

CHAPTER 3

THERMAL AND DIELECTRIC PROPERTIES OF CADMIUM(II),
BARIUM(II) AND LEAD(II) PERRHENATES

ABSTRACT

This Chapter deals with the phase transition behavior of $\text{Cd}(\text{ReO}_4)_2$, $\text{Ba}(\text{ReO}_4)_2$ and $\text{Pb}(\text{ReO}_4)_2$. Phase transitions have been investigated by DTA and dielectric measurements. Both $\text{Cd}(\text{ReO}_4)_2$ and $\text{Ba}(\text{ReO}_4)_2$ undergo three phase transformations in between the ambient temperature and fusion temperatures. $\text{Pb}(\text{ReO}_4)_2$ shows a single phase transition. A characteristic feature of these phase transformations is that they are accompanied by considerable thermal hysteresis. On the basis of thermal and dielectric measurements it has been concluded that the room temperature phases are of low symmetry, and probably monoclinic or triclinic; the high temperature phases appear to have noncentrosymmetric structures.

INTRODUCTION

Perrhenates of metals are known for long time¹⁻³. The monovalent perrhenates, $M\text{ReO}_4$ ^{4,5} ($M = \text{Na}, \text{K}, \text{NH}_4, \text{Rb}, \text{Ag}$) are Scheelite type having space group $C_{4h}^6 - I4_1/a$; CsReO_4 and TlReO_4 are rhombic with pseudotetragonal character ($D_{2h}^{16} - P_{nma}$). Among the bivalent perrhenates⁴, $\text{Ca}(\text{ReO}_4)_2$ and $\text{Sr}(\text{ReO}_4)_2$ appears to be isostructural, while those of others ($\text{Ba}, \text{Cd}, \text{Pb}$ etc) have low symmetries, however, for none of them crystallographic details are available. Quite recently crystal structure of monoclinic $\text{Ca}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been determined⁶.

Phase transition of NH_4ReO_4 has been the subject of several studies during the past few years⁷⁻¹⁷. Anomalies in both temperature and pressure dependence of the ^{187}Re NQR frequency⁷⁻¹³ and an unusual temperature dependence of the dimensions of the unit cell of the NH_4ReO_4 crystal¹¹ have been reported. These as well as variable temperature Raman spectral studies^{14,15} have revealed a broad discontinuity with a peak near 200 K that has been implicated due to a higher order phase transition involving ordering of NH_4^+ ion. On the other hand in a recent NMR study¹⁶, measurement of the proton relaxation time T_1 from 60-300K lends no support to this suggestion.

The heat capacity measurement¹⁷ made with NH_4ReO_4 shows a broad bump with a maxima around 200K, but the data show no obvious order-disorder phase transition. Similar studies made with the other isostructural salts^{11,13,17}, however, do not show these anomalies.

Phase transitions in several anhydrous bivalent perrhenates at higher temperatures has been reported¹⁸ to take place. $\text{M}(\text{ReO}_4)_2$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}$) do not show any transition between the ambient and the melting temperatures. On the other hand the DTA of $\text{M}(\text{ReO}_4)_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Cd}, \text{Pb}$) show¹⁸ one or more reversible phase transitions which are accompanied by thermal hysteresis.

In this chapter we have examined the phase transitions of $\text{Cd}(\text{ReO}_4)_2$, $\text{Ba}(\text{ReO}_4)_2$ and $\text{Pb}(\text{ReO}_4)_2$ by the thermal methods of analysis and by measuring the dielectric constants at varying temperatures.

EXPERIMENTAL SECTION

Preparation metal perrhenates, $\text{M}(\text{ReO}_4)_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Cd}, \text{Ba}, \text{Pb}$).

These compounds were obtained by the metathetical reaction between the metal carbonates and perrhenic acid



Perrhenic acid was prepared by passing a solution of NH_4ReO_4 (Johnson-Matthey) through a column of cation exchanger, Amberlite IR-120 in the hydrogen ion form. An excess of metal carbonate was digested with aqueous perrhenic acid on a water bath for 0.5h. The solution was filtered and the filtrate was evaporated almost to dryness on water bath. The compounds were dried over CaCl_2 at the ambient temperature.

Physical Methods.

