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On the Formation of Semiconductor of Spinel Type*

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Synopsis

The property of the ferromagnetic semiconductor often varies according to the process of its formation. In the present paper, the outline of and some precaution for the preparation of NiO, Fe_2O_3 and Fe_3O_4 are mentioned, their properties being observed by means of the magnetic measurement. Furthermore the best procedure for obtaining the synthetic magnetite by wet method is described, thereby stressing to avoid the employment of NH_4OH as OH^- .

It has been frequently pointed out, that semiconductor displays the different properties according to the process of its formation, and consequently, the examination of the results of experiments on it must be very careful. Considerations on physical as well as chemical aspects of the preparation of samples should go hand in hand.

Magnetite, found in considerable quantities in the nature, is one of the ferromagnetic semiconductors of spinel type, which has the composition of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$; it is well known, that when the ferrous ion is replaced with the other monovalent or bivalent metal ion, or the ferric ion with the other trivalent metal ion in magnetite, the products have also the same crystal structure of spinel type and many of them show ferromagnetism. Especially, the former is prominent as a group of compounds giving the name of ferrite.

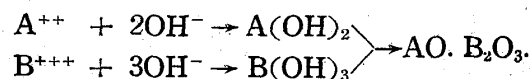
Though some of these spinel oxides, besides magnetite, are found in the nature like chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, or franklinite, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, it is difficult to obtain them as pure state because of its rare occurrence and coexistence with other minerals and elements. Hence, they have to be prepared artificially, and then the results of measurement of their physical properties must be investigated in combination with the condition of the process

of formation. The same is said about artificial magnetite, as reported formerly.⁽¹⁾

Next, the preparation of spinel oxide will be mentioned. Except a small number of particular methods,⁽²⁾ the method of preparation is generally as follows; the mixture of each constituent oxides of the compound is heated at high temperature up to finish of the reaction. This is a sort of additive oxide reaction.⁽³⁾ But, the practical procedure being considered, is roughly classified into the following two methods:

(1) The method, in which two constituent oxides are pulverized and mixed mechanically and let them to be reacted one another:
 $\text{AO} + \text{B}_2\text{O}_3 = \text{AO} \cdot \text{B}_2\text{O}_3$

(2) The method, in which the hydroxides are precipitated from the mixed solution of two constituent cations at the same time and let them to be reacted: Provided that,



A; Fe^{II} , Co, Ni, Cu, Zn, Mn.

B; Fe^{III} , Cr, Al, etc.

The former is called "dry method" and the latter "wet method" in the present report. If these two method are compared with each other, the latter, namely wet method, is preferable except special case.

Generally spoken, in order to react perfectly in usual solid reactions, the following are considered commonly as important factors

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besides temperature; the smallest size of particles, the highest activity and the sufficient mixing of reacting substances. Hence, these conditions are almost satisfied in the case of wet method.

Now, the outline and the ordinary precaution for the formation of spinel oxide, will be mentioned below with respect to the wet method. To begin with, the notes for the precipitation of hydroxide are given. It is desired that the amounts of added alkali are as close as possible to the calculated, not to mention the amounts of the both constituent ions, and the existence of excess alkali seems to bring unexpected difficulties for the reaction of subsequent heat treatment of the obtained oxides. Moreover, it is necessary that the solution should be prepared as dilute as possible, in order to finish completely the reaction, because the precipitation from conqueous solution lowers the degree of mixing owing to adsorbed impurities. Fig. 1. in which $\text{NiO}, \text{Fe}_2\text{O}_3^{4)}$ is

