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Thermal Properties of Pure and Doped BTMC and BTZS Single Crystals

Sethu Gunasekaran[1], Padmapriya Venkatesan[1]*,

Govindarajulu Anand[2], Subramanian Kumaresan[3]

[1]PG and Research Department of Physics, Pachaiyappas College, Chennai – 600 030. India
[2]Department of Physics, Arulmigu Meenakshi Amman College of Engineering, Vadamavandal – 604 410, India
[3]Department of Physics, Government Arts College, Stone House Hill, Ooty – 643 002. India

Corres. Author : padmapriya0506@gmail.com

Abstract: Thermal analysis is very essential method to study the thermal behavior of materials and finds widespread applications in diverse industrial and research fields. In addition to providing valuable information on the thermal stability of the compounds and the decomposition products, these studies often provide an insight into their mode of decomposition. The thermal stability of the grown crystal and their melting point were found by subjecting the samples to TG – DTA studies.
Keywords: Differential Scanning Calorimetry (DSC), Differential thermal analysis (DTA), Thermogravimetry analysis (TGA).

Introduction and Experimental

Thermal Studies

Thermal analysis is a very essential method to study the thermal behavior of materials and finds widespread applications in diverse industrial and research fields [1-5]. It is a general term, which covers a group of related techniques in which the temperature dependence of the parameters of any physical property of a substance is measured. In addition to providing valuable information on the thermal stability of the compounds and the decomposition products, these studies often provide an insight into their mode of decomposition.

Methods of thermal analysis

Thermoanalytical methods involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined conditions of heating rate, temperature range and gaseous atmosphere or vacuum. In many cases, the use of a single thermoanalytical technique may not provide sufficient information to solve the problem on hand and hence, the use of other thermal techniques, either independently or simultaneously for complementary information becomes necessary.

Thermo analytical analysis incorporates three closely related techniques. Thermo gravimetric analysis (TGA), which involves monitoring weight while varying temperature. Thermogravimetry is

widely used to determine the thermal stability, decomposition temperature, temperature of desorption and drying, oxidative stability, etc.,

Differential thermal analysis (DTA), which involves comparing the precise temperature difference between a sample and an inert reference material, while heating both. DTA is more versatile and yields data of a considerably more fundamental nature. The thermal effects are observed as peaks whose sequence, sign (endothermic or exothermic), magnitude and shape reflect the physical or chemical changes taking place. DTA method is applicable to all studies listed for TGA and also to phase transformations including polymerization, phase equilibrium and chemical reactions.

Differential scanning calorimetry (DSC), similar to DTA except that electrical energy is used to restore the cooler of the two materials to the same temperature as the other. This allows direct measurement of energy changes.

These techniques are useful for determining glass points, phase changes, water of crystallization and mixtures where the components have different melting or decomposition points. Among the thermal methods, the most widely used techniques are TGA, DTA and DSC, which find extensive use in all fields of inorganic and organic chemistry, metallurgy, mineralogy and many other areas. In the present work, thermal behavior of the grown crystals has been investigated using TGA and DTA techniques.

Thermogravimetry analysis (TGA)

Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature or time, while the substance is subjected to a controlled temperature program. The curve obtained in a thermogravimetric analysis is called a thermogram (TG) and its first derivative is called derivative thermogram (DTG). The inflection point in the program corresponds to the peak point in the derivative thermogram. Modern commercial TGA instruments consist of the following:

(i) A sensitive analytical balance.
(ii) A temperature programmable furnace.
(iii) A pure gas system for providing suitable gas atmosphere.
(iv) A microprocessor for instrument control, data acquisition and display.

Even though different types of balance mechanism are available today, those employing null-point-weighing mechanism are favoured as the sample remains in the same zone of furnace irrespective of changes in mass. The furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from ambient to 1000-2000 ^{o}C. Thermogravimetry is widely used to determine the thermal stability, decomposition temperature, temperature of desorption and drying, oxidative stability, etc.

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) though, often considered an adjunct to TGA is, in fact, far more versatile and yields data of a considerably more fundamental nature. The technique is simple as it involves the measurement of the temperature difference between the sample and inert reference materials, as both are subjected to identical thermal regimes, in an environment heated or cooled at a constant rate. The origin of the temperature difference in the sample lies in the energy difference between the products and the reactants or between the two phases of a substance. This energy difference is manifested as enthalpy changes, either exothermic or endothermic.

