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Kinetics of Thermal Decomposition of Co_3O_4 Powder and Single Crystals

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Kinetics of thermal decomposition in vacuum of Co_3O_4 powder as well as single crystals has been investigated. Discrepancies with the results of previous authors have been discussed. Decomposition of Co_3O_4 proceeds through formation of a compact layer of CoO and hence diffusion is the rate-limiting factor. The experimental curves $\alpha(t)$ can be described for $0.05 < \alpha < 0.85$ using a modified Ginstling–Brounshtein equation: $1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt^n$ where the activation energy varies with the degree of decomposition.

Introduction

Single crystals of Co_3O_4 have been prepared and characterized for the purpose of photoelectrochemical studies. However, crystals grown by standard C.V.T. techniques were highly stoichiometric, they are practically insulators at room temperature. For photoelectrochemical studies it was necessary actually to obtain semiconducting crystals. The methods which could be considered for that purpose were doping, slight reduction, or decomposition. A slight reduction process could not be used as Co_3O_4 is easily reduced to cobalt metal even at the relatively low temperature of 570 K. Hence the decomposition method was chosen as a first step in the preparation of semiconducting crystals of Co_3O_4 for electrodes.

An examination of the existing literature on the thermal decomposition of Co_3O_4 reveals that many of the previous authors (*1–5*) confined their studies to the temperature and heat of decomposition, only a few (*6–9*) extended their investigations to the chemical kinetics of decomposition. Several discrepancies and contradictions in these studies could justify a reinvestigation of the kinetics of the generally accepted reaction: $Co_3O_4 \rightleftarrows 3CoO + \frac{1}{2}O_2$.

The previous investigators carried out their kinetic studies using different types of Co_3O_4. Ichimura and Komatsu (*6*) used only powders, Deshmukh *et al.* (*8*) powders as well as sintered spherical pellets, Berthod (*7*) both powder and single crystals. Joly and Gerard (*9*) did not indicate

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which material they used, but it was probably a powder sample. It is worthwhile to note that only Berthod attempted to investigate single crystals, but he could not obtain reliable results by isothermal decomposition and instead used only the polythermal method applying the Satava model (*10*) to calculate the activation energy of the process. For describing the kinetic curves $\alpha(t)$, (where α is the degree of decomposition and t the time), Ichimura and Komatsu (*6*), Joly and Gerard (*9*), Deshmukh *et al.* (*8*), used the equation

$$1 - (1 - \alpha)^{1/3} = kt \qquad (1)$$

However, in Ref. (*8*), this equation was considered as valid for the powder and for the so-called first decomposition stage of the pellets. The second decomposition stage of these pellets was described by these authors using Jander's equation

$$[1 - (1 - \alpha)^{1/3}]^{2/3} = kt \qquad (2)$$

Berthod (*7*) for $\alpha < 0.4$ proposed a so-called Carter–Valensi equation

$$\frac{\Delta}{\Delta - 1} - (1 - \alpha)^{2/3} - \frac{1}{\Delta - 1}[1 + (\Delta - 1)\alpha]^{2/3} = kt \qquad (3)$$

where Δ is the ratio of the molar volume of the product to the molar volume of substrate, and also the relation

$$\alpha^2 = kt \qquad (4)$$

But Joly and Gerard extended the validity of (4) up to $\alpha = 0.7$ and 0.8.

It seems that, except for Ichimura and Komatsu, the previous authors could not fit the experimental data with an equation that describes correctly the results over the whole decomposition range.

Various values of activation energy were reported by the previous authors. For powders the values given by Ichimura and Komatsu (*6*) and Deshmukh (*8*) were 366.6 kJ/mole (87.7 kcal/mole) and 392.9 ± 8.4 kJ/mole (94 ± 2 kcal/mole), respectively. But for pellets Deshmukh gave two different values, 397.7 ± 25.1 kJ/mole (95 ± 6 kcal/mole) and 539.2 ± 29.3 kJ/mole (129 ± 7 kcal/mole) corresponding to his first and second stage of decomposition. Berthod (*7*) could not find an activation energy for a powder sample and ascertained that the apparent value determined from the reaction speed, changed with α, being between 627 and 1254 kJ/mole (150–300 kcal/mole). But for single crystals, using the Satava method of polythermal analysis, he obtained two different values: 309.3 kJ/mole (74 kcal/mole) and 384.6 kJ/mole (92 kcal/mole) for α either below or above 0.35, respectively.

