Thermochimica Acta, 13 (1975) 305–314

CRYSTAL STRUCTURE TRANSFORMATIONS IN AMMONIUM AND ALKALI METAL PERCHLORATES

V. R. PAI VERNEKER* AND K. RAJESHWAR
High Energy Solids Laboratory, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012 (India)

(Received 19 June 1975)

ABSTRACT

A comparative study of the polymorphic transformations in ammonium and the alkali metal perchlorates has been made using differential thermal analysis. Certain correlations have been attempted between the observed trends in the transformation temperatures and available crystallographic and thermodynamic data. The transformation in the case of sodium perchlorate shows pronounced second-order effects. Considerable hysteresis is observed in the transformations in ammonium, potassium, rubidium and caesium perchlorates. Doping of ammonium perchlorate with ammonium phosphate is seen to result in an upward shift in the transformation temperature and an increase in the thermal hysteresis. Prior mechanical and thermal treatment is also seen to result in a broadening of the hysteresis loops in the case of ammonium and potassium perchlorates. The results are explained in terms of contrapolarization effects and the production of strain in the material as a result of prior treatment.

1. INTRODUCTION

The crystal structure of ammonium and the alkali metal perchlorates is bipyramidal orthorhombic at low temperatures and cubic at high temperatures. Lithium perchlorate is an exception in that it melts in the low-temperature modification. The phase change from orthorhombic to cubic has been studied by X-ray diffraction methods and by differential thermal analysis (DTA)[1–11]. However, the information regarding the thermodynamic, structural, kinetic and reversibility aspects of these transformations is limited. We have now investigated all these aspects of polymorphic transformations of these materials using DTA. DTA has been shown to be a powerful tool in the quantitative study of the thermodynamic and kinetic aspects of crystal structure transformations[12]. Although the transformations in ammonium and the alkali metal perchlorates have been classified as "reversible", considerable hysteresis is observed in these transformations in terms of fairly large differences in the transformation temperatures in the forward and reverse directions[13,14]. One of our main objectives was to investigate the thermal hysteresis in

---

*To whom all correspondence should be addressed.

these materials and to study the effects of mechanical and thermal pre-treatment on the forward and reverse transformation temperatures. We have also tried to find a correlation between the observed trends in the transformation temperatures and the thermal hysteresis with certain parameters obtained from available crystallographic and thermodynamic data.

2. EXPERIMENTAL

The materials employed in the investigation were: ammonium perchlorate and sodium perchlorate (Fluka A.R., as received), and potassium perchlorate (Lab. Chemicals, India, A.R., twice recrystallized from distilled water). Rubidium and caesium perchlorates were prepared from the corresponding carbonates. The materials were then recrystallized twice.

Ammonium perchlorate was doped with PO_4^{3-} by cocrystallization from an aqueous solution containing the desired concentration of the dopant.

