

ONE CONSIDERATION ON THE SINTERING MECHANISM OF ORE

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1. Introduction

Now it is generally thought that sintering of materials occurs at high temperature owing to some binder included in them and the surface energy of their particles. Especially at the oxidizing roasting of lead sulphide concentrates, we recognized that they showed the strong phenomena of sintering and sludging. This sintering phenomenon has been considered that the lead sulphide ore-particles will sinter and sludge each other at higher temperatures.

But we found that the degree of sintering at the oxidizing roasting of lead sulphide concentrates was larger in higher crystallinity (*i.e.* the crystallization degree) of lead sulphide, and had little relations with lead sulphates, lead oxides or other impurities (in very small amount) included at that time.

Hence, we considered, the crystallinity of materials, particularly of ores, has a great influence on sintering at higher temperature.

On the basis of this idea, we investigated the changes of sintering phenomenon of many materials (lead sulphide, zinc sulphide, copper sulphide, iron sulphide, and so on) in oxidizing, vacuum or argon gas atmosphere, for the various kinds of their crystallinities, at the temperature range of 300°–700°C.

We examined their sintering phenomena chiefly in hardness number and degree of crystallinity with X-ray diffraction analysis.

We shall subsequently describe the experimental data in details.

2. Experimental Details

2.1. *Experimental apparatus*

A. Sintering apparatus: The apparatus is shown in Fig. 1. Sintering reaction room (left) is made of stainless steel retort and is able to be vacuum-pumped to 10^{-3} – 10^{-6} mmHg. Reaction temperature is regulated by temperature controller (Alumel-Cromel thermocouples and automatic pyrometer) and other electronic regulator (details in Fig. 1). The system diagram (right) shows reaction system, vacuum system, argon gas system, and temperature controlling system.

B. X-ray diffraction apparatus: We used Geigerflex diffraction apparatus for crystallinities of specimens by powder method, which has X-ray tube: Cu, Co etc, Current 0–30 mA, Voltage 0–90 kV, D. Slit 1°, R. Slit 1° etc.

C. Hardness tester: We used Shore hardness tester for observing hardness of sintering materials.

2.2. *Experimental specimens*

Experimental specimen is made by compressing the sample materials under 1 t/cm² pressure, of which particle-size is 200 mesh and grade is chemical pure, and concentrate.

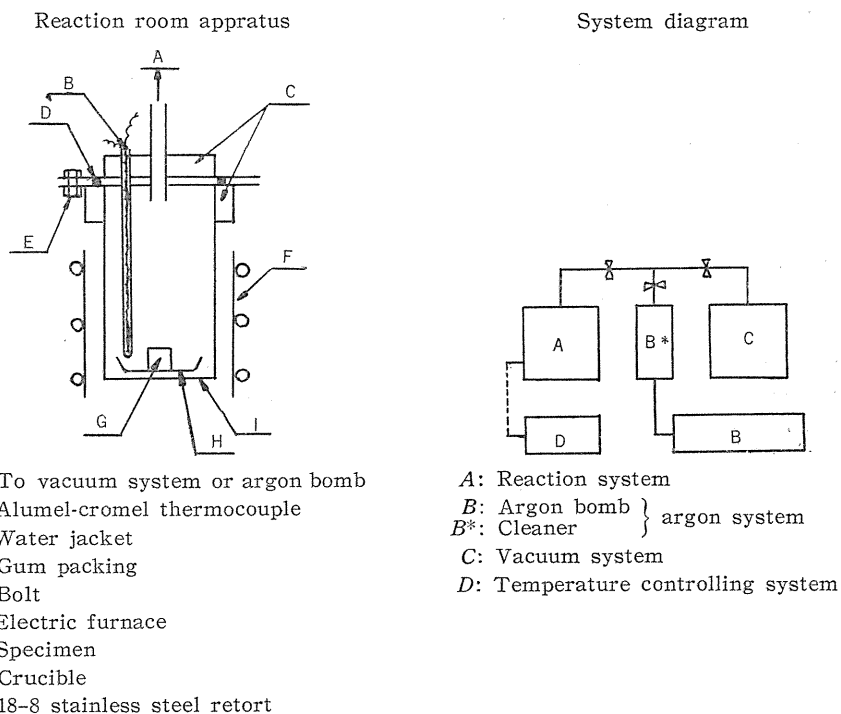


FIG. 1. Experimental apparatus

It is formed into a block of 10 mm dia. 20 mm height and the raw-material for it is lead sulphide, zinc sulphide, iron sulphide, cupric sulphide, calcopyrite, cadmium sulphide, or zinc metal.

