. Curr Sci. 1977;46:557.
6. Lis T, Matuszewski J. Manganese (II) malonate dihydrate: a re-investigation. Acta Cryst. 1979;B35:2212–4.
7. Blank Z. The growth of cadmium mercury thiocyanate and zinc mercury thiocyanate crystals in gels. J Cryst Growth. 1973;18: 281–8.
8. Mathew V, Joseph J, Jacob S, Abraham KE. Crystallization and spectroscopic studies of manganese malonate. Bull Mat Sci. 2010;33:433–7.
9. Perumal S, Mahadevan CK. Growth and characterization of multiphased mixed crystals of KCl, KBr and KI–part 2: Electrical measurements. Physica B. 2005;367:172–81.
10. Neelakanda Pillai N, Mahadevan CK. Preparation and electrical properties of $(NaCl)_x$ $(NaBr)_{y-x}$ $(NaI)_{1-y}$ crystals. Mater Manuf Proc. 2007;22:393–9.
11. Gabbott Paul. Principles and applications of thermal analysis. Oxford: U. K. Blackwell; 2008.
12. Brown ME. Handbook of thermal analysis and calorimetry, vol. 1. Amsterdam: Elsevier; 2003.
13. Nabar MA, Jukar BN. Studies on double malonates-II. Potassium rare earth malonates, K5Ln (C3H2O4)4 (Ln = Gd–Ho or Y). Bull Chem Soc Jpn. 1985;58:3582–6.
14. Muraishi K. Thermal decomposition of alkali metal malonate anhydrides in various atmospheres. Thermochimica Acta. 1990; 164:401–9.
15. Muraishi K, Suzuki Y, Takahashi Y. Thermal behavior of alkaline earth metal malonate hydrates and their anhydrides. Thermochimica Acta. 1996;286:187–98.
16. Varughese PA, Saban KV, George J, Paul I, Varghese G. Crystallization and structural properties of calcium malonate hydrate. J Mat Sci. 2004;39:6325–31.
17. Doreswamy BH, Mahendra M, Sridhar MA, Shashidhara Prasad J, Varughese PA, Saban KV, Varghese G. Structural studies on praseodymium malonate hydrate. J Mol Struct. 2003;659:81–8.
18. Mathew V, Joseph J, Jacob S, Abraham KE. Spectroscopic characterization of gel grown strontium malonate crystals. Indian J Pure Appl Phys. 2011;49:21–4.
19. Caires FJ, Lima LS, Carvalho CT, Giagio RJ, Ionashiro M. Thermal behavior of malonic acid, sodium malonate and its compounds with some bivalent transition metal ions. Thermochimica Acta. 2010;497:35–40.
20. Rzaczynska Z, Danczowska-Burdon A, Sienkiewicz-Gromiuk J. Thermal and spectroscopic properties of light lanthanides (III) and sodium complexes of 2,5-pyridinedicarboxylic acid. J Therm Anal Calorim. 2010;101:671–7.
21. Wyrzykowski D, Chumurzynski L. Thermodynamics of citrate complexation with Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} ions. J Therm Anal Calorim. 2010;102:61–4.
22. Meena M, Mahadevan CK. Growth and dielectric properties of L-arginine acetate and L-arginine oxalate single crystals. Mater Lett. 2008;62:3742–4.
23. Goma S, Padma CM, Mahadevan CK. Dielectric parameters of KDP single crystals added with urea. Mater Lett. 2006;60: 3701–5.
24. Meena M, Mahadevan CK. Growth and electrical characterization of L-arginine added KDP and ADP single crystals. Cryst Res Technol. 2008;43:166–72.