Due to these discrepancies the present authors report new experimental results and a new description of the kinetics of thermal decomposition of Co_3O_4, both in powder and single-crystal forms.

Experimental Techniques and Sample Preparation

The powder samples studied were commercial Co_3O_4 (Cerac Inc. 99.95%). Single crystals were obtained by a standard C.V.T. technique using quartz ampoules. The transport agents were Cl_2, HCl, or $TeCl_4$. Crystals grown after about a 1-week run, ranged in a size between 1 and 3 mm (Fig. 1). The identity of the crystals was confirmed by powder X-ray diffraction.

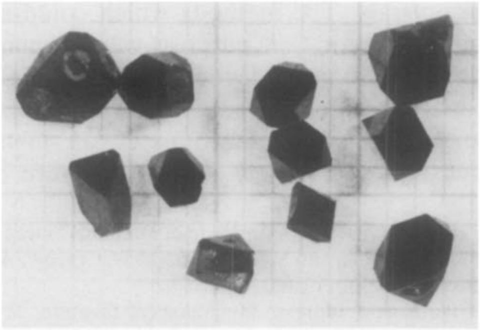

FIG. 1. Single crystals of Co_3O_4.

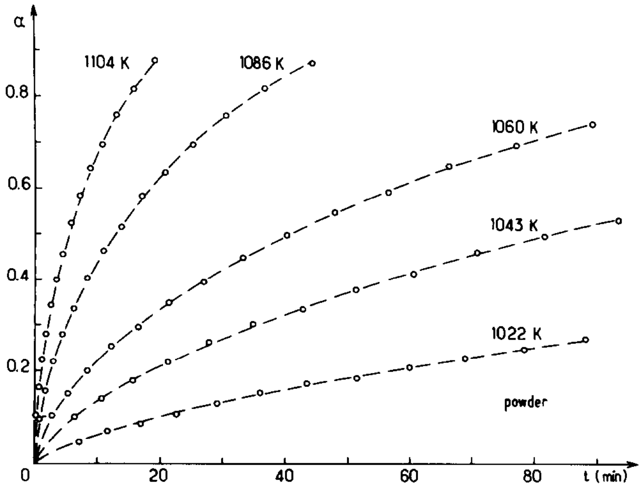

FIG. 2. The $\alpha(t)$ curves for thermal decomposition of Co_3O_4 powder.

Kinetics determination were made with a SETARAM thermal balance (±0.05 mg). Thermal decomposition studies in isothermal conditions were carried out under an oxygen partial pressure of 0.67 Pa. For each experiment a 100-mg sample was used in a platinum holder. The single crystals chosen for these measurements had approximately the same dimensions, each edge being about 1 mm. A rapid heating rate for 40–50°C/mm was used so as to reach the desired temperature as quickly as possible. When a constant temperature was attained the loss of mass as a function of time was automatically recorded. The degree of decomposition was calculated as the ratio of the loss of mass to the total loss of mass at the end of the reaction.

Results and Discussions

Kinetic measurements for powder and single crystal samples were made at five selected temperatures; 1022, 1043, 1060, 1086, 1104 K for powder samples, 1158, 1175, 1183, 1211, and 1231 K for single crystals. The $\alpha(t)$ curves for powder and single crystals are given in Figs. 2 and 3.

In order to choose an appropriate kinetic equation it was necessary to know whether the decomposition product formed a layer or was dispersed in the crystal bulk. From Figs. 4a and b showing the cross section of crystals decomposed up to $\alpha = 0.1$ and 0.6, respectively, the formation of a layer is clearly visible. In order to describe the experimental curves, several so far used kinetic equations corresponding to layer-type decomposition were tried, but it was apparently impossible to find a single equation accounting satisfactorily for the entire range of α. However, a relatively good agreement with the experimental data for both powder and single crystals could be achieved, thanks either to Eq. (1) or to the Ginstling–Brounshtein equation

$$1 - \tfrac{2}{3}\alpha - (1 - \alpha)^{2/3} = kt \qquad (5)$$

A plot against t of $1 - (1 - \alpha)^{1/3}$ and $1 - 2\alpha/3 - (1 - \alpha)^{2/3}$ for Eqs. (1) and (5), respectively, gave linear dependencies for $0.15 < \alpha < 0.75$. The coefficient of correlation obtained from least-squares methods were in the range of 0.985 to 0.995, values which appear to be satisfactory. However, the intercept which should have been at the

