

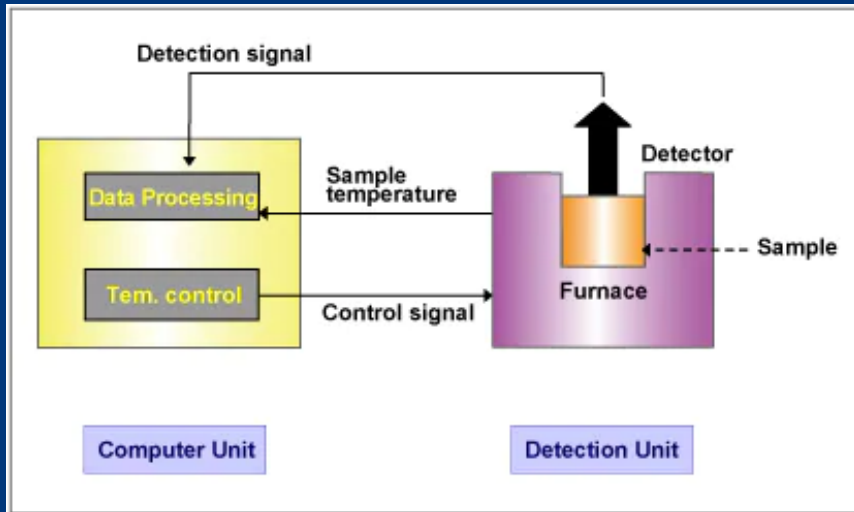
SERAMİK KARAKTERİZASYONUNDA TERMAL ANALİZ KULLANIMI

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toplano@sakarya.edu.tr

Termal Analiz Nedir?

Termal analiz; sıcaklık değişmesine karşı bir katı maddenin fiziksel ve kimyasal reaksiyonlar sonucunda özelliklerindeki değişimlerin ölçülmesi ve yorumlanmasıdır.

Sıcaklığa bağlı değişkenin ne olduğuna (enerji, ağırlık, boyut, vs.) bakılmaksızın ölçüm yapılır.



Temperature programmer



Sample in furnace with controlled atmosphere

↓ x axis

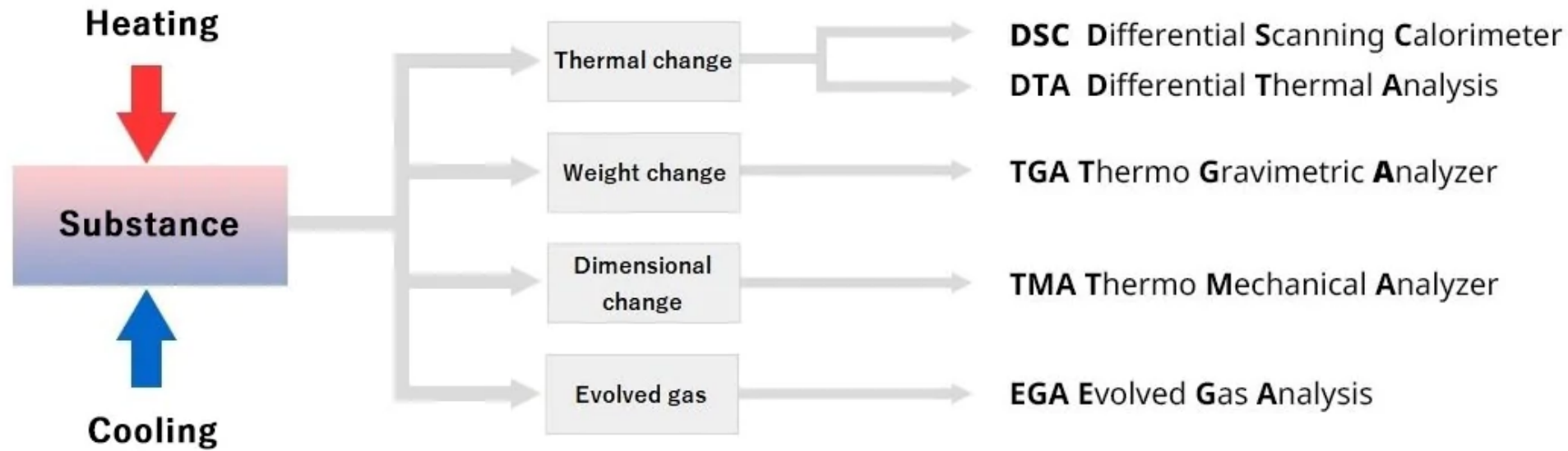
temperature

↓ y axis

property

Output: Plot of the property (y axis) versus T.

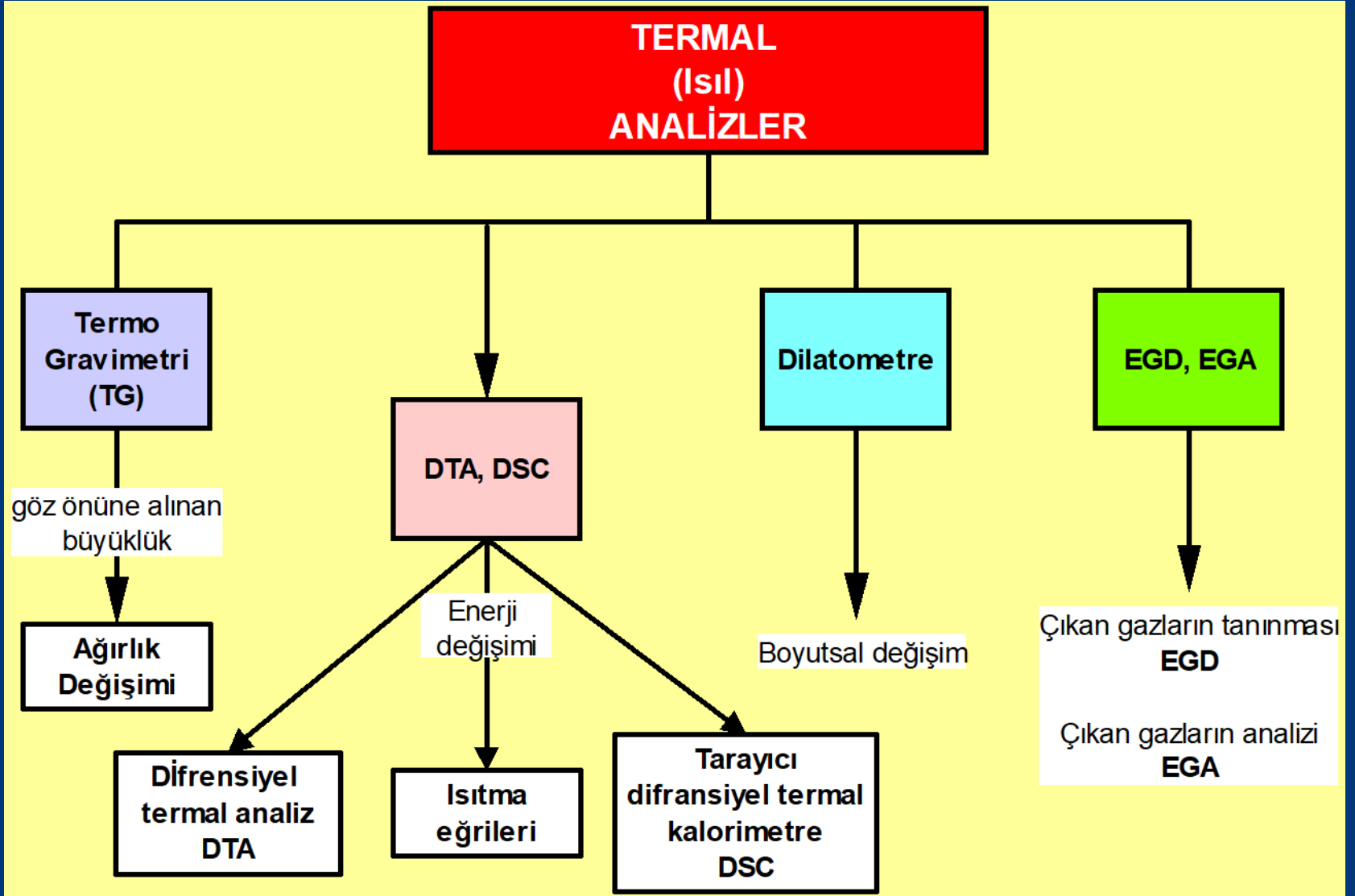
Termal Analiz Yöntemleri



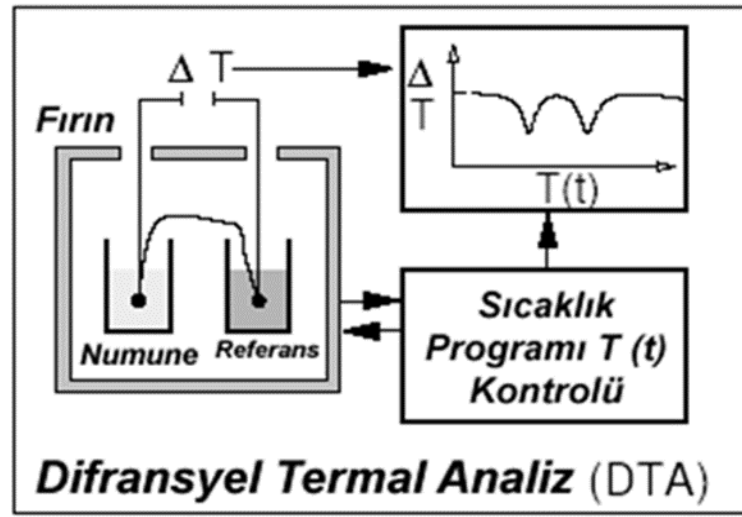
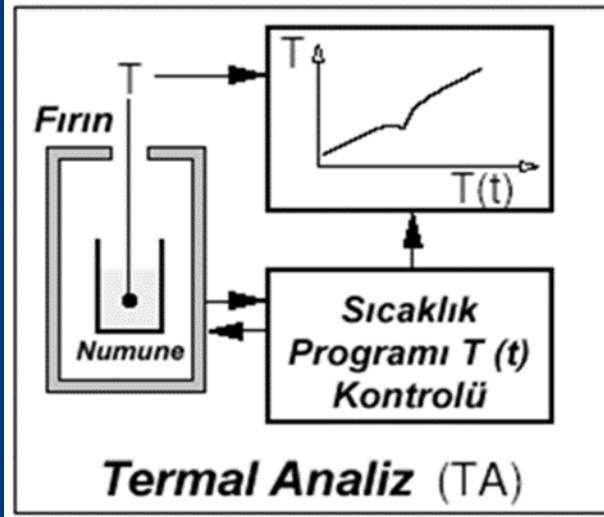
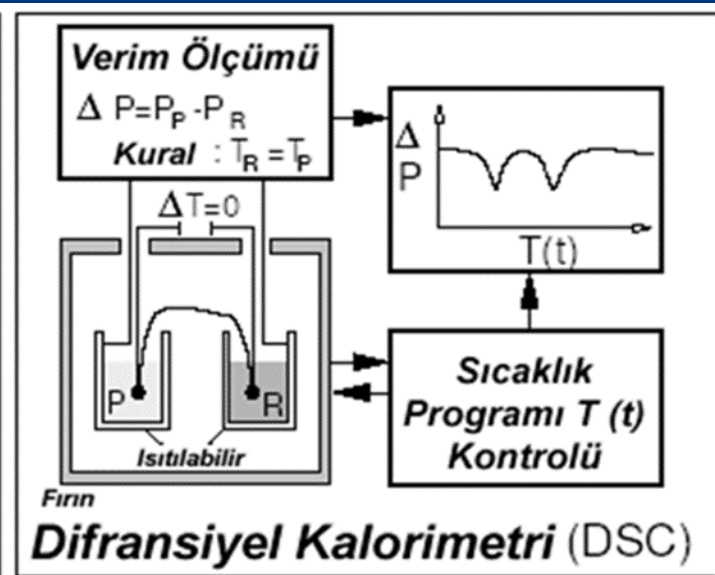
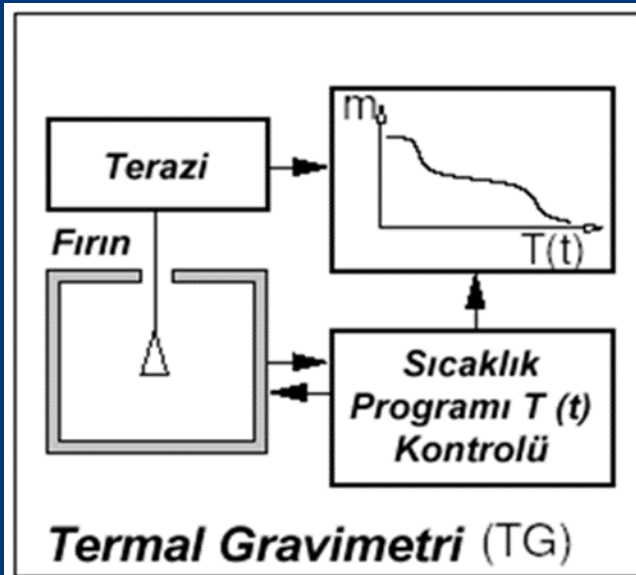
- Faz dönüşümleri
- Ergime
- Sublimasyon
- Termal parçalanma

- Cam geçişleri
- Oksitlenme
- Redüklenme
- Boyutsal değişimler

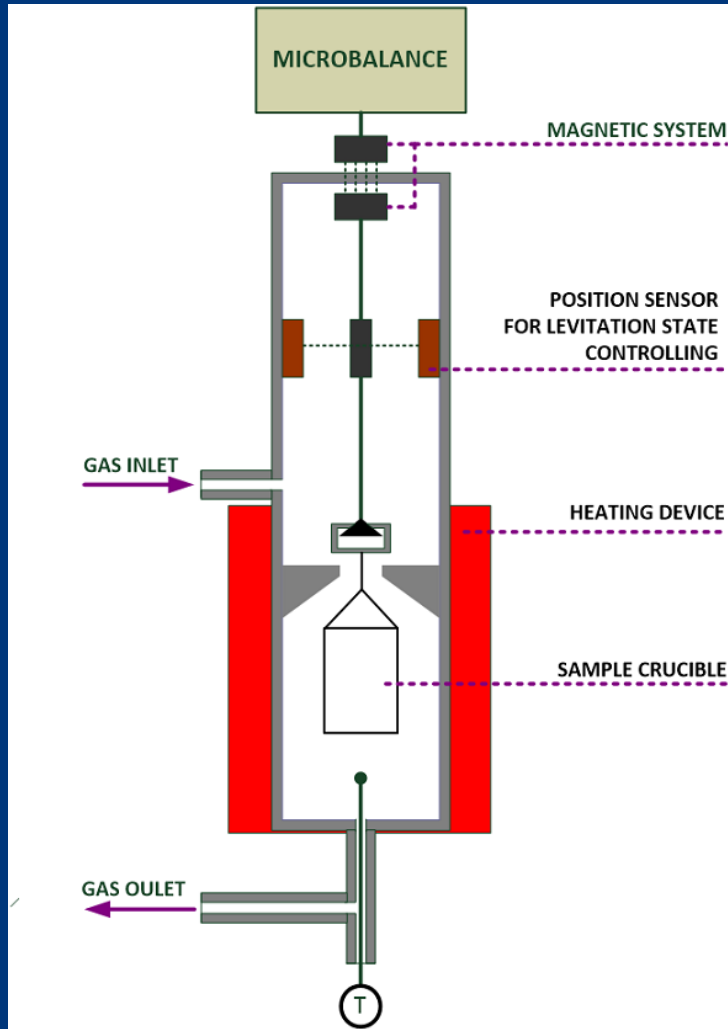
Termal Analiz Yöntemleri



Termal Analiz Yöntemleri



Thermo Gravimetric Analyzer (TGA/TG)



Bir maddenin deęiřik řartlarda kütlesini koruyabilme kabiliyetini (termal stabilite) incelemek için kullanılan bir yöntemdir.

Termo-gravimetrimin esası, bir maddenin sıcaklıęa baęlı olarak meydana gelen reaksiyonların, kütlesindeki deęiřimlerin özel bir terazide sürekli olarak tartılması yardımı ile incelenmesidir.

Bu gibi cihazlara da Termo-balans denilmektedir.

Kısaca, termo-gravimetrik analiz (TG), numunenin kütlesindeki deęiřmeyi sıcaklıęın fonksiyonu olarak kaydeden bir tekniktir.

Thermo Gravimetric Analyzer (TGA/TG)

İzoterm veya statik TG: Numune kütlesi sabit sıcaklıkta zamanın fonksiyonu olarak ölçülür.

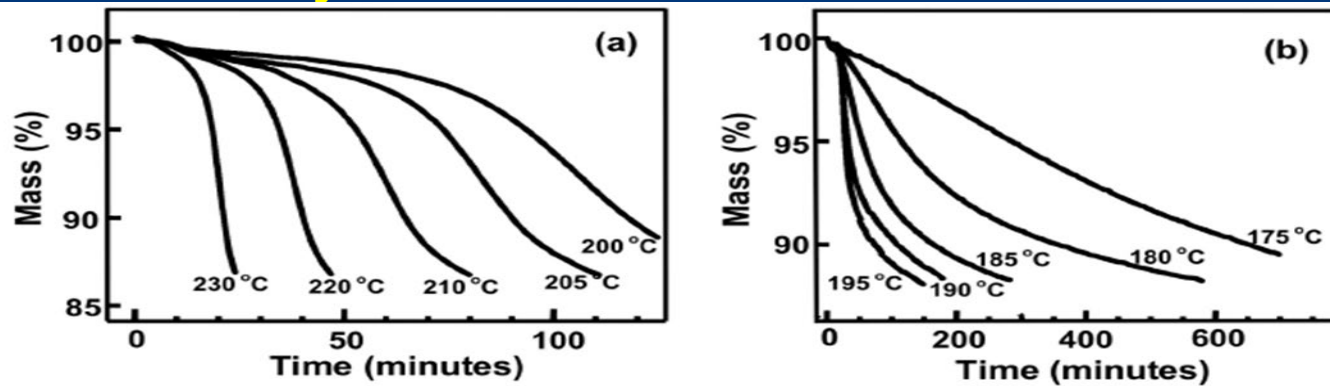


FIGURE 7 - TG curves obtained under isothermal conditions and dynamic air atmosphere ($50 \text{ mL} \cdot \text{min}^{-1}$) for the rifampicin samples: (a) polymorph I and (b) polymorph II.

Dinamik TG : Numune önceden belirlenen ve belli oranda artan (tercihan linear) bir sıcaklık ortamına ısıtılır.

