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Thermal, Dielectric, and Electrical Transport Properties of Some Bivalent Metal Perrhenates

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Thermal, dielectric, and electron transport properties of dihydrated and anhydrous perrhenates of strontium, barium, cadmium, and lead have been investigated. The DTA of anhydrous $M[ReO_4]_2$ (M = Sr, Ba, Cd) compounds exhibit three reversible phase transitions with considerable thermal hysterisis for the first phase transformation. A single reversible phase transition occurs for $Pb[ReO_4]_2$. The parent phases of $Ba[ReO_4]_2$, $Pb[ReO_4]_2$, and $Cd[ReO_4]_2$ behave as semiconductors at elevated temperatures. The dielectric constants measured for $Sr[ReO_4]_2$ in the temperature range 30 to −160°C give a broad inflection between −40 and −70°C, which probably indicates a phase transition.

Introduction

Phase transitions of inorganic materials in the solid state are often accompanied by many interesting change in properties (*1–3*). We recently reported (*4, 5*) the thermal and dielectric behavior of different phases of rare earth iodates. Presently we are concerned with phase transition behavior of simple perrhenate salts. A survey of literature revealed that the structurally characterized perrhenate salts are $M[ReO_4]$ (M = alkali metals, NH_4, Ag, Tl) (*6–8*) and $Ca[ReO_4]_2 \cdot 2H_2O$ (*9*). Powder diffraction data of $M[ReO_4]_2$ (M = Ba, Pb, Cd) have also been reported (*7, 10*), but not indexed. $NH_4[ReO_4]$ has received considerable attention in recent years because a broad discontinuity has been noted at around 200 K in its unit cell dimension (*11*), heat capacity (*12*), Raman spectra (*13*), and ^{187}Re NQR frequency (*14*). More recently the molecular metals bis-(ethylenedithio)tetrathiafulvalene perrhenates, $[BEDT{-}TTF]_m[ReO_4]_n$, are receiving considerable attention (*15–17*) due to their $1 - D/2 - D$ conduction behavior. Differential thermal analysis of the products obtained by heating a mixture of several bivalent metal carbonates and ammonium perrhenate has been reported (*18*) to undergo one or more phase transformations. During the course of our preliminary studies we noted that $Ln[ReO_4]_3$ (Ln = lanthanides), and $M[ReO_4]_2$ (M = Cu, Ni, Co, Fe, Mn) compounds do not exhibit any phase transition prior to their thermal decomposition. We report here that the anhydrous perrhenates of strontium, barium, lead, and cadmium, however, undergo one or more phase tran-

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sitions, and the electrical conductivity of the low temperature phase of these compounds increase by 3 to 4 orders of magnitude with the increase of temperature. The dielectric behavior of $Sr[ReO_4]_2 \cdot 2H_2O$ also shows a broad discontinuity at subambient temperatures.

Experimental

Preparation of $M[ReO_4]_2 \cdot 2H_2O$ *(M = Sr, Ba, Pb, Cd).* These compounds were prepared by reacting excess of metal carbonates (reagent grade) with aqueous perrhenic acid, which was obtained by passing an aqueous solution (0.1 *M*) of $NH_4[ReO_4]$ (Koch-Light, >99%) through a cation exchanger, Amberlite IR-120, in the H^+ ion form. The mixture was digested on a steam bath till the solution became neutral (pH paper). After removal of the unreacted metal carbonate by filtration, the filtrate was concentrated and then allowed to crystallize at the ambient temperature. The hydrated salts were dried over $CaCl_2$.

The thermogravimetric analysis of the hydrated perrhenates showed that dehydration of these compounds take place in the temperature range 80 to 120°C. The anhydrous compounds were prepared by heating the hydrated salts isothermally at 120°C for 2 hr. The thermograms of the dehydrated products did not show any weight loss before their decomposition temperatures were reached.

Thermal analysis. Thermogravimentric analysis (TGA) and differential thermal analysis (DTA) were performed on a Shimadzu DT-30 thermal analysis system. About 20 mg of a specimen in finely ground state was heated in flowing nitrogen atmosphere at a rate of 20°C/min. Heats of phase transformation were determined as described earlier (*19*).

