

Analysis of Dolomite of Balochistan (Pakistan) by Using X-Ray Fluorescence Spectroscopy (XFS), Simultaneous Differential Thermal Analysis (SDTA), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

¹SALMA JABEEN, ¹SYED MOHSIN RAZA*, ²KHALID MEHMOOD, ³SHABBAR ATIQ*
AND ⁴ZIA-UL-HAQ FAROOQI,

¹Department of Physics, University of Balochistan, Quetta, Pakistan.

²Institute of Bio Chemistry University of Balochistan, Quetta, Pakistan.

³PCSIR, Mustung Road, Quetta, Pakistan.

⁴PCSIR Complex, Off University Road, Karachi, Pakistan.

(Received 12th July 2006, revised 31st October 2006)

Summary: We deciphered new methods for calculation of thermodynamic parameters from SDTA, TGA & DSC techniques. The stretching of ionic bonds between Mg⁺⁺ and CO₃ and Ca⁺⁺ and CO₃, respectively is conformed on TGA curve at a temperature of 427 °K. At 728 K, an ore of dolomite is decomposed due to release of carbon dioxide and carbon monoxide gases and the left over substance is a mixture of MgO and CaO. The ionic bond breaking occurs at 723 °K. After this, there is reshuffling of ions due to which MgO and CaO are produced at 816 °K and 835 K, respectively. The chemists have to think about the chemical processes to separate MgO, a refractory material, from CaO, after baking dolomite upto about 840 °K.

Introduction

We used amorphous dolomite (MgCO₃ CaCO₃) collected from deposits of dolomite (raw material) found at Lak Baran village a distance of about 100 km., south in the vicinity of Khuzdar, a city in Balochistan. The X-Ray Fluorescence spectroscopy was performed by using XFS Machine (Model EDX-700) Shimadzu, Japan. The quantitative results of dolomite with all constituent elements and their oxides are shown in Tables-1 and 2, respectively. The peak lists are shown in Figs. 1 and 2. Fig. 2 is a resolved XFS. By employing diverse techniques, the results are shown in Tables 3-7 respectively.

Table-1: XFS analysis on Dolomite.

Analyte	Result	(Std. Dev)	Proc-Calc.	Line	Int.(cps/ uA)
Mg	92.167 %	(0.451)	Quan-FP		1.170
Eu	2.240 %	(0.156)	Quan-FP		0.427
Ca	2.150 %	(0.016)	Quan-FP		0.562
Si	1.639 %	(0.039)	Quan-FP		0.073
Tm	0.578 %	(0.043)	Quan-FP		0.427
K	0.567 %	(0.040)	Quan-FP		0.023
Ti	0.276 %	(0.020)	Quan-FP		0.306
Fe	0.175 %	(0.013)	Quan-FP		0.370
S	0.115 %	(0.002)	Quan-FP		0.123
Cu	0.059 %	(0.005)	Quan-FP		0.384
Cl	0.033 %	(0.002)	Quan-FP		0.048

The SDTA-TGA [1] for dolomite sample was used with simultaneous differential thermal

Table-2: XFS analysis with constituent oxide of Dolomite.

Instruments: EDX-700	Atmosphere ac.			Collimator: 10 (mm)		Spin off	
	TG	KV	uA	Fl Acq. (keV)	Anal. (keV)	Time (sec)	D.T. (%)
Ti-U	Rh	50	260-Auto	0.0-40.		Real - 99	26
Na-Sc	Rh	15	506-Auto			Real - 100	
Analyte	Result	(Std. Dev.)	Proc-Calc	Line	Int. (cps/ uA)		
MgO	92.167%	(0.470)	Quan-FP	mgKa	1.170		
SiO ₂	2.240 %	(0.031)	Quan-FP	SiKa	0.071		
CaO	2.150 %	(0.008)	Quan-FP	CaKa	0.562		
Eu203	1.639 %	(0.058)	Quan-FP	EuLa	0.427		
m	0.578 %	(0.017)	Quan-FP	K Ka	0.023		
Tm 203	0.567 %	(0.015)	Quan-FP	TmLa	0.427		
m	0.276 %	(0.011)	Quan-FP	TiKa	0.306		
SO ₃	0.175 %	(0.002)	Quan-FP	S Ka	0.123		
Fe ₂ O ₃	0.115 %	(0.001)	Quan-FP	FeKa	0.370		
CuO	0.059 %	(0.005)	Quan-FP	CuKa	0.384		
Cl	0.033 %	(0.002)	Quan-FP	ClKa	0.048		