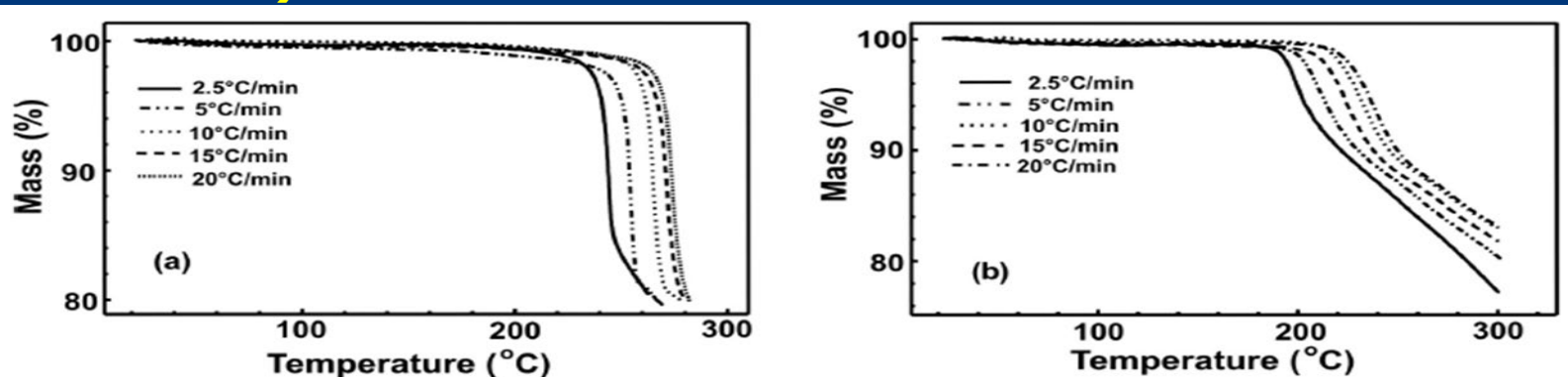
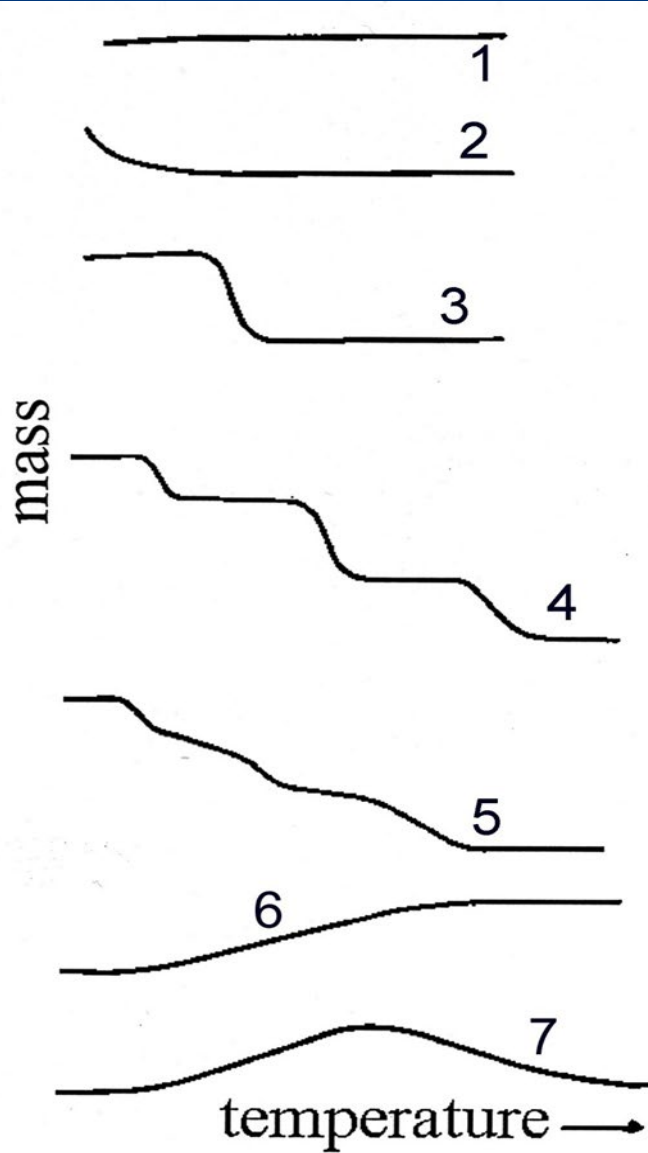


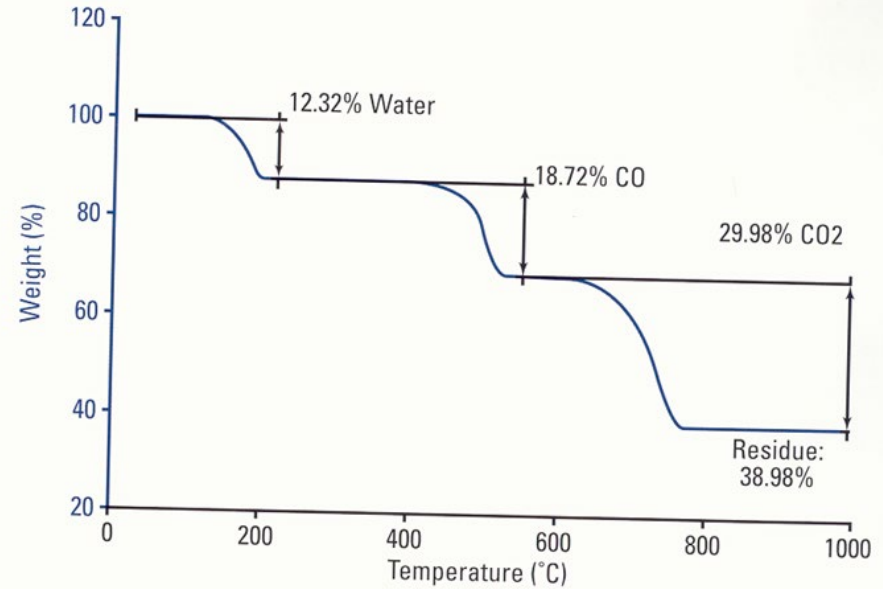
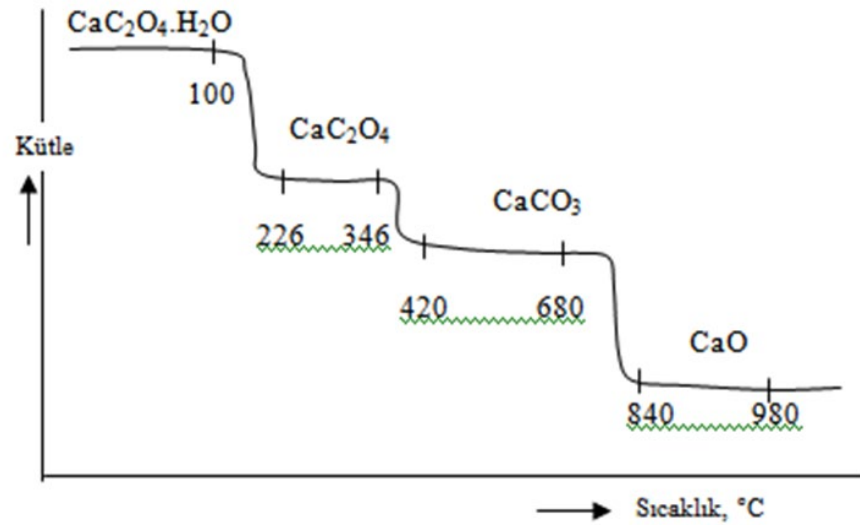
FIGURE 5 - TG curves obtained under dynamic air atmosphere and with different heating rates for the rifampicin samples: (a) polymorph I and (b) polymorph II.

Thermo Gravimetric Analyzer (TGA/TG)

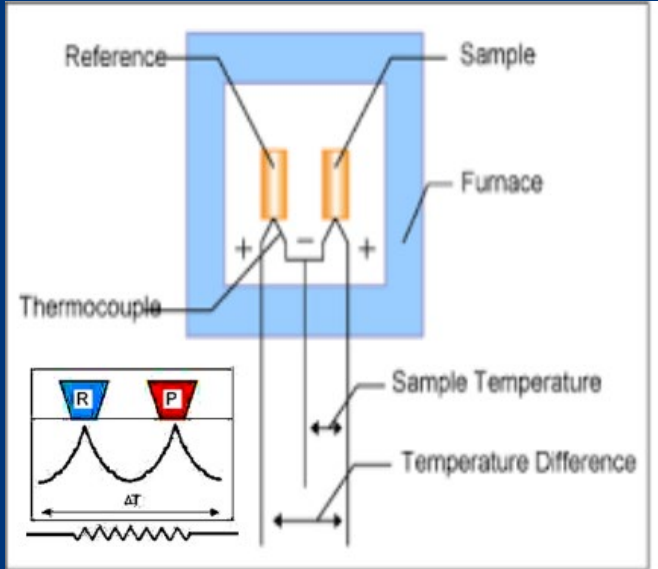


1. Kütlesel bir değişim yok
2. Kuruma sonunda meydana gelen kütlede azalma
3. Tek adımda dekompozisyon (parçalanma) sonucunda meydana gelen kütlede azalma
4. Birkaç adımda dekompozisyon (parçalanma) sonucunda meydana gelen kütlede azalma
5. (4)'e benzer fakat her adım sonucunda oluşan bir ara faz yok veya ısıtma hızı çok yüksek
6. Oksitlenme sonucunda meydana gelen kütle artışı
7. (6)'ya benzer fakat oluşan ürün yüksek sıcaklıkta dekompozisyona uğruyor

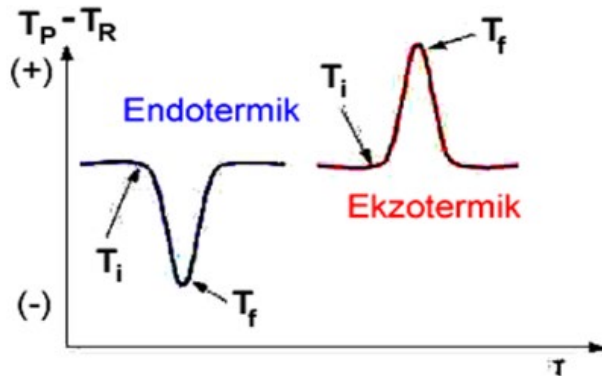
Thermo Gravimetric Analyzer (TGA/TG)



Differential Thermal Analyzer (DTA)

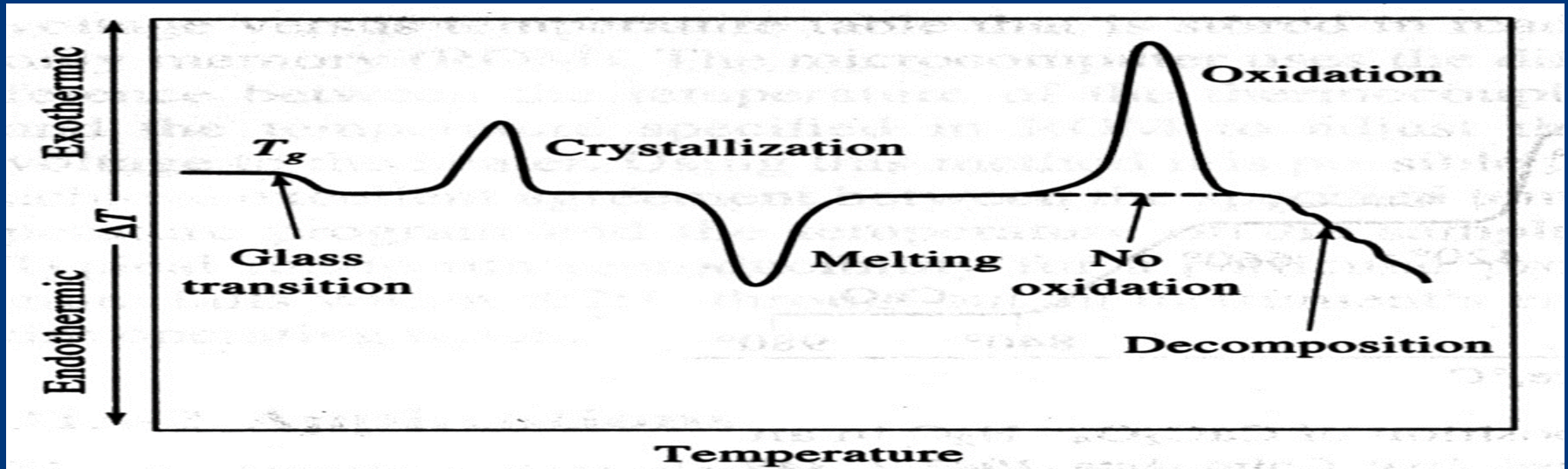


Detekte edilen termal sonuç için T_i ve T_f , başlangıç ve bitiş sıcaklığı



- Bu yöntemde numune ve termal olarak inert ($\alpha\text{-Al}_2\text{O}_3$) olan referans maddeye aynı sıcaklık programı uygulanır.
- İkisi arasındaki fark, sıcaklığın bir fonksiyonu olarak ölçülür.
-
- Bu iki madde birlikte ısıtılır ve sıcaklık lineer bir şekilde arttırılır.

Differential Thermal Analyzer (DTA)



Endotermik

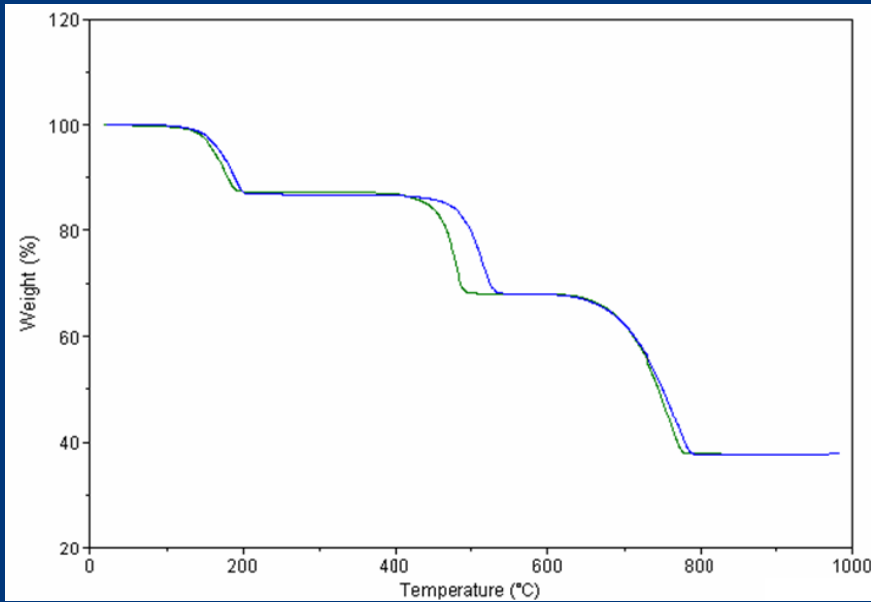
- Dehidratasyon
- Dekompozisyon
- Ergime
- Buharlaşıma
- Süblimasyon

Exotermik

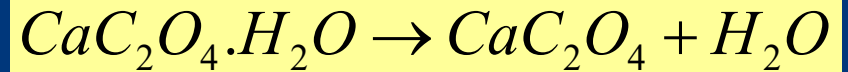
- Amorflaşma
- Amorf halden kristalleşme
- Katılaşma
- Kristal yapıdan yeni bir kristal yapı oluşumu

Differential Thermal Analyzer (DTA)

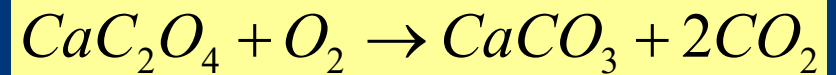
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in air and nitrogen



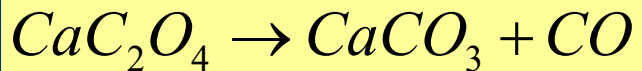
(1) Endo



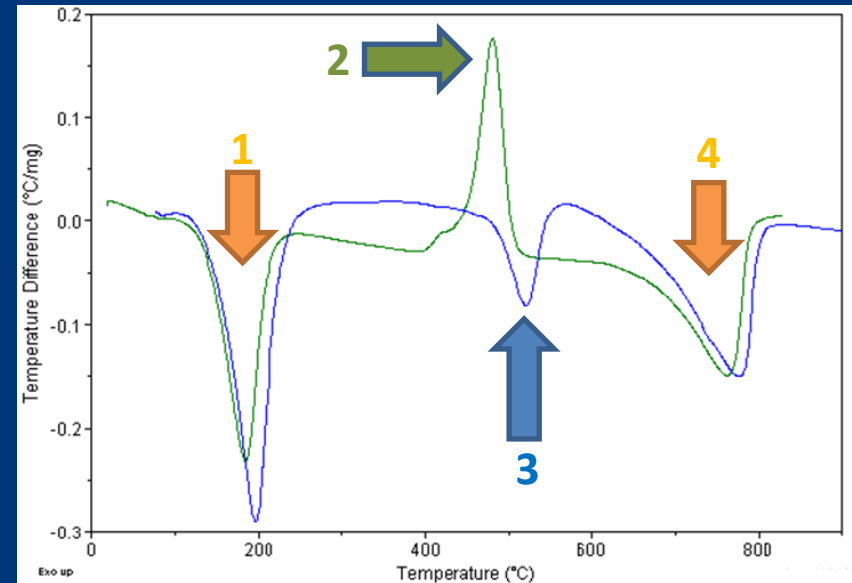
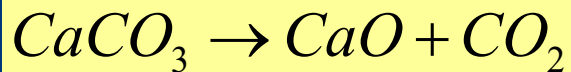
(2) Exo (Hava)



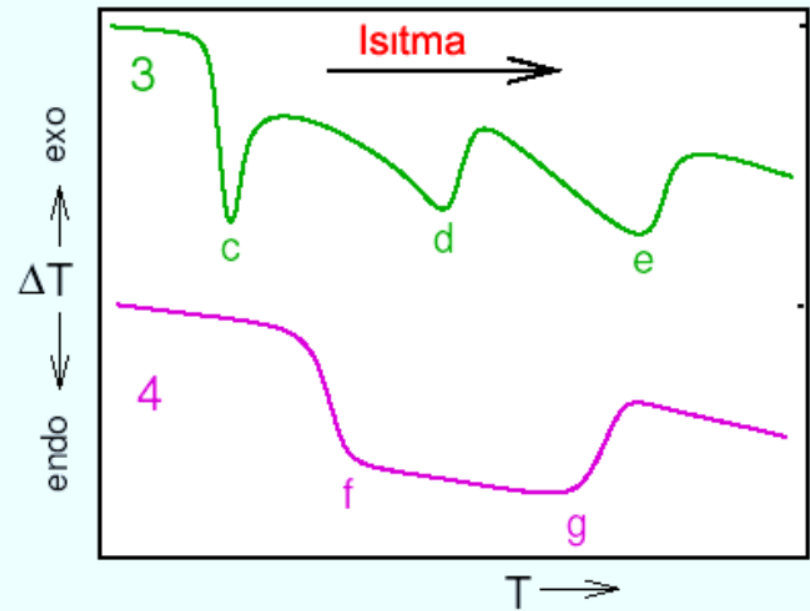
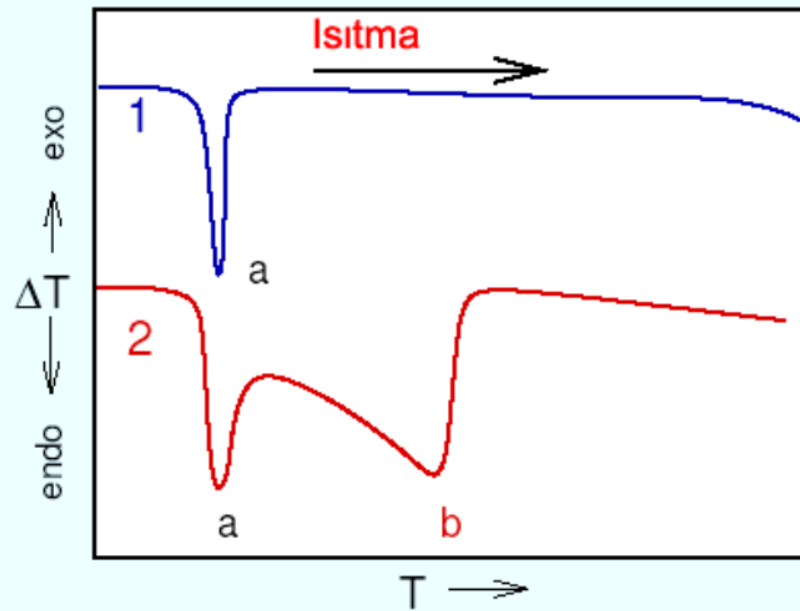
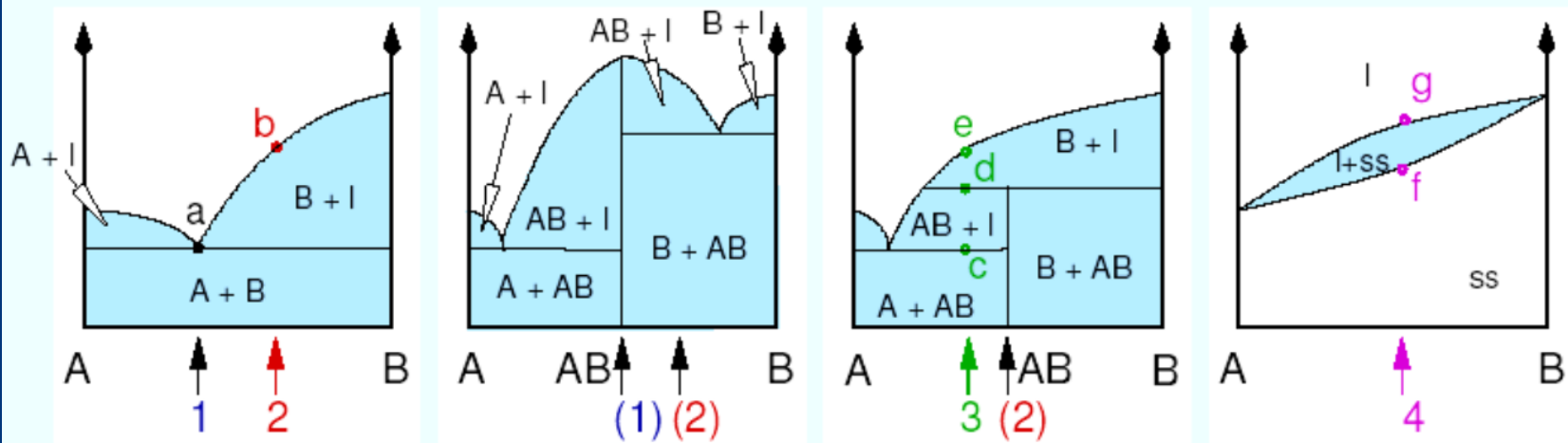
(3) Endo (Azot)