Electrical conductivity measurement. Electrical conductivity measurements were carried out with a General Radio Type 1620-A capacitance-measuring assembly consisting of Type 1615-A capacitance bridge, Type 1311-A audio oscillator, Type 1232-A tuned amplifier and null detector. The conductance, G (Ω^{-1}) of a specimen was obtained by measuring the capacitance, $C(F)$ and dissipation factor, D at a given frequency, f (Hz), by using the relation $G = 2\pi fDC$. The conductivity of a pelletized specimen with thickness l and area a is σ (Ω^{-1} cm^{-1}) $= Gla^{-1}$. The diameter and thickness of the pellets used were 1.35 and ca. 0.2 cm, respectively. The pellets were coated with a thin layer of palladium paste (Dow-Corning) on both the sides to ensure good electrical contact. A spring-loaded locally fabricated two-probe sample holder was used for conductivity measurements. The probes were made of polished stainless steel of diameter 1.4 cm. The sample holder was fitted in a stainless steel cylinder which was evacuated to 10^{-3} Torr. A chromel-alumel thermocouple was located close to the specimen and the potential drop was measured with a Leeds-Northup Type K4 potentiometer. The cell assembly was heated by a cylindrical furnace whose power input was regulated by a proportionating-type temperature controller.

Dielectric measurement. The relative dielectric constant, ε_r of a material was determined as the ratio $\varepsilon_r = \varepsilon/\varepsilon_0 = C/C_0$, where C and C_0 are the capacitance of the sample and empty space in vacuum, respectively. The dielectric measurements were carried out at a frequency of 20 kHz. The pelletized specimens in these experiments were coated with a very thin layer of silver paste. All measurements were made at 10^{-5} Torr using a cell assembly similar to the one described above, and in these experiments a calibrated copper–constantan thermocouple was used for temperature measurements. Dielectric measurements at subambient temperatures were made by inserting the cell assembly in a locally fabricated cryostat (*20*).

Results and Discussion

All of the perrhenate salts were obtained as dihydrates as indicated by TGA. The powder diffraction data of the anhydrous compounds were in agreement with the reported values (*7*, *9*). The observed *d* spacings could not be indexed with unit cells of higher symmetries, and appear to be monoclinic or triclinic. The TGA and DTA of the anhydrous compounds taken together indicated that the observed thermal changes prior to decomposition are due to solid state phase transitions. The DTA of $Cd[ReO_4]_2$, $Pb[ReO_4]_2$, and $Ba[ReO_4]_2$ are shown in Fig. 1. Both $Cd[ReO_4]_2$ and $Ba[ReO_4]_2$ are characterized by three endothermic changes, whereas a single endotherm is observed for $Pb[ReO_4]_2$. The cooling curves showed considerable supercooling of the product phases. The phase transition temperatures observed during heating and cooling, and their differences (ΔT) indicating the width of thermal hysterisis are given in Table I. In the case of $Ba[ReO_4]_2$, the first phase transition which occurred at 595°C in the heating mode did not appear in the cooling curve. It appeared, however, on reheating the quenched-cooled specimen after standing at room temperature for 2 hr. Figure 2 shows the gradual changes that occurred on reheating the quenched-cooled sample after various time intervals.

TABLE I

Differential Thermal Analysis Data for $M[ReO_4]_2$

$M[ReO_4]_2$	Transition temperature (°C)[a] Heating	Cooling	Ref. (*18*)	ΔT(°C)[b]	ΔH(kcal/mole)
$Cd[ReO_4]_2$	300	75	220	225	4.1
	335	295	320	40	0.3
	380	370	595	10	0.4
$Sr[ReO_4]_2$	650	*c*	580	*d*	0.3
	780	770	750	10	1.6
	840	830	825	10	1.1
$Ba[ReO_4]_2$	595	*c*	495	*d*	0.7
	680	640	560	40	3.7
	725	710	600	15	2.2
$Pb[ReO_4]_2$	480	430	385	50	8.2

[a] Refers to the temperature at the onset of the peak, which was obtained as the point of intersection of the extrapolated base line and the linear ascending/descending part of the heating or cooling curve.

[b] Width of thermal hysterisis.

[c] Not observed during cooling.

[d] Large value, to be reckoned as a metastable phase.

