

THE EFFECT OF DEFECT STRUCTURE DUE TO DOPING  
AND IRRADIATION ON THE THERMAL DECOMPOSITION  
OF POTASSIUM CHLORATE

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The thermal decomposition of potassium chlorate was investigated as a function of doping and there seems to be a correlation between the polarizing nature of the dopant cation and the thermal degradation temperature of potassium chlorate. In particular, transition metal cations influence strongly the temperature of decomposition. Irradiation and mechanical shock defects influence also the process. A possible mechanism in terms of the semi-conductive properties of the defective chlorates is discussed.

Chlorine oxy-salts are subject to thermal decomposition at relatively low temperatures. Their thermal stability depends on various conditions. In particular, the coordinative saturation of the oxygen surrounding the chlorine atom within the complex anions and the nature of the cations seem to determine the outcome of the thermal decomposition of these salts.

Thus, the thermal stability decreases apparently from the perchlorates to the chlorates to the chlorites and hypochlorites [1, 2], since only the chlorine atom in the perchlorate anions is coordinatively saturated with four oxygen atoms. Also, bonding energies between the central chlorine and the surrounding oxygens decrease quantummechanically in that order [3].

On the other hand, the nature of the cations of an oxy-chlorine compound affects significantly the stability and reaction path [4, 5]. In fact, there seems to be a distinct correlation between the polarizing power of the cations [6] or the ionic character of the cation-oxychlorine bond [7, 8] and the thermal stability. The less ionic the bond, or the stronger the polarization power of the cation, the less stable is the compound.

The apparent heterogeneous catalytic effects of metal oxides on the solid state and molten phase decomposition of potassium chlorate and perchlorate have been studied previously [9], and it was found that the defect nature of the metal oxides played an important part in the catalytic efficiency with respect to the thermal decomposition of the chlorates and perchlorates [10].

As a logical consequence of these studies we investigated the influence which intra-crystalline defects such as cationic impurities might have on the thermal decomposition of potassium chlorate. To this end, chlorate samples were prepared

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with controlled amounts of impurity defects. Undoped material was subjected to radiation and mechanical stresses and the created defects correlated to the thermal stability of the host chlorates. Thermal analysis was applied to study relative trends in the thermal stability of the prepared samples.

The results are discussed in terms of possible decomposition mechanisms as a charge transfer between dopant and host compound and/or polarization power of the dopant cation.

## Experimental

### *Preparation and standardization of samples*

#### *Heterocrystalline<sub>v</sub> doped samples of potassium chlorate*

The following doped chlorates were prepared by evaporating to dryness solutions of reagent grade  $\text{KClO}_3$  containing one mole per cent of the dopants on a hot water bath:

- (a)  $\text{KClO}_3$  - 1 mole % LiCl
- (b)  $\text{KClO}_3$  - 1 mole % KCl
- (c)  $\text{KClO}_3$  - 1 mole % CsCl
- (d)  $\text{KClO}_3$  - 1 mole %  $\text{CaCl}_2$
- (e)  $\text{KClO}_3$  - 1 mole %  $\text{CdCl}_2$
- (f)  $\text{KClO}_3$  - 1 mole %  $\text{CuCl}_2$
- (g)  $\text{KClO}_3$  - 1 mole %  $\text{FeCl}_3$
- (h)  $\text{KClO}_3$  - 1 mole %  $\text{LiNO}_3$
- (i)  $\text{KClO}_3$  - 1 mole %  $\text{Pb}(\text{NO}_3)_2$

The crystallized samples were gently broken into smaller crystals in a mortar, and sieve fractions between 240 and 270 mesh sieves (about 53 to 63 micron size) obtained. The samples were stored in a desiccator for further use.

#### *Preparation of doped single crystals of potassium chlorate by slow crystallization procedures*

Various reagent grade chlorates obtained from K & K Laboratories were put into solution with  $\text{KClO}_3$  in varying concentration. The concentration of the dopants were 0.1, 1, and 10 mole per cent. These solutions were subsequently transferred to large dishes and subjected to slow crystallization at room temperatures.