*To whom all correspondence should be addressed.

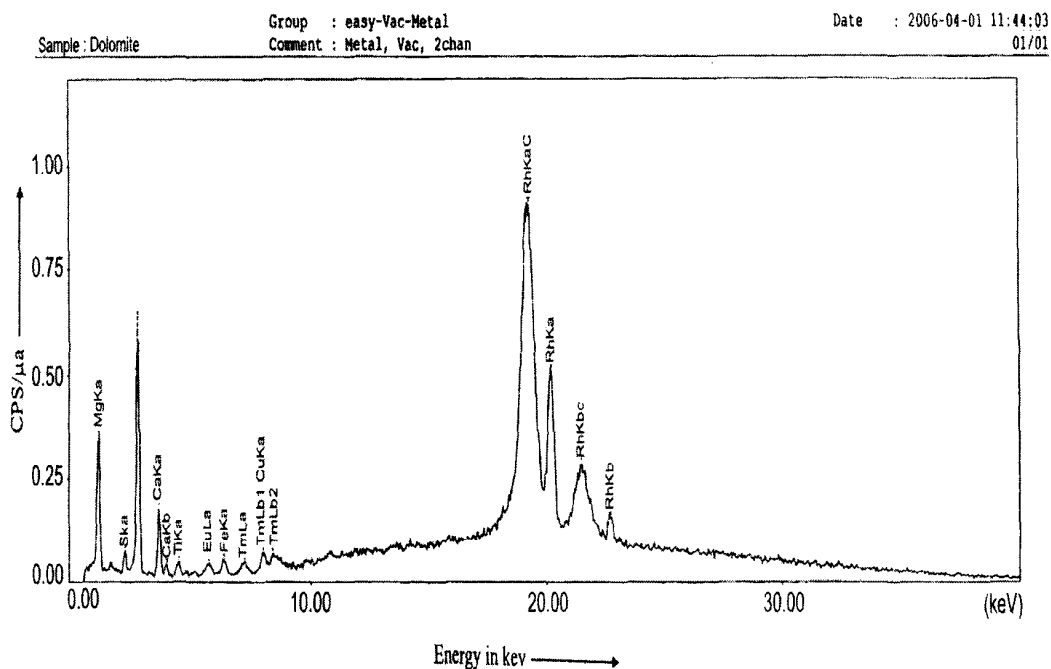


Fig. 1: Shows X-ray fluorescence spectroscopic analysis on dolomite.