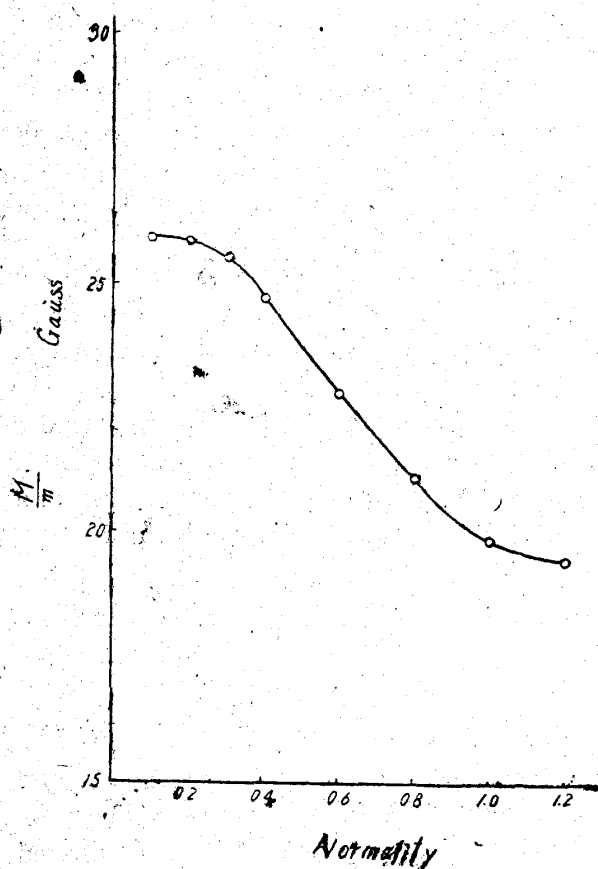


Fig. 1

taken as an example, illustrates the results of experiment; abscissa shows concentration of reacted solution, ordinate magnetic mo-

ment per unit mass at the external field of 820 Oe, after heating the precipitate obtained in respective concentration at 900°C in 10^{-2} mm. Hg for two hours. It is seen from this figure that the magnetic moment increases with the decrease of concentration.

In the next place, the reaction temperature for the formation of spinel is considered. Generally, solid reaction hardly takes place at low temperature, and the raise of temperature becomes the most important factor, in order to proceed the reaction. Now, the reaction of spinel formation of $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ is investigated by means of magnetic measurement by using Ballistic galvanometer. The following reaction, $\text{NiO} + \text{Fe}_2\text{O}_3 \rightarrow \text{NiO} \cdot \text{Fe}_2\text{O}_3$, arises at first observably in the neighbourhood of 450°C , and is accelerated remarkably with the raise of temperature. Fig. 2 indi-

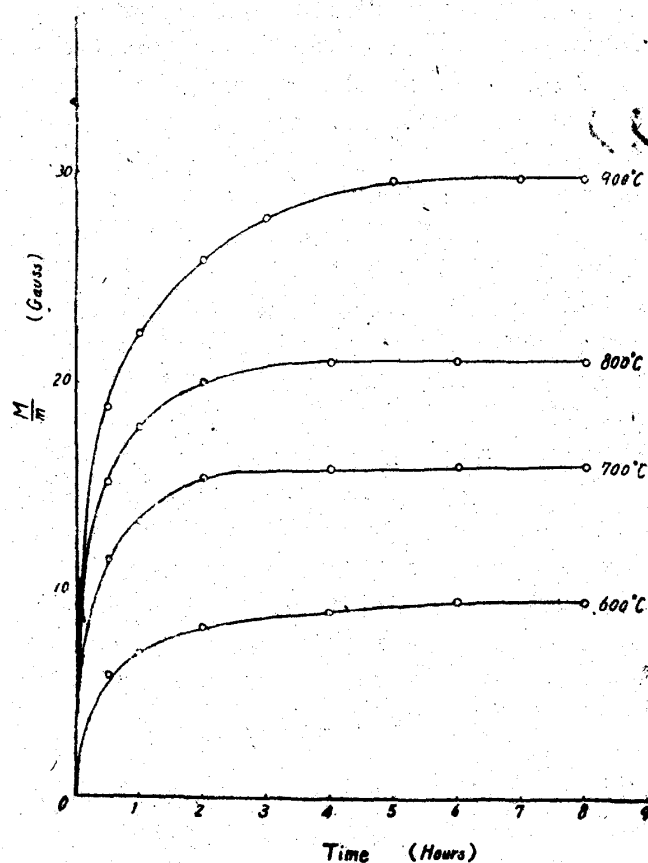


Fig. 2

cates the advancing degree of the reaction at the respective temperature, abscissa shows duration of the reaction, ordinate magnetic moment per unit mass at the external field of 820 oe, after heating at respective temperature, where vacuum degree was always at 10^{-2} mm. Hg. kept. Now, the following two points are noticeable from the figur.