Methods of measurement were similar to those described in Chapter 2.

RESULTS AND DISCUSSION

Thermogravimetric analysis of the perrhenates showed that cadmium and barium salts are dihydrates, whereas the lead salt is anhydrous. Before melting none of these compounds decomposed. Anhydrous cadmium perrhenate is very much hygroscopic and therefore cannot be handled under open atmospheric condition. X-ray powder data of $\text{Ba}(\text{ReO}_4)_2$, $\text{Pb}(\text{ReO}_4)_2$ and $\text{Cd}(\text{ReO}_4)_2$ summarized in Table 3.1 are in good agreement with those reported in literature^{18,19}.

Table 3.1

Observed d -spacings (\AA) and intensities of anhydrous
 $\text{Cd}(\text{ReO}_4)_2$, $\text{Ba}(\text{ReO}_4)_2$ and $\text{Pb}(\text{ReO}_4)_2$.

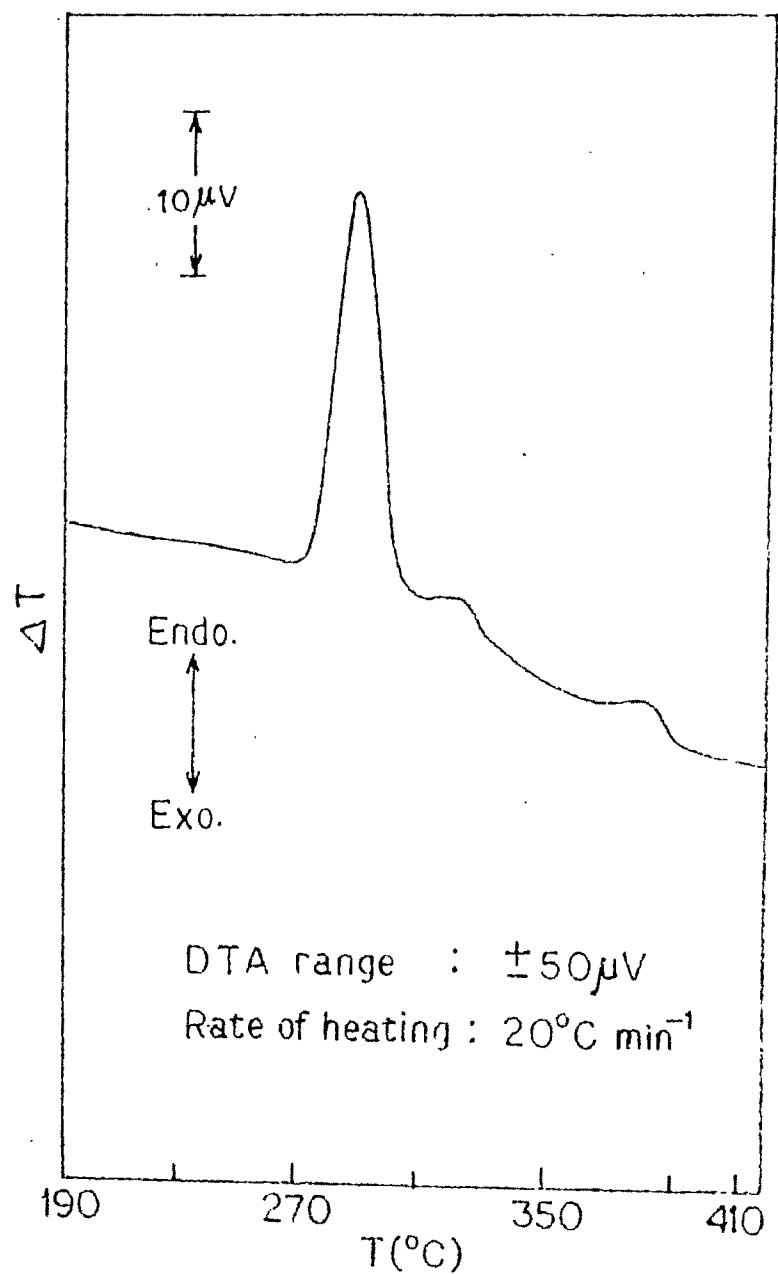
$\text{Cd}(\text{ReO}_4)_2$		$\text{Ba}(\text{ReO}_4)_2$		$\text{Pb}(\text{ReO}_4)_2$	
d_{obs} (\AA)	I	d_{obs} (\AA)	I	d_{obs} (\AA)	I
3.902	w	4.836	w	4.628	w
3.521	vs	4.780	w	4.206	w
3.375	w	3.766	vs	3.723	m
3.032	vs	3.521	s	3.559	vs
2.924	vw	3.341	vs	3.341	s
2.380	vw	3.209	w	3.241	vs
2.314	m	2.977	m	3.118	vw
2.166	w	2.924	m	2.873	m
2.087	w	2.330	m	2.708	m
1.945	w	2.298	w	2.643	w

