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MECHANISM FOR CONTROLLING THE REACTIVITY OF LEAD AZIDE (U)

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Introduction

A great deal of work has been done on the thermal de-composition of α -PbN$_6$ (1-5). However the role of crystal defects (vacancies, dislocations, interstitials and foreign ions) has not been studied in any great detail. Jach (6) investigated the effects of defects created by reactor irradiation and showed that the rate of thermal decomposition of α -PbN$_6$ can be enhanced. The defects caused by reactor irradiation could be of different kinds and so it is hard to attribute the sensitization of α -PbN$_6$ to any one or two principal defects. Jach explains his results in terms of nuclei or potential nuclei created by reactor irradiation. In attempting to explain the initial stages of the thermal decomposition of unirradiated α -PbN$_6$, Jach states that the activation energy for the surface reaction is lower than that for the bulk reaction and so at lower temperatures the surface reaction predominates over the bulk reaction.

The object of the present investigation is to determine how the reactivity (sensitivity) of α -PbN$_6$ is influenced by particle size, the incorporation of an impurity (iron) and the method of preparation of α -PbN$_6$.

Experimental

Material Preparation: α -PbN$_6$ was prepared in two ways by reacting an aqueous solution of lead nitrite with an acetone solution of hydrazoic acid and by reacting aqueous solutions of lead acetate and sodium azide or barium azide. The acidity was controlled in the first process by adjusting the concentration of hydrazoic acid and in the second by the addition of nitric acid.

An aqueous solution of ferric azide was prepared by reacting metallic iron of spectral grade with hydrazoic acid. An excess of acid had to be maintained to avoid hydrolysis. Fe^{59} was

obtained from Oak Ridge National Laboratory, Tennessee, in the form
of ferric chloride. This was diluted with hydrazoic acid in such a
way that the final solution contained only traces of chloride.

Lead azide doped with iron was prepared in the following
manner. To a known amount of an acetone solution of hydrazoic acid
was added a calculated amount of ferric azide solution and one
micro-micro curie of Fe^{59}. To this solution a known amount of an
aqueous solution of lead nitrite was added with constant stirring.
The final volume in all cases was kept constant as was the ratio of
acetone to water. Before filtering to separate the lead azide formed,
a known amount of the supernatent liquid was pipetted into a measuring
vial to determine the radioactivity due to Fe^{59} remaining in
solution. Lead azide doped with iron was then separated, dried and
desiccated. The dried product was then sieved so as to collect sam-
ples of a desired particle size. When lead azide was prepared by the
second method, the dopant (iron) was added to the aqueous solution of
either sodium or barium azide and the rest of the procedure was the
same as described above.

Uptake of Iron by Lead Azide: In order to determine the mechanism of
uptake of iron by lead azide the azide was partially precipitated
from the solution and a study was made of the distribution of iron in
both the solid and the solution. Details of this type of study are
discussed by Wahl and Bonner (7).

Determination of the Reactivity of the Solid: The thermal sensitivity
of lead azide was determined by measuring the time for a sample
(constant particle size) to explode at a fixed temperature. To
study the thermal decomposition of α-PbN$_6$ a conventional vacuum
system was used and an alphatron gauge served to monitor the pressure
of the nitrogen gas evolved in the decomposition. The sample was
contained in a glass cell and this was heated by immersion in an oil
bath which was maintained at a temperature fixed within $\pm$ 0.1°C.
Reactivity was determined by measuring the time taken for the gas
pressure to build from one arbitrary value to another. This procedure
was adopted because to obtain a full pressure time curve at the
temperatures under investigation, required six to eight hours.
Furthermore, α-PbN$_6$ undergoes what is termed an ageing effect, i.e.,
its reactivity changes with time.

Except when a study was made of the effect of particle
size, in all experiments where a comparison of the sensitivities of
different samples was made, care was taken to use the same amount of
sample (by weight) and the same particle size. Finally, measure-
ments of the optical absorption were done using a diffuse reflect-
ance technique.

Results and Discussion

Figure 1 shows the effect of the surface on the sensitivity of α-PbN$_6$. The surface area was not measured but was calculated from the average particle size considering the particles as spheres. Although this assumption is not strictly true, the results definitely show that the sensitivity increases as the surface increases. This may mean that the thermal reaction starts at defect centers and that these are more abundant on the surface.