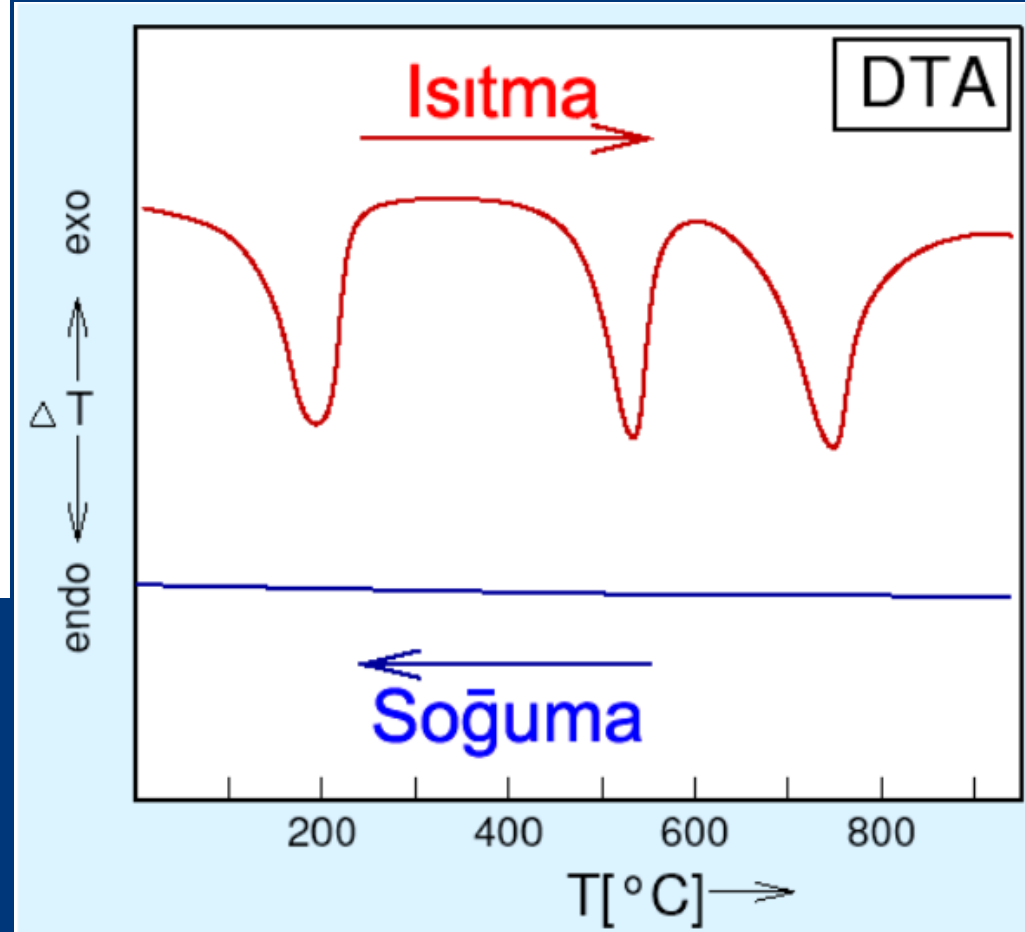
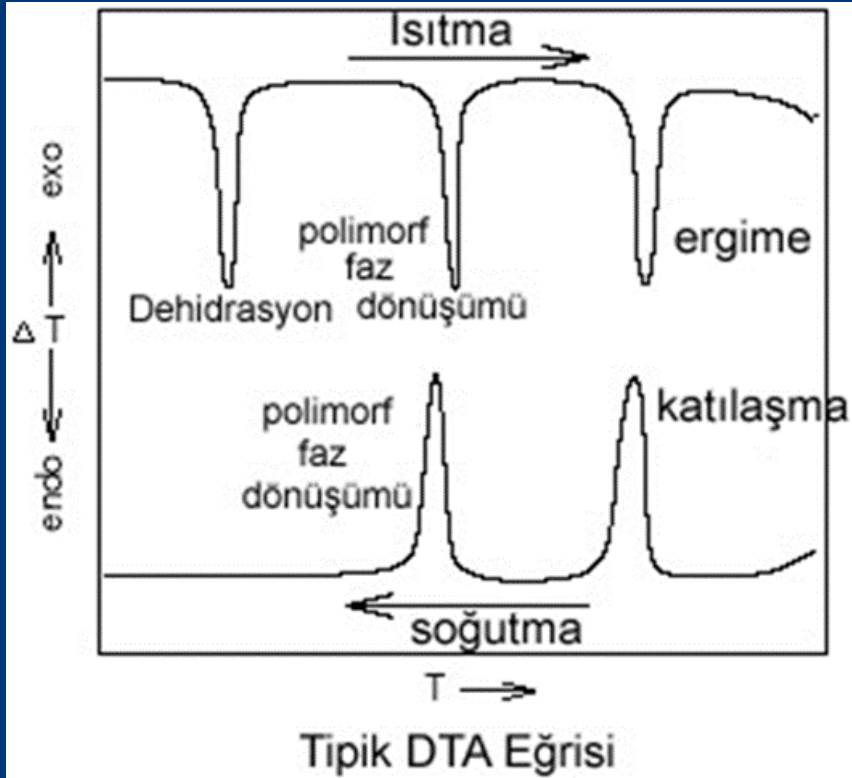
(4) Endo



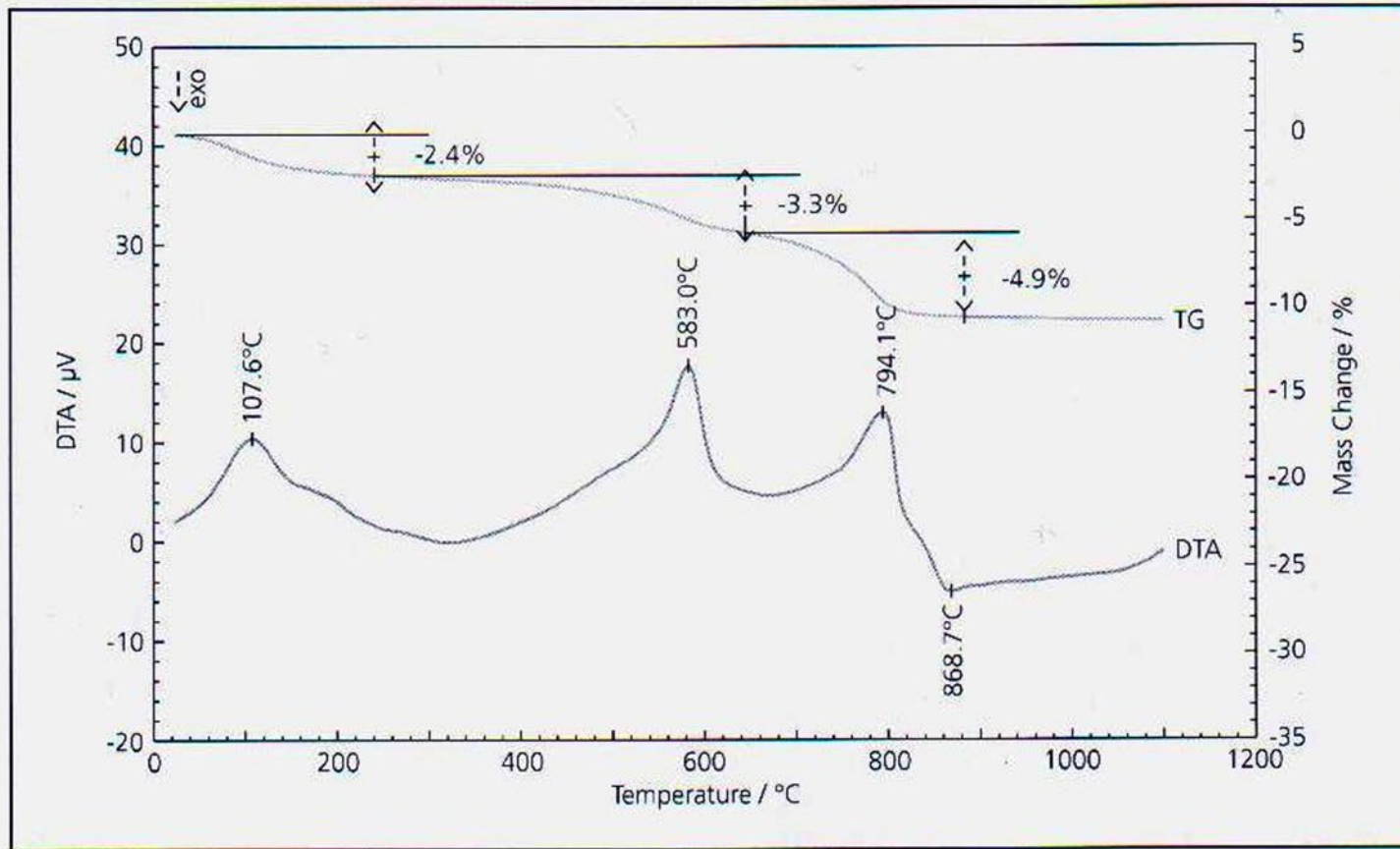
Differential Thermal Analyzer (DTA)



Differential Thermal Analyzer (DTA)

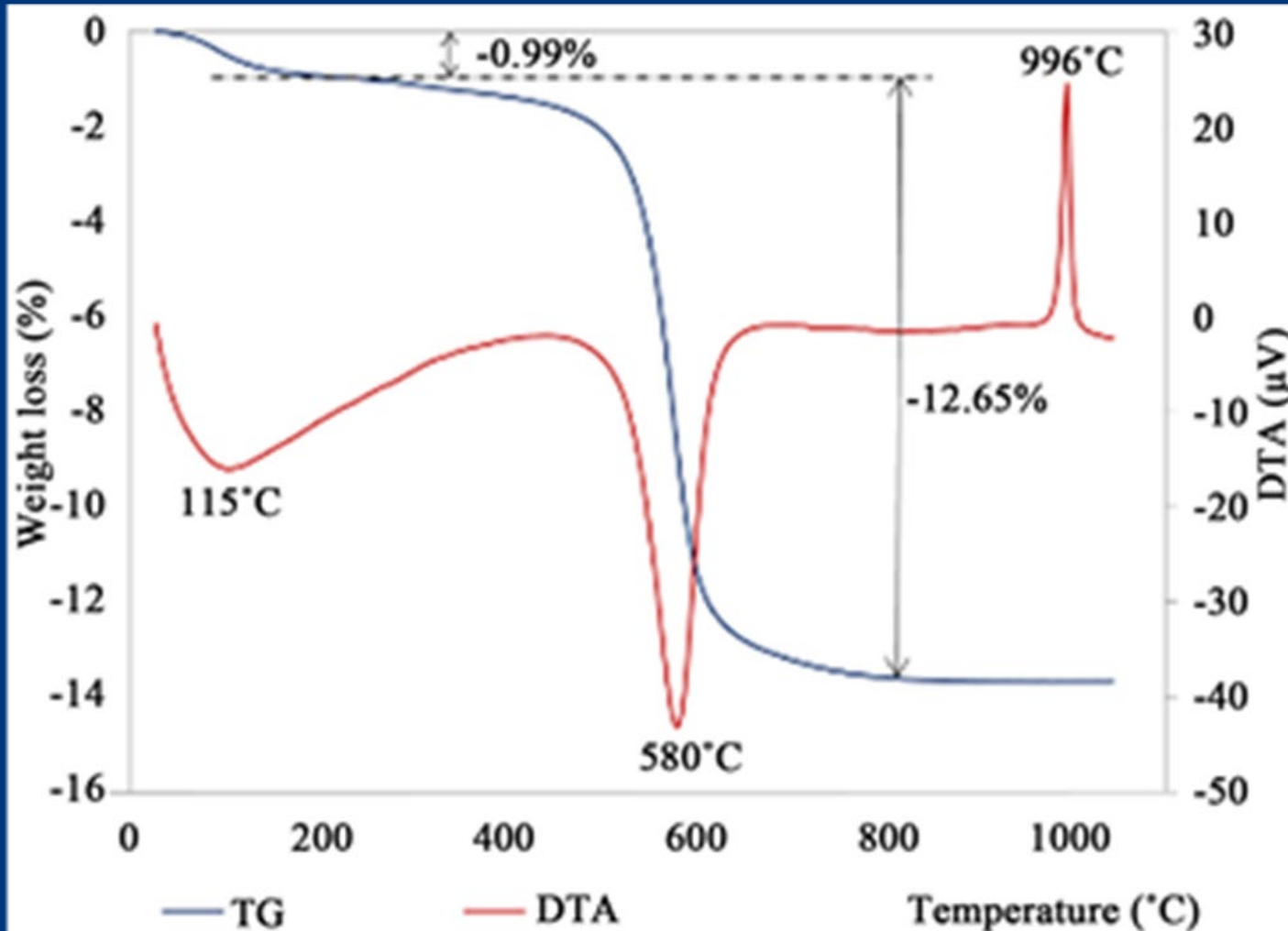


Differential Thermal Analyzer (DTA)



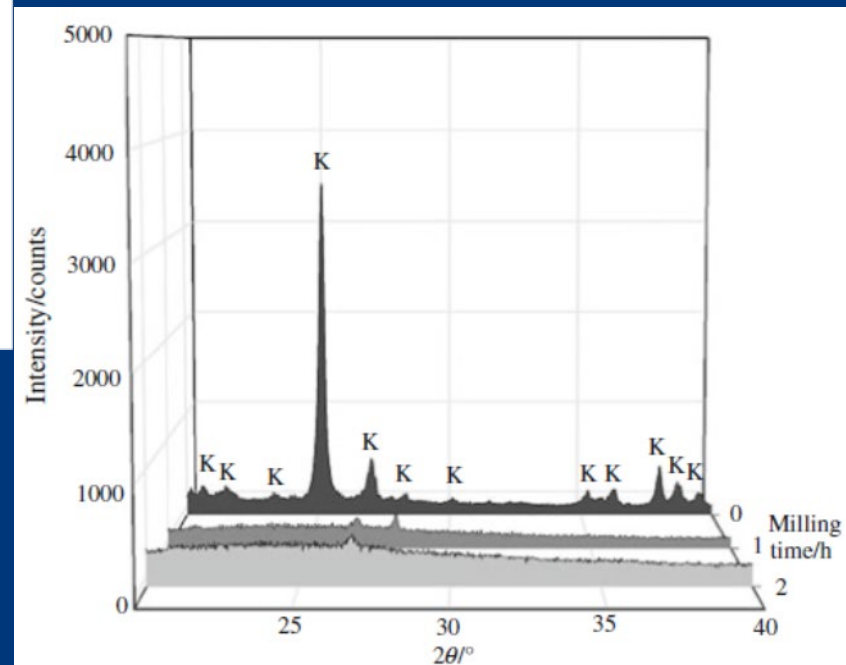
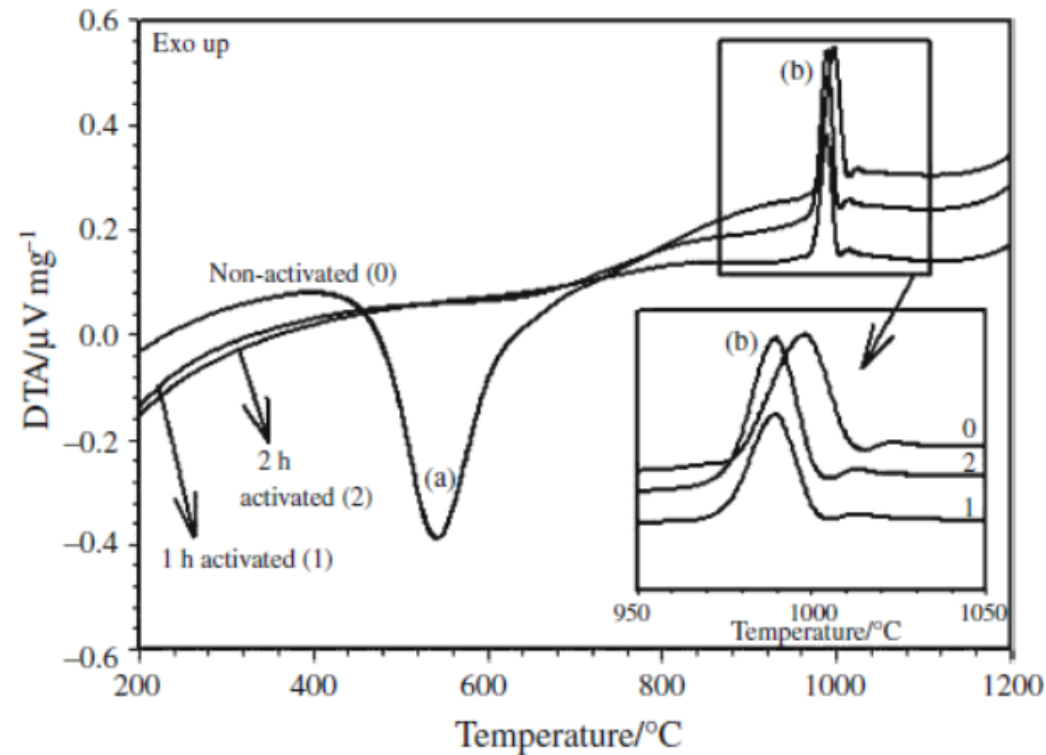
Yer Karosu Kili

Differential Thermal Analyzer (DTA)