contd..

Table 3.1(contd)

<u>Cd(ReO₄)₂</u>		<u>Ba(ReO₄)₂</u>		<u>Pb(ReO₄)₂</u>	
<u>d_{obs}^o(Å)</u>	<u>I</u>	<u>d_{obs}^o(Å)</u>	<u>I</u>	<u>d_{obs}^o(Å)</u>	<u>I</u>
1.872	m	2.267	w	2.380	m
1.842	s	2.087	w	2.283	m
1.804	w	1.990	vw	2.252	w
1.768	s	1.842	w	2.112	w
1.700	w	1.733	w	1.990	s
1.528	s			1.946	w
1.423	m			1.923	m
1.407	m			1.862	s
1.362	w			1.824	w
				1.804	m
				1.735	m
				1.624	w

The DTA for the heating curve of $\text{Cd}(\text{ReO}_4)_2$ is shown in Figure 3.1. It may be noted that there are three endothermic changes for the compound, of which the one observed at the lowest temperature is much stronger relative to the two higher temperature transitions. The DTA obtained during cooling is characterized by the three corresponding exotherms with shift of the transition temperatures to the lower side. In Table 3.2 the peak temperatures for phase transitions observed during the heating and cooling cycle has been compared. It may be noted that the width of hysteresis (ΔT) is very much pronounced for the first transition ($\Delta T = 225^\circ\text{C}$), less for the second ($\Delta T = 40^\circ\text{C}$) and least for the third one ($\Delta T = 10^\circ\text{C}$). With the increased order of temperature the four phases of $\text{Cd}(\text{ReO}_4)_2$ are designated as δ , γ , β and α , that is, the room temperature phase is δ and the highest temperature one is α . Table 3.2 also includes the enthalpy changes occurred during these phase transitions. X-ray powder patterns of the high temperature phases could not be recorded due to the lack of facility. The room temperature phase (δ) has not been indexed but appears to be of low symmetry, and most likely monoclinic or triclinic. In terms of Buerger's structural classification²⁰ it may be conjectured that the phase undergoes transformation involving the first coordination as indicated by high ΔH value ($\delta - \gamma$, $4.1 \text{ kcal mol}^{-1}$), and probably it is reconstructive type. Nothing can be said