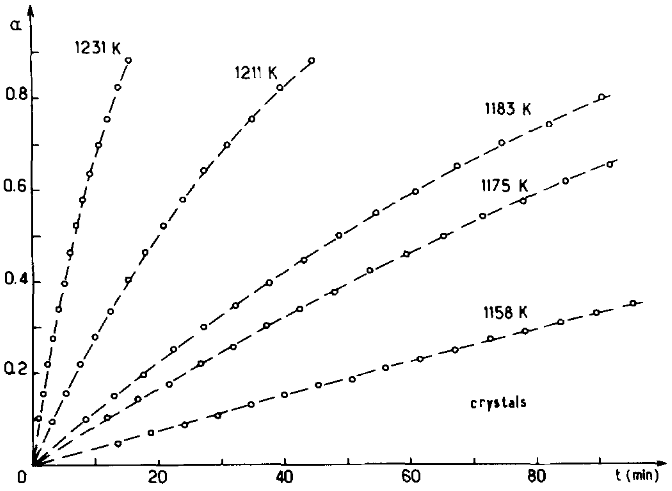

FIG. 3. The $\alpha(t)$ curves for thermal decomposition of Co_3O_4 single crystals.

origin showed a conspicuous shift. This shift could be attributed to an experimental error, but statistical tests showed that the probability of a zero intercept did not exceed 5% and hence that the shift could not be ignored. It was therefore thought that none of these equations truly described the experimental data and that the agreement with the experimental value of α in the range of 0.15–0.75 was in fact only a numerical coincidence. It became thus impossible to use any of the known kinetic equations to describe our experimental data. A similar situation prevailed actually before in the studies carried out by Berthod and Deshmukh. While Berthod failed to find a suitable equation, Deshmukh *et al.* attempted to describe their data for the kinetics of decomposition of pellets using two different equations, (1) and (2). The second decomposition stage, for $\alpha > 0.6$, was described by Deshmukh using Jander's equation (2), a choice which is rather surprising as this equation is in principle only valid for small values of α (0.15 or 0.20). One may assume that this apparent fitting with Jander's equation for $\alpha > 0.20$ is merely a numerical agreement and has in fact no physical meaning.

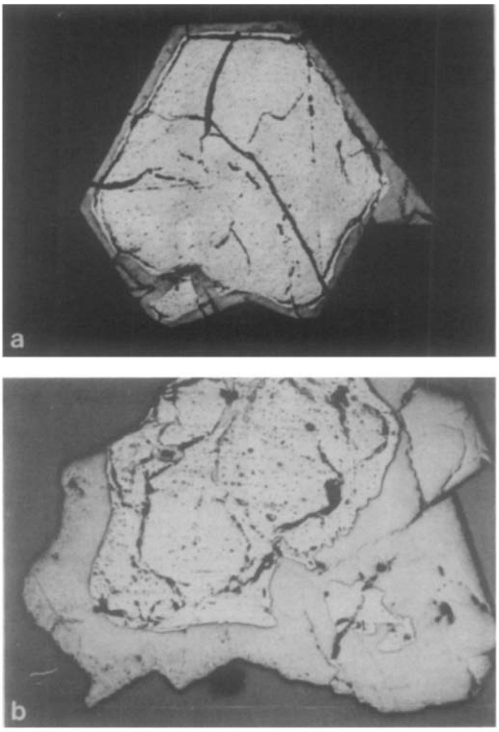

FIG. 4. Cross section of partially decomposed single crystals of Co_3O_4: (a) $\alpha = 0.1$; (b) $\alpha = 0.6$.

Before considering the ability of Eq. (1) to describe the reaction, it is necessary to take into consideration two important factors, namely the compactness of the layer of the material and then the reversibility of the reaction. Indeed this equation does not take into account the influence of the layer on the surface reaction. In the thermal decomposition of Co_3O_4 a dense and compact layer of CoO is formed as observed by Deshmukh *et al.* (*8*) and also in the present work (Figs. 4a and b). Such a layer should hinder the transport of oxygen from the surface on which the reaction occurs and therefore should have an influence on the speed of the reversible reaction itself. This is quite in contradiction with the assumption under which Eq. (1) is derived.