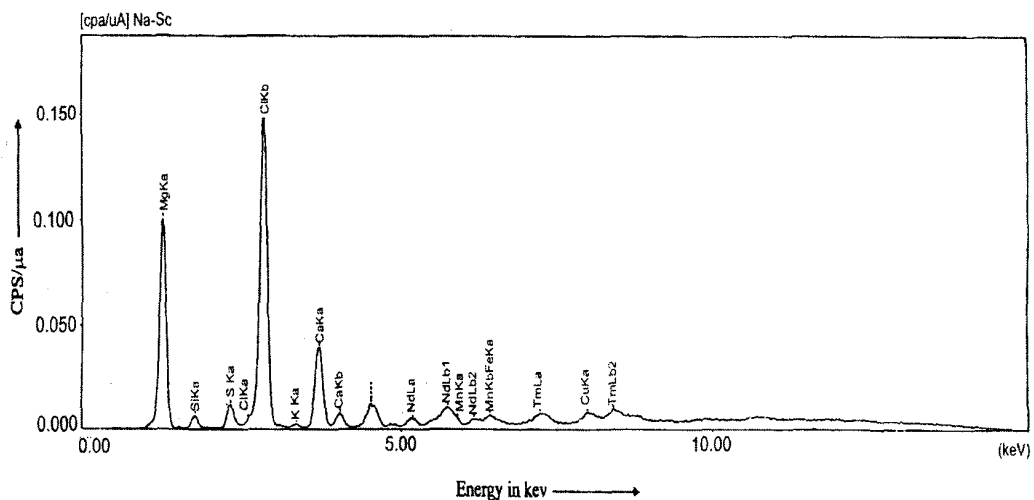


Fig. 2: Shows X-ray fluorescence spectroscopic analysis (XFS) on dolomite with better resolution.

Table-3: Shows simultaneous differential thermal analysis with exothermic peaks on dolomite.

Sample	Mass of the sample (kg)	Exothermic Peak	Peak Temp T_p (K)	Peak width ΔT (K)	Specific heat capacity (mcal/ kg.K)	Enthalpy ΔH (kJ)
MgCO ₃ CaCO ₃	56.0760x10 ⁻⁶	1	725	437	384	9.40

Table-4: Shows simultaneous differential thermal analysis with endothermic peaks on dolomite.

Sample	Mass of the sample (kg)	Peak nature	Peak temp. T_p (K)	Peak width ΔT (K)	ΔU (Internal energy) pp JK^{-1}
$\text{MgCO}_3\text{CaCO}_3$	56.0760×10^{-6}	1. Endothermic Peak.	449	491	6771
		2. Endothermic Peak.	928	370	5104

analysis (Model 8511^e Mattler Toledo, Switzerland). The sharp exothermic and endothermic peaks were observed and considered for the calculation of following parameters. For enthalpy, we used

$$\Delta H = m \int_{T_1}^{T_2} c(T) dT \text{ or } \Delta H = mc\Delta T \text{ Joules.}$$

Where 'm' is the sample mass in kilogram (kg).

ΔT is the width of exothermic peak in kelvin, $c(T)$ is the specific heat capacity measured in joules. Ordinarily, the masses are considered by the chemists in grams but the physicists practice SI units. This is why the mass was taken in kilogram and temperature in kelvin. The specific heat, *i.e.*, $c(T)$ in SI units was measured in $\text{cal/ kg. } ^\circ\text{K}$. There are two types of chemical reactions, *i.e.*,

- (i) Exothermic in which energy is required or absorbed.
- (ii) Endothermic in which energy is released due to any physical or chemical changes. In our results, we have one exothermic and two endothermic peaks in DTA and one exothermic and two endothermic peaks in TGA, respectively.

The presence of endothermic peaks confirms the structural changes associated with energy releasing processes, such as thermal stresses causing heating and annealing. Gibbs free energy is also associated with this reaction.

The enthalpy energies are calculated from exothermic peaks. With differential scanning calorimetry analysis (DSCA) (Model 822^e Mattlertoledo Switzerland), we calculated the internal energy from exothermic peaks and the latent heat of fusion from endothermic peaks. We utilized the formula mostly utilized by chemical engineers [2] *i.e.*,

$c(T) = C = 0.132 + 1.56 \times 10^{-4}T_p + 2.64 \times 10^{-7}T_p^2$

$$c(T) = C = 0.132 + 1.56 \times 10^{-4}T_p + 2.64 \times 10^{-7}T_p^2$$

where T_p is the observed exothermic peak temperature in DTA.

For Gibb's free energy we utilized the classical formula, $\Delta U = k\Delta T$

where $^{\circ}\text{K}$ is the Boltzman constant for endothermic peaks and ΔT is the peak width observed in DTA.