The differential thermal curve would be parallel to the temperature (time) axis till the sample undergoes any physical or chemical change of state. However, as soon as the sample has reached the temperature of this change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appear as a peak. The differential signal would return to the base line only after the change of state of the sample is completed and the temperature becomes equal to that of the reference material.

The thermal effects are observed as peaks whose sequence (on the temperature scale), sign (endothermic or exothermic), magnitude and shape reflect the physical or chemical changes taking place. Since any change in the chemical or physical state of a substance is accompanied by changes in energy that are manifested as heat changes, the DTA method is applicable to all studies listed for TGA and also to phase transformations including polymerization, phase equilibrium and chemical reactions.

Differential Scanning Calorimetry (DSC)

DSC measures the amount of energy or power absorbed/released by a sample when it is heated / cooled or held at a constant temperature.

Differential scanning calorimetry has become the most widely used thermal analysis technique. In this technique, the sample and reference materials are subjected to a precisely programmed temperature change. When a thermal transition (chemical or physical change that results in the emission or absorption of heat) occurs in the sample, thermal energy is added to either the sample or the reference containers in order to maintain both the sample and reference at the same temperature. Because the energy transferred is exactly equivalent in magnitude to the energy absorbed or evolved in the transition, the balancing energy yields a direct calorimetric measurement of the transition energy. Since DSC can directly measure both the temperature and enthalpy of a transition or the heat of a reaction, it is often substituted for differential thermal analysis as a means of determining these quantities except in certain high-temperature applications.

In general, each substance gives a DSC curve in which the number, shape, and position of the various endothermic and exothermic features serve as a means of qualitative identification of the substance. Endotherms generally represent physical rather than chemical changes. Sharp endotherms are indicative of crystalline rearrangements, fusions, or solid-state transitions for relatively pure materials. Broader endotherms cover behavior ranging from dehydration and temperature-dependent phase behaviors to the melting of polymers. Exothermic behavior (without decomposition) is associated with the decrease in enthalpy of a phase or chemical system. Narrow exotherms indicate crystallization of a metastable system. Broad exotherms denote chemical reactions, polymerization, or curing of thermosetting resins. Exotherms with decomposition can be either narrow or broad depending on the kinetics of the behavior.

Experimental

In the present work, simultaneous TGA and DTA have been carried out for the pure and doped BTMC and BTZS crystals in the temperature range of 30 º C to 500 º C with a heating rate 20 º/min in the nitrogen atmosphere by using SDT Q 600V 8.3 instrument

Results and Discussion

The TGA-DTA traces of pure, Cd^{2+} and Zn^{2+} doped BTMC crystals are shown in Fig. 1, Fig. 2 and Fig. 3 respectively and the TGA-DTA traces of pure, Cd^{2+} and Cu^{2+} doped BTZS crystals are shown in Fig. 4, Fig. 5 and Fig. 6.