Crystallization took place slowly over several weeks and resulted in large single crystals. These single crystals were separated from the solution, washed with water, and dried and stored in a desiccator for further use. They were subsequently

analyzed for their dopant content. The following dopants were used:

- (a)  $\text{NaClO}_3$
- (b)  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$
- (c)  $\text{Ca}(\text{ClO}_3)_2 \cdot 2 \text{H}_2\text{O}$
- (d)  $\text{Cu}(\text{ClO}_3)_2$

*Gamma irradiation and shock treatment of reagent grade potassium chlorate*

Portions of 240–270 mesh  $\text{KClO}_3$  (reagent grade) were subjected to  $\text{Co}^{60}$  gamma irradiation of varying doses. The irradiation cell has been described previously [10]. Portions of the irradiated samples were placed in a desiccator at room temperature, and were dried in an oven at  $100^\circ$ . Portions were also used for DTA/TG experiments directly after they were taken from the hot cell.

*Analytical methods*

DTA and TG experiments were done on a combination DTA/TG Chevenard thermobalance which has been described previously [9]. In some cases X-ray analysis and microscopic investigation under the polarizing microscope were done to obtain some idea on possible gross defect structures of the doped single crystal samples.

Table 1

a) EDTA titration of  $\text{KClO}_3$  single crystals for Ca and Ba against metals and/or Eriochrome Black T indicators

Crop No.	% Dopant in original mother liquid	% Dopant against metal	% Dopant against Black Eriochrome
<b>Ca</b>			
1.1*	10	—	0.0042
1.2	10	0.0064	0.0060
1.3	10	—	0.0112
2.1	1	0.0020	—
2.2	1	0.0037	—
3.1	0.1	0.0007	—
3.2	0.1	0.0017	—
<b>Ba</b>			
1.1	10	0.0013	
1.2*	10	0.0024	
1.3	10	0.0020	
2.1*	1	0.0015	
3.1	0.1	0.0003	

\* These samples were used in the DTA/TG runs of Fig. 2.

Table 1

b) Analysis of doped  $\text{KClO}_3$  crops for  $\text{Na}^+$  by flame photometry and for  $\text{Cu}^+$  with Neocuproine

Sample	% Cu in original mother liquid	% Cu
Crop # 1	0.1	0.000086
Crop # 2	0.1	0.000086
Crop # 1	1	0.00018
Crop # 2*	1	0.00014
Crop # 1	10	0.0069
Crop # 2*	10	0.010
Crop # 3	10	0.0076

Sample	% Na in original mother liquid	% Na
Crop # 1	0.1	0.0021
Crop # 2*	0.1	0.0027
Crop # 1	1	0.0036
Crop # 2*	1	0.0071
Crop # 1	10	0.0028
Crop # 2	10	0.0056
Crop # 3	10	0.0092

\* These samples were used in the DTA/TG runs of Fig. 2.

Wet analysis was performed on some crops of doped single crystals of potassium chlorate before they were used in thermal decomposition studies. Copper was colorimetrically determined with neocuproine, sodium by flame spectrophotometry, and  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  were initially analyzed titrimetrically with EDTA against Eriochrome Black T. Poor reproducibility in the titration results for  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  due to the low concentration present made it advisable to use a different indicator (Metab-Indicator) in order to check the rather low concentrations. Table 1 summarizes the analytical results.

### Experimental results

Potassium chlorate samples which were prepared by evaporating solutions of 1 mole % dopant with  $\text{KClO}_3$  at  $100^\circ$  to dryness were heterocrystalline; and with the exception of  $\text{FeCl}_3$  and  $\text{CuCl}_2$  doped samples, were white. Since the samples were obtained by way of water evaporation, no analysis was necessary.

Doped single crystals were obtained by fractional crystallization from slowly evaporating solutions of the dopants and the potassium chlorate. The crops were analyzed for their dopant content and some typical results are listed in Table I.

The growth of the single crystals from water solutions was influenced by the amount and type of dopants. Large single crystals in the form of platelets were obtained from solutions containing 0.1% or less of dopant. If higher percentages of dopants were used the crystals were smaller in size. An exception was  $\text{NaClO}_3$ , where the single crystals formed in solutions of higher  $\text{NaClO}_3$  concentrations were as large as the pure  $\text{KClO}_3$  crystals. Observations with a polarizing microscope showed gross surface defects which are possibly due to etching by water during the washing process. Aside from this, structural defects were observed in some cases as judged from the birefringence patterns of the crystals under the crossed polarizer and analyzer of the microscope.