For internal energy we utilized the universal formula, *i.e.*, $\Delta U = k\Delta T$

where ΔT is the exothermic peak width observed in DSC.

For latent heat of fusion we utilized $\Delta U = k\Delta T$,

where ΔT is the endothermic peak width observed in DSC.

We observed threshold, *i.e.*, a transition, in thermogravimetry analysis, which can be associated with entropy (measure of thermal disorder in a system). We utilized the standardized formula

$$\Delta S = \frac{mc\Delta T}{T_t} \text{ J/K}$$

where ΔT is the peak width and T_t is the transition temperature of threshold.

Tables-3, 4, 5, 6 and 7 show all the details along with above mentioned calculated parameters. We calculated useful thermodynamic parameters for dolomite by employing diverse techniques. Some of the new methods for calculating the thermodynamic

Table-5: Shows differential scanning calorimetry analysis with exothermic peaks on dolomite.

Sample	Mass of the sample (kg)	Exothermic peak	Peak temp. T_p (K)	Peak width ΔT (K)	Specific heat capacity (m cal/ kg.K)	Internal energy (mJ)
$\text{MgCO}_3\text{CaCO}_3$	8.8×10^{-6}	1	47	298	247.	0.7

Table-6: Shows differential scanning calorimetry analysis with endothermic peaks on dolomite.

Sample	Mass of the sample (kg)	Peak nature	Peak Temp T_p (K)	Peak width ΔT (K)	Latent heat of fusion (pp JK^{-1})
$\text{MgCO}_3\text{CaCO}_3$	8.8×10^{-6}	1. Endothermic Peak.	816	289	3994
		2. Endothermic Peak.	835	281	3877

Table-7: Shows calculation of entropy with thermo gravity analysis on dolomite.

Sample	Mass of the sample (kg)	Peak nature	Transition temp. T_i (K)	Transition width ΔT (K)	Entropy ($\mu\text{J/K}$)
$\text{MgCO}_3\text{CaCO}_3$	57.0118×10^{-6}	Threshold	892	333	0.1

where k stands for 10^3 , p for 10^{12} , pp for 10^{24} , μ for 10^{-6} and m for 10^{-3} .

parameters are deciphered such as for entropy, latent heat of fusion, Gibbs free energy and internal energy by employing the already mentioned techniques. We