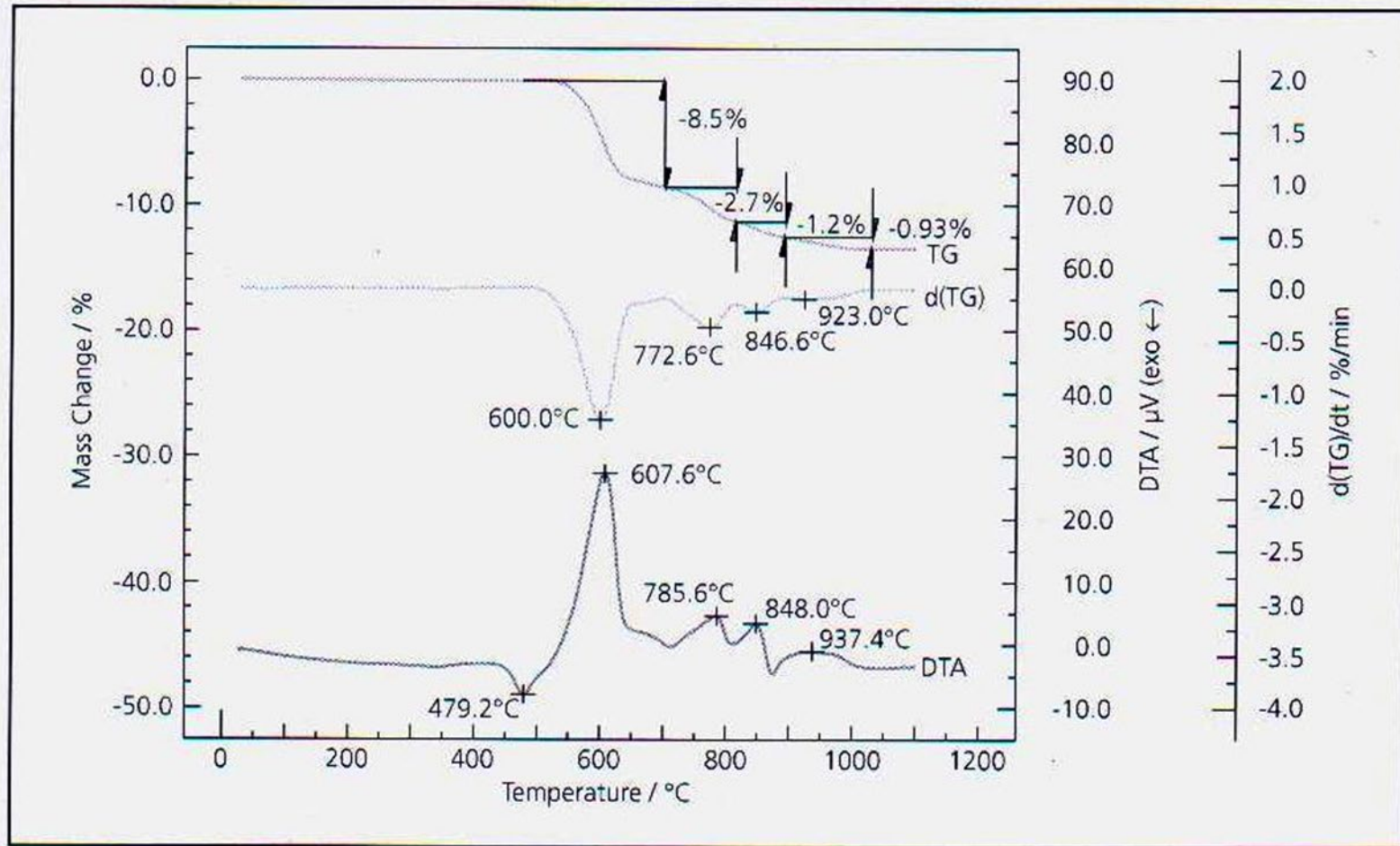


Kaolen

Differential Thermal Analyzer (DTA)

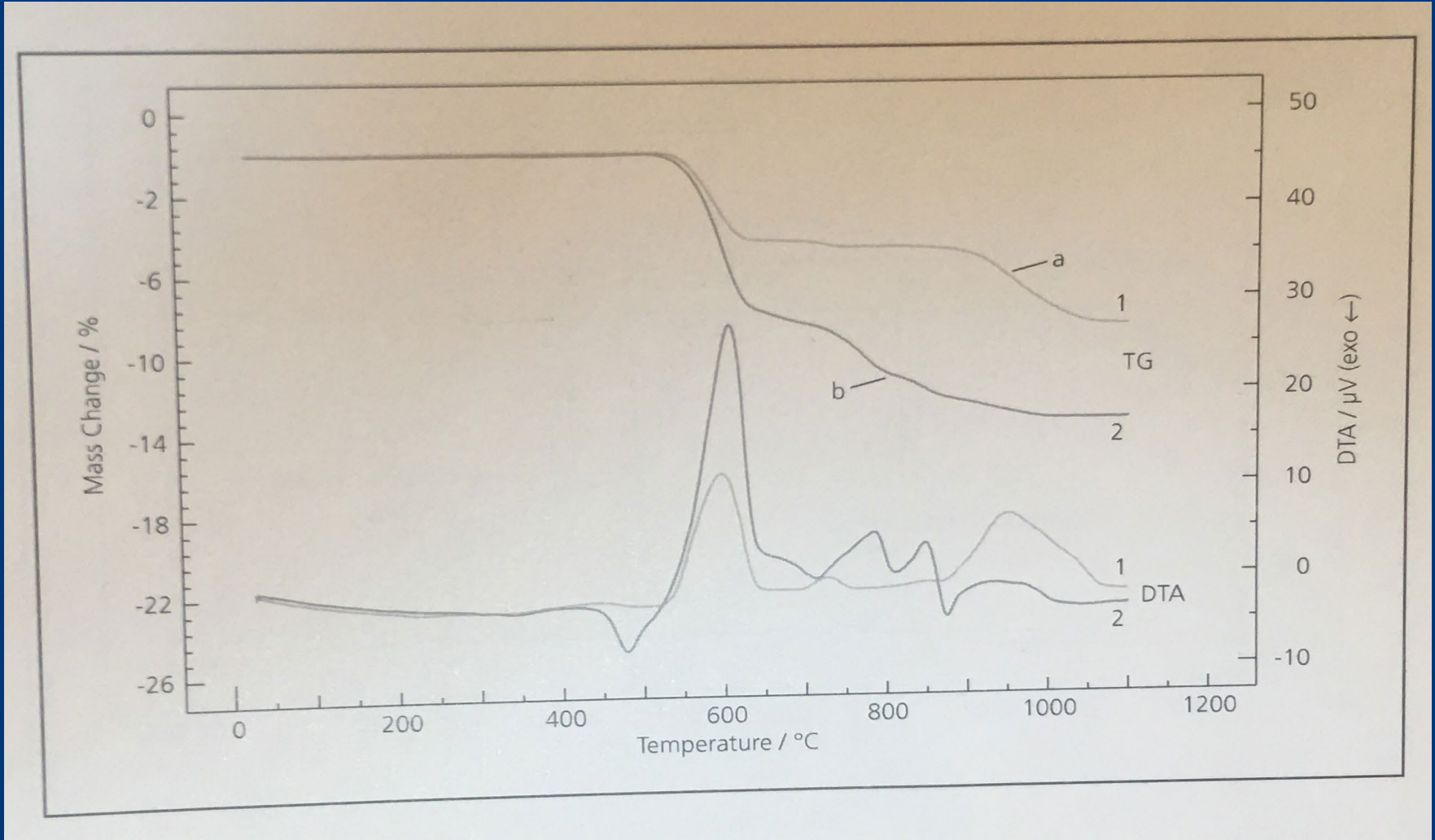


Differential Thermal Analyzer (DTA)



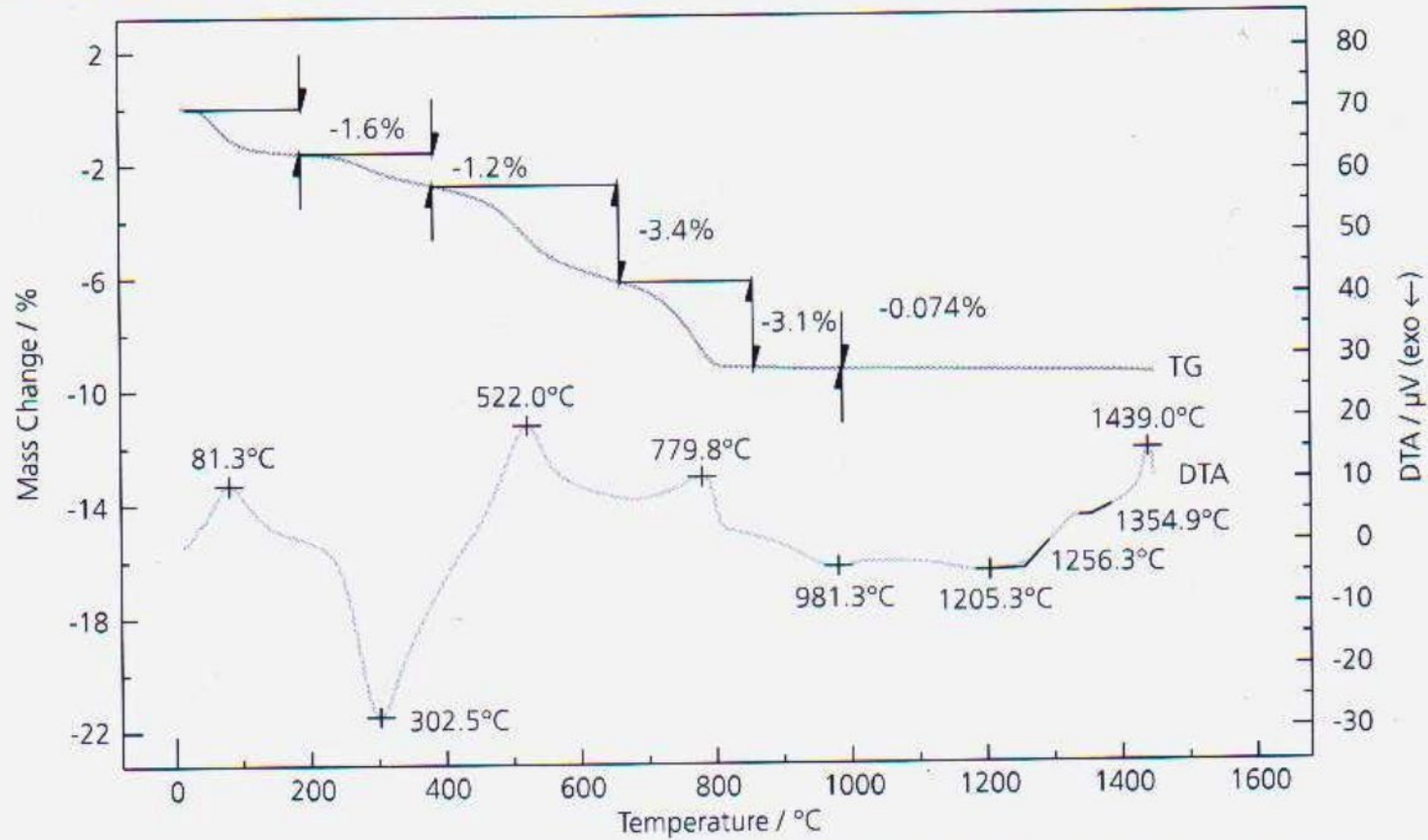
Talk

Differential Thermal Analyzer (DTA)



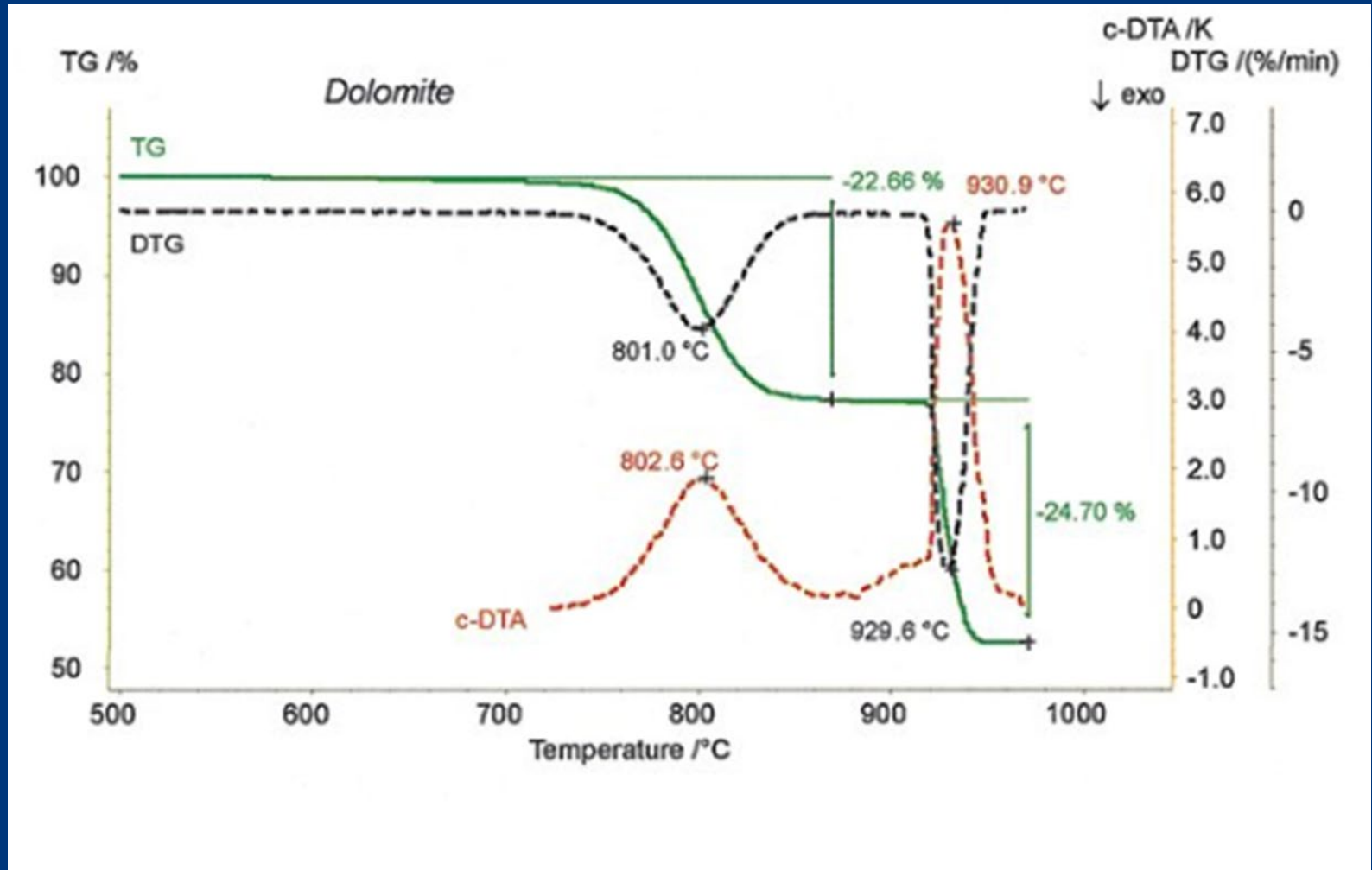
Talk

Differential Thermal Analyzer (DTA)

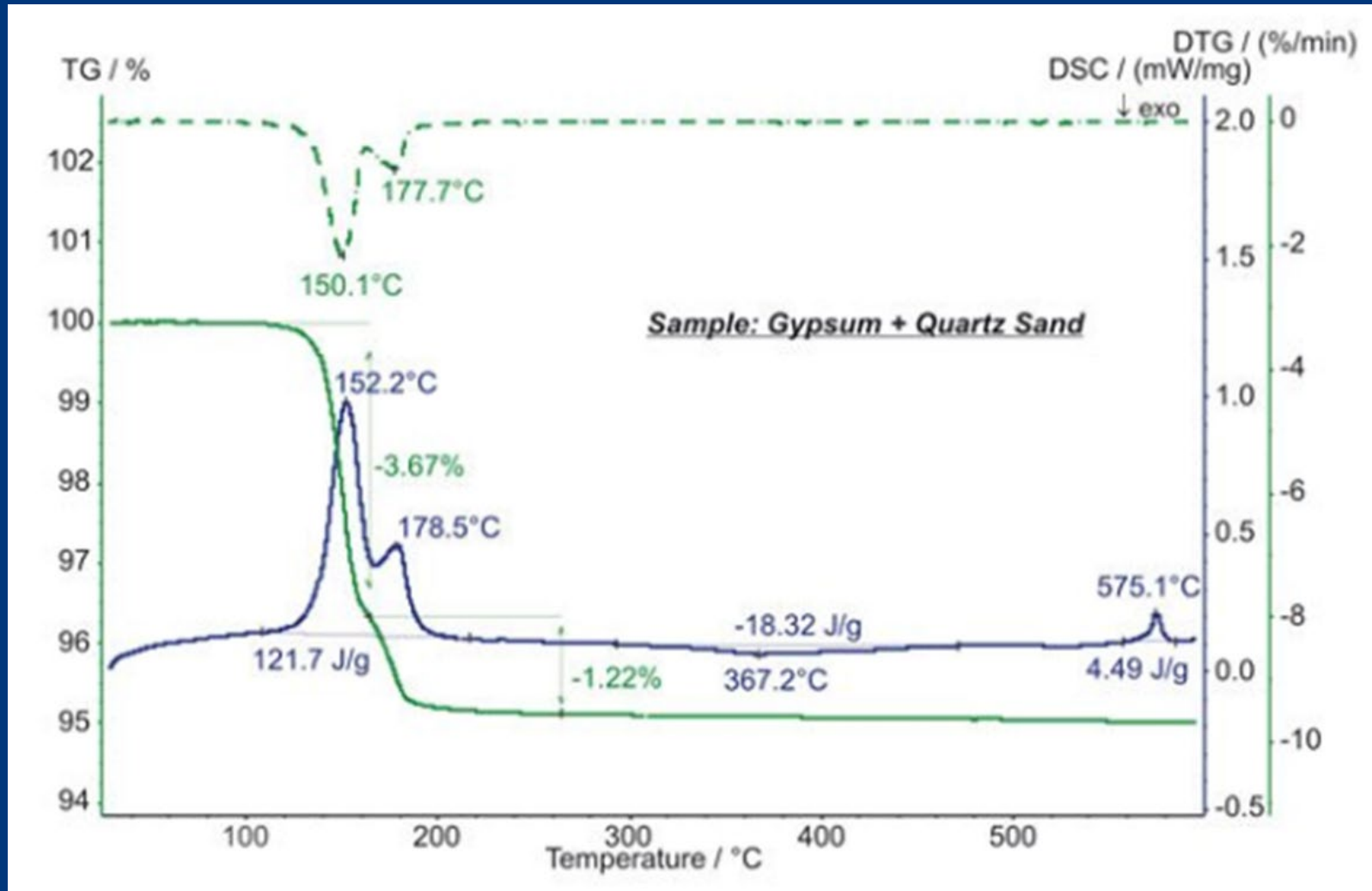


Kemik Porseleni

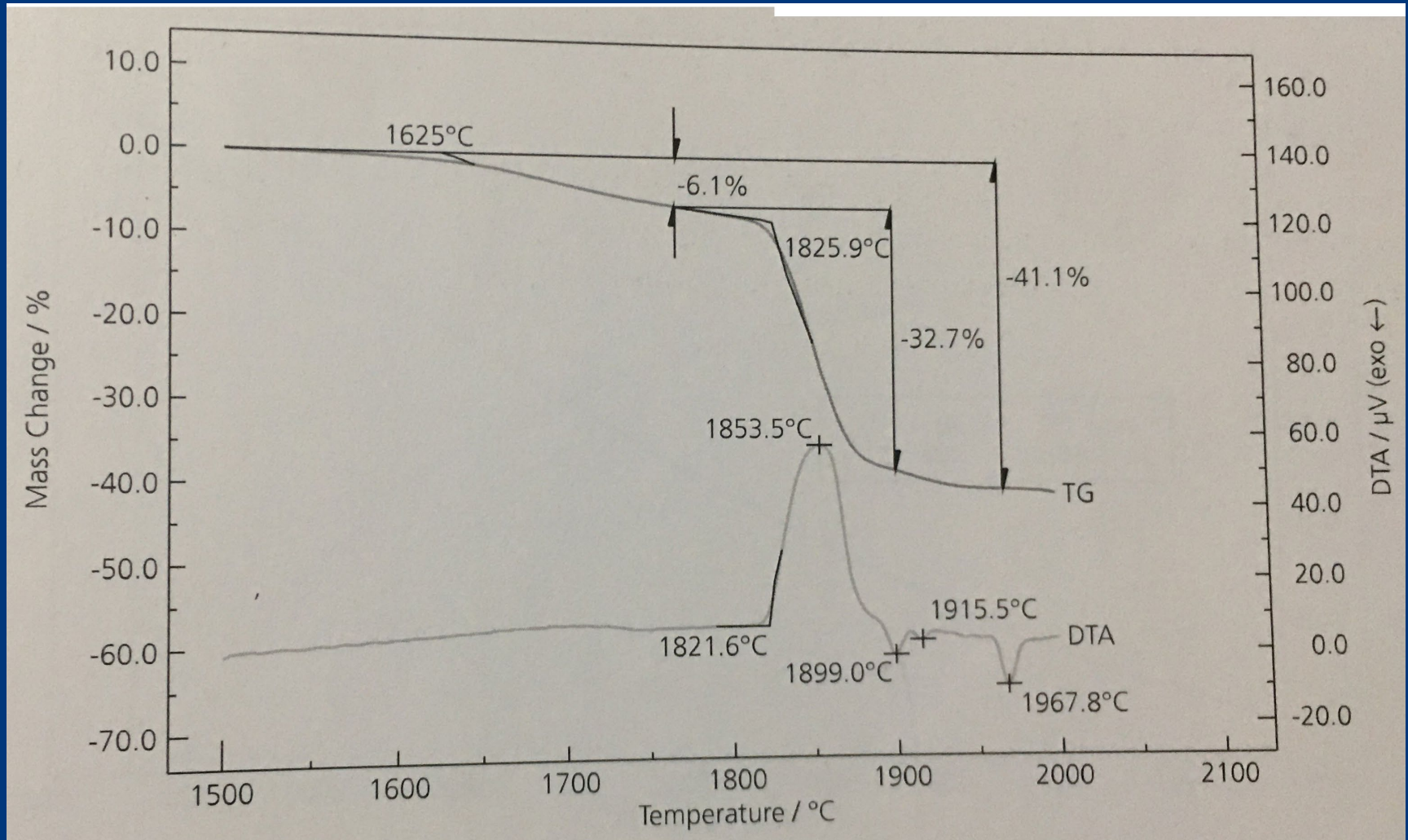
Differential Thermal Analyzer (DTA)