2.3. Experimental procedure

We put the specimen on a porcelain dish in the stainless steel retort and close the retort, and pump up to 10^{-3} – 10^{-4} mmHg.

Then we induce the specified gas into the retort as to show the specified atmosphere, and elevate the temperature to the specified condition at the rate of $50^{\circ}\text{C}/\text{min}$, regulating the gas condition. After getting to the required temperature, we let the specimen sinter for an hour. And then we cool the retort down to the room temperature. we take out the specimen from the retort and observe the Shore hardness number on the polished surface, and carry out the X-ray diffraction analysis of the specimen.

In determining the crystability of specimen, we used the wellknown formula for the crystallization degree as follows;

$$y_c = kxIW$$

k : Constant

x : Crystability of materials

I : Initial X-ray intensity

y_c : Diffraction X-ray intensity

W : Weight

In the above formula, κ value shows the crystallinity, but it is difficult to calculate the absolute value of crystallinity, then we used diffraction X-ray intensity, of the personal lattice plane which personal d shows, in relative comparison of crystallinity of materials, which is proportional to the crystallinity of materials, and we shall discuss the crystallinity by means of the relative crystallinity. Lattice plane distances are as follows; PbS $d=2.97$ Å, ZnS $d=3.12$ Å, Cu_2S $d=2.75$ Å, FeS_2 $d=1.64$ Å, CuFeS_2 $d=3.03$ Å, CdS $d=3.35$ Å, Zn $d=2.08$ Å.

In the figures, we represent the relative crystallinity in letters in bracket after the name of material, for example PbS(higher). PbS is the name of material. (higher) shows the relative crystallinity among the used materials. In the case of iron sulphide, though in initial crystallinity FeS_2 was lower, after cooling successively from the state treated at elevated temperature the specimen showed higher crystallinity. Then we described FeS_2 (higher-lower) in this case vice versa.