Fig. 1 The TGA-DTA traces of pure BTMC crystal

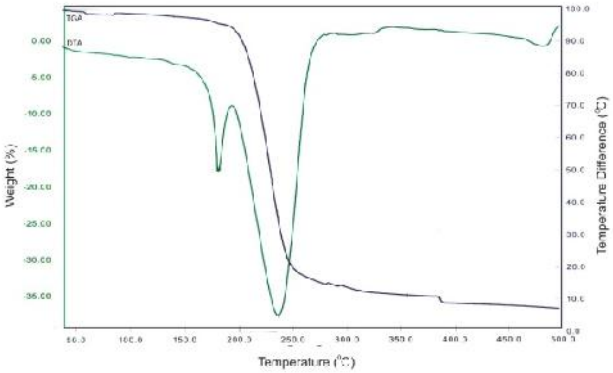


Fig. 2 The TGA-DTA traces of Cd^{2+} doped BTMC crystal

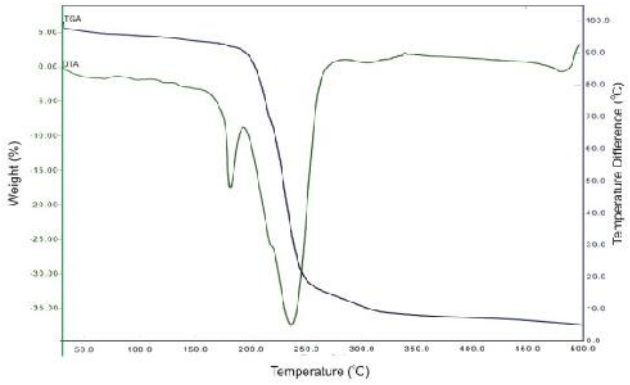


Fig. 3 The TGA-DTA traces of Zn^{2+} doped BTMC crystal

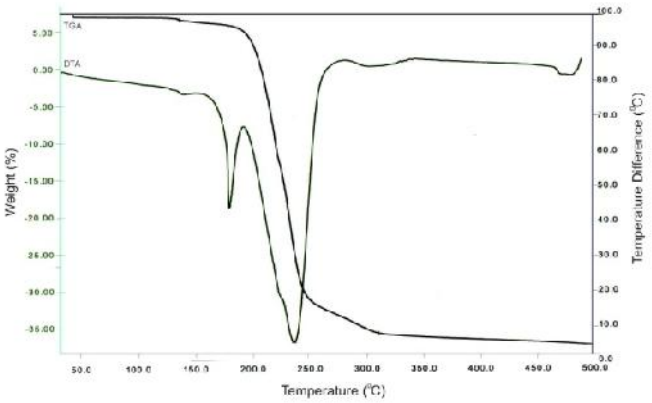


Fig. 4 The TGA-DTA traces of pure BTZS crystal

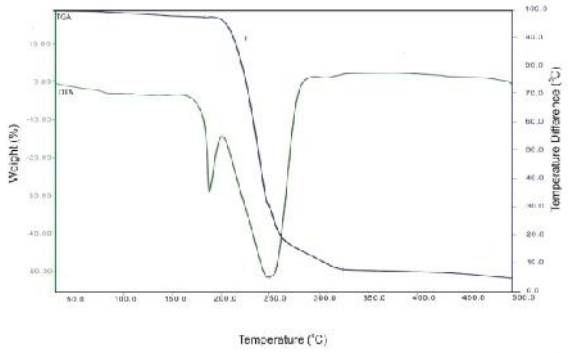


Fig. 5 The TGA-DTA traces of Cd^{2+} doped BTZS crystal

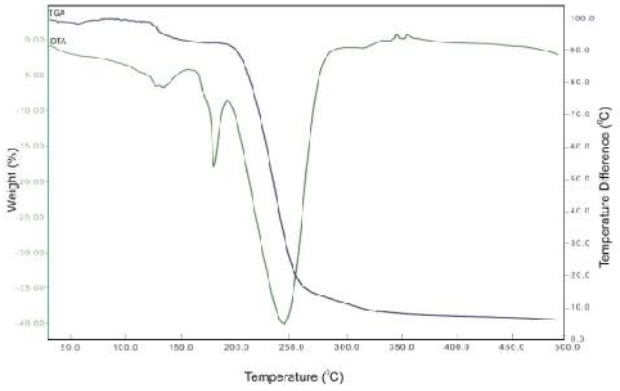
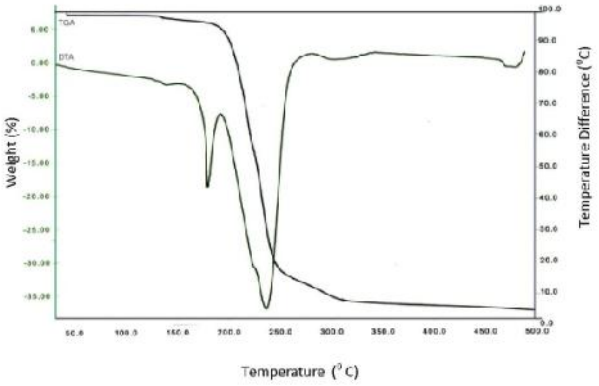


Fig. 6 The TGA-DTA traces of Cu^{2+} doped BTZS crystal



The thermograms of pure and doped BTMC crystals appear with three stages of decompositions between 180 and 500 ^{o}C. The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100 º C.The first stage of decomposition for the pure BTMC occurs between 185 and 258 ^{o}C. The first peak decomposition temperature is seen at 242 ^{o}C, which is due to the removal of hydrogen from the thiourea molecule. The second stage of decomposition occurs between 268 and 318 ^{o}C. This may be attributed to the removal of nitrogen from the thiourea molecule. The third stage occurs between 378 and 460 ^{o}C. The removal of carbon from the thiourea molecule indicates the third stage of decomposition temperature.