Attempts were made to analyze doped samples by X-ray, to investigate whether gross structural defects could be detected. No significant differences were observed which in essence means that the different phases are too small to be detected or that the dopants were incorporated substitutionally into the chlorate lattice. The exceptions are, perhaps, the  $\text{LiNO}_3$ -doped sample which exhibits slightly lower intensities of the major peaks at a diffraction angle of about  $20.9^\circ$  and  $21.8^\circ$ , the lead nitrate-doped sample which shows additional lines in the X-ray spectrum, and  $\text{CdCl}_2$ -doped samples which also show an additional peak.

TG and combination DTA/TG analysis experiments were performed on doped and undoped potassium chlorate. The heating rate was nominally  $10^\circ/\text{min}$ . Figure 1 represents a comparison of the thermal decomposition characteristics of pure  $\text{KClO}_3$  with those of the doped materials. The results indicate that chloride anions do not appreciably influence the thermal decomposition of  $\text{KClO}_3$  at the concentrations present. The chloride dopants include  $\text{LiCl}$ ,  $\text{KCl}$ , and  $\text{CsCl}$ .

The data based on these experiments are tabulated in Table 2 and reveal several interesting points.

1. The average temperatures of the endothermal minimum at the melting point of  $\text{KClO}_3$  are only slightly decreased upon addition of chloride anions. The decrease in temperature is much more pronounced upon addition of the nitrate impurities.

2. Doping with the nitrates has the effect of decreasing the average decomposition temperatures from  $25^\circ$  to  $50^\circ$  below the temperatures of the decomposition of pure  $\text{KClO}_3$  and chloride doped (with singly charged cations) chlorates.

3. The most effective dopants are  $\text{FeCl}_3$  and  $\text{CuCl}_2$ . In particular, doping with  $\text{FeCl}_3$  causes appreciable thermal decomposition of  $\text{KClO}_3$  to occur below the temperature of the melting endotherm as is seen in Fig. 1.

In Fig. 2 the effect of cation doping on the thermal characteristics of single crystals is demonstrated. It is seen that dopants such as  $\text{Na}^+$  and  $\text{Ba}^{2+}$  have, if at all, only little influence on the thermal decomposition characteristics of  $\text{KClO}_3$ . Even crystals which were crystallized from solutions containing 10%  $\text{Na}^+$  (which coincides with the curve obtained from 1%  $\text{Na}^+$ ), and 10%  $\text{Ba}^{2+}$  do not differ appreciably in their thermal behavior from the undoped material. In the case of  $\text{Na}^+$  this is not unexpected, since  $\text{Na}^+$  is in the same group of the periodic system as  $\text{K}^+$  with only slightly smaller cationic diameter than  $\text{K}^+$ .

The decomposition behavior of  $\text{KClO}_3$  doped with  $\text{Ca}^{2+}$  (from 10% solution) is, however, significantly different from the behavior of pure  $\text{KClO}_3$ . The most pronounced differences in thermal characteristics are found, if the solutions are