Differential Thermal Analyzer (DTA)

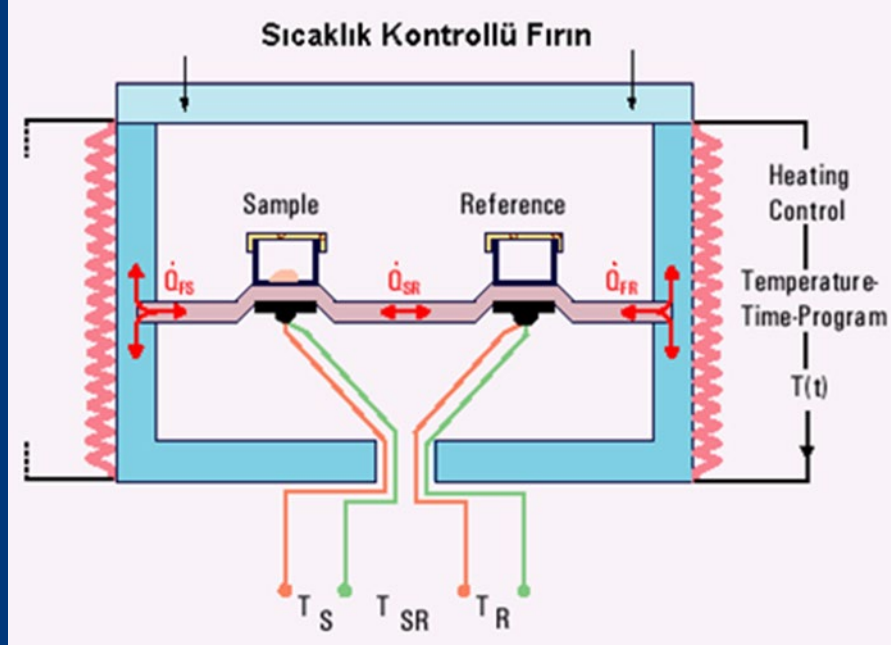


Differential Thermal Analyzer (DTA)



Silisyum Nitrür Si_3N_4

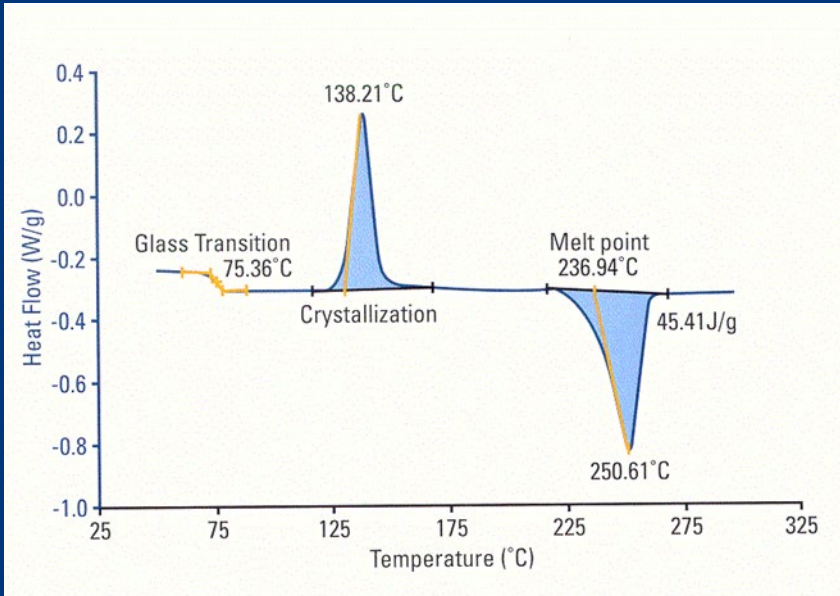
Differential Scanning Calorimetry (DSC)



- ✓ Termal benzer davranışta ısı akışı fırından numuneye doğru (dQ_{FS}/dt) ve referans malzemesi için (dQ_{FR}/dt) mükemmel derecede eşittir, ikisi arasında ölçülebilir bir sıcaklık farkı T_{SR} yoktur.
- ✓ Şayet numunede bir reaksiyon ısıya ihtiyaç duyar veya ısı açığa çıkarırsa, bir sıcaklık farkı meydana gelir.
- ✓ Bu ısı akışı, denge dışı durumu eşitlemeye çalışır.

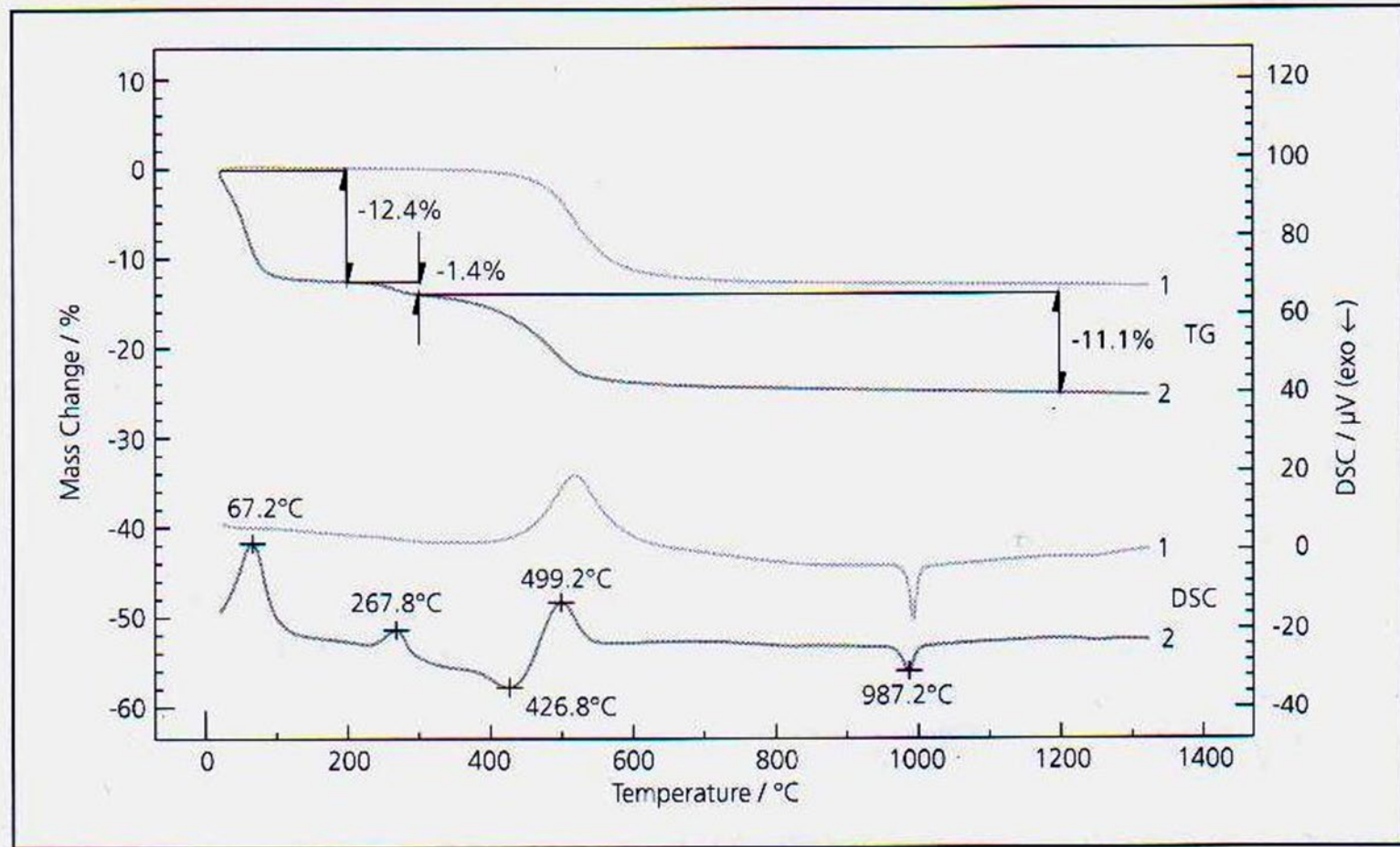


Differential Scanning Calorimetry (DSC)



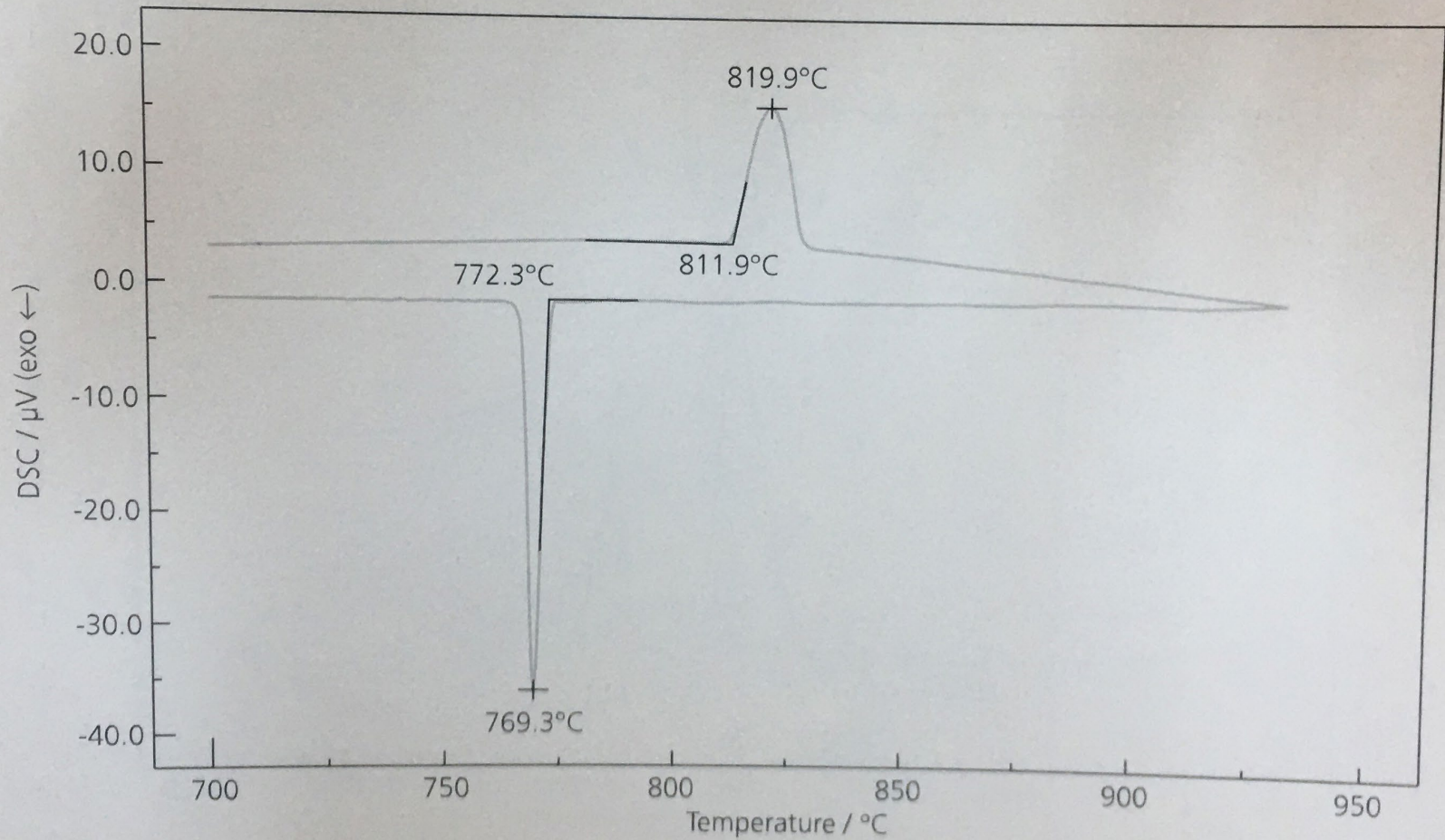
- ✓ Tüm katı malzemelerin faz durumlarında değişikliklerin belirlenmesi için kullanılabilir.
- ✓ Yanma, buharlaşma ve süblimleşme entalpilerinin bulunması,
- ✓ Kozmetik ürünlerin saflık derecesinin belirlenmesi,
- ✓ Teknolojik önemi olan malzemelerin ısı kapasitelerinin tespit edilmesi ve
- ✓ Camların faz dönüşüm sıcaklıklarının T_g ve cam dönüşüm entalpilerinin belirlenmesinde kullanılır.

Differential Scanning Calorimetry (DSC)



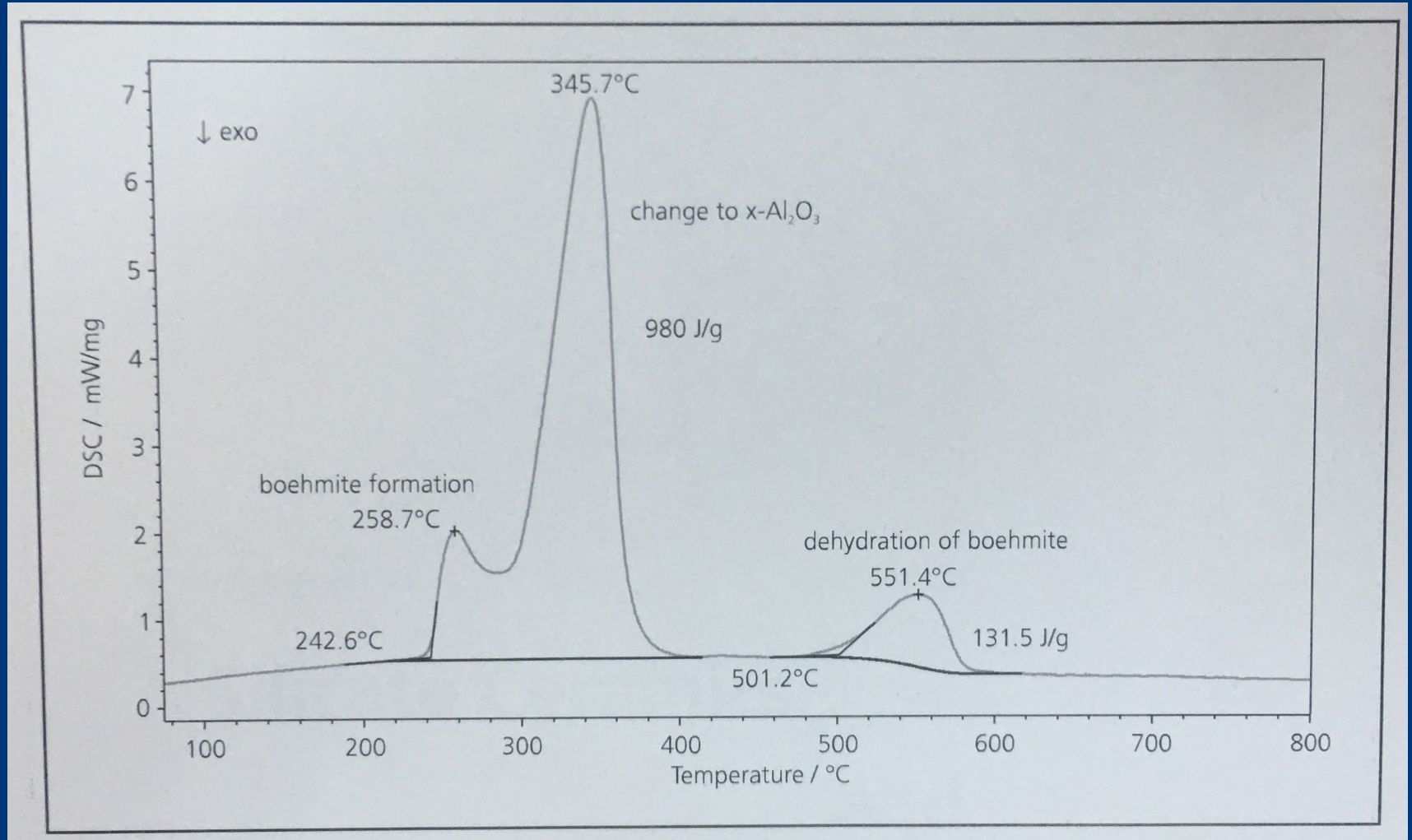
Kaolen

Differential Scanning Calorimetry (DSC)



Baryum Karbonat

Differential Scanning Calorimetry (DSC)



Gibbsite - Al(OH)_3

Dilatometre (DIL)