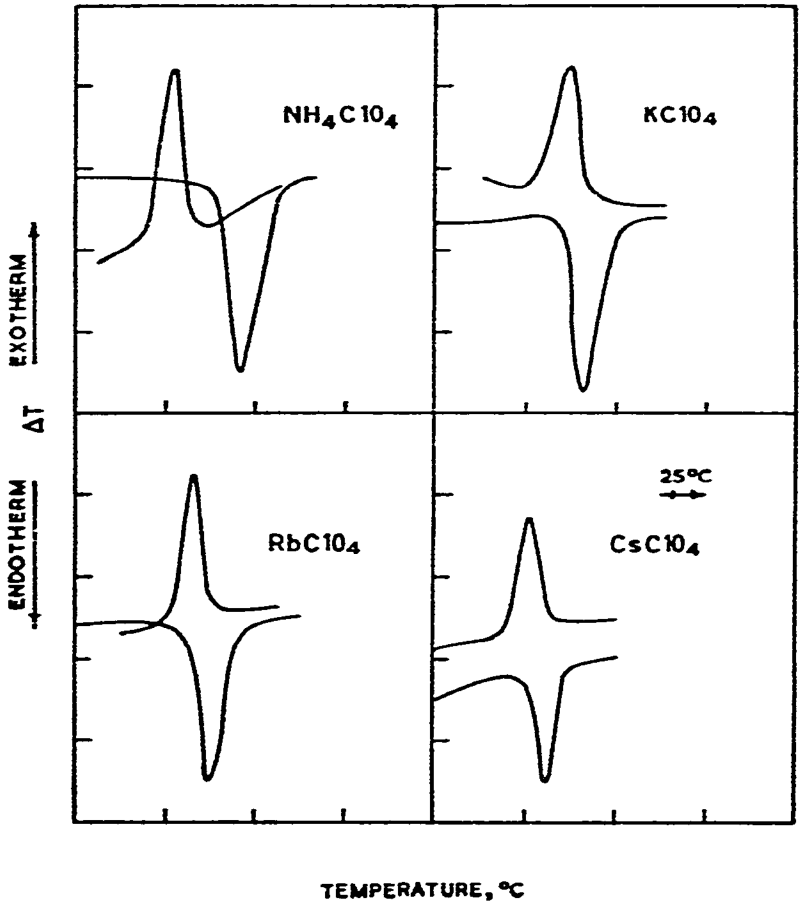

Fig. 1. Typical DTA peaks for the transformations in ammonium and alkali metal perchlorates (the transformation temperatures are listed in Table 1).

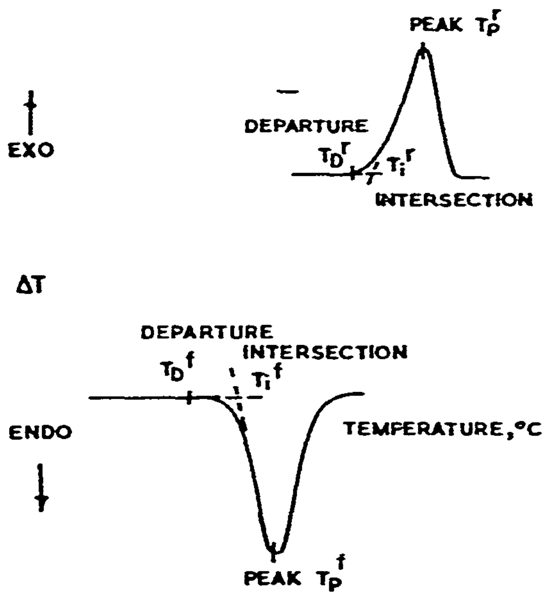

Fig. 2. Representation of the departure, intersection and peak temperatures in the forward and reverse directions.

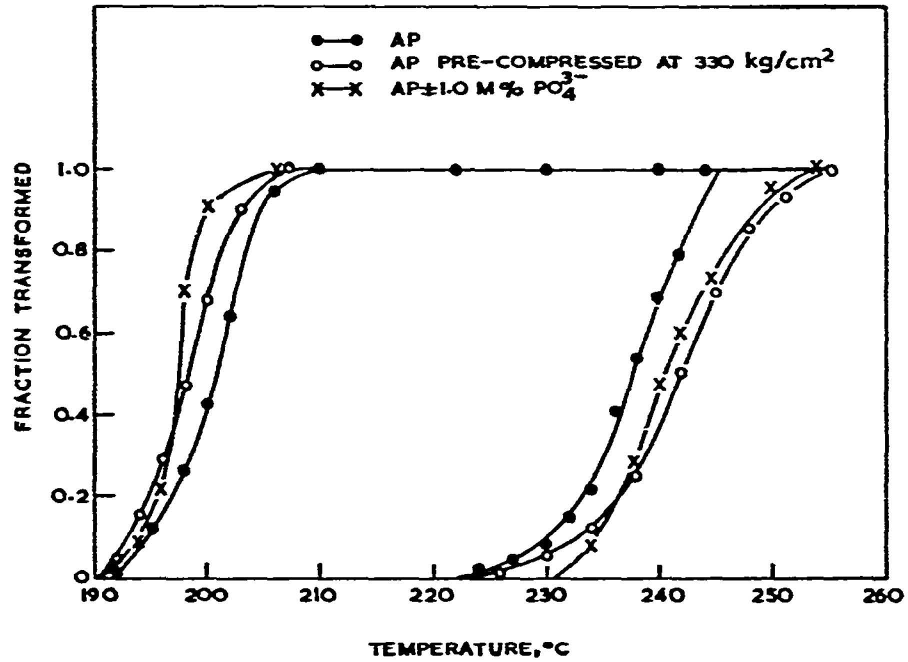

Fig. 3. Typical hysteresis loops obtained in thermal transformations.

All the materials were dried and stored in powder form over phosphorus pentoxide before subjecting them to DTA.