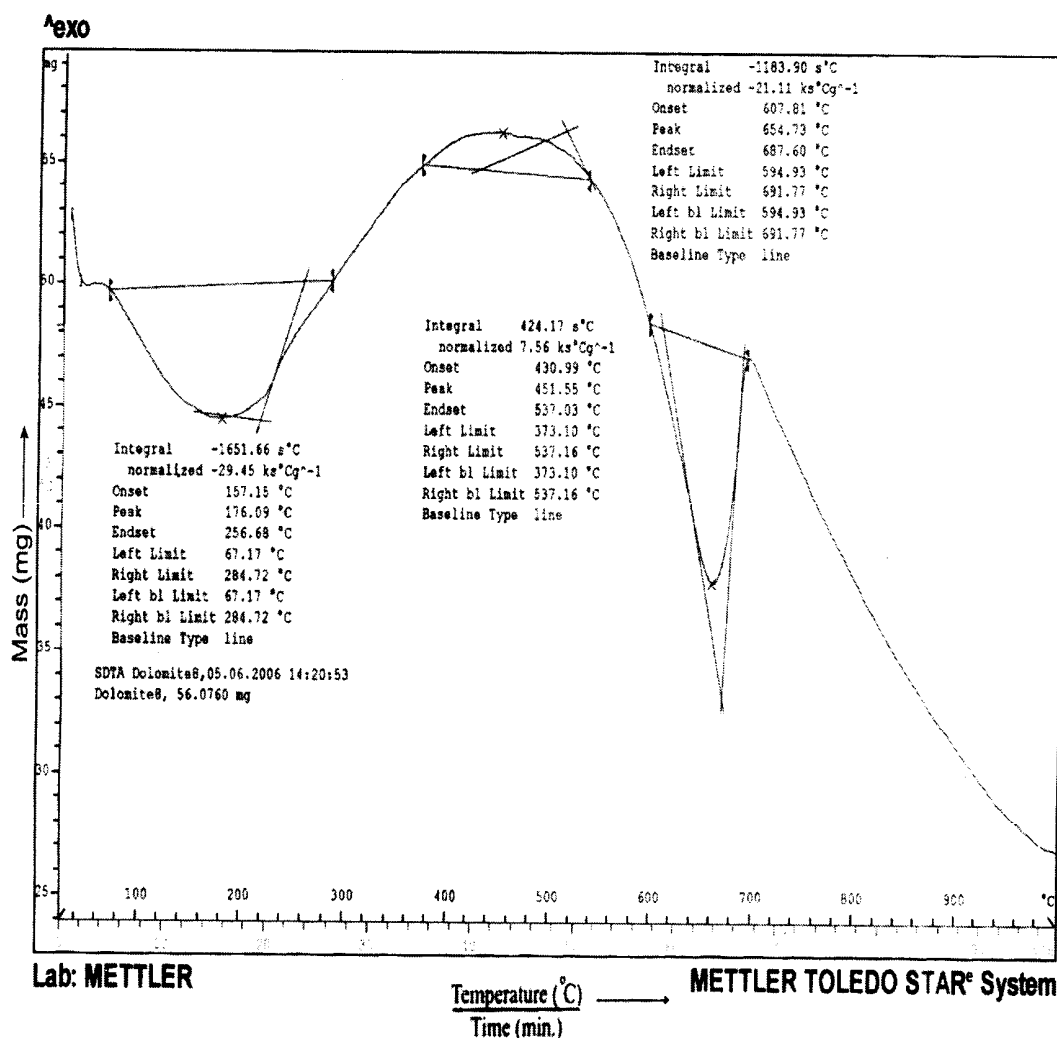


Fig. 3: Shows differential thermal analysis on dolomite.