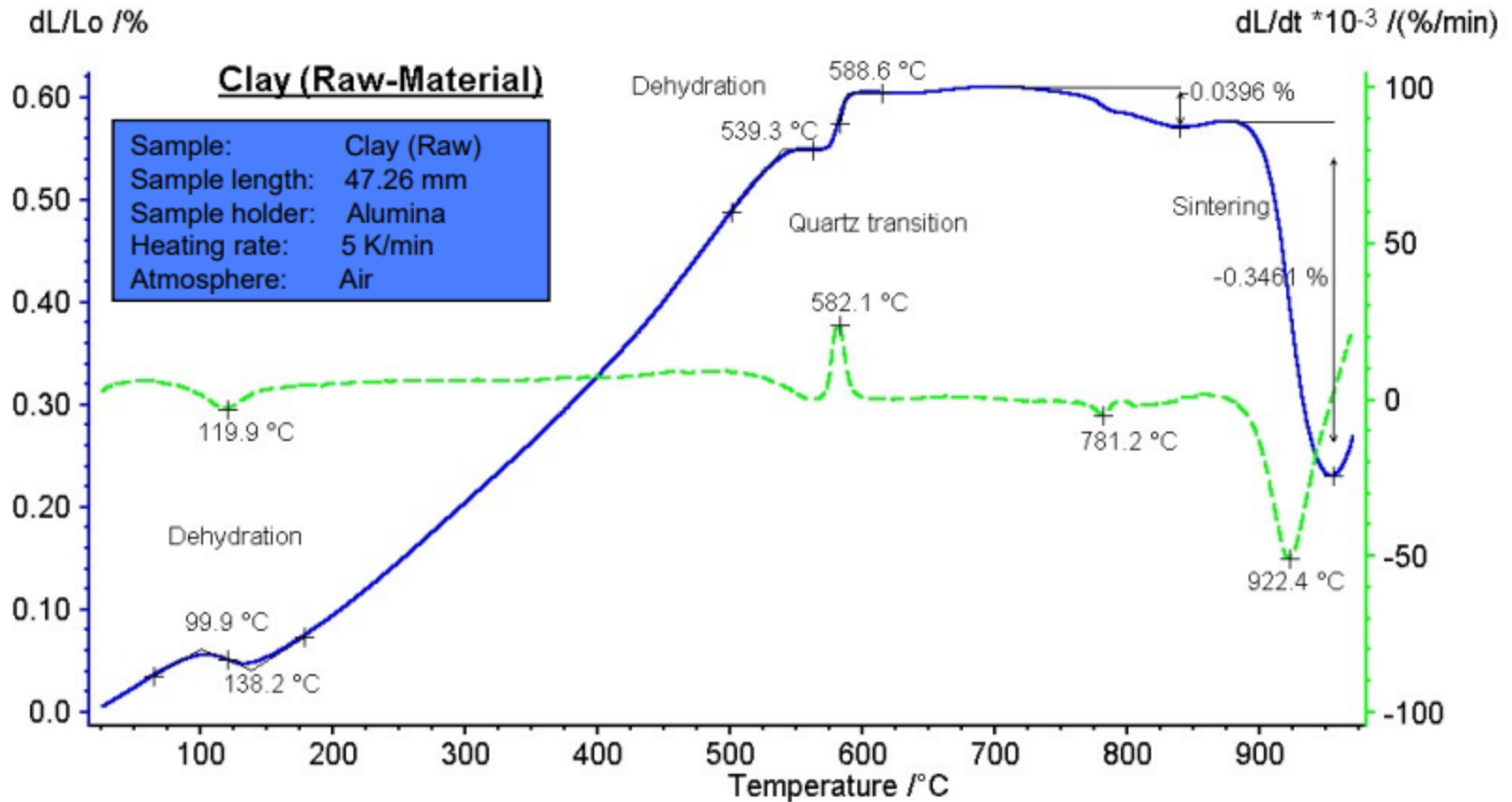
DIL 402 C

- ✓ Dilatometre, katıların sıcaklığa bağlı olarak uzama veya çekmelerin (büzülme) analitik ölçümü için kullanılan bir metottur.
- ✓ Farklı malzemelerin genleşme katsayısını belirlemek amacıyla uzun yıllardır kullanılan bir prosestir.
- ✓ İlk zamanlar proses metallerin uzama veya çekme davranışının belirlenmesi için kullanılırken son zamanlarda seramik malzemelerin sinter prosesi sırasındaki büzölmelerin incelenmesinde kullanılmaktadır.
- ✓ Prensip olarak bir numune çubuğunun sıcaklık değişimi esnasındaki genleşme ölçölür.

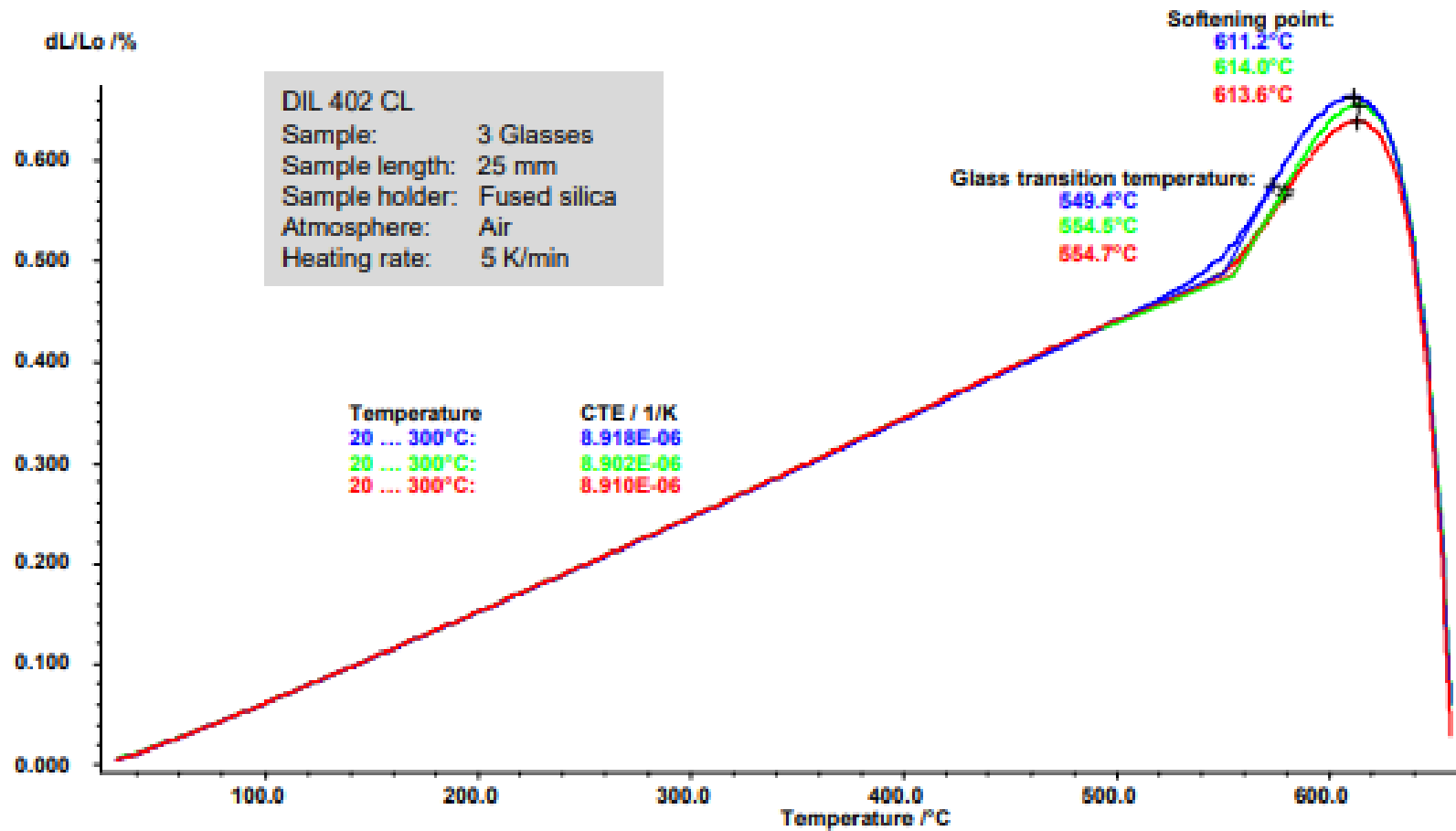
Dilatometre

- Dilatometre ile bir örneğin sıcaklık değişimi ile genleşmesi ölçülür.
- Sıcaklık veya zamana karşı Genleşme veya ısı genleşme katsayısı hesaplanır.
- Ölçümler sonucunda; numunenin
 - **termal genleşme katsayısı,**
 - **hacimsel genleşme,**
 - **faz dönüşümleri,**
 - **cam geçiş sıcaklığı ve**
 - **yumuşama noktası**
- tespit edilebilir.

Dilatometre (DIL)

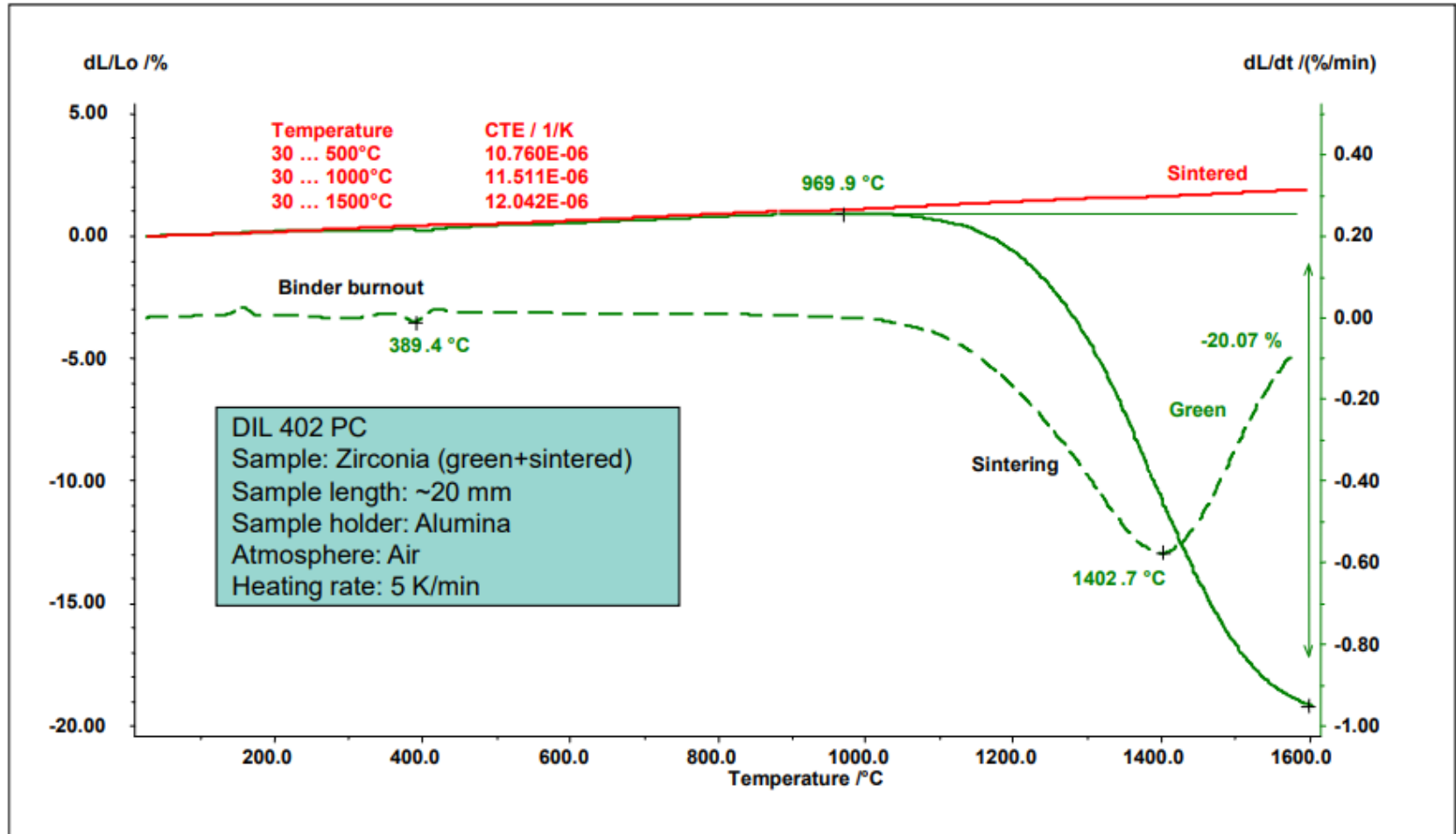


Dilatometre (DIL)

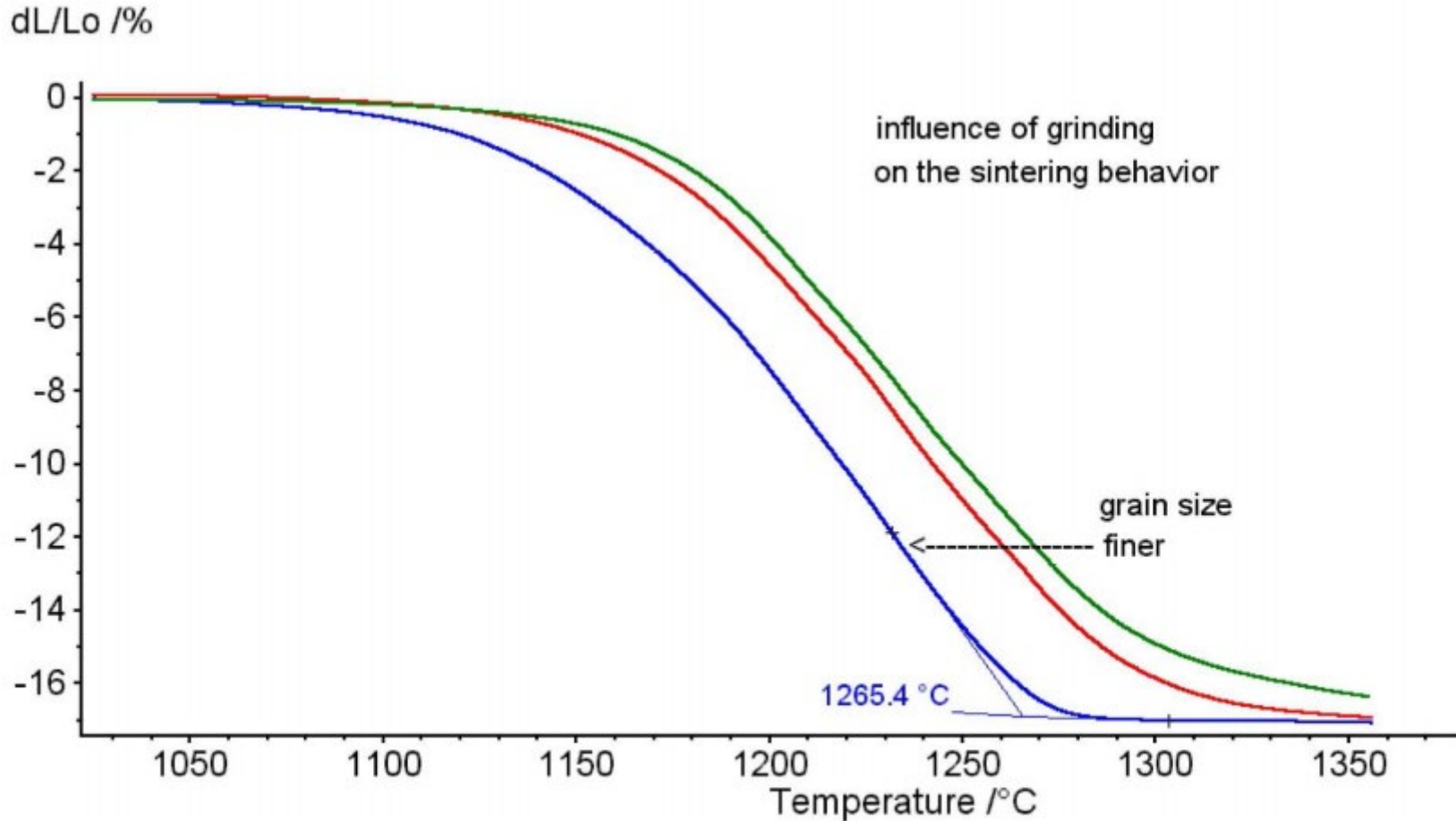


Dilatometre (DIL)

Application – Sintering of Zirconia

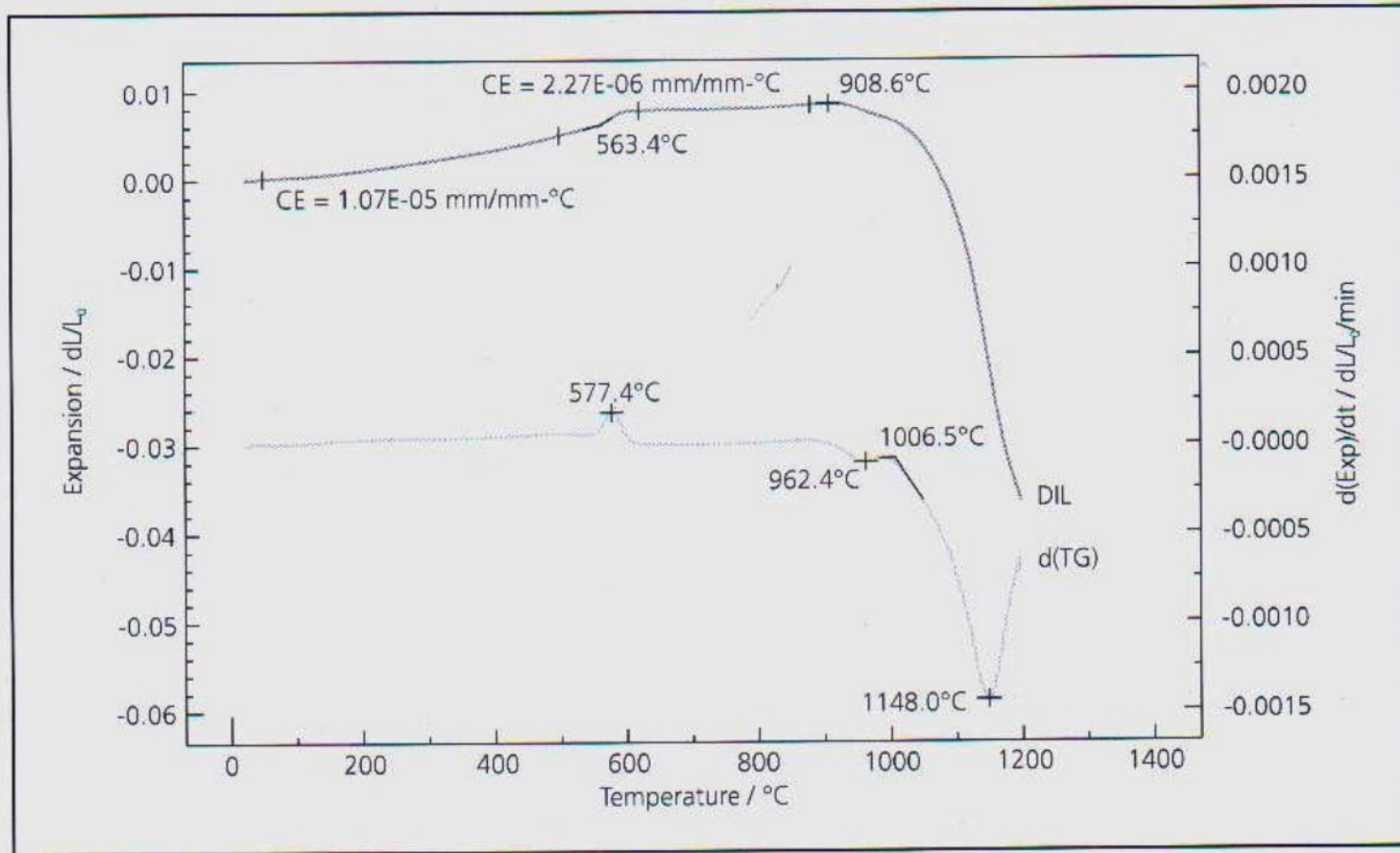


Dilatometre (DIL)



Nanosized Bariumtitanate sinters 80 $^{\circ}\text{C}$ earlier than normal powder