From the above considerations, and also from the observations of the previous authors (*7, 8*), it may be assumed that the speed of the Co_3O_4 decomposition is diffusion controlled. As it has already been emphasized that none of the known diffusional models could be applied, it became necessary to look for a more satisfactory description of the present results.

During different trials made to fit experimental data with the kinetic equations, it was found that when $\ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}]$ was plotted against $\ln t$, extremely high values of straight-line coefficients of correlation (0.9992–0.9999) were obtained for a large α domain: 0.05–0.85. This corresponds to fitting of data to the Ginstling–Brounshtein equation using logarithmic coordinates instead of those mentioned earlier. Using such a system of coordinates the Ginstling–Brounshtein equation takes the form

$$F(\alpha) = \ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}] = \ln k + \ln t \quad (6)$$

If this equation is suitable for the experimental data, then the plot of $F(\alpha)$ against $\ln t$ should give a straight line with a slope equal to 1. In our case, although a good straight line was observed, the slope was found to be between 1.82 and 2.07 or 1.18 and 1.30 for single crystals or powders, respectively. Statistical tests confirmed that this difference between the obtained and the expected value of the slope was quite significant. The probability of the event that the true value of the slope was 1 rather than those observed, due to experimental errors, was not greater than 1%. Simultaneously statistical tests for the coefficient of correlation of the straight-line dependency given by Eq. (6) showed that the probability was smaller than 1%, i.e., it was really a straight-line dependency. As a result of these tests, the following equation was able to describe our experimental data:

$$\ln[1 - 2\alpha/3 - (1 - \alpha)^{2/3}] = \ln k + n \ln t \quad (7)$$

or

$$1 - 2\alpha/3 - (1 - \alpha)^{2/3} = kt^n \quad (8)$$

Assuming this to be a true kinetic equation, it was used to work out our results. Tables I and II give the parameters n and k

TABLE I

RESULTS OF FITTING OF EXPERIMENTAL DATA FOR POWDER

T (K)	n	k	r
1022	1.385	1.871×10^{-5}	0.99997
1043	1.358	9.312×10^{-5}	0.99988
1060	1.295	3.078×10^{-4}	0.99997
1086	1.229	1.618×10^{-3}	0.99987
1104	1.184	5.203×10^{-3}	0.99973

TABLE II

RESULTS OF FITTING OF EXPERIMENTAL DATA FOR SINGLE CRYSTALS

T (K)	n	k	r
1158	2.072	1.290×10^{-6}	0.99971
1175	2.028	7.660×10^{-6}	0.99932
1183	1.981	1.671×10^{-5}	0.99947
1211	1.899	1.271×10^{-4}	0.99938
1231	1.823	1.178×10^{-3}	0.99917

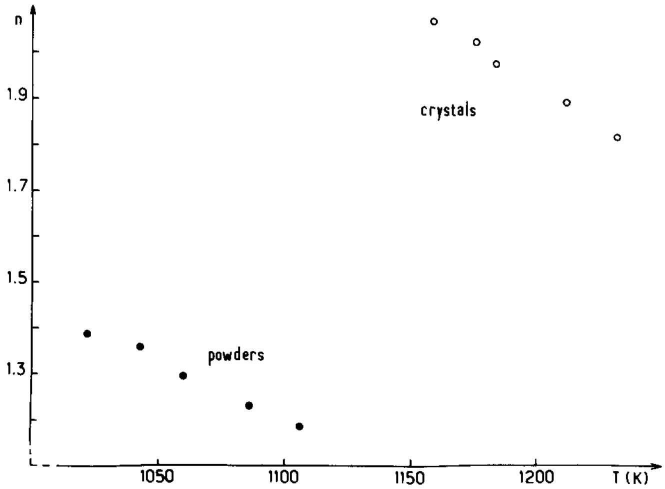

FIG. 5. Temperature dependency of n in Eq. (8) for powder and single crystal.

and the correlation coefficient r for the thermal decomposition of powder and single crystals, respectively.

In Figs. 2 and 3, it is possible to find out the quality of the fitting (the points correspond to experimental data and the curves to the calculated values using n and k from Tables I and II). It can be pointed out that the parameters n and k are temperature dependent, as illustrated for n in Fig. 5.