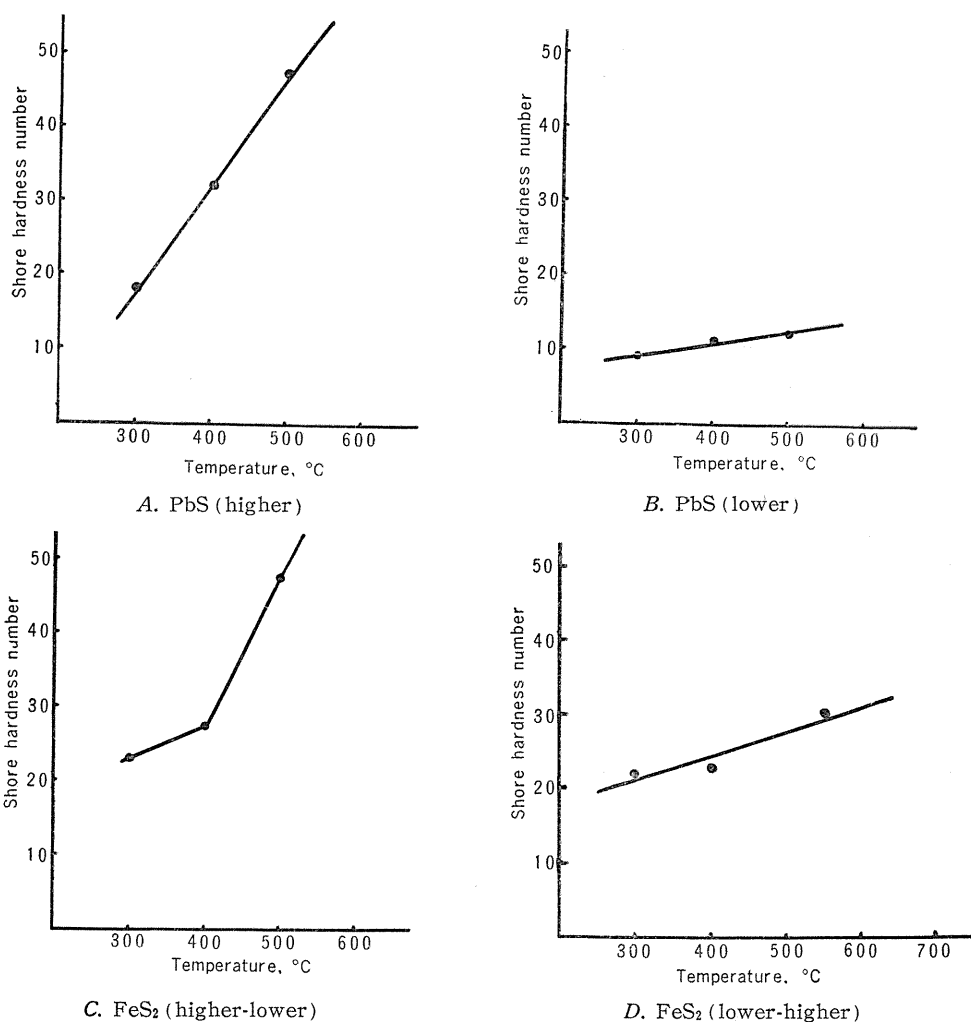


FIG. 2. Sintering in oxidizing atmosphere.

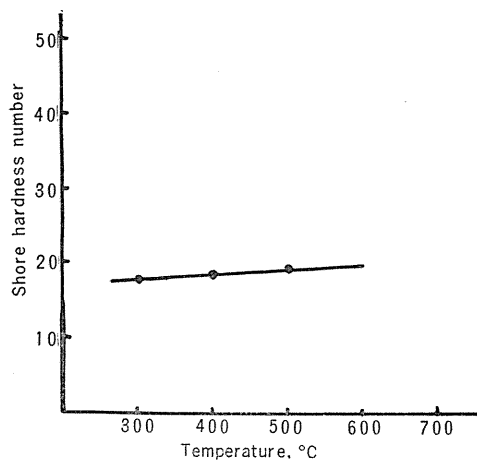
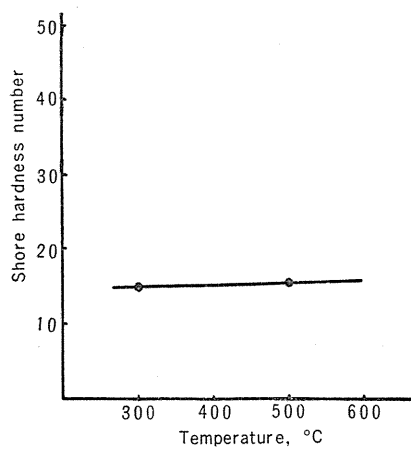
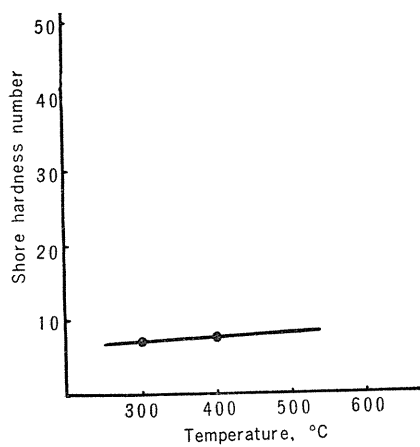
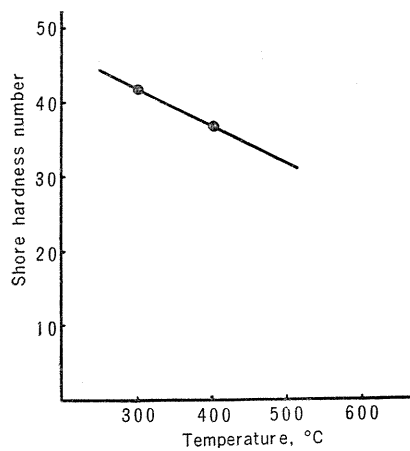
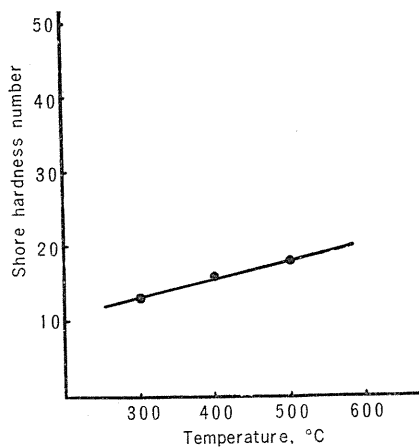
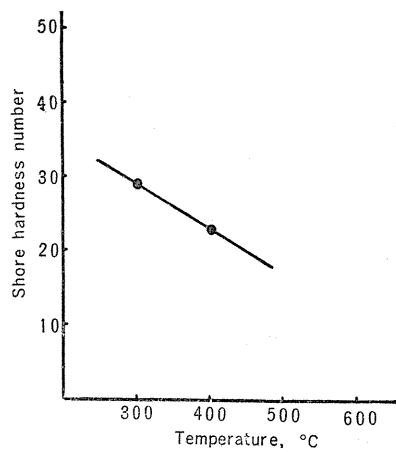
*E. ZnS (higher)**F. ZnS (lower)**G. Cu₂S (lower)**H. Cu₂S (higher)**I. Zn**J. CdS*