The first and third stages of decompositions have produced maximum weight loss when compared to the second stage. In order to study the influence of dopants on the thermal stability of BTMC, the temperature corresponding to peak maximum of first stage of decomposition is taken into account for comparison. The maximum decomposition temperature for the parent sample is found to be 242 ^{o}C, whereas for the Cd^{2+} and Zn^{2+} doped BTMC the corresponding temperatures are 247 and 249 ^{o}C respectively. The total weight loss of pure, Cd^{2+} and Zn^{2+} doped BTMC are 74.54%, 68.98% and 64.38 % respectively. The high melting point of BTMC when compared with organic crystals arises due to the stronger bonding existing between the conjugation layers of thiourea molecules and metal ion[6].

In BTZS crystals three stages of decomposition take place. The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100 º C. Ramajothi et al [7] reported the melting point at 233 º C of ZTS crystals (Tris thiourea zinc sulphate) and the decomposition of the crystals starts at 236 º C. The sharp endothermic peak at 241 º C is assigned to the melting point of BTZS crystals.

The first stage of decomposition occurs between 180 º and 270 º C. The second stage of decomposition occurs between 270 º and 330 º C and may be attributed to the removal of nitrogen from the thiourea molecule. In the third stage of decomposition takes place in between 370 and 430 º C. The thermal stability of the doped crystals is slightly greater than the pure crystals. The lesser ionic radius of Mg^{2+} and Cd^{2+} can give more bonding interaction with thiourea, thus giving more thermal stability to the crystal[8-11]. The melting points and decomposition temperature of all the crystals are higher than the ligand-thiourea. The increase in the decomposition temperature is due to the formation of metal complexes.

Conclusion

The TGA thermograms of pure, Cd^{2+} and Zn^{2+} doped BTMC reveal that the substitution of dopants

slightly increases the decomposition temperature of the BTMC crystals. The doped crystals of BTMC undergo four stages of thermal decompositions similar to the pure one. The thermal analysis by TG-DTG technique indicates that the presence of metallic dopants (Cd^{2+} and Cu^{2+}) slightly increases the decomposition temperature of the BTZS crystals. The DTA analysis clearly indicates the change in the exothermic nature of the BTZS, due to the presence of dopants.

References

[1] Gunjan Purohit Joshi G.C.,Indian J. Pure Appl. Phys, 41, 922-927, (2003).
[2] Ushashree P.M., Jayavel R., Subramanian C., and Ramasamy P.,J. Cryst. Growth, 197, 216, (1999).
[3] Rajasekaran R., Ushashree P.M., Jayavel R., and Ramasamy P., J. Cryst. Growth, 218,365, (2000).
[4] Marey H.O., Rosker M.J., Warren L.F, Cunningham P.C., Thomas A., Deloach L. A., Velsko S.P.,EbbersC.A.,Liao J.H and Kanatzidis M.G., Opt. Lett., 20, 252 (1995).
[5] Long N.J., Angew. Chem, 34, 21, (1995).
[6] VenkataramananV., Maheswaran S., Sherwood J.N. and Bhat H.L.(1997), J.Crystal Growth, Vol.179, pp.605-610.
[7] Ramajothi J., Dhanushkodi S. and Nagarajan K. Cryst. Res. Technol.39, (2004) 414–420
[8] Ushasree P.M., Jayavel R. and Ramasamy P. (1999), Mater.Chem.Phys., Vol. 61, pp. 270–274.
[9] Selvakumar S., Rajasekar S.A., Thamizharasan K., Sivanesan S., Ramanand A. and Sagayaraj P. (2005), Materials Chemistry and Physics, Vol.93, pp. 356-360.
[10] Albert Cotton F. and Wilkinson G. (1970), 'Advanced Inorganic Chemistry', second Ed., Wiley Eastern limited, New Delhi.
[11] Ushasree P.M., Jayavel R. and Ramasamy P. (1999b), Materials Science and Engineering, Vol. B65, pp.153-158.

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