It has been shown that particle size has marked effects on the transformation temperatures[15]. To preclude the effects of particle size, all the materials were graded through standard BSS sieves to 144–179 μm range. Comparative runs were always made on materials of the same particle size.

DTA was carried out on an apparatus similar to that described by Sawant and Patel[16]. The DTA assembly was housed in a tubular quartz furnace which was programmed to a constant heating rate of 10°C min^{-1}. Temperatures were measured on a calibrated chromel–alumel thermocouple connected in series with the block thermocouple and immersed in an ice–water mixture so as to maintain 0°C as the reference temperature. Platinum sample cups (M/s. Ravindra Herauss and Co., India) were used in all the experiments. All the substances studied were polycrystalline. Ignited powdered alumina was used as the reference standard. For thermal hysteresis studies, the DTA curves were obtained under conditions where the heating and cooling rates were nearly identical (10°C min^{-1}). Typical DTA curves obtained in the present study are shown in Fig. 1. From the DTA curves, the peak temperature T_p (at which the transformation goes to completion), the departure temperature T_d and the intersection temperature T_i were noted as shown in Fig. 2. The values for the departure, intersection and peak were recorded wherever possible for both the forward and reverse directions. The precision of a transition temperature measurement was ± 1 °C.

The energies of activation E_a were calculated by the method of Piloyan[17]. Activation energies calculated by this method have an uncertainty of $\pm 15\%$. In spite of this limitation, it is nevertheless reasonable to compare values of E_a in a related series of systems under identical conditions. The analysis of the DTA peaks, in all the cases, gave good linear Arrhenius plots and this seems to confirm the fact that meaningful values of activation energies can be obtained by this method. The hysteresis loops (shown in Fig. 3) were constructed from the DTA peaks by calculating the fraction of material transformed at the different temperatures in the forward and reverse directions. The fraction transformed at any one temperature was calculated from the ratio of the deviation of the curves from the baseline at that temperature and the peak height maximum.

The strain energies were calculated by the method suggested by Rao et al.[12].

Pre-compression was effected on a hydraulic pellet press using a stainless-steel die for holding the material. After compression, the material was crushed in a mortar (avoiding circular motion on the pestle) and then sieved to the same particle size as the uncompressed material. For pre-heating, the material was maintained in a sealed tube in an air oven at 110°C for 24 h.

3. RESULTS AND DISCUSSION

3.1 Crystal structure transformations in ammonium and the alkali metal perchlorates

The transformation temperatures, the enthalpies of transformation, the energies of activation and relevant crystallographic data for the phase transformations in ammonium, sodium, potassium, rubidium and caesium perchlorates are shown in Table 1. All the materials listed in Table 1 show a phase change from the low-temperature bipyramidal orthorhombic to the high-temperature cubic structure. The transformation temperatures reported in the literature for ammonium and the alkali perchlorates show a considerable variation as can be seen in Table 2. This is largely due to the differences in the method of DTA measurement, as e.g., in the position of the thermocouples, the type of sample holder and the heating rate employed. However, the influence of other factors like purity of the material and particle size are undoubtedly equally important[12,18]. An examination of Table 1 shows that the transformation temperatures progressively decrease in going from potassium to caesium perchlorate. This is not altogether surprising since the transformations are all similar and all the crystal structures are isomorphous. The enthalpies of transformation (ΔH) and the energies of activation for the transitions also decrease from potassium to caesium perchlorate. Sodium perchlorate, however, shows a strikingly small value of

TABLE 1

CRYSTALLOGRAPHIC, THERMODYNAMIC AND KINETIC DATA ON THE CRYSTAL STRUCTURE TRANSFORMATIONS IN AMMONIUM AND THE ALKALI METAL PERCHLORATES

Material	T_d^f (°C)	T_i^f (°C)	T_p^f (°C)	T_d^r (°C)	T_i^r (°C)	T_p^r (°C)	ΔH[a] (*kcal mol*$^{-1}$)	E_a (*kcal mol*$^{-1}$)	*Volume*[b] *available for perchlorate ion* (Å^3)	*Radius ratio,* ρ
$NaClO_4$	268	298	320	—	—	—	0.6 ±0.2	48	77.39[c] 91.66	0.44
$KClO_4$	282	292	302	270	278	292	3.29	184	80.49 104.91	0.61
$RbClO_4$	246	260	270	246	250	264	3.00 ±0.1	129	88.45 98.98	0.68
$CsClO_4$	210	216	228	202	204	220	2.00 ±0.1	92	94.59 106.84	0.78
NH_4ClO_4	218	230	246	194	197	210	2.30 ±0.2	110	86.76 99.18	0.65

[a] Values taken from Markowitz and Boryta, *J. Am. Rocket Soc.*, 32 (1962) 1941; *J. Phys. Chem.*, 69 (1965) 1114. [b] Calculated from the unit cell dimensions and ionic radii. [c] The two values refer to orthorhombic and cubic phases, respectively.