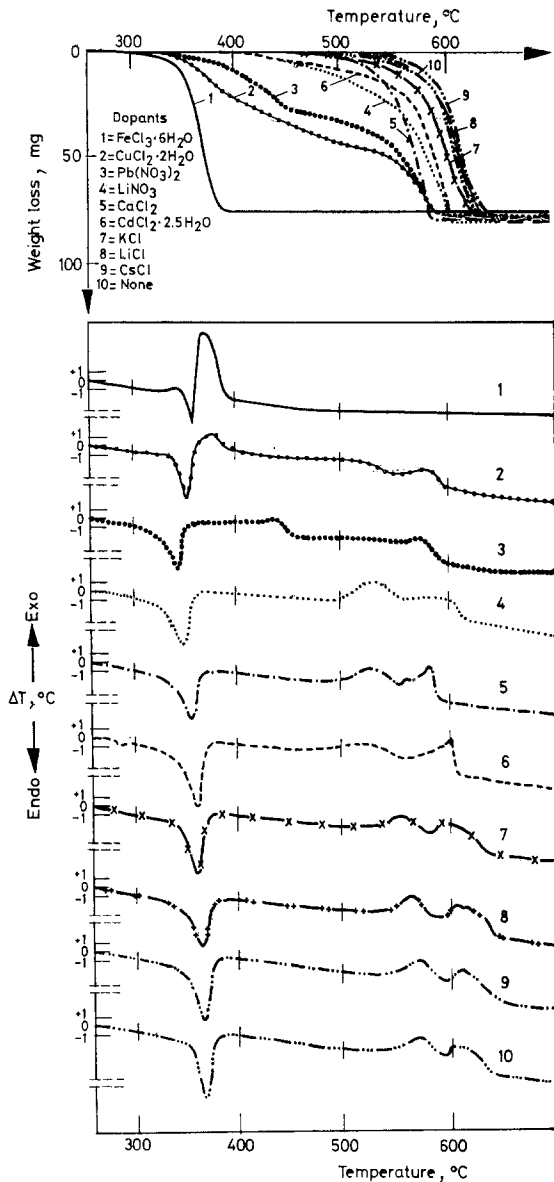


Fig. 1. Thermogravimetric analysis and differential thermal analysis of doped potassium chlorates. Amount of dopants: in mole%. Heating rate:  $10^\circ\text{C}/\text{min}$ , sample size: 200 mg, atmosphere: air

doped with  $\text{Cu}^{2+}$ . The single crystals obtained from 10% solutions were most reactive (the total concentration in the crystals is  $\sim 0.01\%$ ). Slow decomposition begins much below the melting point of  $\text{KClO}_3$  and the melting point is shifted towards lower temperatures. At least two steps are seen in the weight loss curves of  $\text{Cu}^{2+}$  doped  $\text{KClO}_3$ .

A few experiments were done to elucidate possible effects of irradiation and mechanical shock on the thermal decomposition of potassium chlorate (Fig. 3).

Table 2  
Summary of thermal analysis results

Dopant	Average peak endothermic temperature	Average decomposition temperature at 25% wt loss	Average decomposition temperature at 50% wt loss	Charge density of cationic dopant positive charge/ $\text{Å}^2$
LiCl	363 $\pm$ 2.6	588.7 $\pm$ 8.1	607.3 $\pm$ 2.6	0.69
KCl	360 $\pm$ 0.0	581.5 $\pm$ 2.1	606.5 $\pm$ 0.7	0.179
CsCl	367.7 $\pm$ 2.5	601.7 $\pm$ 7.6	618 $\pm$ 5.3	0.114
$\text{CuCl}_2$	353.3 $\pm$ 1.5	398.3 $\pm$ 2.9	485 $\pm$ 5.0	1.240
$\text{CdCl}_2$	360.7 $\pm$ 9.3	562.3 $\pm$ 6.8	586 $\pm$ 7.9	0.678
$\text{CaCl}_2$	355.3 $\pm$ 19.6	554.3 $\pm$ 14.3	568.3 $\pm$ 12.8	0.650
$\text{FeCl}_3$	357.5 $\pm$ 3.5	354 $\pm$ 1.4	375 $\pm$ 0.0	2.42
$\text{Pb}(\text{NO}_3)_2$	342.5 $\pm$ 0.7	441.5 $\pm$ 0.7	543.5 $\pm$ 9.2	0.442 (1.800)*
$\text{Li}(\text{NO}_3)$	349 $\pm$ 15.5	549 $\pm$ 8.5	585 $\pm$ 7.1	0.69
NONE	368 $\pm$ 4.2	606.5 $\pm$ 2.1	620 $\pm$ 2.8	0.0

\* Second number refers to four-valent lead.

The results are very interesting. It was observed that the data appeared to be poorly reproducible, if time and atmospheric conditions during storage were not kept under careful control. If the irradiated samples were taken directly from the hot cell, a chlorine odor was discernible, and the samples were of tannish color. When the samples were dried at about  $110^\circ$ , the color faded and the smell disappeared.

A DTA/TG experiment on a sample placed on the thermobalance immediately after it was taken from the hot cell, showed exothermal and endothermal decomposition steps at low temperatures. Partial weight loss is observed at temperatures below  $100^\circ$ . This low temperature weight loss is approximately 17% of the total weight. The total weight loss after complete decomposition is approximately 55%.

If the sample is left in a desiccator or if it is stored for a longer period of time under ambient conditions, the low temperature weight loss in the TG curve is no longer observable. A sample dried in an oven at  $110^\circ$  loses its tannish color and again, low temperature weight loss is no longer apparent. The melting endotherm of irradiated  $\text{KClO}_3$  shows two pronounced shoulders, while the higher temperature exotherms appear similar to those of unirradiated material. One sample of  $\text{KClO}_3$  which had been subjected to mechanical shock showed a similar but smaller weight loss at low temperature as the irradiated material directly after irradiation (Fig. 3, curve 4).