The DTA of $Sr[ReO_4]_2$ gave three endotherms with peaks at 650, 780, and 840°C. In the cooling curve, only two exotherms appeared with peaks at 830 and 770°C. The weak thermal change at 650°C could be observed only on reheating the specimen after

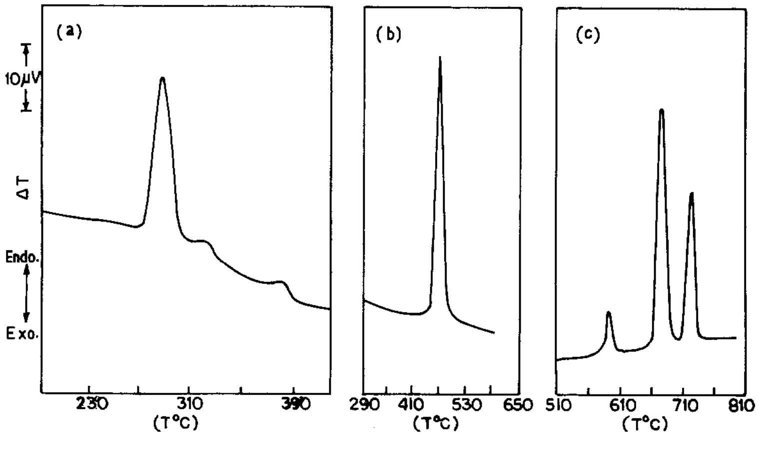

Fig. 1. DTA for $Cd[ReO_4]_2$ (a), $Pb[ReO_4]_2$ (b), and $Ba[ReO_4]_2$ (c).

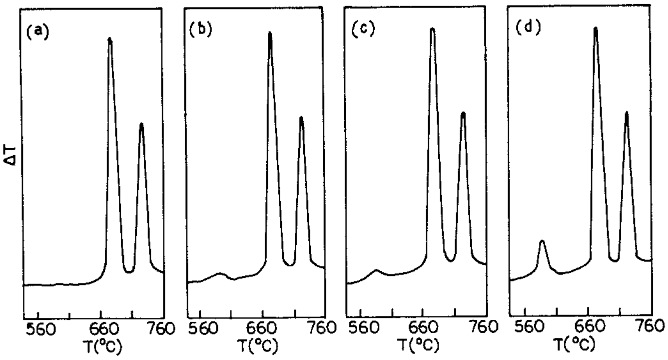

FIG. 2. DTA for a quench-cooled specimen of Ba$[ReO_4]_2$ after various time intervals of standing at room temperature. Reheated immediately (a), after 0.5 hr (b), after 1 hr (c), after 2 hr (d).

several hours, indicating it to be a metastable phase.

We note that the phase transition temperatures recorded in the present work are at variance with the reported values (*18*) (see Table I). The enthalpy changes for phase transitions are also given in Table I. It is worth noting that the ΔH value for Pb$[ReO_4]_2$ due to a single phase transformation is considerably more than the other compounds exhibiting three successive endotherms.

Of particular interest is the large thermal hysterisis observed for some of these phase transitions. It may be noted that for the compounds undergoing multiple phase transitions, the transition that occurred at the lowest temperature exhibited maximum supercooling. Normally, thermal hysterisis is observed either in terms of differences in transformation temperatures, or by the existence of a metasteable phase. Factors such as creation of an interface between the product and parent phases, and the elastic strain resulting from transformation are responsible for hysterisis (*21*). Usually, the magnitude of thermal hysterisis is related to the volume change in transformation (*2, 22*). Close packed structures tend to be stable at lower temperatures and transform to a more open structure at a higher temperature (*21*). Although structural information for the compounds under consideration are lacking, it may be reasonably assumed that in the cases of strontium, barium, and cadmium perrehates the lowest temperature low symmetry structures transform to ones of high symmetry through three successive endothermic processes.

The dielectric behavior of $M[ReO_4]_2 \cdot 2H_2O$ (M = Sr, Ba, Pb) were investigated in the temperature range 30 to −160°C at a frequency of 20 kHz. Figure 3 shows the variation of relative dielectric constant of Sr$[ReO_4]_2 \cdot 2H_2O$ with temperature. A broad inflection between −40 and −70°C may be noted for this compound. The appearance of such a plateau can be suspected as due to a phase transition, but would require confirmation from other evidences. In any case, if the change is *real*, then most likely it is a second-order transition. For such a phase transition, the parent and product phases should be crystallographically closely related. In contrast to Sr$[ReO_4]_2 \cdot 2H_2O$, no special features were noted for the hydrated salts of barium and lead, for which ε_r remained practically unchanged throughout the entire temperature range of study.