TABLE 2

COMPARISON OF THE TRANSFORMATION TEMPERATURES OBTAINED IN THE PRESENT INVESTIGATION WITH THE VALUES REPORTED IN LITERATURE

Material	*Transformation temp.* (°C)	*Reference*
$NaClO_4$	308	1
	313	4
	305	8
	309	8
	320	Present investigation
$KClO_4$	299–300	1
	303	8
	302	11
	302	Present investigation
$RbClO_4$	279	1
	281	4
	278	8
	284	8
	270	Present investigation
$CsClO_4$	219	1
	224	4
	225	8
	221	8
	228	Present investigation
NH_4ClO_4	240	1
	250	7
	255	9
	244	10
	246	Present investigation

TABLE 3

RELATION BETWEEN THE TRANSFORMATION TEMPERATURE, FUSION TEMPERATURE AND POLARIZING POWER OF THE CATION

Material	*Transformation*[a] *temp.* (°C)	*Fusion*[b] *temp.* (°C)	*Polarizing power of cation (charge/radius ratio)*
$NaClO_4$	320	468	2.275
$KClO_4$	302	580	1.641
$RbClO_4$	270	597	1.472
$CsClO_4$	228	577	1.282
NH_4ClO_4	246	—	1.538

[a] Taken as the peak temperature in the forward direction. [b] Data taken from Markowitz et al. (ref. 8).

ΔH. Progressive variations in the heats and energies of activation have been reported by Rao et al.[12] for alkali sulphate although the trends are not so regular as in the case of alkali perchlorates. In the case of alkali sulfates, the transformation temperature drops abruptly from Li_2SO_4 to Na_2SO_4 and then increases progressively from Na_2SO_4 to Cs_2SO_4. Bredig[19] has explained this trend in the transformation temperatures on the basis of the strength of the metal–oxygen bond and "contrapolarization" effects (i.e., deformation of the cation in the field of the sulfate ion). However, in the case of alkali perchlorates, the transformation temperatures fall off smoothly from sodium perchlorate to caesium perchlorate. This clearly shows that unlike the case of alkali sulfates, contrapolarization effects are unimportant for the alkali perchlorates. An examination of the fusion temperatures, the transformation temperatures and the polarizing power of the cation (Table 3) clearly shows that deformation of the anion in the field of the cation is more important than contrapolarization in both phase transformation and fusion in the case of alkali perchlorates (the variation in the fusion temperatures shows some proportionality to the polarizing power, increasing with decreasing polarizing power of the cation).

The transformation in the case of sodium perchlorate takes place over a wide temperature range and has considerable second-order effects. In fact, the hysteresis observed for the phase transformations in the case of potassium, rubidium and caesium perchlorates is absent in the case of sodium perchlorate. This anomalous behaviour in the case of sodium perchlorate is different from that observed for the alkali sulfates where rubidium and caesium sulfates show second-order effects presumably because of the large volume available for the sulfate ion[12]. An examination of Table 1 shows that although the volume available for the perchlorate ion increases from sodium perchlorate to caesium perchlorate, second-order effects are pronounced for sodium perchlorate rather than for the rubidium and caesium salts. This is probably because of the difference in the coordination in the case of sodium perchlorate where it is NaO_8[20], whereas it is MO_{12} (M = K, Rb, Cs) for the other alkali perchlorates. The weakening of the coordination around the metal and consequently of the M–O bonding in the case of sodium perchlorate probably facilitates rotation of ClO_4 anions with accompanying second-order effects.

Table 4 shows the results of AP doped with different concentrations of phosphate. The doped samples show an increase in the transformation temperatures in the forward direction and a corresponding increase in the activation energies. The contrapolarization of the cation in the field of the anion must be of a considerably higher order in the case of the doped samples because of the presence of the triply charged phosphate ions. this results in a stabilization of the lower symmetric low-temperature structure up to comparatively higher temperatures. It is possible that the smaller radius ratio of the impurity ($\rho = 0.5$) also has considerable effects on the transformation temperatures.