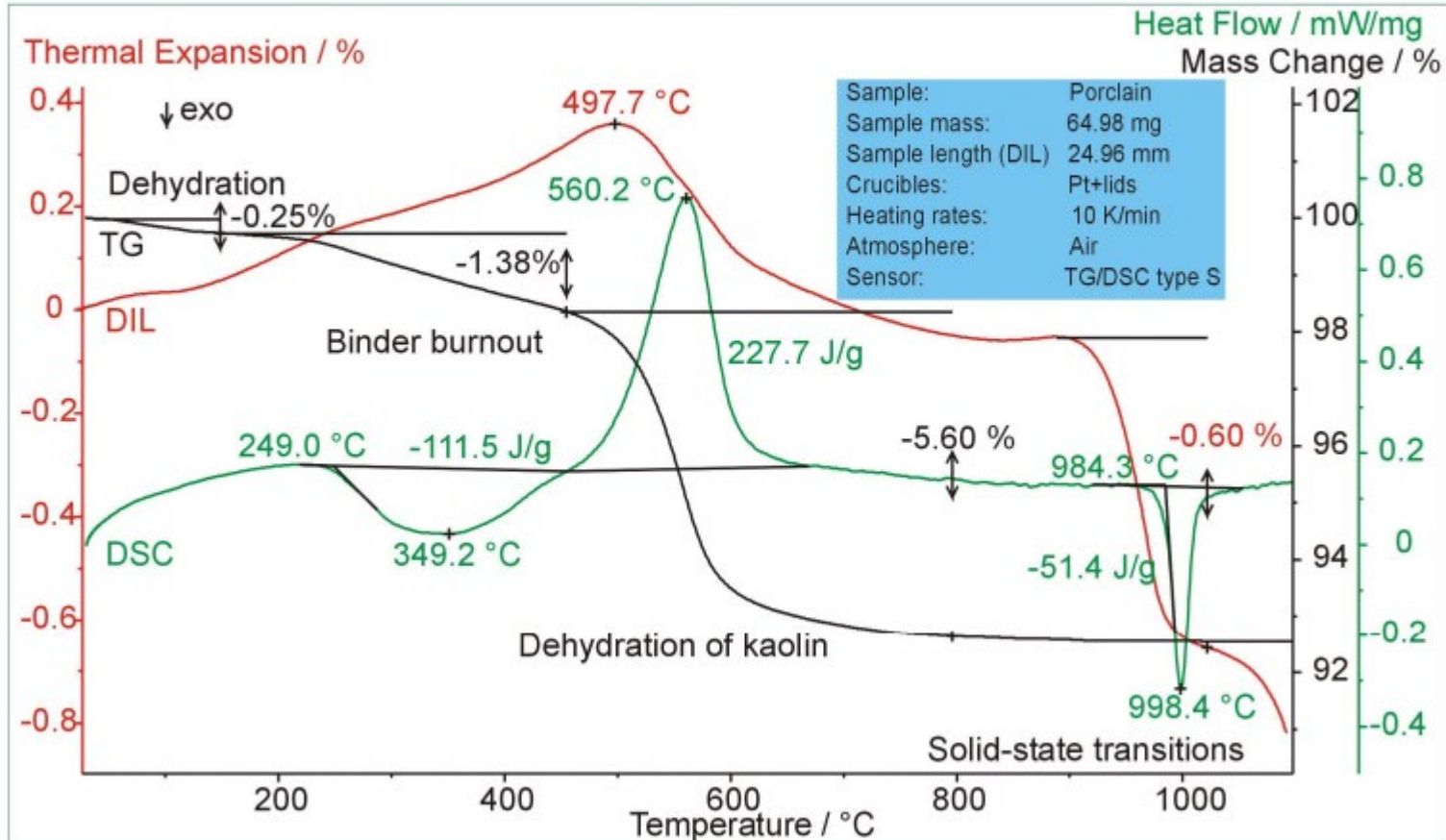
Dilatometre (DIL)



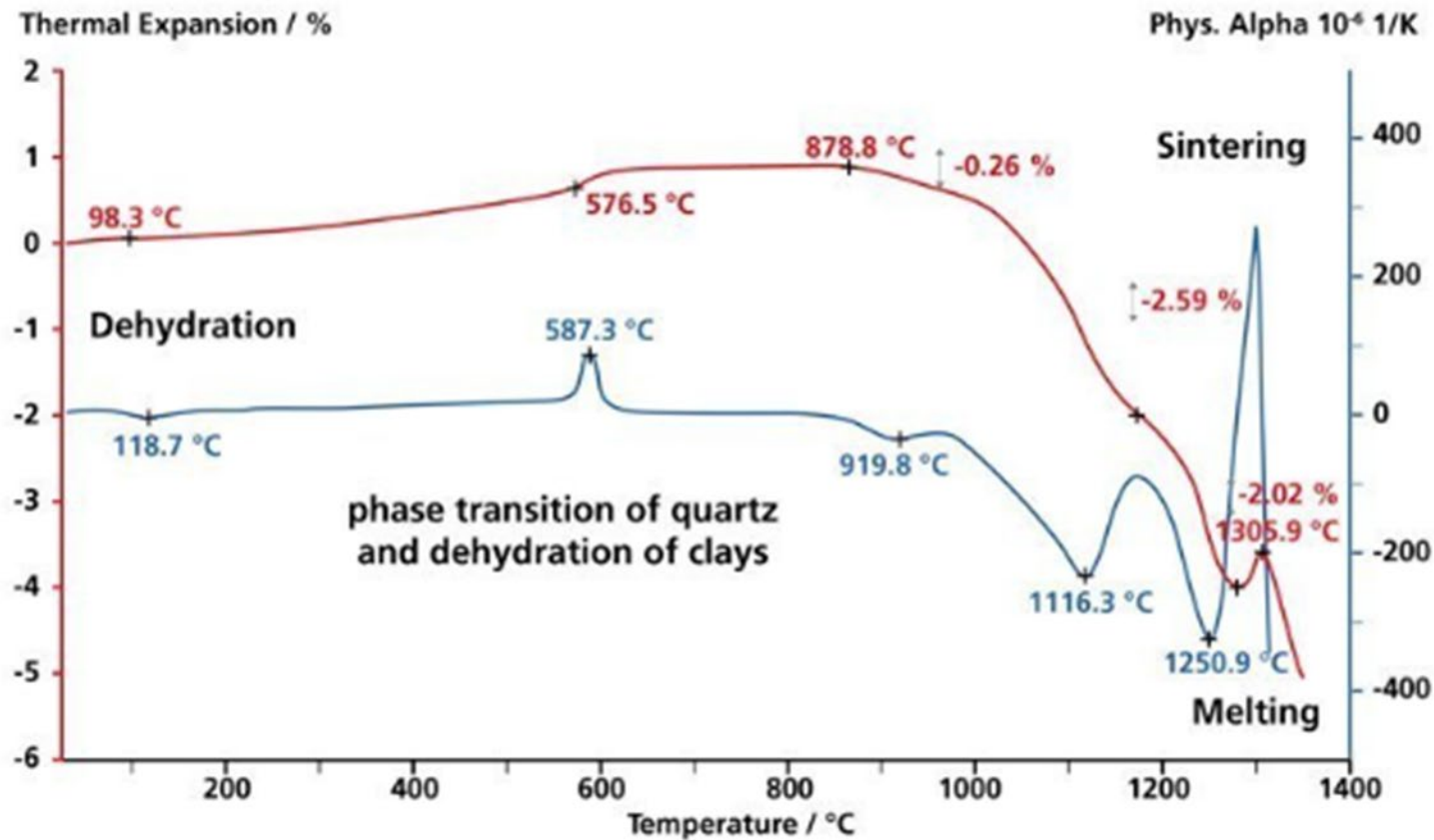
Kuvarslı parça

Dilatometre (DIL)

Porcelain Green Body

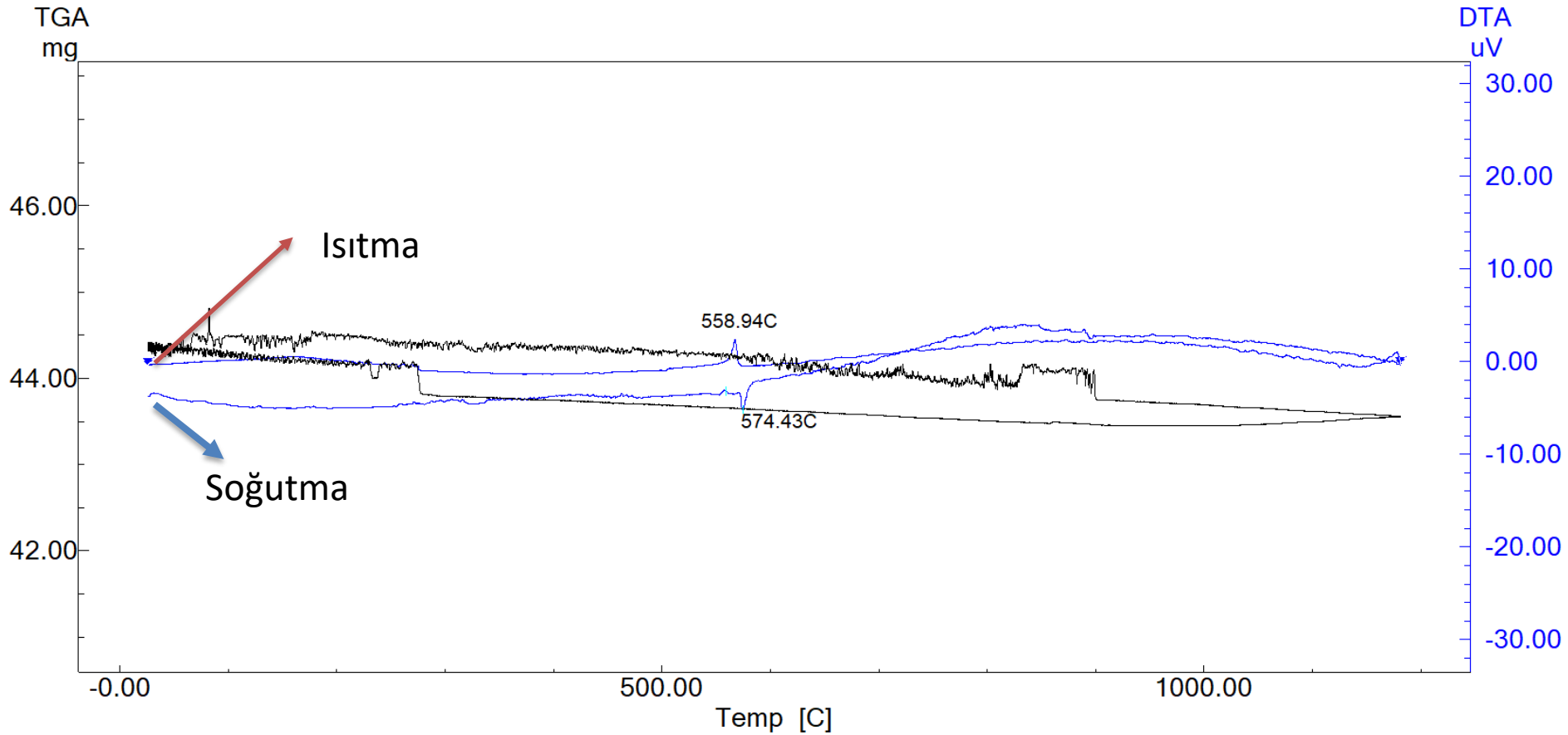


Dilatometre (DIL)

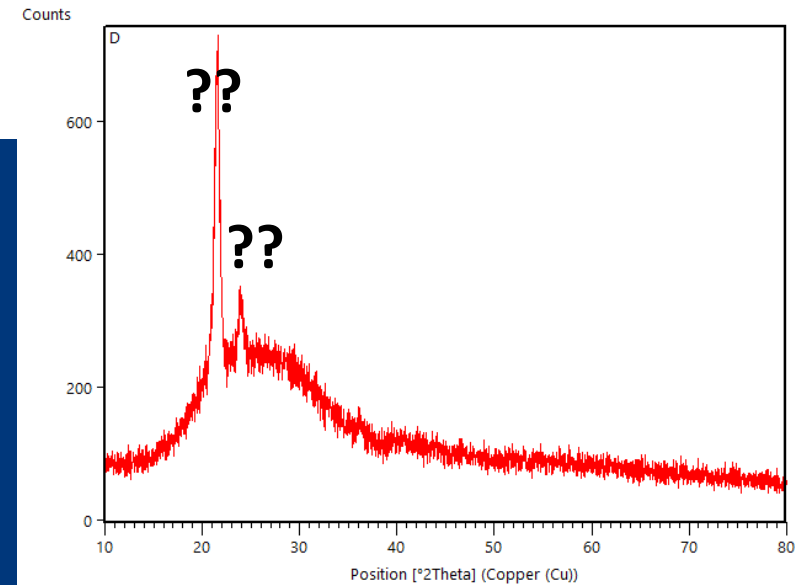
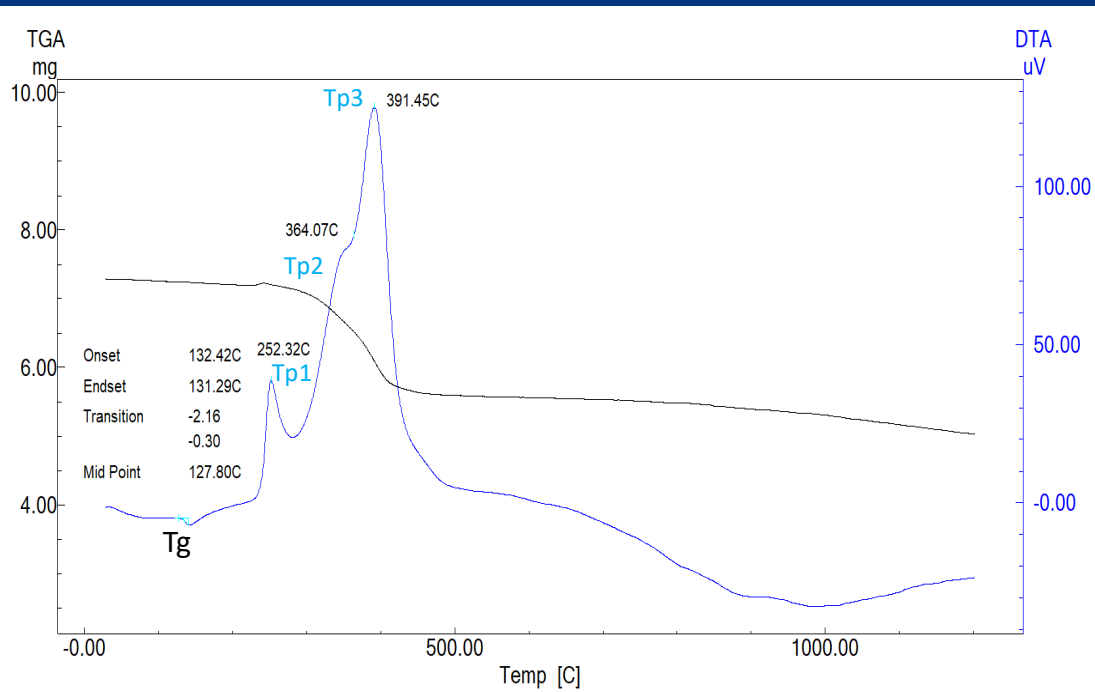


Tuğla kili

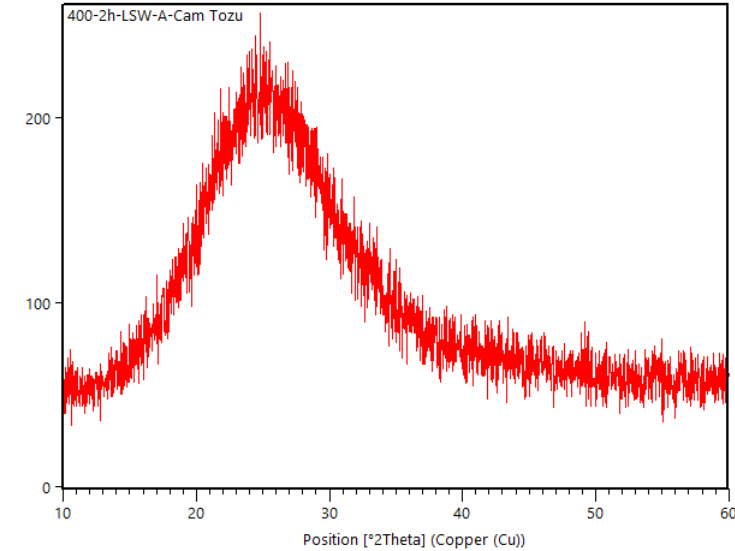
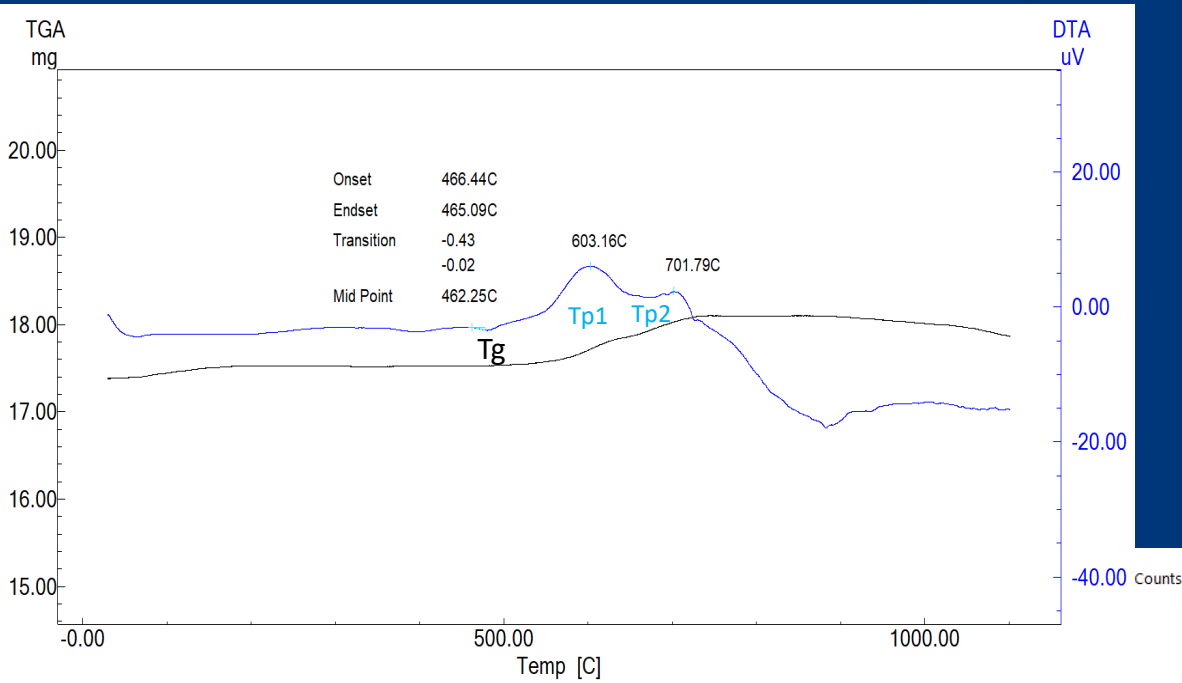
Örnek Çalışmalar