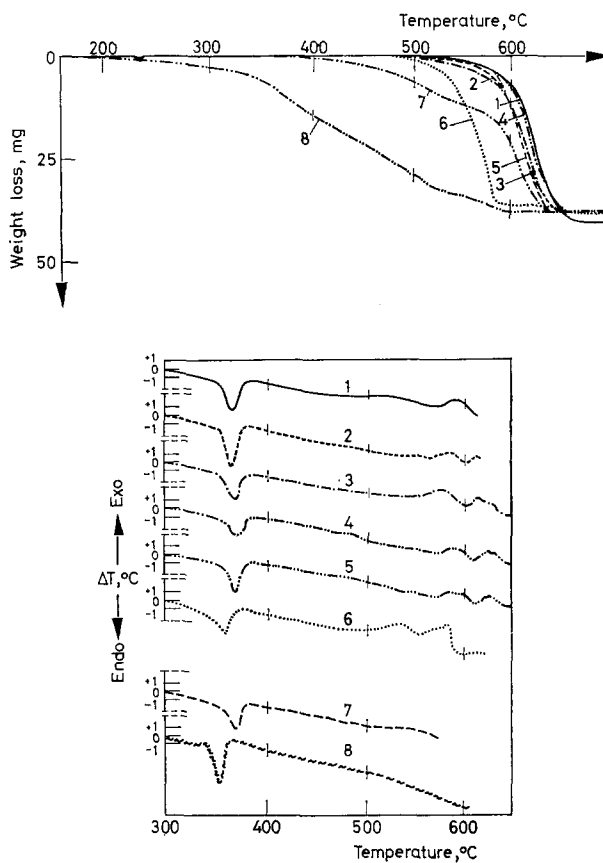


Fig. 2. The effect of cation doping on the thermal characteristics of single crystals

No.	% Dopant Dopant in solu- tion	
1	undoped	0
2	Na	1
3	Na	1
4	Ba	1
5	Ba	10
6	Ca	10
7	Cu	1
8	Cu	10

Heating rate = 10 °C/min.



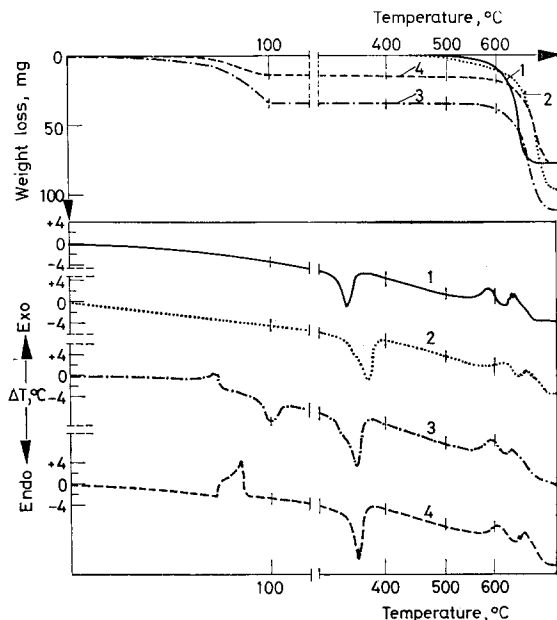


Fig. 3. Influence of irradiation and mechanical shock on the decomposition of potassium chlorate. 1 = unirradiated, 2 = irradiated and dried. Approx. dose  $18 \times 10^7$  rads, 3 = irradiated and not dried. Approx. dose  $54 \times 10^7$  rads. 4 = shock treated. Heating rate:  $10^\circ\text{C}/\text{min}$ , sample size: 200 mg, atmosphere: air

### Discussion

The decomposition of potassium chlorate is significantly altered by small amounts of impurities. Figures 1 and 2 and Table 2 indicate that, in particular, cations of transition elements such as  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  can lower the decomposition temperatures by more than  $200^\circ$ . In fact both the  $\text{Cu}^{2+}$  and the  $\text{Fe}^{3+}$ -doped samples initiate decomposition distinctly in the solid phase before the melting endotherm is visible.