(1) In a very short time such as 5 minutes, the reaction proceeds considerably, and anything like induction period⁵⁾ cannot be found there.

(2) For advancing of the reaction, a restriction exists, which depends upon temperature, and so it is different from the other reactions; such as it proceeds perfectly at some fixed temperature, as found in the case of many solid reactions⁶⁾. With respect to the mechanism of the reaction above mentioned, it will be reported for another opportunity with the aid of the X ray analysis.

Since the reaction of spinel formation takes place at considerably high temperature as remarked above, sufficient precautions are necessary other reactions, accompanied by the reaction of spinel formation, especially the oxidation and the reduction; in the case of nickel ferrite, nickel oxide, NiO, forms no higher oxide without high pressure oxygen or oxidizing reagent, but when the precipitate obtained by wet method are heated by means of the following reaction, $\text{Ni}(\text{OH})_2 \rightarrow \text{NiO}$, it is partially oxidizes and forms nickelic oxide, Ni_2O_3 , within $200^\circ\text{--}300^\circ\text{C}$.⁷⁾ Hence, in such temperature range, heating was accomplished always in vacuum.

As the reduction of NiO occurs frequently rather than the oxidation, sufficient precaution must be taken for it. Namely, NiO is reduced in the neighbourhood of 450°C ⁸⁾ in the air by means of carbon and in more lower temperature in the case of carbon monoxide. Consequently, the mixing of filter paper in the precipitate must be avoided as perfectly as possible. Furthermore, as the dissociation pressure of NiO increases appreciably in a temperature, over 1000°C ,⁹⁾ therefore limitation of vacuum degree must be considered in the case of the heat treatment at very high temperature.

Lastly, the preparation of artificial magnetite is considered.¹⁰⁾ The mixed solution of ferrous and ferric ions in the proportion of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ is slowly added to the OH^- solution in a flask, boiled in vacuo using aspirator after the replacement of the air by nitrogen, and then the black precipitate, namely hydrated magnetite is at once formed. The above reaction is formulated as follows:

$$\begin{array}{l} \text{Fe}^{++} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2 \\ 2\text{Fe}^{+++} + 6\text{OH}^- \rightarrow 2\text{Fe}(\text{OH})_3 \end{array} \rightarrow \text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$$

In this case, it is very interesting to note, that the reaction takes place between the two solid hydroxides, $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, at the considerable low temperature such as 100°C . The same example can be found only in the case of the formation of cobalt ferrite.¹¹⁾

If the reaction is performed at room temperature, the two distinct hydroxides are formed independently in stead of the those immediate combination; when the mixed solution of Fe^{++} and Fe^{+++} is added to OH^- solution, the bluishwhite ferrous hydroxide and the brown ferric hydroxide are obtained. After a very short time, they change into the black precipitate, but that is nonmagnetic at the beginning and, after some minutes, shows the ferromagnetic property, which can be identified by using horse shoe magnet. But the finish of the reaction seems to take a considerable long time.

What sort of results we may expect, when the mixing order of iron ions and OH^- ion are reversed at the room temperature namely, OH^- ion are added to the mixed solution of Fe^{++} and Fe^{+++} ions? Then the precipitation reaction of ferric ion, $\text{Fe}^{+++} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$, only takes place at the beginning owing to the difference of solubility of ferrous and ferric hydroxides. When ferric ion has been consumed, the reaction, $\text{Fe}^{++} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$, arises and the black precipitate is produced. But it seems to take a long time for the finish of the reaction to the formation of magnetite, as in the former case. The present mixing method is quite undesirable at high temperature, because of oxidation of ferrous ion before the reaction. The reaction of spinel formation occurs already in solution in the case of preparation of magnetite by wet method, that is different from the ordinary wet method in some point, such as the formation of $\text{NiO} \cdot \text{Fe}_2\text{O}_3$; the former shows already ferromagnetic property, but the latter nonmagnetic in the room temperature. Remarks above mentioned being considered, the method in which the mixed solution of Fe^{++} and Fe^{+++} ions is added to OH^- solution in the neighbourhood of 100°C , can be considered the best one, though its treatment is somewhat complicated in order to prevent oxidation in the course of form-

ation of precipitation. Because, ferrous and ferric hydroxides are formed at the same time, and its reaction is active, being different from the course of the reaction at a room temperature, moreover, solid reaction takes place before the growth of precipitated hydroxide. In fact, the magnetite prepared by this procedure has stronger magnetic moment, than that of obtained by other methods at the room temperature, because the remaining of unreacted ferrous hydroxide is oxidized at the subsequent treatment like filtration in the case of another methods.