The high energies of activation found for the transformations in the present investigation show that they are of the reconstructive type. Thus factors which affect the nucleation and growth processes should be of considerable importance in the kinetics of these transformations. Since all these transformations involve considerable changes in molar volume (Table 5), the Clausius-Clapeyron equation[21] may be used to calculate dp/dT. The dp/dT values are positive for all the transformations included in this study.

TABLE 4

EFFECT OF DOPING AMMONIUM PERCHLORATE ON ITS CRYSTAL STRUCTURE TRANSFORMATION

Material	T_d^f (°C)	T_i^f (°C)	T_p^f (°C)	T_d^r (°C)	T_i^r (°C)	T_p^r (°C)	ΔT_i^h[a] (°C)	ΔT_p^h[b] (°C)	E_a (*kcal mol*$^{-1}$)	E_a (*kcal mol*$^{-1}$)
Ammonium perchlorate (AP)	218	230	246	194	197	210	33	36	110	141
AP+0.001 M% PO_4^{3-}	230	234	250	190	198	210	36	40	120	920
AP+0.1 M% PO_4^{3-}	230	232	252	193	195	209	37	43	138	1021
AP+0.5 M% PO_4^{3-}	230	232	253	191	191	207	41	46	138	1089
AP+1.0 M% PO_4^{3-}	230	234	254	189	191	206	43	48	138	1072

[a] $\Delta T_i^h = T_i^f - T_i^r$. [b] $\Delta T_p^h = T_p^f - T_p^r$.

TABLE 5

RELATION BETWEEN THE THERMAL HYSTERESIS AND THE CHANGE IN MOLAR VOLUME

Material	ΔT_i^h (°C)	ΔT_p^h (°C)	ΔV[a] (*cc mol*$^{-1}$)
$NaClO_4$	—	—	8.66
$KClO_4$	14	10	8.37
$RbClO_4$	10	6	6.36
$CsClO_4$	12	8	7.46

[a] The molar volumes calculated from unit cell dimensions of the orthorhombic and cubic structures.

3.2 *Thermal hysteresis and the effect of pre-compression and pre-heating*

Ammonium and the alkali perchlorates with the exception of lithium and sodium perchlorates, show considerable hysteresis effects (Table 5). The extent of hysteresis is seen to bear a direct relationship to the change in molar volume. Similar results have been obtained by Staveley et al.[22] in their work on ammonium halides. Tables 6 and 7 show the results on the effect of pre-compression and pre-heating on the transformation temperatures in the forward and reverse directions. There is ar

TABLE 6

EFFECT OF PRIOR MECHANICAL AND THERMAL TREATMENT ON THE TRANSFORMATION IN AMMONIUM PERCHLORATE (AP)

Material	T_d^f (°C)	T_i^f (°C)	T_p^f (°C)	T_d^r (°C)	T_i^r (°C)	T_p^r (°C)	ΔT_i^h (°C)	ΔT_p^h (°C)	E_s (*cal mol*$^{-1}$)
AP	218	230	246	194	197	210	33	36	141
AP 50[a]	218	234	248	194	194	208	40	40	187
AP 100	218	236	248	193	193	204	43	44	299
AP 200	218	236	250	180	192	204	44	46	414
AP 330	218	238	255	180	193	207	45	48	741
AP 110[b]	218	236	254	192	206	216	36	38	468

[a] The number signifies the pressure in kg cm^{-2} at which the sample was precompressed. [b] AP preheated at 110°C for 24 h.

TABLE 7

EFFECT OF PRIOR MECHANICAL TREATMENT ON THE TRANSFORMATION IN POTASSIUM PERCHLORATE (KP)

Material	T_d^f (°C)	T_i^f (°C)	T_p^f (°C)	T_d^r (°C)	T_i^r (°C)	T_p^r (°C)	T_i^h (°C)	T_p^h (°C)	E_s (*kcal mol*$^{-1}$)
KP	282	292	302	270	278	292	14	10	255
KP 100[a]	284	294	307	269	269	287	25	20	299
KP 200	290	296	308	264	270	282	26	26	460
KP 300	285	295	309	251	259	275	36	34	1611

[a] The number signifies the pressure in kg cm^{-2} at which the sample was pre-compressed.