In Fig. 4, the average decomposition temperatures at 50% decomposition are plotted as a function of the surface charge density. The surface charge density in this case is defined as the ratio of the cationic charge divided by the surface area of an assumed spherical model of the impurity cations based on published ionic radii of these cations [11]. It appears that the decomposition temperature is decreased with increasing charge density of the dopant cation. This may indicate that the polarizing power of the doping cation on the asymmetric electron distribution of the  $\text{ClO}_3^-$  anion is an important factor in the reactivity of the doped potassium chlorate. It should be kept in mind that the  $\text{KClO}_3$  was in the molten state during this stage of the reactions.

Doping with  $\text{CuCl}_2$  caused appreciable increases in the chemical reactivity of  $\text{KClO}_3$ . In addition, it is also apparent that the first step of decomposition due to

disproportionation [Ref. 12] is significantly more pronounced in the presence of these cations.

In Fig. 4 the reactivity of the lead dopant is plotted twice. In the first case a doubly charged  $\text{Pb}^{2+}$  ion was assumed and in the second case a valence of +4 was assumed,  $\text{Pb}^{4+}$  ion. The point for the double valent  $\text{Pb}^{2+}$  ion dopant lies left of the line, while that of the +4 valent  $\text{Pb}^{4+}$  dopant lies to the right of the line.

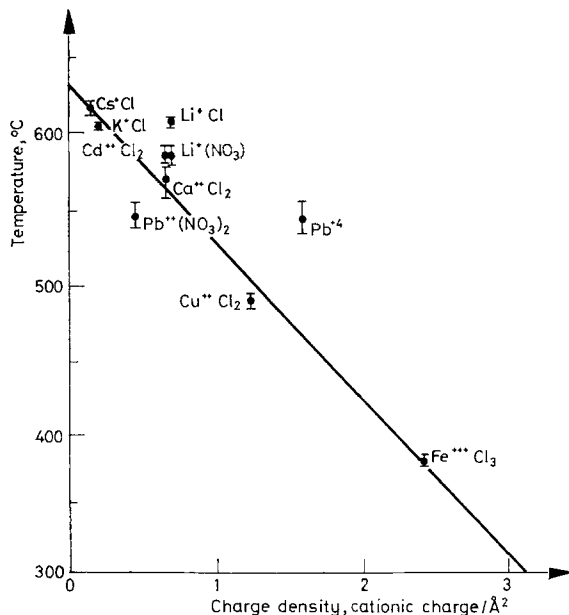
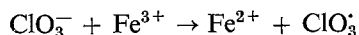
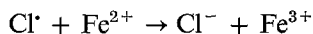
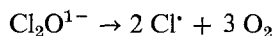
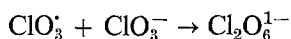


Fig. 4. Reactivity of doped  $\text{KClO}_3$  (Temperature at 50% decomposition of charge density at surface of cationic species)

One interpretation of this observation might be that the lower valent lead dopant is partially oxidized to a higher valence state by the strong oxidant host compound.

The apparent catalytic effects may be considered from another point of view. This concept is based on the finding that the activation energy for thermal decomposition is about 210–230 J/mole [6]. Taking this into account, one would expect that if the rate controlling step in the thermal decomposition of  $\text{KClO}_3$  involved the rupture of the Cl–O bond in the  $\text{ClO}_3^-$  ion, then the marked effects of the  $\text{Fe}^{3+}$  and the  $\text{Cu}^{2+}$  cations could not be accounted for. However, if the impurity cations could act as bridges in an electron transfer rate controlling mechanism, then the marked reduction in decomposition temperatures may be reasonably expected. The reaction involves the formation of an intermediate  $\text{Fe}^{2+}$  ion with a  $\text{ClO}_3$  radical. The radical would be considerably more reactive than the  $\text{ClO}_3^-$  ion. The following equations illustrate this mechanism.





The observation that the  $\text{Fe}^{3+}$  doped sample gave off a distinct odor of chlorine supports this assumption. Also, preliminary mass spectrometric analysis seems to confirm it.

A similar mechanism would apply to the  $\text{Cu}^{2+}$  ion dopant. This mechanism can apply to the molten or solid state decomposition. The activation energy for the interaction of two chlorate species would be reduced because of the formation of the intermediate chlorate radical. In the case of solid state decomposition, however, another factor such as defect state also becomes important which determines the concentration and mobility of charge carriers during charge transfer. The addition of higher valent cations may cause a reduction of positive holes in the valence band or an increase of electrons in the conduction band. A third possibility is that the concentration of cationic vacancies would increase.