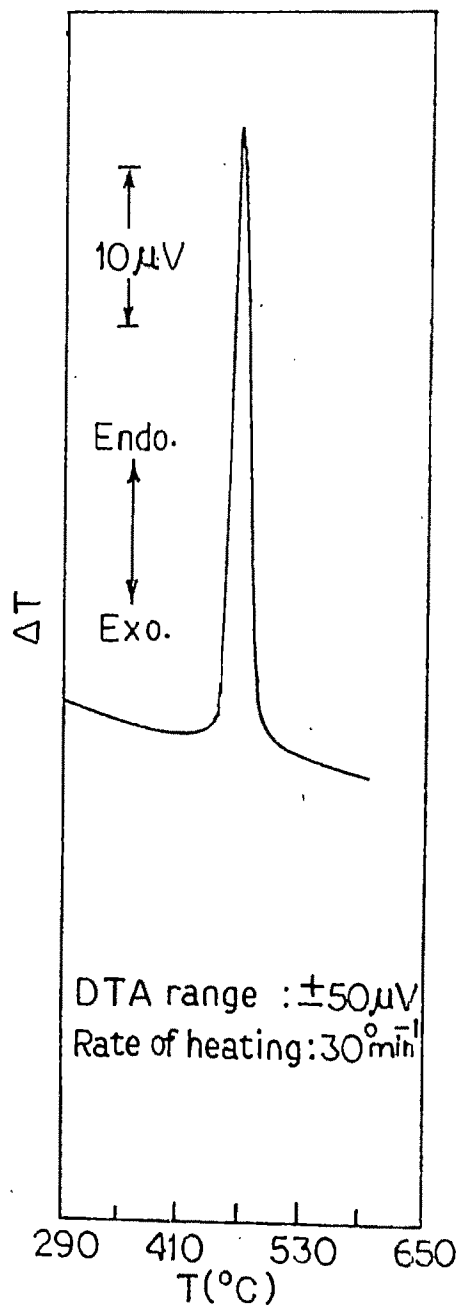


DTA of $\text{Cd}(\text{ReO}_4)_2$
Figure. 3.1

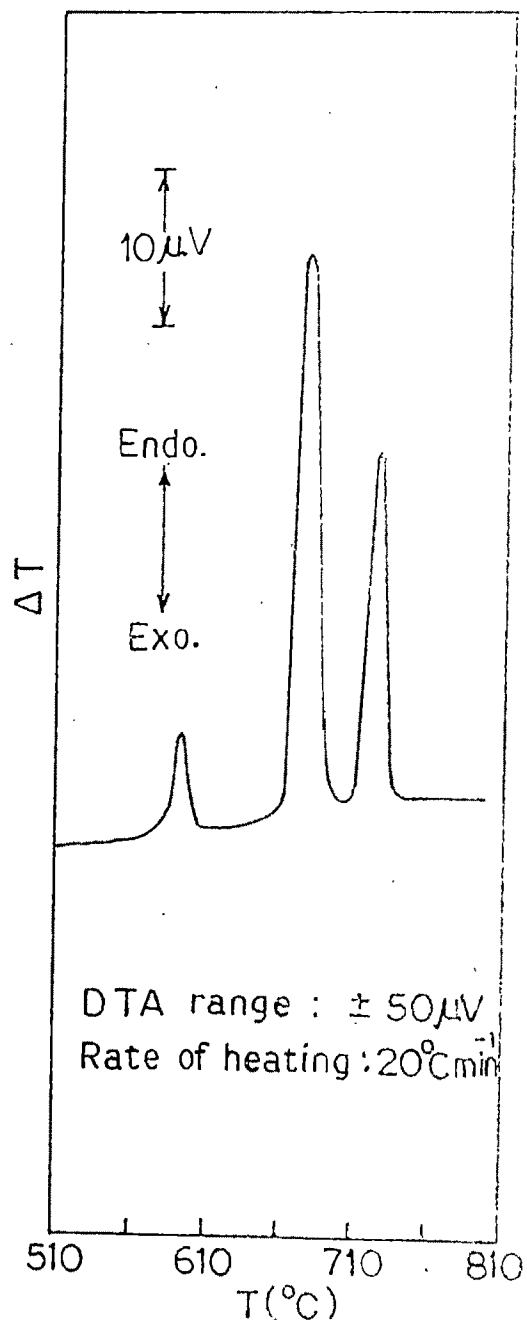
about $\sqrt{\text{---}} - \beta$ and $\beta - \alpha$ transformations, however, it is quite likely that the α -phase has the highest symmetry and there is a good probability of its belonging to the cubic class.

$\text{Pb}(\text{ReO}_4)_2$ on heating exhibits a single very strong endothermic change (Figure 3.2). On reversal of temperature the exotherm is observed again at a lower temperature. In this case the width of hysteresis is 50°C . High enthalpy change ($8.6 \text{ kcal mol}^{-1}$) for $\text{Pb}(\text{ReO}_4)_2$ is a clear indication for the drastic change occurred on phase transition. The relevant thermal data for $\text{Pb}(\text{ReO}_4)_2$ are collected in Table 3.2.