In Figure 2 are depicted results on the uptake of iron by α-PbN$_6$. The distribution coefficients plotted were calculated from the following:

(1) Homogeneous distribution:

$$\frac{\text{Iron in the solid}}{\text{Iron in the solution}} = D\left[\frac{\text{Azide in the solid}}{\text{Azide in the solution}}\right].$$

(2) Inhomogeneous or logarithmic distribution:

$$\log\left[\frac{\text{Total iron}}{\text{Iron in solution}}\right] = \lambda\log\left[\frac{\text{Total azide}}{\text{Azide in solution}}\right]$$

Of the two coefficients D is seen to be constant, i.e., iron is distributed homogeneously within the azide crystal (7). The data does not fit any adsorption isotherm. The D value is independent of the pH from 4-6 and does not show any change when the iron/lead ratio is changed from 10^{-3} mole % to 10^{-5} mole %. As iron azide and lead azide are not isomorphous, this mechanism of uptake is called anomalous mixed crystal formation (7) where iron goes into the crystal either substitutionally or interstitially.

Figure 3 shows how the sensitivity of α-PbN$_6$ is affected by doping α-PbN$_6$ with different concentrations of iron. The α-PbN$_6$ used in this experiment was prepared by reacting spectral grade lead nitrite with HN$_3$. Besides the iron no other significant impurities were present. One sees a marked initial desensitization which peaks when the doping is of the order of 1×10^{-2} mole %. Thereafter the drop in sensitivity decreases and when the doping is of the order of 1×10^{-1} mole % the sensitivity attains the value of the sensitivity of the undoped sample. The only variable, apart from the concentration of iron, which was changed was the ratio $[\text{Fe}]/[\text{HN}_3]$. It is reported in the work of Ricca (8) and Wallace (9) that iron can exist either as Fe^{3+} or $[\text{Fe}(N_3)]^{2+}$ and that, as the proton concentration drops, $[\text{Fe}(N_3)]^{2+}$ is favored $[\text{Fe}^{3+} + \text{HN}_3 \rightleftharpoons [\text{Fe}(N_3)]^{2+} + \text{H}^+]$. In these experiments, as the doping increased, so did the ratio Fe/HN$_3$. It is, therefore, possible that with high dopant concentrations some $[\text{Fe}(N_3)]^{2+}$ could have been incorporated in the α-PbN$_6$. Although it is extremely dangerous to work with high concentrations of HN$_3$, one experiment was done to dope α-PbN$_6$ with iron and to bring the ratio of

Fe/HN_3 down from 1×10^{-2} to 1×10^{-5}. It can be seen from Figure 3 that the sensitivity (as measured by the gas evolved) dropped from 4.1 to 2.5. Under the conditions of the experiment, therefore, one may say that iron is incorporated into α-PbN_6 in the form of Fe^{3+}. This then would give rise to cation vacancies in the crystal of α-PbN_6. It is very tempting, therefore, to say that cation vacancies desensitize α-PbN_6. However, as there is a limit to the number of cation vacancies which can exist in the crystal, one would expect a saturation effect for desensitization. If the result of the single experiment ($Fe/HN_3 = 1 \times 10^{-5}$ mole %) is valid then this is explained. Experiments were then conducted to determine the effect of high doping with Fe^{3+} using a different method to prepare α-PbN_6.

Lead acetate was treated with sodium azide in a nitric acid solution keeping the pH between 2 and 2.5. The results of these experiments are presented in Figure 4. One sees that, after the initial desensitization, there is in fact a sensitization. Since there is a high concentration of sodium ions present in the solution along with Fe^{3+}, Na^{1+} can also get into the crystal. Sodium doping would then produce anion vacancies. To overcome this α-PbN_6 was prepared from the following reaction

$$Pb(\bar{A}C)_2 + BaN_6 \longrightarrow PbN_6 + Ba(\bar{A}C)_2$$
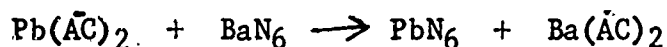
The results of these experiments are shown in Figure 5. One can see an initial desensitization but, on further doping the sensitivity attains the value of the sensitivity of undoped α-PbN_6. In the same figure one can also see that the sensitivity of α-PbN_6 prepared from NaN_3 is much greater than that prepared from BaN_6. α-PbN_6 is partially ionic and partially covalent. As a result it will have both Schottky as well as Frenkel type of defects. Thus, as Fe^{3+} is incorporated in the crystal it will create cation vacancies and so the concentration of lead interstitials will drop. In an undoped crystal diffusion may arise from interstitial lead ions. However, as the concentration of interstitials drops so will the diffusion and so may the sensitivity. When, however, the doping concentration is high, the predominent diffusion may arise from vacancies which are now in abundance. This may explain why the sensitivity drops initially and with increased doping it regains its original value. Experiments on the conductivity of AgBr doped with Cd^{2+} show similar results (10).