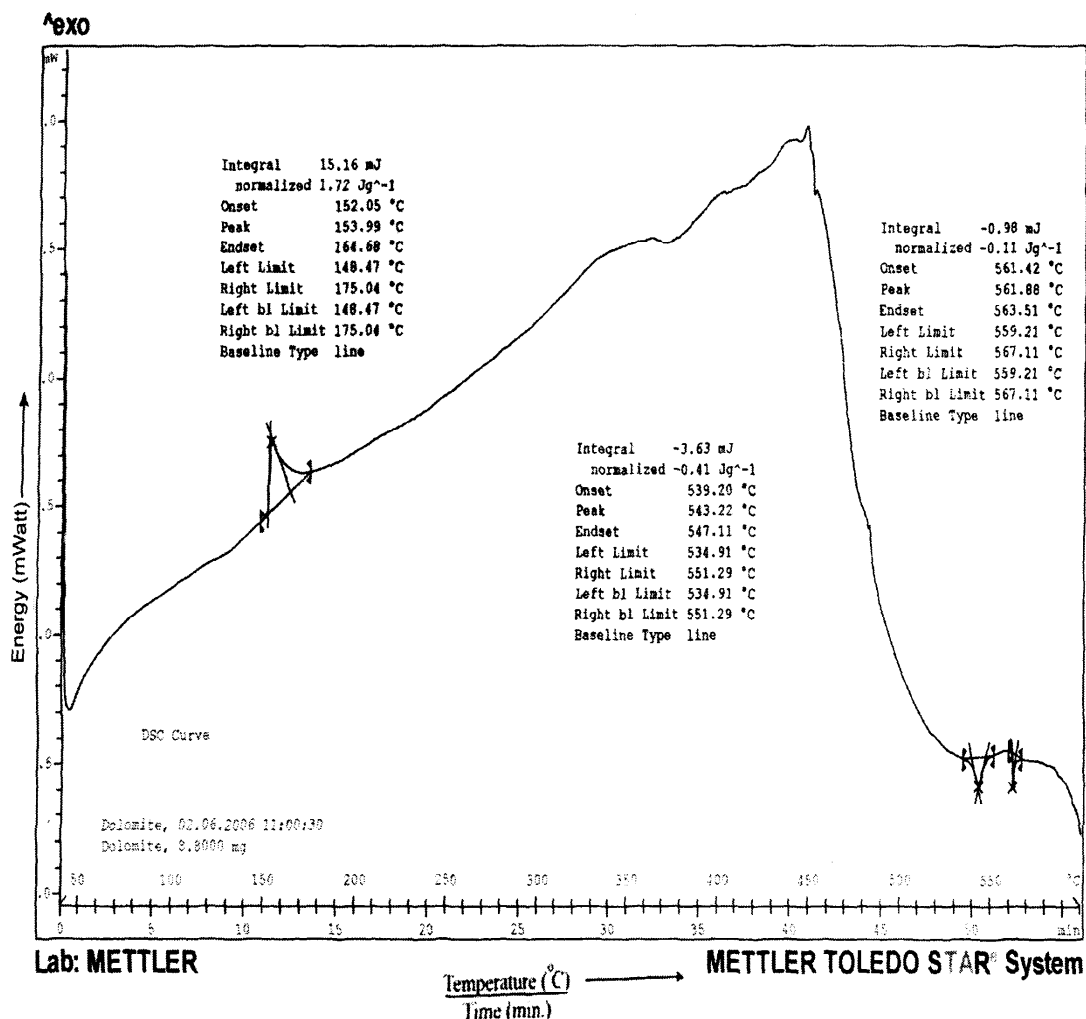


Fig. 4: Shows thermogravimetry analysis on dolomite.

used new methods also for the calculation of thermodynamic parameters by using DTA [3]. The same method is repeated for SDTA. The SDTA, TGA, DSC results are shown in Fig. 3, Fig. 4 and Fig. 5 respectively.

Results and Discussion

We observed a change at a transition temperature of 728 °K which is indicated with sudden drop in TGA. With the sudden drop of TGA at 728 K, inverted peaks at 816 °K and 835 °K are observed. These peaks after the threshold are indicative of the fact that there are some microscopic

changes such as interstitial formation or vacancies due to migration of ions are produced. We can, therefore, ascertain that magnesium and calcium oxides are produced at such temperatures with release of carbon dioxide and carbon mono oxide gases. We have to evolve a chemical process to separate CaO from MgO.

MgO is a refractory material used to sustain temperatures of the order of 2,273 °K to 3,273 °K without heat transfer to the surrounding. We offer the chemists to look into the chemical processes for separation of CaO from MgO after treating dolomite at 816 °K and 835 K, respectively.