FIG. 2. Sinteting in oxidizing atmosphere

3. Experimental Results

3.1. *Some sintering phenomena at oxidizing atmosphere—influences of the sintering temperature upon the hardness of sintering products.*

The results are shown in Fig. 2(A...J). Curve A or B shows the Shore hardness number changes of lead sulphide. In this case the higher the sintering temperature was, the greater the hardness number was. This phenomenon, later, we shall name "Temperature effect". And also its hardness was greater in higher initial crystallinity than in lower, as shown in the figure. That phenomenon, later, we shall name "Crystallinity effect". Curve C or D shows the hardness changes of iron sulphide. We recognized the temperature effect and the crystallinity effect only at 500°C and at 300°–400°C little effect was shown as in Curve E or F (ZnS). Curve G or H shows the hardness changes of cupric sulphide. We could know that temperature effect did not nearly appear in this temperature range, but crystallinity effect was appreciable. In curve H(Cu₂S) or J(CdS) there is a negative temperature effect. In curve I(Zn) or J(CdS), we observed the possible tendency to sinter zinc or cadmium sulphide at oxidizing atmosphere.

3.2. *On the sintering in vacuum atmosphere*

In oxidizing atmosphere sintering phenomena may be affected by a little oxidizing chemical reaction, then we did not exactly observe the influences of crystallinity upon the sintering characteristics.

Therefore we examined the sintering phenomena in vacuum atmosphere.

The results are shown in Fig. 3(A...J). In curve A or B(PbS), curve C or D(FeS₂), and curve G or H(CuFeS₂), they showed the temperature effect and crystallinity effect. In curve E or F(ZnS) both phenomena did not nearly appear, and in curve I(Cu₂S) the hardness suddenly dropped at 600°C, where we observed the lowest crystallinity of cupric sulphide in the temperature range.

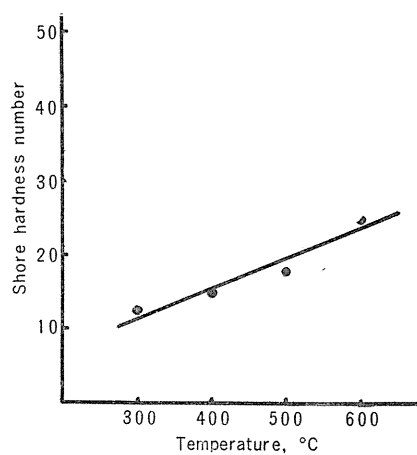
3.3. *On the sintering in argon gas atmosphere*

We examined the sintering phenomena in argon atmosphere, where we protected the materials from various chemical and physical reaction.