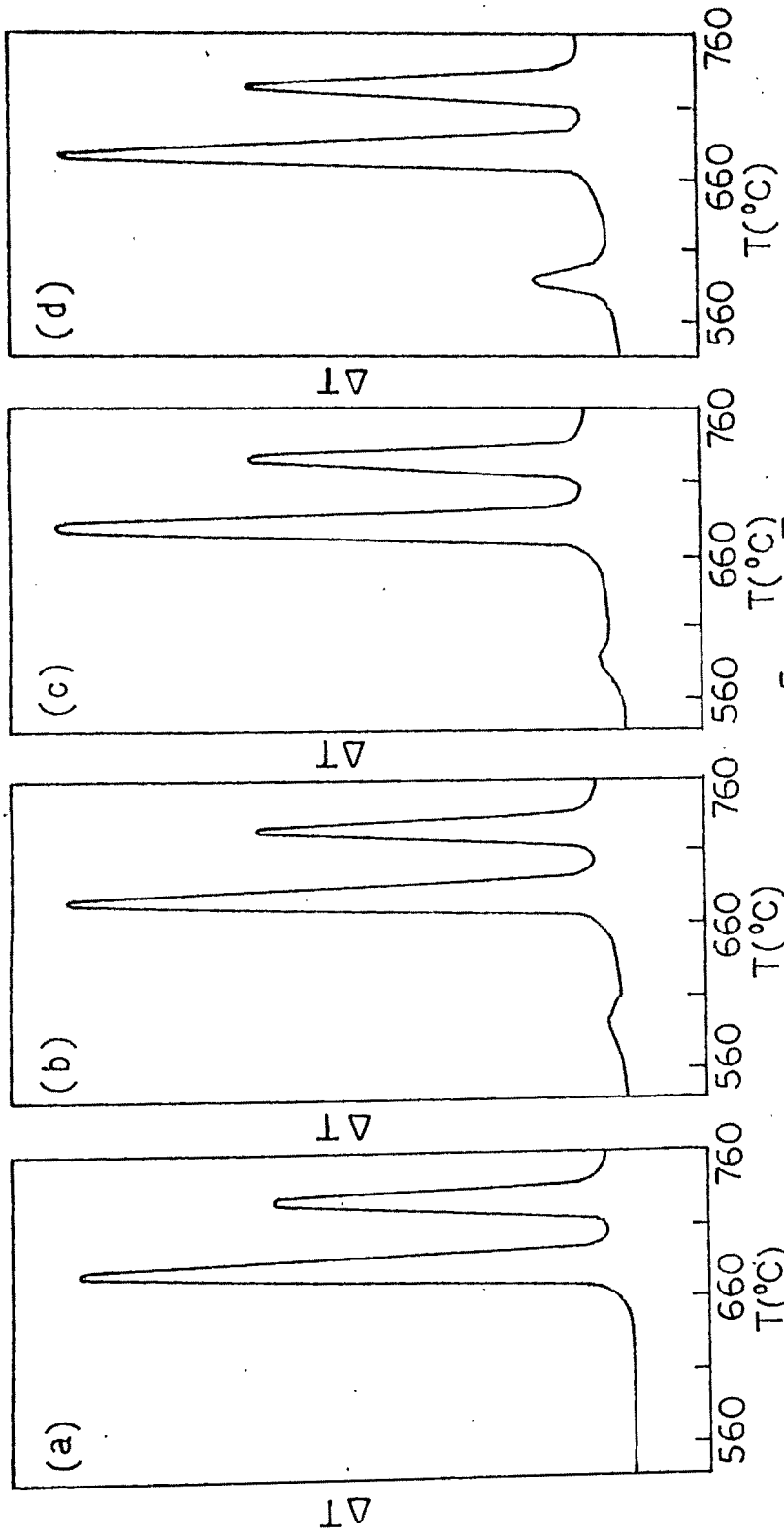
Figure 3.3 shows the thermal behavior of $\text{Ba}(\text{ReO}_4)_2$ during heating. It may be noted that there are three endotherms and the decreased for ΔH are $\sqrt{\text{---}} - \beta > \beta - \alpha > \delta - \sqrt{\text{---}}$. On cooling, only two exotherms, namely, $\alpha - \beta$ and $\beta - \sqrt{\text{---}}$ are observed. In order to follow the nature of $\sqrt{\text{---}} - \delta$ transition, the sample after it reached the α -phase was quench-cooled and then reheated at different time intervals. Figures 3.4(a-d) show the changes in DTA that occurred during reheating of the quench-cooled specimens immediately (a), after 0.5h (b), after 1h (c) and after 2h (d). It may be noted that the $\delta - \sqrt{\text{---}}$ endotherm reappears with the passage of time and the complete conversion takes place after ca. 2h. This shows that the hysteric effect in this case is very high and is associated with kinetic barrier. The width of the hysteresis for the two