The reagents used in the present research, are KOH, ferrous and ferric sulphates. It is noteworthy, that KOH is used as OH^- ion; on the other hand, any soluble salt, like ion chloride etc., may be satisfactorily used as iron ion. Commonly, NH_4OH is often employed as OH^- ion, due to the possibility of removing the adsorbed impurities by heating, the facility of filtration, and the other reasons, but when this artificial magnetite obtained by using NH_4OH is heated, adsorbed NH_4OH in the precipitate easily decomposes into nitrogen and hydrogen, and this active hydrogen reduces constituent oxide and lessens the effect of excess oxygen in the oxide in the case of heat treatment. Therefore, especially the employment of NH_4OH must be avoided.

Summary

The outline and the ordinary precaution for the preparation of spinel oxide are remarked with respect to the wet method, as $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ is taken as an example.

In the first place, the notes for the precipitation of hydroxide are given as follows; the amounts of reacting ions is as close as possible to the calculated; moreover, the precipitated hydroxide should be formed in solution as dilute as possible. Next, the reaction for the spinel formation of $\text{NiO} \cdot \text{Fe}_2\text{O}_3$ is investigated by means of magnetic measurement. From the results of the measurement, the following two points are noticeable.

(1) In a very short time such as 5 minutes, the reaction proceeds considerably, and anything like induction period can not be found

there.

(2) For advancing of the reaction, a restriction exists, which depends upon temperature.

With respect to the mechanism of the reaction above mentioned, it will be reported for another time with the results of X-ray investigation.

Lastly, the preparation of artificial magnetite by wet method is mentioned. From examinations for the experimental results, the procedure in which the mixed solution of Fe^{2+} and Fe^{3+} ions is added to OH^- solution in the neighbourhood of 100°C can be considered the best one, though its treatment is somewhat complicated in order to prevent oxidation. Moreover, the employment of NH_4OH as OH^- ion should be avoided in the course of formation of precipitation.

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References

- (1) T. Okamura, Y. Torizuka and J. Simoizaka, Sci. Rep. RITU, A-Vol 1, No. 3.
- (2) S. Hilpert u. A. Wille, Z. physik. Chem., B 18 (1932), 291.
- (3) T. A. Hedvall, Reaktionsfähigkeit fester Stoffe, (1938), 188.
- (4) T. A. Hedvall, K. List u. S. Holgersson, Z. anorg. Chem., 93 (1915), 318.
H. Forestrer et G. Chaudron, Compt. rendu., 180 (1925), 1294.
- (5) Frhr v. Göler u. G. Sachs, Z. Physik, 77 (1932), 281.
- (6) T. A. Hedvall, Reaktionsfähigkeit fester stoffe, (1938).
- (7) Ipateef, J. Prak. Chem., (2) 77 (1908), 513.
M. Prasad and M. G. Tenduklar, J. Chem. Soc., 1403, 1407 (1931).
- (8) G. Tammann u. A. Y. Sworykin, Z. anorg. Chem., 170 (1928), 62.
W. Bankloh u. R. Durrer, Z. anorg. Chem., 222 (1935), 189.
- (9) H. W. Foot and E.K. Smith, J. Am. Chem. Soc., 30 (1908), 1344.
G. Kröger, Z. anorg. Chem., 205 (1932), 369.
- (10) S. Hilpert, Ber., 44 (1911), 1911.
L. A. Wello u. O. Baudisch, Phil. Mag., (6) 50 (1925), 399.
L. A. Wello u. O. Baudisch, Phil. Mag., (7) 3 (1927), 397.