In Figure 6 are presented results showing how the sensitivity of α-PbN_6 is influenced by doping α-PbN_6 with iron in the form of the complex $[FeN_3]^{2+}$. As stated earlier whether iron exists as Fe^{3+} or $[FeN_3]^{2+}$ is primarily determined by the pH. From the experiments conducted to this point it was not clear whether $[FeN_3]^{2+}$ is adsorbed either on the surface or internally at dislocations or whether this complex gets into the crystal either substitutionally or interstitially. It is possible that $[FeN_3]^{2+}$ itself is unstable at the temperature of the experiment and thus

starts the reaction. It is equally conceivable that the incorporation of a colored ion like $[FeN_3]^{2+}$ may well change the bulk properties of α-PbN$_6$. Until this is resolved it is not possible to define the exact mechanism of sensitization.

In Table 1 are presented data on the optical absorption of α-PbN$_6$ prepared by different methods and α-PoN$_6$ doped with Fe^{3+} or $[Fe(N_3)]^{2+}$. As single crystals of α-PbN$_6$ are difficult to grow the measurements were made using the reflectance technique on powders. From the data it is clear that α-PbN$_6$ prepared from NaN$_3$ or BaN$_6$ starts to absorb at 420 mμ. This is not dependent on the pH and doping with Fe^{3+} does not change the absorption edge. However, doping with $[FeN_3]^{2+}$ shifts the edge to 680 mμ. It is not clear from the spectrum whether the absorption due to the colored $[FeN_3]^{2+}$ is superimposed on the intrinsic absorption of α-PbN$_6$ or whether the intrinsic absorption itself has changed. Further, it is also noted that when α-PbN$_6$ is prepared by reacting lead nitrite with HN$_3$ the absorption edge shifts to 300 mμ. From the table one can see that this α-PbN$_6$ is the least sensitive. All of the other un-doped preparations absorb at 420 mμ but still show differences in sensitivities. The samples prepared from an acidic medium are less sensitive than those prepared from a neutral medium. It is difficult to draw inferences from this set of experiments because samples prepared from acidic medium could well have contained nitrate ions and nitrate ions could desensitize α-PbN$_6$. However it can be inferred with reasonable certainty that sodium ions sensitize α-PbN$_6$ and that the least sensitive preparation of α-PbN$_6$ is from the reaction:

$$Pb(NO_2)_2 + 4HN_3 \rightarrow PbN_6 + 2NO + 2H_2O + 3N_2.$$
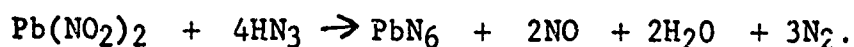
Conclusion

In conclusion, it has been shown that (1) the sensitivity of α-PbN$_6$ increases as the surface area increases, (2) iron can be carried by α-PbN$_6$ either as Fe^{3+} or as $[FeN_3]^{2+}$, (3) when iron is incorporated as Fe^{3+} up to 1×10^{-2} mole % (acidic medium) it is possible to desensitize α-PbN$_6$, (4) when iron is carried by α-PbN$_6$ as $[FeN_3]^{2+}$ a very marked sensitization results and (5) a change in the optical absorption of α-PbN$_6$ is also caused by iron doping. α-PbN$_6$ prepared from lead nitrite and hydrazoic acid is the least sensitive and the absorption edge of this preparation is at 300 mμ in contrast to 420 mμ which is the absorption edge of α-PbN$_6$ prepared by other conventional methods.