DTA of $\text{Pb}(\text{ReO}_4)_2$
 Figure 3.2



DTA of $\text{Ba}(\text{ReO}_4)_2$
 Figure 3.3



Reheating of the quench-cooled specimen $[\text{Ba ReO}_4]_2$; immediately (a), after 0.5 h (b), after 1 h (c) and after 2 h (d).

Figure 3.4

Table 3.2

Thermal data for $M(\text{ReO}_4)_2$

$M(\text{ReO}_4)_2$	Transition temperature ^a (°C)		ΔT^b (°C)	ΔH (kcal mol ⁻¹)
	onset	peak (heating) peak (cooling)		
$\text{Ca}(\text{ReO}_4)_2$	275	300	75	4.1
	315	335	40	0.3
	365	380	370	0.4
$\text{Ba}(\text{ReO}_4)_2$	580	595		0.7
	665	680	640	3.7
	710	725	710	2.2
$\text{Pb}(\text{ReO}_4)_2$	465	480	430	8.6
			50	

^a All thermal transitions are endothermic. ^b Width of hysteresis.

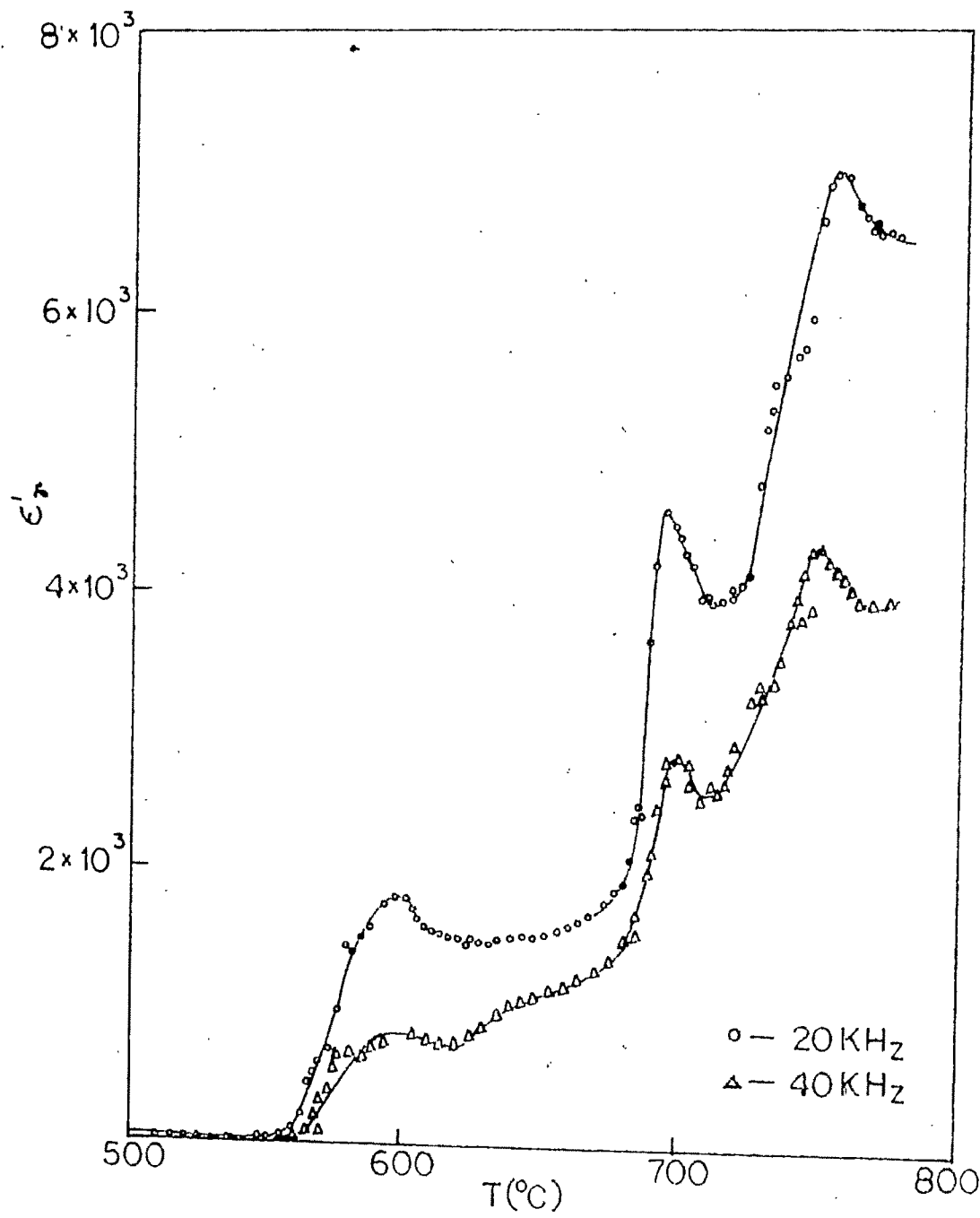
other transitions and the enthalpy changes for all three transitions are summarized in Table 3.2.