The electrical conductivities of the parent phases of Ba$[ReO_4]_2$, Pb$[ReO_4]_2$, and Cd$[ReO_4]_2$ were measured as a function of temperature. All three compounds behave as insulators from ambient to 200°C. In the case of $Ba[ReO_4]_2$, the conductivity increased from 2.4×10^{-9} to $5.6 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ in between 330 and 550°C. For $Pb[ReO_4]_2$, similar increase in conductivity occurred between 290 and 410°C (1×10^{-9} to $5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$). The conductivity of $Cd[ReO_4]_2$ changed from 1×10^{-9} to $2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ in the narrow temperature range 250 to 300°C. Beyond 300°C, a sharp decrease in conductivity was observed for this compound, which was later identified to be due to the development of a crack in the pellet. This problem was found to be inherent with $Cd[ReO_4]_2$ since repitition of the experiment met with the same experience. We presume that the development of multiple fracture in the measuring pellet is associated with considerable change in volume that takes place at the phase transition temperature, which incidentally is 300°C for $Cd[ReO_4]_2$. Large thermal hysterisis observed for this phase transition is also consistent with this view.

The electrical conductivity of the anhydrous perrhenates appears to arise due to defect structures (*23*). Conduction due to the presence of foreign impurities is possible, but less probable. For a material having one type of charge carrier, the expression for conductivity is

$$\sigma = nqu \tag{1}$$

where n is the concentration of charge carrier, q is the magnitude of charge, and u is the mobility. When the charge carrier moves through an activated diffusion process, the expression for the mobility becomes

$$u = u_0(T)_e = \varepsilon_u/kT \tag{2}$$

where $u_0(T)$ is a function which depends weakly on T, ε_u is mobility activation energy, and k is Boltzmann's constant. The electrical transport property of a semiconductor whose charge carriers are localized, as should be the case with the perrhenates, the expressions for σ can be distinguished in the high, intermediate-, and low-temperature ranges (*24*)

$$\sigma(\text{high}) = (N_d - N_a)qu_0(T)_e - \varepsilon_u/kT \tag{3}$$

$$\sigma(\text{intermediate}) = [(g_i/g)N_t(N_d - N_a)]^{1/2}qu_0(T)_e - (\varepsilon_g/2 + \varepsilon_u)/kT \tag{4}$$

$$\sigma(\text{low}) = (N_t g_i/g)[(N_d - N_a)/N_a]qu_0(T)_e - (\varepsilon_g + \varepsilon_u)/kT. \tag{5}$$

In these expressions N_d and N_a are the donor and acceptor site concentrations, N_t is the total concentration of all cations, g_i and g are degeneracy factors, and $\varepsilon_g = \varepsilon_t - \varepsilon_d$, where ε_t and ε_d are the energies of the charge carrier at transport levels and near donor sites, respectively.

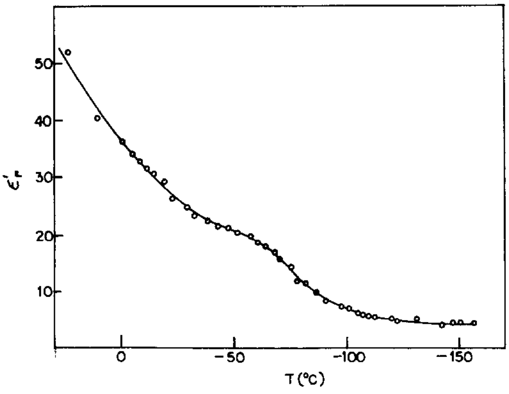

FIG. 3. Variation of dielectric constants of $Sr[ReO_4]_2$ $2H_2O$ with temperature. Frequency used, 20 kHz.

The plots of log σ against $1/T$ for anhydrous barium, lead, and cadmium perrhenates are shown in Fig. 4. For barium and lead compounds the conductivity profiles exhibit sigmoidal feature. From the linear part of the plots, which correspond to the intermediate temperature range, the gross activation energies have been obtained. These values are $Ba[ReO_4]_2$, 2.3 eV; $Pb[ReO_4]_2$, 3.2 eV; $CD[ReO_4]_2$, 4.3 eV. In absence of data related to the thermoelectric powers it is not possible to decide whether the charge carriers in the perrhe-