In solids which are purely ionic or purely covalent one can speak in terms of either Schottky or Frenkel defects. However, α-PbN$_6$ is partly ionic and partly covalent and this makes it hard to argue in favor of any one kind of defect. In spite of this one can speculate on models to explain these results, i.e., initial desensitization followed by the regaining of the original sensitivity.
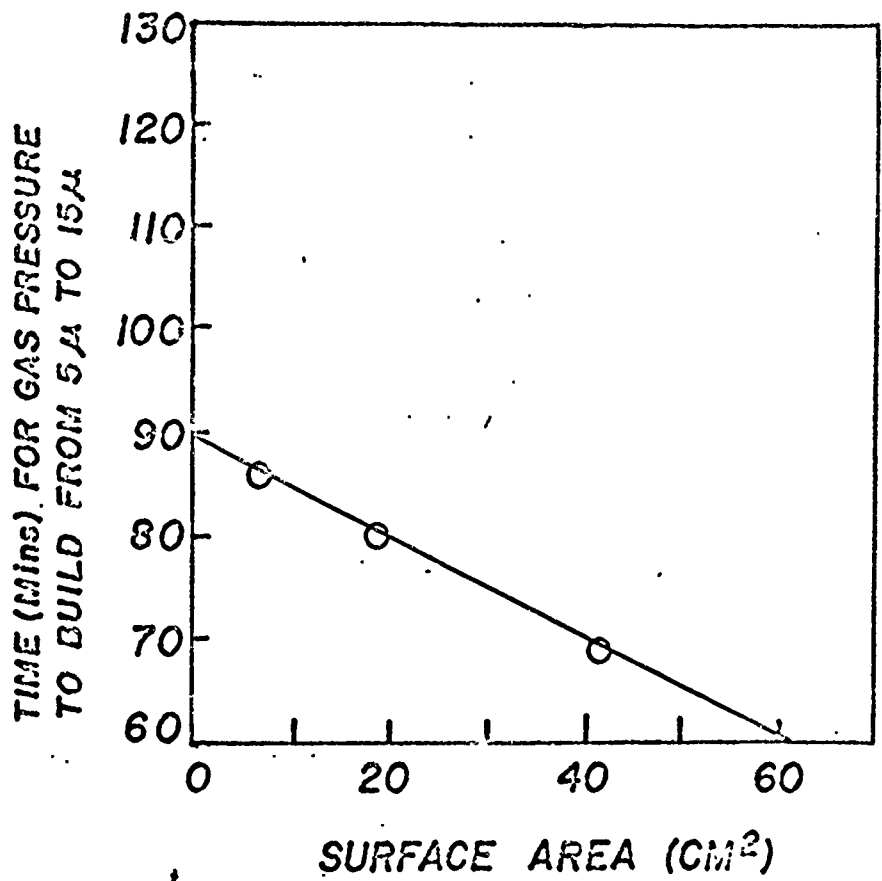
When Fe^{3+} is incorporated in a crystal of α-PbN_6, cation vacancies are created and, to maintain an equilibrium following the law of mass action, this results in a decrease in anion vacancies. Since anion vacancies are good electron traps, a decrease in their concentration will result in drop in sensitivity. As the doping increases there results, along with the production of cation vacancies, an increasing concentration of Fe^{3+}. This Fe^{3+} can form an associated complex with a cation vacancy and also act as a good electron trap. This will result, therefore, in an apparent sensitization. If one now considers Frenkel defects, then it follows that as the iron doping increases the vacancy concentration likewise increases and the added vacancies depress the equilibrium concentration of interstitial lead ions. The ionic conductivity would therefore decrease and so would the sensitivity. However, as the doping increases further the vacancy diffusion mechanism becomes more important than the interstitial diffusion of lead ions and so the conductivity, and usually the sensitivity, could increase. Further investigations will have to be done to determine the conductivity, color center behavior and similar properties of α-lead azide before the actual sensitization mechanism can be defined. However, it is believed that these studies have, for the first time, highlighted the close relationship between sensitivity and doping in an explosive material.