increase in the upward transition temperature and a decrease in the downward transition temperature on pre-compression and pre-heating and the thermal hysteresis ($T^h = T^f - T^r$) increases with increasing pelleting pressure. Bogardus and Roy[23] have made similar observations on pelleting NH_4Cl where they found a 6°C increase in the upward transition temperature and a 12°C decrease in the downward transition temperature. They attribute the observed effects to the average strain on the individual grains as a result of pelleting and this manifests itself in the increased hysteresis. We have calculated the strain energies by the method of Rao et al.[12] and the results are shown in Tables 6 and 7. The doped samples also show an increased hysteresis and a corresponding increase in the strain energies (Table 4). The increased strain energies in the case of the pre-compressed, pre-heated and the doped samples clearly show the increased difficulties associated with the nucleation step and a consequent shift in the thermal hysteresis to higher values. The increased strain energy can also be associated with an increased thickening of the *G–P–T* surfaces of the two phases[24] in the neighbourhood of the transformation temperature with a consequent increase in the thermal hysteresis. It is therefore reasonable to assume that doping and pre-compression give rise to large local discontinuities of structure.

It may be pointed out at this stage that the observed effects of prior mechanical and thermal treatment on the transformation temperatures of these materials disappear on subjecting them to thermal cycling. For example, pre-compressed ammonium perchlorate on heating to 250°C and cooling back to room temperature, does not show an upward shift in the transformation temperature. Thermal cycling of the materials in this manner, presumably produces annealing of the imperfections and/or the strain produced by the prior treatment.

In summary, therefore, it has been shown that the trends in the phase transformation characteristics in the alkali perchlorates are significantly different from those observed in a similar system, viz., the alkali sulfates. The transformation in sodium perchlorate shows pronounced second-order effects. Prior mechanical and thermal treatment of the material has marked effects on the transformation temperatures and on the thermal hysteresis.

REFERENCES

1 D. Vorlander and E. Kaascht, *Ber.*, 56B (1923) 1157.
2 R. W. G. Wyckoff, *Crystal Structures*, The Chemical Catalog Co., New York, 1931.
3 W. Bussem and K. Herrmann, *Z. Kristallogr.*, 67 (1928) 405.
4 S. Gordon and C. Campbell, *Anal. Chem.*, 27 (1955) 1102.
5 M. M. Markowitz and D. A. Boryta, *J. Am. Rocket Soc.*, 32 (1962) 1941.
6 M. W. Evans, K. W. Beyer and L. McCulley, *J. Chem. Phys.*, 40 (1964) 2431.
7 G. Krien, *Explosivestoffe*, 13 (1965) 205.
8 M. M. Markowitz, D. A. Boryta and M. Harris, *J. Phys. Chem.*, 65 (1961) 261; 69 (1965) 1114.
9 J. N. Maycock and V. R. Pai Verneker, *Proc. Roy. Soc.*, A 307 (1968) 303.
10 E. S. Freeman, D. A. Anderson and J. J. Campisi, *J. Phys. Chem.*, 64 (1960) 1727.
11 P. D. Garn, *Anal. Chem.*, 41 (1969) 447.
12 C. N. R. Rao and K. J. Rao, *J. Mater. Sci.*, 1 (1966) 238.
13 H. Mauras, *C.R. Acad. Sci. Ser. C*, 272 (1971) 973.
14 S. R. Yoganarasimhan and S. K. Syal, *Inorg. Nucl. Chem. Lett.*, 9 (1973) 1193.
15 M. Natarajan, A. R. Das and C. N. R. Rao ,*Trans. Farad. Soc.*, 65 (1969) 3081.
16 V. V. Savant and C. C. Patel, *Ind. J. Tech.*, 6 (1968) 231.
17 G. O. Piloyan, *Nature*, 212 (1966) 1229.
18 K. J. Rao, G. V. S. Rao and C. N. R. Rao, *Trans. Faraday Soc.*, 63 (1967) 1013.
19 M. A. Bredig, *J. Phys. Chem.*, 49 (1945) 543.
20 W. H. Zachariasen, *Z. Kristallogr.*, 73 (1930) 141.
21 S. Glasstone, *Thermodynamics for Chemists*, Van Nostrand, New York, 1958.
22 L. A. K. Staveley and D. C. Thomas *J. Chem. Soc.*, (1951) 2572.
23 E. H. Bogardus and R. Roy, *J. Am. Chem. Soc.* ,48 (1965) 205.
24 A. R. Ubbelohde, in J. H. de Boer (Ed.), *Proceedings of the 4th Symposium on the Reactivity of Solids*, Elsevier, Amsterdam, 1961, p. 249.