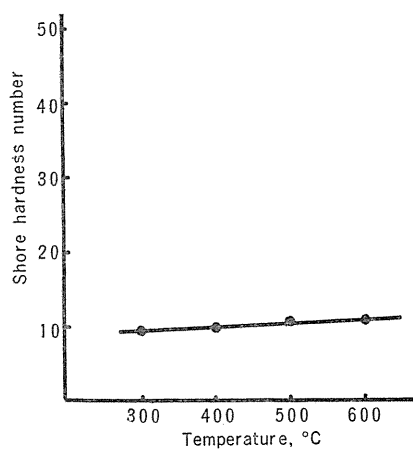
The results are shown in Fig. 4(A...L). In curve A, B, C(PbS) there were both temperature effect and crystallinity effect. In curve D or E(FeS₂) influences upon sintering characteristics were higher in the secondary crystallinity than in the initial primary crystallinity as shown in curve H or I(CuFeS₂). That is owing to the speedy crystal growth of the lower crystallinity materials. After crystal growth their conditions were the same as in PbS. In curve F or G(ZnS), lower crystallinity showed greater values in hardness than higher crystallinity at lower temperature.

It will be owing to the good sludging possibility of lower crystallinity.

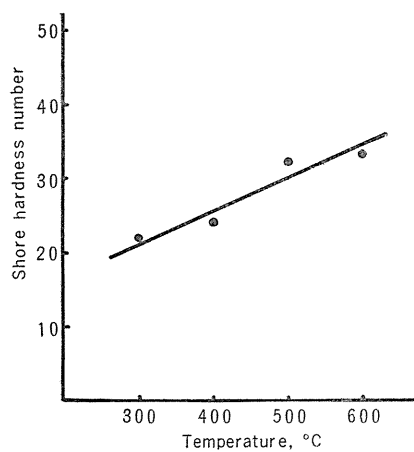
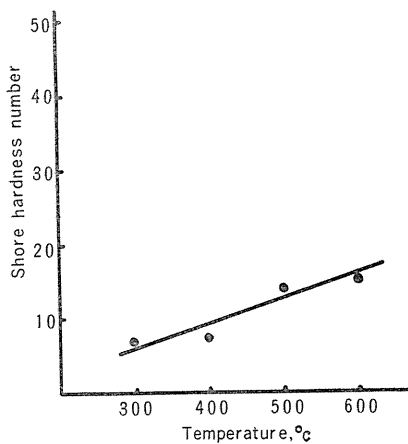
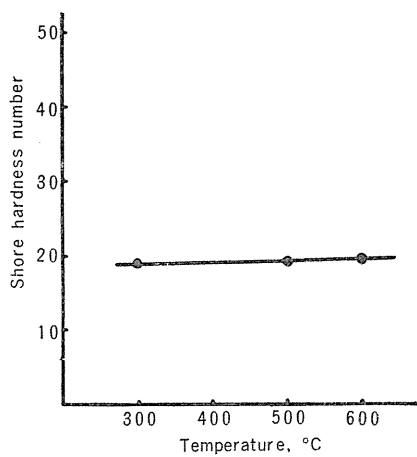
In general, the hardness number was greater in the case of showing higher relative crystallinity, (even if the relative crystallinities in initial condition were equal) when at elevated temperature the relative crystallinity material was greater than the other, which had lower relative crystallinity at this time. In Fig. 5 are shown there the various relative crystallinities of materials in diffraction X-ray intensity at the same scale factor. In curve D or E(FeS₂) as shown in Fig. 4, in that temperature range, the phenomena were the same as zinc sulphide at lower temperature.



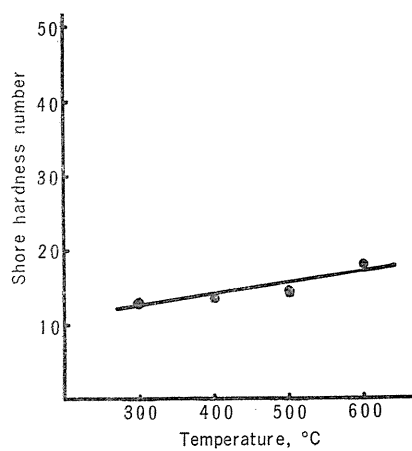
A. PbS (higher)



B. PbS (lower)

C. FeS₂ (higher-lower)D. FeS₂ (lower-higher)

E. ZnS (higher)



F. ZnS (lower)

FIG. 3. Sintering in vacuum.