References

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TABLE 1

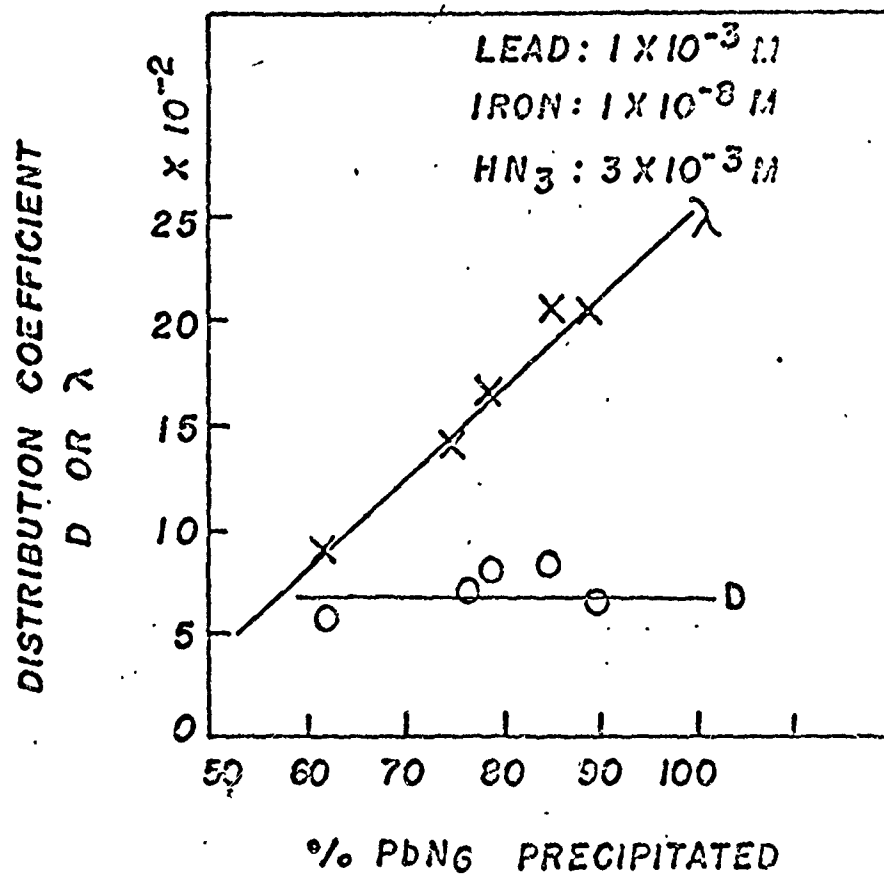### EFFECT OF DOPING ON THE OPTICAL AND THERMAL PROPERTIES OF LEAD AZIDE

Iron (Mole %)	Method of Preparation	pH	Absorption Edge	Time for Gas Pressure to build from 0 to 5 μ (220°)
0	$BaN_6 + Pb(AC)_2$	2.5	420 mμ	95 mins.
0	$BaN_6 + Pb(AC)_2$	7.0	420 mμ	48 mins.
0	$NaN_3 + Pb(AC)_2$	2.5	420 mμ	65 mins.
0	$NaN_3 + Pb(AC)_2$	7.0	420 mμ	33 mins.
0	$HN_3 + Pb(NO_2)_2$	3.5	300 mμ	120 mins.
from 10^{-4} to 10^{-1} (Fe^{3+})	$BaN_6 + Pb(AC)_2$	2.0	420 mμ	-
from 10^{-4} to 10^{-1}	$NaN_3 + Pb(AC)_2$	2.0	420 mμ	-
from 10^{-4} to 10^{-1} $[(FeN_3)^{2+}]$	$BaN_6 + Pb(AC)_2$	7.0	680 mμ	-
from 10^{-4} to 10^{-1}	$NaN_3 + Pb(AC)_2$	7.0	680 mμ	-

SENSITIVITY OF α - PbN_6 VS SURFACE
AREA (240°C)

FIGURE 1

LEAD: 1×10^{-3} M

IRON: 1×10^{-8} M

$HN_3 : 3 \times 10^{-3}$ M

DISTRIBUTION COEFFICIENT D OR λ $\times 10^{-2}$

% PbN$_6$ PRECIPITATED

UPTAKE OF IRON BY α — PbN$_6$

FIGURE 2

SENSITIVITY OF α-PbN₃ VS
IRON DOPING

FIGURE 3

CONCENTRATION OF IRON
IN α-PbN₆ (MOLE %)

SENSITIVITY OF α-PbN₆ VS
IRON DOPING

FIGURE 4

CONCENTRATION OF IRON IN
α-PbN₆ (MOLE %)

O — Pb (AC)₂ + BaN₆
□ — Pb (AC)₂ + NaN₃

SENSITIVITY OF α-PbN₆ VS
IRON DOPING

FIGURE 5

CONCENTRATION OF IRON III
α - PbN₆ (MOLE %)

O - Pb (AC)₂ + BaN₆
□ - Pb'(AC)₂ + NaN₃

SENSITIVITY OF α - PbN₆ VS
IRON DOPING

FIGURE 6