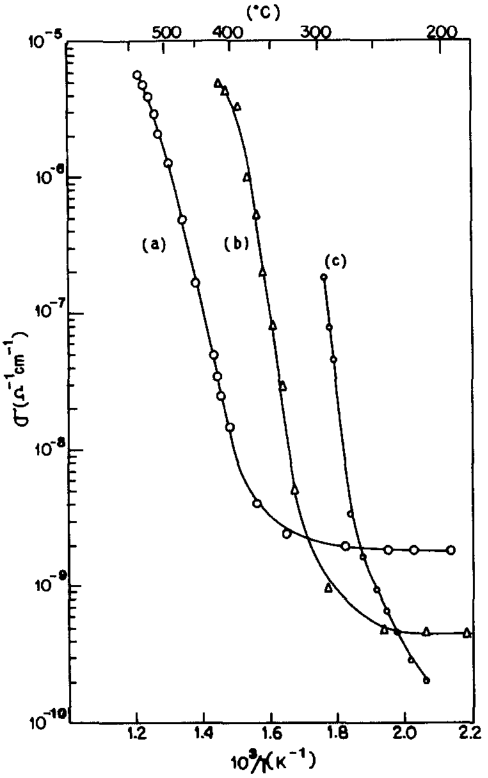

FIG. 4. Electrical conductivity vs reciprocal temperature for $Ba[ReO_4]_2$ (a), $Pb[ReO_4]_2$ (b), and $Cd[ReO_4]_2$ (c).

nates are electrons or holes. Nevertheless, if it is assumed that some of the Re(VII) sites in the crystal lattices are occupied by Re(VI) ions, then an extra electron which is introduced per Re(VI) ion can migrate in an electrical field. On this basis $M[ReO_4]_2$ compounds are expected to act as n-type semiconductors.

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References

1. T. Tsakalakos (Ed), "Phase Transformations in Solids," North-Holland, New York, 1984.
2. C. N. R. Rao and K. J. Rao, "Phase Transitions in Solids," McGraw-Hill, New York, 1978.
3. H. K. Henisch, R. Roy, and L. E. Cross (Eds.), "Phase Transitions," Pergamon, New York, 1973.
4. B. P. Ghosh, A, K. Ray, and K. Nag, *J. Mater. Sci. Lett.* **2,** 638 (1983).
5. B. P. Ghosh and K. Nag, *J. Mater. Sci.* **20,** 2335 (1985).
6. R. Scholder and K. L. Huppert, *Z. Anorg. Allgem. Chem.* **334,** 209 (1964).
7. K. Ulbricht and H. Kriegsmann, *Z. Anorg. Allg. Chem.* **358,** 193 (1968).
8. B. Krebs, *Acta Crystallogr. Sect. B* **32,** 1334 (1976).
9. R. G. Matveeva, V. V. Ilyukhin, M. V. Varfolomeev, and N. V. Belov, *Sov. Phys. Dokl.* **25,** 321 (1980).
10. L. L. Zaitseva, M. I. Konarev, A. V. Velichko, and N. N. Morgunova, *Russ. J. Inorg. Chem.* **23,** 978 (1978).
11. R. J. C. Brown, J. G. Smeitzger, and R. D. Heyding, *J. Magn. Reson.* **24,** 269 (1976).
12. R. D. Weir and L. A. K. Stavely, *J. Chem. Phys.* **73,** 1386 (1980).
13. J. Korppi-Tommola, R. J. C. Brown, H. F. Shurvell, and O. Sala, *J. Raman Spectrosc.* **11,** 363 (1981).
14. R. A. Johonson and M. T. Rogers, *in* "Advances in Nuclear Quadrupole Resonance," Vol. 1, p. 297, Heyden, London, 1974.
15. S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, *Phys. Rev. Lett.* **50,** 270 (1983).
16. S. S. P. Parkin, E. M. Engler, V. Y. Lee, and R. R. Schumaker, *Mol. Cryst. Liq. Cryst.* **119,** 375 (1985).
17. H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, H. Inokuchi, *Chem. Lett.* **183,** (1984).
18. D. Schultze, *in* "Proceedings of 4th International Conference On Thermal Analysis," Vol. 1, p. 717, Heyden, London, 1975.
19. B. P. Ghosh and K. Nag, *J. Thermal Anal.* **29,** 433 (1984).
20. B. P. Ghosh, M. Chaudhury, and K. Nag, *J. Solid State Chem.* **47,** 307 (1983).
21. V. I. Raghavan and M. Cohen, *in* "Treatise On Solid State Chemistry" (N. B. Hanny, Ed.), Plenum, New York, 1975.
22. N. G. Parsonage and L. A. K. Stavely, "Disorder in Crystal," Oxford Univ. Press, London/New York, 1977.
23. F. A. Kroger, "The Chemistry of Imperfect Crystals," 2nd. ed., North-Holland, Amsterdam, 1974.
24. J. M. Honig, *in* "Preparation and Characterization of Materials" (J. M. Honig and C. N. R. Rao, Eds.), Academic Press, New York), 1981.