An estimate of the order of activation energies of the doped potassium chlorates were made from the thermogravimetric curves obtained in the Chevenard DTA/TG experiments. A method is described in the literature [13], where the inflection point in the TG curve is determined. The final equation is as follows:

$$E^*/n = - (RT_i^2/W_i)(dw/dt)_i$$

where  $E^*$  is the activation energy,  $T_i$  the temperature at the inflection point,  $w_i$  the weight loss at the inflection point,  $n$  is the order of reaction. It should be noted that using this expression we are comparing  $E^*/n$ , rather than the activation energy alone. This, however, does give information concerning the relative activation energies for comparison purposes.

Table 3 summarizes some of the values of  $E^*/n$ . It can be seen that there is wide scatter which is due to the qualitative nature of the Chevenard TG runs. In particular,  $(dw/dt)_i$  is rather difficult to determine. The table shows, nevertheless, definite trends in the activation energies: The order of activation energies is in the order of dopants: none >  $\text{CsCl} \sim \text{CaCl}_2 > \text{LiCl} > \text{Pb}(\text{NO}_3)_2 > \text{CdCl}_2$ .

The activation energies for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ -doped samples were not evaluated, since the transition from solid to molten state decomposition complicates the TG curves.

Irradiation with gamma rays and mechanical shock introduce apparent changes in reactivity with respect to the decomposition of  $\text{KClO}_3$ . In order to be able to deduce possible mechanisms, we have to reconcile the following observations:

1. The odor of chlorine and/or chlorine oxides and the tannish color observed right after irradiation disappear upon drying at  $100^\circ$ .
2. The total weight loss of an irradiated sample is significantly higher for both, the dried and undried, chlorates than would be expected from the normal thermal

Table 3

Apparent activation energies of doped  $\text{KClO}_3$ 

Dopant	$E^*/n$ , J/mole	Average, J/mole
None	238	234
None	261	
None	219	
None	220	
None	211	
None	257	
$\text{CaCl}_2$	212	219
$\text{CaCl}_2$	217	
$\text{CaCl}_2$	229	
$\text{CsCl}$	194	218
$\text{CsCl}$	256	
$\text{CsCl}$	205	
$\text{LiCl}$	169	175
$\text{LiCl}$	137	
$\text{LiCl}$	220	
$\text{Pb}(\text{NO}_3)_2$	89	96
$\text{Pb}(\text{NO}_3)_2$	103	
$\text{CdCl}_2$	87	74
$\text{CdCl}_2$	72	
$\text{CdCl}_2$	63	

decomposition equation:



(theoretical weight loss: 39.3%).

3. The low temperature exotherm and endotherm disappear after drying, and overall weight loss is reduced as compared to the sample not dried at  $110^\circ$ .

4. The eutectic shoulder in the melting endotherm between  $350$  and  $400^\circ$  remains even after drying.

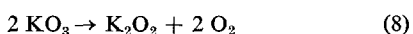
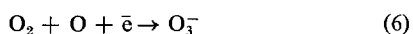
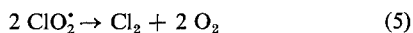
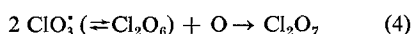
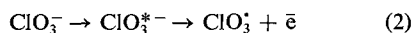
5. The temperature of the final decomposition steps is shifted towards higher values as compared to that of the unirradiated material.

6. The mechanically shocked sample shows a low temperature exotherm and no endotherm as observed with the irradiated sample, but the overall weight loss corresponds to Eq. (1).

7. There is experimental evidence from EPR measurements that both,  $\text{KClO}_4$  and  $\text{KClO}_3$  decompose under gamma- and X-ray irradiation to relatively stable radical species such as  $\text{ClO}_2^\cdot$ ,  $\text{Cl}^\cdot$ ,  $\text{O}_3^-$ ,  $\text{ClO}_3^\cdot$  [14, 15] and some unidentified species, X, [14]. The stability of these radicals within the lattice increases apparently in the order,  $\text{Cl}^\cdot$ ,  $\text{ClO}_3^\cdot$ ,  $\text{ClO}_2^\cdot$ , X,  $\text{O}_3^-$  [14].