The next problem was to determine the activation energy, which required the knowledge of the ratio constant. Since both n and k parameters are temperature dependent, none of them could be used as ratio constant. Using Eq. (8), it was possible to find for the reaction speed:

$$\frac{d\alpha}{dt} = \frac{K(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}[1 - 2\alpha/3 - (1-\alpha)^{2/3}] \quad (9)$$

where

$$K = (\tfrac{3}{2})nk^{1/n}[1 - 2\alpha/3 - (1-\alpha)^{2/3}]^{-1/n} \quad (10)$$

The temperature dependency of the reaction speed concerns only K. But it is mathematically impossible to separate Eq. (9) into two parts, one depending on α and the other one on the temperature. Therefore it was necessary to assume that the expression (10) corresponded to the reaction constant as supposed previously by one of the authors (*11*).

In such a case we can expect, for a given value of α, K to obey an Arrhenius law

$$K = K_0 e^{-E/RT} \quad (11)$$

where K_0 is a constant, E the energy of activation, R the perfect gas constant.

TABLE III

FITTING OF K VALUES TO THOSE GIVEN BY AN ARRHENIUS EQUATION FOR DIFFERENT VALUES OF α (POWDER)

α	E (kJ/mole)	k_0	r	ΔE (kJ/mole)
0.1	457.3	1.89×10^{22}	0.9999	4.3
0.2	436.8	6.00×10^{20}	0.9998	4.9
0.3	424.3	7.51×10^{19}	0.9997	5.6
0.4	415.1	1.63×10^{19}	0.9997	6.1
0.5	407.6	4.74×10^{18}	0.9996	6.5
0.6	401.3	1.64×10^{18}	0.9996	6.9
0.7	395.4	6.28×10^{17}	0.9995	7.3
0.8	390.0	2.51×10^{17}	0.9994	7.7

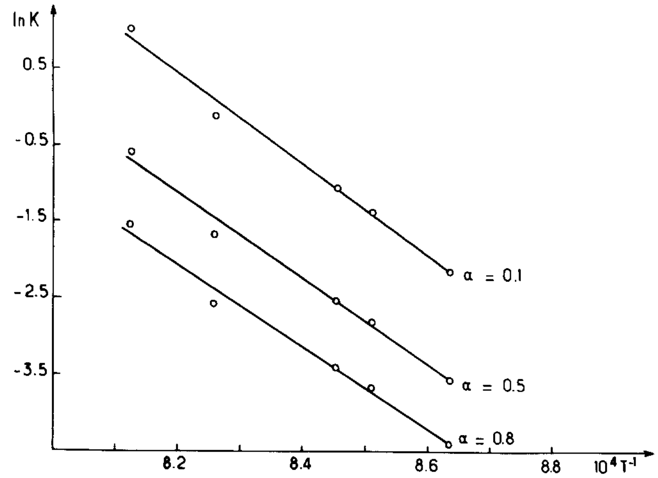

FIG. 6. Plot of ln K against $10^4 \times T^{-1}$ for Co_3O_4 single crystals for different values of α.

Because K is also a function of α, we must expect that either K_0 or E or both of them depend on α. Tables III and IV give results of the fitting of the K values with those of the Arrhenius equation for different values of α. The tables also give the correlation coefficients and the most probable error on the determination of the activation energy, ΔE.

Figures 6 and 7 show examples of fittings of ln K to the values given by an Arrhenius equation for different values of α (0.1, 0.5, and 0.8). It can be seen from these plots that the activation energy is a function of α, as illustrated in Fig. 8. This observation is in good agreement with the difficulties encountered by Berthod (7) who also noticed such a dependency. Table IV shows clearly however that the uncertainty ΔE is large relative to the influence of α on the activation energy E.