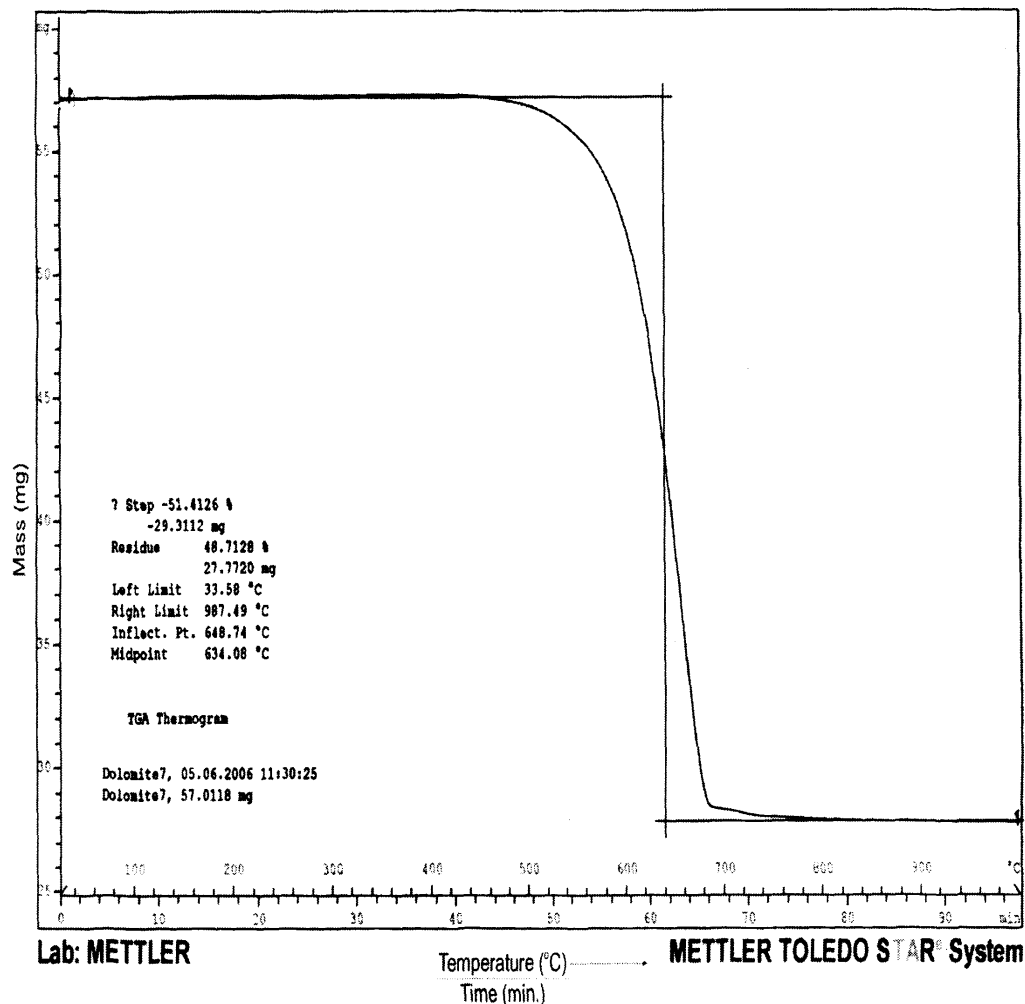


Fig. 5: Shows differential scanning calorimetry analysis on dolomite.

TGA curve at temperature 427 °K shows a new behaviour related to stretching of ionic bonds due to absorption of thermal energy. This is confirmed with dielectric measurements at about the same temperature in dolomite [4].

Experimental

We used EDX-700 Shimadzu, Japan for XFS (X-ray fluorescence spectroscopy). The measurements are performed with X-Ray tube with Rh (rhodium) source and that without any filter. We used the software DXP-700E and performed the measurements in Vacuum.

We used Model 8511^c Mettler Toledo, Switzerland Stare System for SDTA (Simultaneous differential thermal analysis), DSC (differential

Scanning 21 Calorimetry) and TGA (thermogravimetry analysis) for our sample.

References

1. S. M. M. R. Naqvi, N. Shams, S. D. H. Rizvi, S. Fatima and S. M. Raza, Proc. of 5th National Chemistry Conf. Quaid-e-Azam University Islamabad, Pakistan, 200. (25, Oct. 1993).
2. C. Chapra and R. P. Canale, *Numerical Methods for Engineers*, McGraw Hill, New York, 438, (1985).
3. S. M. M. R. Naqvi, S. D. H. Rizvi, S. M. Raza, S. Rizvi, A. Hussain and F. Rehman, *Jour. Chem. Soc. Pak.*, **24**, 1 (2002).
4. Mushtaq Gormani, Fazl-ur-Rehman, M. Ashfaq Ahmed and Syed Mohsin Raza, *Jour. Chem. Soc. Pak.*, **28**, 414 (2006).