Table 4

Possible mechanism of the decomposition of irradiated potassium chlorate



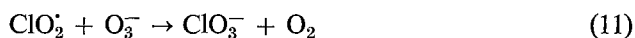
In order to reconcile the above experimental evidence, we may postulate the mechanism as described in Table 4 which can account for the low temperature curve of irradiated  $\text{KClO}_3$ .

The initiation reaction (2) leads to the formation of  $\text{ClO}_3^*$  radicals which are in equilibrium with  $\text{Cl}_2\text{O}_6$  molecules. Equation (4) is very likely, because it leads to a relatively stable complex molecule which is coordinatively saturated:

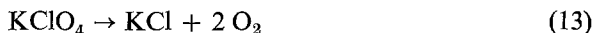


Formation of this complex would explain the initial exotherm at low temperature and partial weight loss. Also,  $\text{Cl}_2\text{O}_7$  boils at about  $83^\circ$  [16] and desorption from the lattice would account for the small endotherm and the corresponding weight loss below  $100^\circ$ .

The solid reactants  $\text{KO}_3$  and  $\text{K}_2\text{O}_2$  of Eqs (7) and (8) are sufficiently stable to enter the liquified  $\text{KClO}_3$  phase as a eutectic shoulder in the melting endotherm. Recombination reactions such as,



may also be possible. This together with the bulk of undecomposed  $\text{KClO}_3$  gives rise to the normal thermal decomposition observed at higher temperatures [12]:



The mechanically shocked sample experiences apparently a different mechanism, since its overall decomposition corresponds to Eq. (1), and several features in the thermal curves are different from those observed in the irradiated sample.

### Conclusions

The order of dopants with respect to decreasing stability of  $\text{KClO}_3$  was found to be: The most effective,  $\text{FeCl}_3 > \text{CuCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{CdCl}_2 > \text{CaCl}_2 > > \text{LiNO}_3 > \text{LiCl} > \text{KCl} \sim \text{CsCl} \sim$  no dopant. This order may be correlated to charge density (or equivalently to percent of ionic cation-oxygen bond, see [7, 8]) or to charge transfer. Doping the  $\text{KClO}_3$  with nitrates reduces the temperature of the DTA endotherm for melting.

It is most remarkable that even relatively small amounts of dopants (See Table 1) can influence strongly the thermal decomposition of  $\text{KClO}_3$  (Fig. 2).

Gamma irradiation and mechanical shock affects the decomposition path of  $\text{KClO}_3$  as reflected in the thermal curves. Low temperature weight loss and exothermic as well as endothermic reactions indicate defect creation within the crystalline lattice such as  $\text{ClO}_2^-$ ,  $\text{O}_3^-$ , and other relatively stable radicals.

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RÉSUMÉ — On a étudié la décomposition thermique du chlorate de potassium en fonction de l'ajout d'additifs. Il semble qu'une corrélation existe entre la nature polarisante du cation de l'additif et la température de la dégradation thermique du chlorate de potassium. En particulier, ce sont les cations des métaux de transition, qui exercent une forte influence sur la température de décomposition. L'irradiation et des défauts causés par choc mécanique influencent aussi le processus. On discute un mécanisme possible à partir des propriétés semi-conductrices des chlorates présentant des défauts.

**ZUSAMMENFASSUNG** — Die thermische Zersetzung von Kaliumchlorat wurde in Abhängigkeit von der Zugabe von Zusätzen untersucht und es scheint eine Korrelation zwischen der polarisierenden Beschaffenheit des Additivkations und der thermischen Zersetzungstemperatur von Kaliumchlorat zu bestehen. Besonders die Übergangsmetallkationen beeinflussen die Zersetzungstemperatur stark. Bestrahlung und mechanische Stoßdefekte beeinflussen den Vorgang ebenfalls. Ein möglicher Mechanismus wird anhand der Halbleiter-Eigenschaften der defekten Chlorate erörtert.

**Резюме** — Исследовано термическое разложение хлората калия в зависимости от легирования и установлена корреляция между поляризационным характером катиона примеси и температурой разложения хлората калия. Значительное влияние оказывают на температуру разложения хлората калия катионы переходных металлов. Дефекты, вызванные облучением и механическим ударом, также затрагивают процесс разложения. Обсужден возможный механизм на основе полупроводниковых свойств хлоратов с нарушенной структурой.