The values of the activation energy are

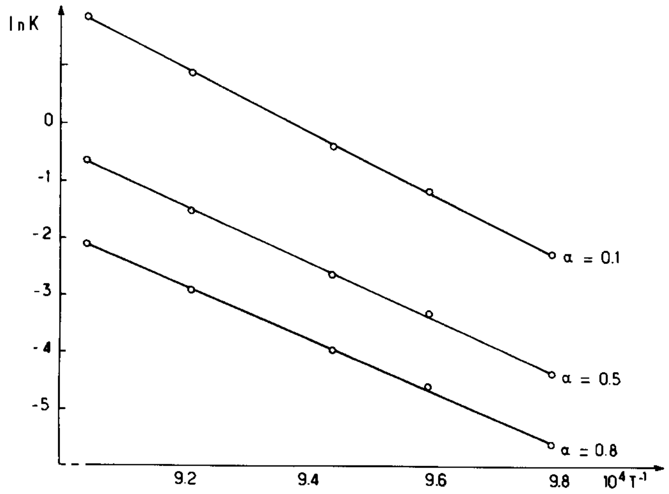

FIG. 7. Plot of K against $10^4 \times T^{-1}$ for Co_3O_4 powder for different values of α.

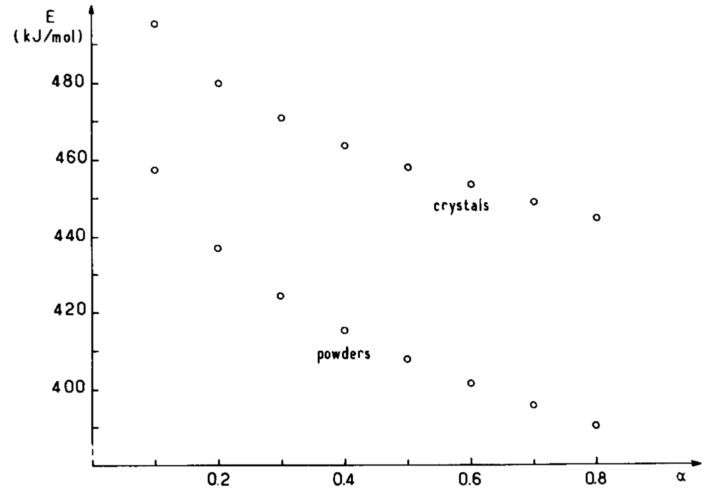

FIG. 8. Dependency of activation energy on α for single crystals and powders.

close to those given by Deshmukh *et al.* (*6*), however it must be emphasized that the values found here show a dependency on α.

Conclusions

In conclusion we may say that we obtained an equation which has the following features: (i) it describes experimental curves α(*t*) for a wide range of α-values with high accuracy; (ii) it leads to determination of activation energy as a function of α; (iii) it derives from Ginstling–Brounshtein equation.

Therefore, Eq. (8) can be considered as kinetic equation. The only difference between this equation and that of Ginstling–Brounshtein lies in the introduction of *n* parameter which actually takes into account the observed change of activation energy with α. Such an interpretation is analogous to that reported earlier for the modification of the Zhuravlev equation used to explain kinetics of the reduction of V_2O_5 by gaseous ammonia (*11*). However, the apparently linear temperature dependency of *n* as well as the large difference obtained for the *n*-values between single crystals and powder (Fig. 5) remains to be explained.

Equation (8) is able to describe the thermal decomposition of both powder and single crystals with comparable efficiency. The activation energy for powder seems to be lower than that obtained for single crystals. However, statistical tests do not confirm this hypothesis with high enough probability (not greater than 80%).

Finally, it may be ascertained that due to the layer-type decomposition of the single crystals of Co_3O_4, semiconducting homoge-

TABLE IV

FITTING OF *K* VALUES WITH THOSE OF AN ARRHENIUS EQUATION FOR DIFFERENT VALUES OF α (SINGLE CRYSTALS)

α	*E* (kJ/mole)	k_0	*r*	Δ*E* (kJ/mole)
0.1	495.3	1.94×10^{21}	0.9947	29.4
0.2	479.9	1.96×10^{20}	0.9946	29.0
0.3	470.7	4.93×10^{19}	0.9944	28.8
0.4	463.6	1.79×10^{19}	0.9944	28.6
0.5	458.1	7.87×10^{18}	0.9943	28.4
0.6	453.5	3.89×10^{18}	0.9942	28.3
0.7	448.9	2.06×10^{18}	0.9941	28.2
0.8	444.8	1.12×10^{18}	0.9941	28.1

neous crystals cannot be obtained by partial decomposition. It will be necessary to investigate the possibility of doping single crystals of Co_3O_4 by transition elements to get such a material.

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