Örnek Çalışmalar



Örnek Çalışmalar

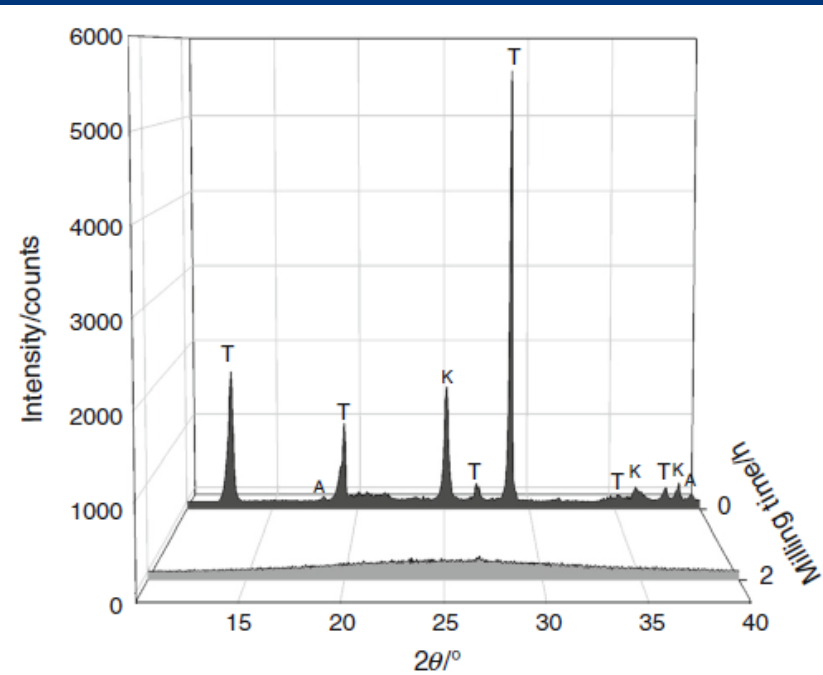


KİNETİK YAKLAŞIMLAR

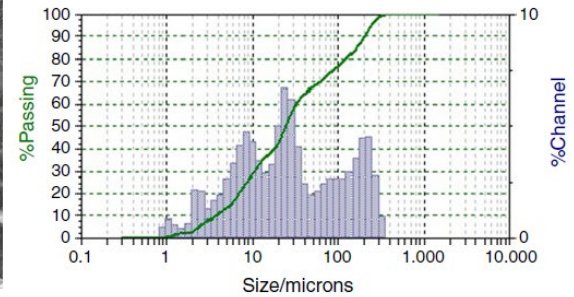
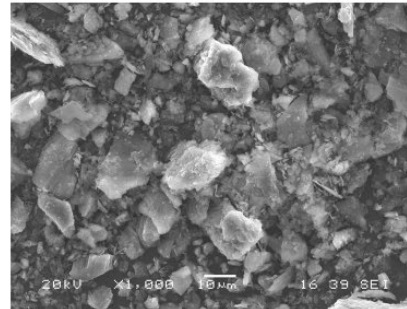
Components (wt.%)	CaO	Al ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	Fe ₂ O ₃	MgO	TiO ₂	I.L.
Talc	0,25	0,40	63,0	0,04	0,08	0,25	30	-	4,83
Kaolin	0,15	33,83	52,12	0,13	0,01	0,55	0,05	-	12,45
Alumina	-	99,425	0,52	-	0,055	-	-	-	-

Cordierite ($2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$)

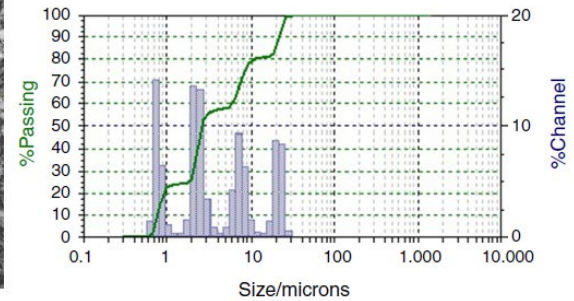
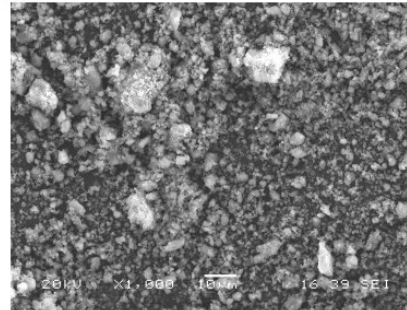
J Therm Anal Calorim (2016) 125:803–808

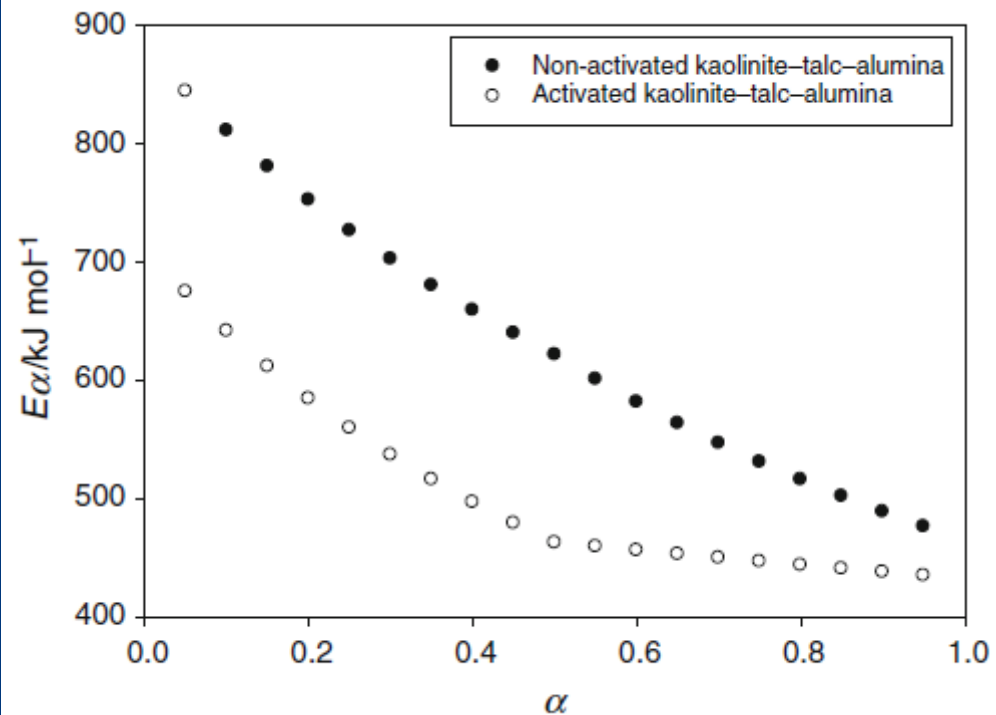
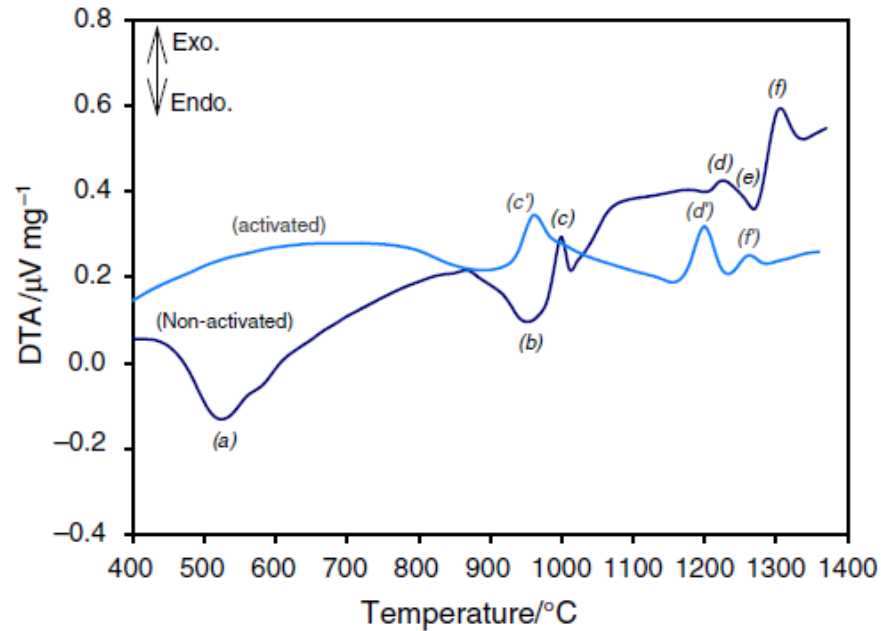


(a)

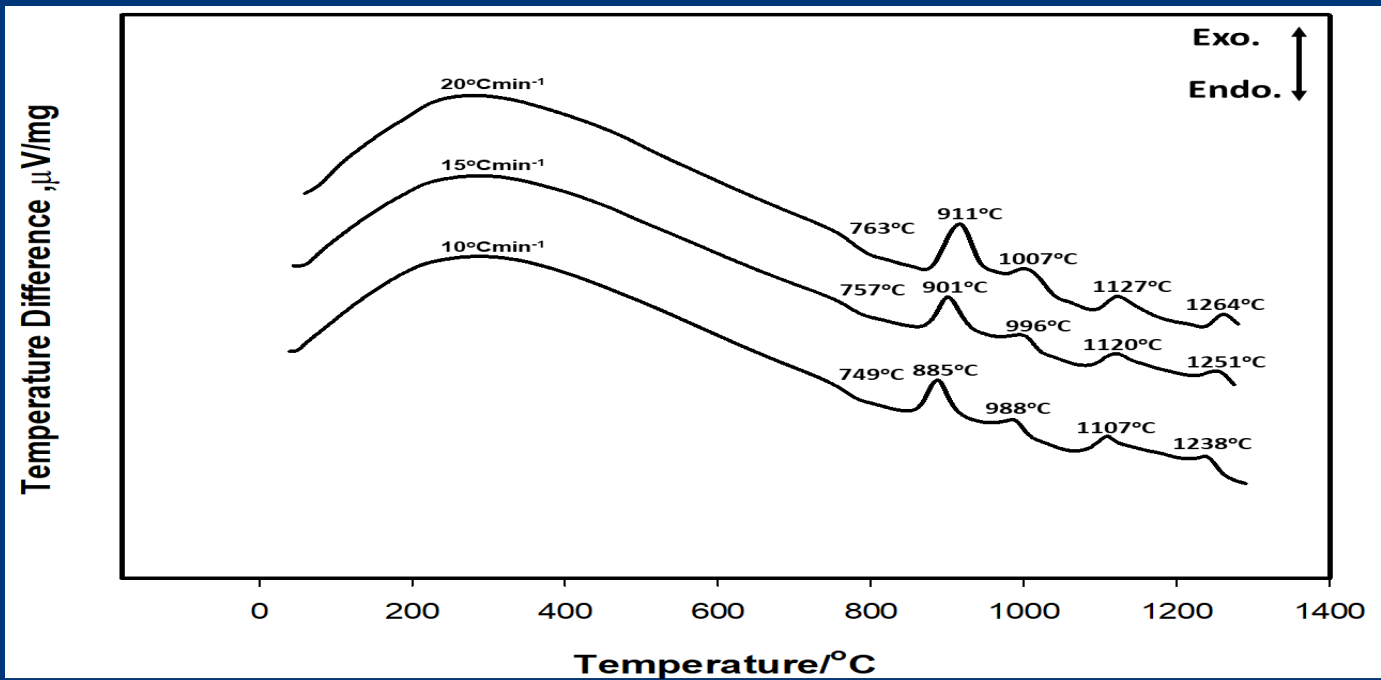


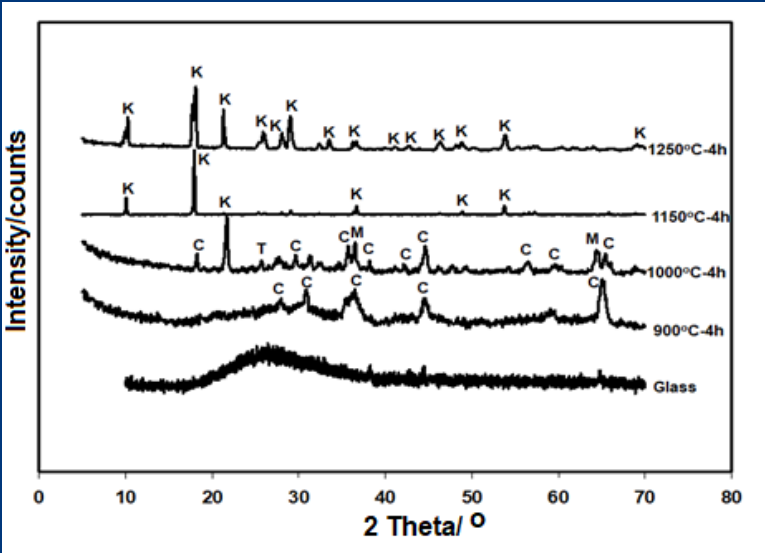
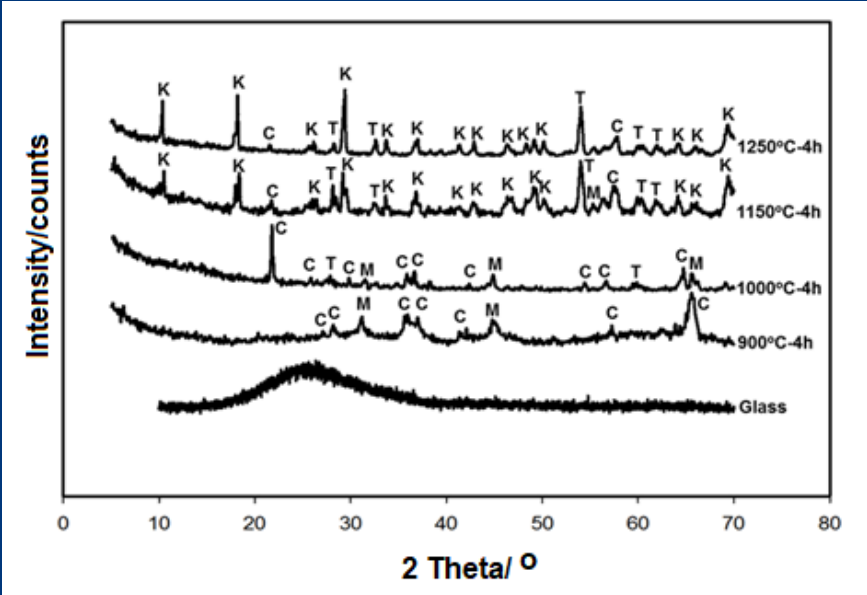
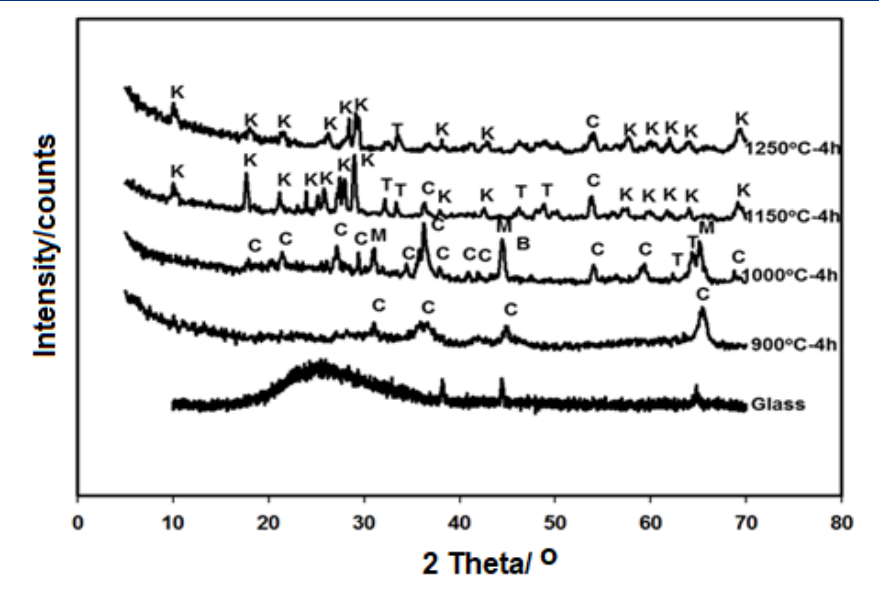
(b)



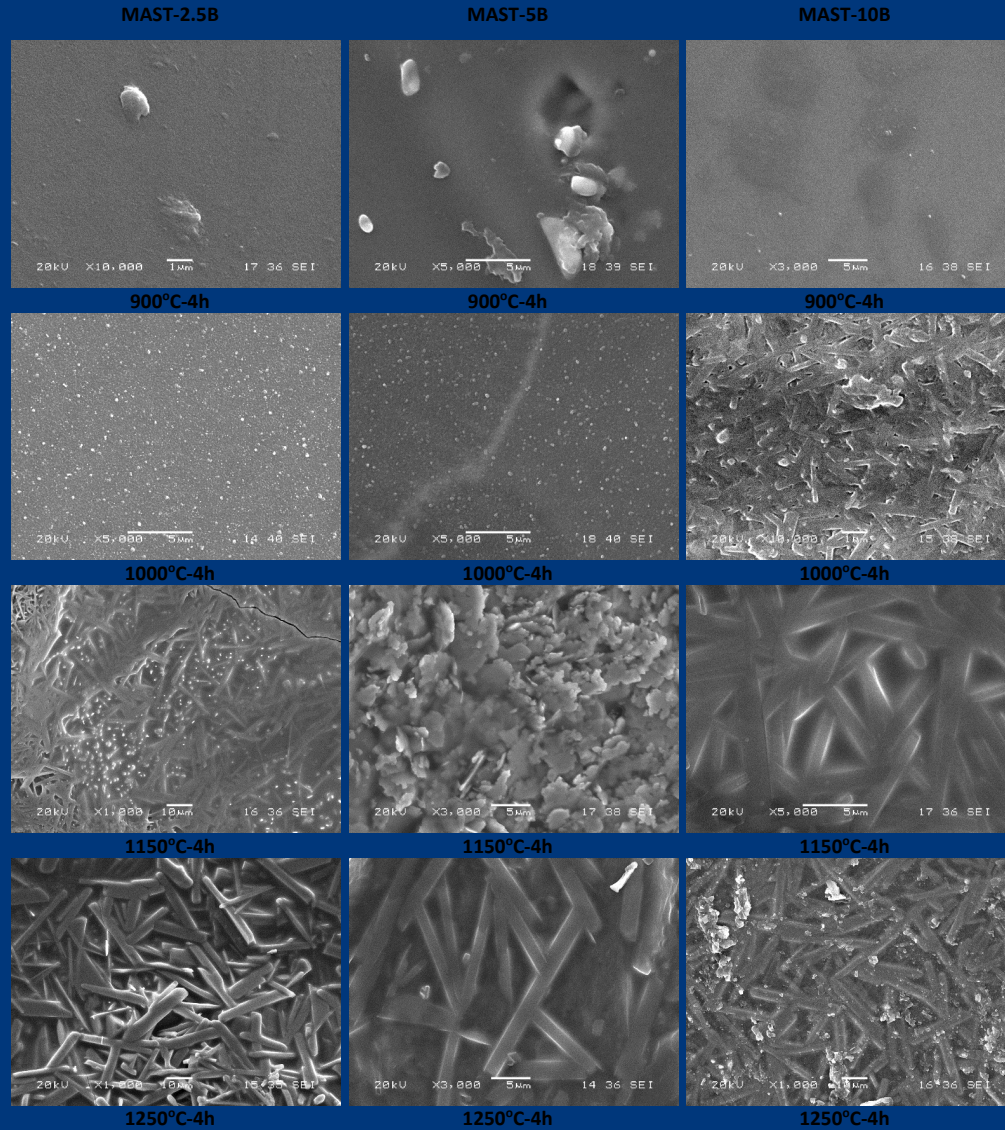


	MAST-2.5B	MAST-5B	MAST-10B
Magnesite Waste	35	35	35
Kaolinite	25	25	25
Quartz	20	20	20
Alumina	20	20	20
Titanium Oxide	8	8	8
Bismuth Oxide	2,5	5,0	10,0





C: $\text{Ca}_{0.965}\text{Mg}_2\text{Al}_{16}\text{O}_{27}$
T: Fe_2TiO_5
M: MgAl_2O_4 Spinel
K: $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ (Cordierite)



Code	Heating rate /Kmin ⁻¹	Crystallization activation energy E _a / kJmol ⁻¹	Viscous flow activation energy E _c / kJmol ⁻¹	n	Mechanism	ΔT/K
	10			3.36	Bulk nucleation	32
MAST-2.5B	15	336±4	377±2	3.43	Bulk nucleation	35
	20			3.68	Bulk nucleation	36
	10			6.23	Bulk nucleation	29
MAST-5B	15	218±1	403±7	6.12	Bulk nucleation	30
	20			5.99	Bulk nucleation	30
	10			5.17	Bulk nucleation	55
MAST-10B	15	170±3	407±21	5.33	Bulk nucleation	43
	20			4.05	Bulk nucleation	43

Dilediğiniz için Teşekkür Ederim....