

DISTRIBUTION COEFFICIENT OF Co_2O_3 IN NaCl
SINGLE CRYSTALS

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ABSTRACT: The distribution coefficient of Co_2O_3 in NaCl single crystals from the melt is determined by atomic absorption spectrophotometry. The crystals were grown by a method similar to that described by Kyropoulos. An analysis of the decomposition reaction of $\text{Na}_3\text{Co}(\text{NO}_2)_6$ at the growth temperature was made.

INTRODUCTION

Among the different analytical methods utilized for the determination of the distribution coefficients of metal impurities in NaCl crystals, atomic absorption spectrophotometry has been used successfully for some divalent impuri-

ties¹. In this work we report its use in the determination of the distribution coefficient of Co_2O_3 in NaCl single crystals. The knowledge of this impurity distribution in these crystals is important, due to the investigations that are done in EPR² by which the valence change and the stability in the lattice of the compound $\text{Na}_3\text{Co}(\text{NO}_2)_6$ can be studied.

EXPERIMENTAL

The method of Kyropoulos³ in the open atmosphere (with some modifications⁴) was used to grow the single crystals, starting with 100 g of sodium chloride of reagent grade (J. T. Baker Chemical Co.), the impurity $\text{Na}_3\text{Co}(\text{NO}_2)_6$ was added in 1 and 0.5 wt% respectively. The growing conditions are the same that those described elsewhere¹. The crystals obtained were single and nearly cylindrically shaped.

From each crystal we get about fifteen samples by cleaving slices perpendicular to the cylinder axis at 3 mm intervals. For the analysis it was considered that the concentration of impurity in a sample represents the concentration at the average height of the sample in the crystal. The quantitative analysis was made with a Perkin atomic absorption spectrophotometer, Model 403.

It was found that the distribution of impurities in the crystal obeys Pfann's Equation:⁵

$$\frac{C_s(X)}{C_0} = k(1 - f(X))^{k-1}$$

where $C_s(X)$ is the impurity concentration in the solid at height X , measured from the sees along the crystalization axis; C_0 is the initial concentration in the melt, $f(X)$ is the ratio of the volume of the crystal at height X to the initial volume of melt and k the distribution coefficient.

The value of k for each crystal is is taken as the average value for the various samples from a single crystal.

RESULTS AND CONCLUSIONS

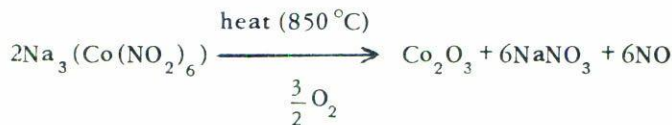
The distribution coefficients and the rates of growth for the two crystals grown are in Table I, where the errors quoted correspond to one standard deviation. The error in the determination of the distribution coefficients was estimated less than 10 percent.

TABLE 1

Crystal N ^o	Rate of growth (mm/h)	Initial concen- tration Wt. %	<k>
1	4	1	0.00817 ± 0.00027
2	6	0.5	0.01786 ± 0.00068

It was observed that in the lower part of the crystals appeared certain dark conglomerates which were also analysed by atomic absorption spectrophotometry finding that these regions were cobalt oxide aggregates.

In order to verify the composition of the final products, the thermal decomposition of $\text{Na}_3(\text{Co}(\text{NO}_2)_6)$ alone, and in the presence of NaCl, was carried out at several heating rates up to the melting point of NaCl. Evolution of nitric oxide starts with the heating and ceases near 400°C. At the end of the decomposition, the residue was extracted with hot water and the filtered solution analysed for nitrates. According to the results, the total reaction in the presence of air proceeds as follows:



in agreement with the results reported for the corresponding potassium derivative⁶.

This confirms that in the final product we only got the two first substances shown in the right side of reaction.

REFERENCES

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RESUMEN

En este trabajo se determinó el coeficiente de distribución de Co_2O_3 en monocristales de NaCl . Los cristales fueron creados a partir del fundente por un método similar al descrito por Kyropoulos. Para el análisis de las muestras se utiliza la técnica de espectrofotometría por absorción atómica. También se analizó la reacción de descomposición del $\text{Na}_3\text{Co}(\text{NO}_2)_6$ a la temperatura de crecimiento.