The phase transformations under consideration are all thermodynamically first order. In a first order transition the free energy curves intersect at the transition temperature, T_t when the free energies G_I and G_{II} become equal. The occurrence of hysteresis suggests that the transformation does not occur at the point where the free energies are exactly equal. It has been suggested²¹ that for such a situation the strain energy, ϵ , and the interfacial energy, η , should also be taken into consideration in the free energy expression. Thermal hysteresis may arise either due to the formation of hybrid crystal or kinetic reasons. In the hybrid crystal the domain of the product and parent phases exist in a kind of metastable equilibrium, the termination of this metastable region in the two directions away from the true transition temperature, T_t , measures the width of the hysteresis^{21,22}. Due to the existence of the kinetic barrier, the new phase may not be able to nucleate at T_t . The nucleation barriers should be higher and hence ΔT (width of hysteresis) greater, for transitions involving larger change in volume.

Inspection of the data in Table 3.2 reveals that transformation in $Ba(ReO_4)_2$ is kinetically controlled and presumably involves considerable change in volume (ΔV) due to $\delta - \sqrt{\quad}$ transformation. Similarly it seems likely that the $\delta - \sqrt{\quad}$

transition in $\text{Cd}(\text{ReO}_4)_2$ also is accompanied by a large change in volume. Such large change in volume is possible if a low symmetry phase (triclinic/monoclinic) transforms to one with a greater symmetry. In the case with $\text{Pb}(\text{ReO}_4)_2$, the ΔT is quite high (50°C), but not as high as observed for $\delta - \sqrt{}$ transformation in $\text{Ba}(\text{ReO}_4)_2$ or $\text{Cd}(\text{ReO}_4)_2$. It may be also noted that the magnitude of hysteresis for $\sqrt{} - \beta$ phases in $\text{Cd}(\text{ReO}_4)_2$ and $\text{Ba}(\text{ReO}_4)_2$ are almost equal. Similarly for both the compounds the $\beta - \alpha$ transformation is accompanied by small width of hysteresis showing that there is small change in volume due to phase transition, which means, that both the phases have high symmetries. Thus although $\text{Cd}(\text{ReO}_4)_2$ and $\text{Ba}(\text{ReO}_4)_2$ are not isostructural at the ambient temperature, however, there is great similarity in the phase transitions of these two compounds.

Figure 3.5 shows the variation of dielectric constants of $\text{Pb}(\text{ReO}_4)_2$ with temperature at 20 KHz. Prior to the phase transition the dielectric constants remain invariant with temperature and have very low values (Table 3.3). A sharp increase in dielectric constant occurs from 470°C and attains the peak at 500°C . Low dielectric constant of $\text{Pb}(\text{ReO}_4)_2$ before transition indicates that the room temperature phase is centrosymmetric, while the high temperature form is noncentrosymmetric.



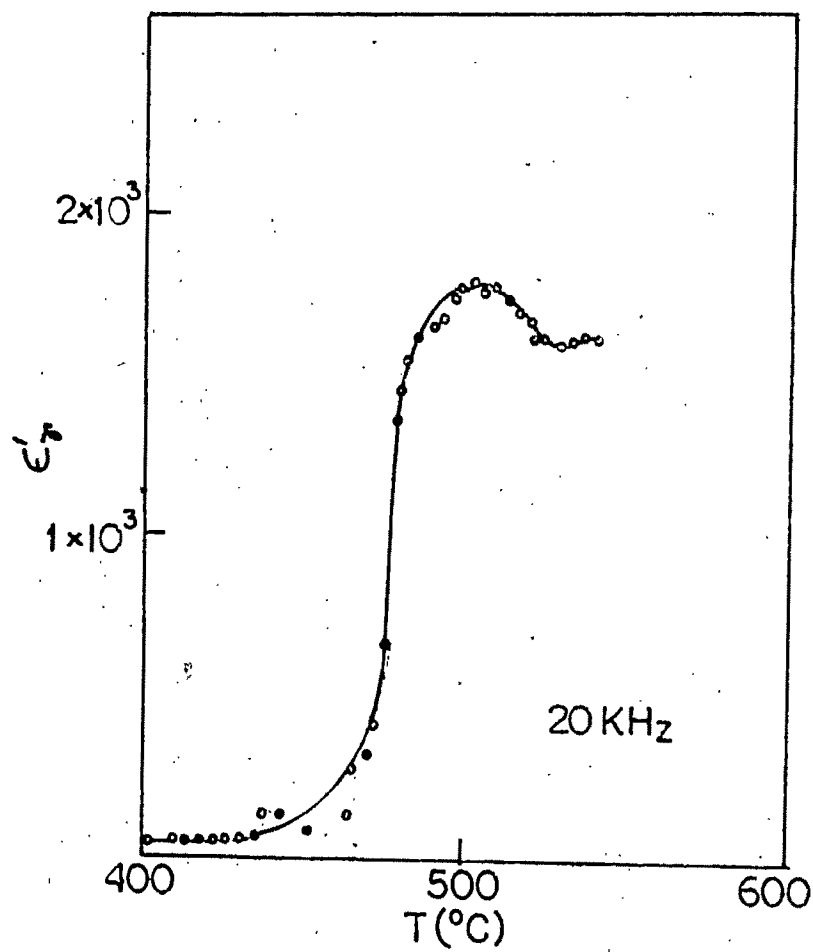
Dielectric study of $Ba(ReO_4)_2$
Figure 3.5

Table 3.3

Dielectric data for $\text{Ba}(\text{ReO}_4)_2$ and $\text{Pb}(\text{ReO}_4)_2$

Compound	T_m^a ($^{\circ}\text{C}$)		ϵ_r' (at T_m)		ϵ_r' (at 30°C)	
	DTA	Dielectric	20 KHz	40 KHz	20 KHz	40 KHz
$\text{Ba}(\text{ReO}_4)_2$	595	605	1800	800	15	3
	680	700	4650	2880		
	725	750	7000	4360		
$\text{Pb}(\text{ReO}_4)_2$	480	500	1750		40	

^a Peak temperature for transition.



Dielectric study of $\text{Pb}(\text{ReO}_4)_2$
Figure 3.6

The variation of dielectric constants of $\text{Ba}(\text{ReO}_4)_2$ measured at 20 and 40 KHz as a function of temperature is shown in Figure 3.6. As observed with DTA here also three phase transitions can be noted. The peak temperatures correspond well with the DTA values. Similar to $\text{Pb}(\text{ReO}_4)_2$ in this case also the δ -phase has very low dielectric constant, however, with successive phase transitions ϵ'_r undergoes large increase in value. From the magnitude of ϵ'_r (Table 3.3) it appears that the higher temperature phases are all noncentrosymmetric.

Attempts to measure dielectric constants of $\text{Cd}(\text{ReO}_4)_2$ phases were unsuccessful due to highly hygroscopic nature of this compound. Making of pellets for measurement turned out to be a formidable problem; slight exposure to atmosphere caused flaking of the pellets during compaction. Nevertheless, from similar thermal behavior it may be predicted that the gross dielectric features of $\text{Cd}(\text{ReO}_4)_2$ will be similar to $\text{Ba}(\text{ReO}_4)_2$.

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