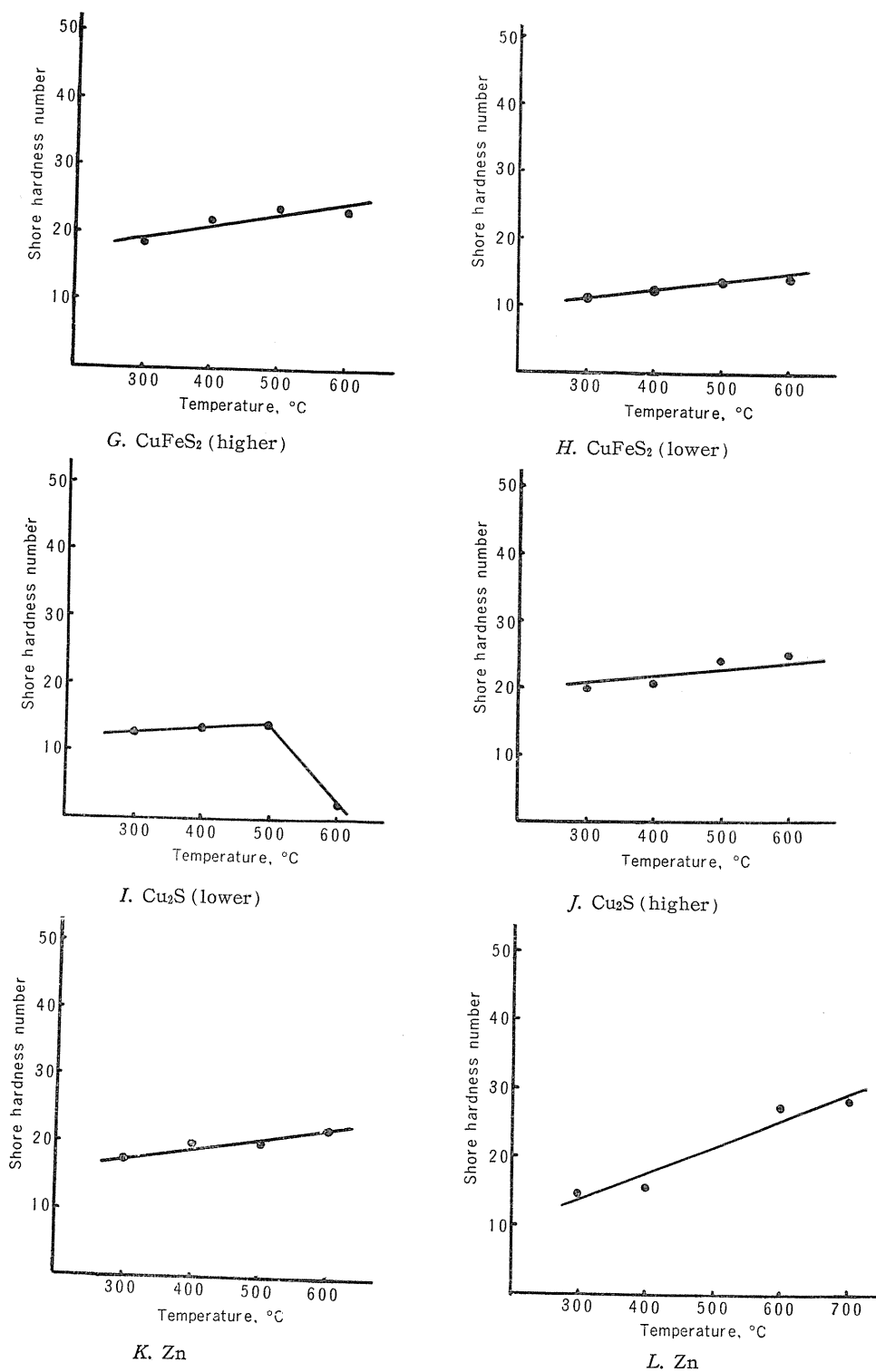
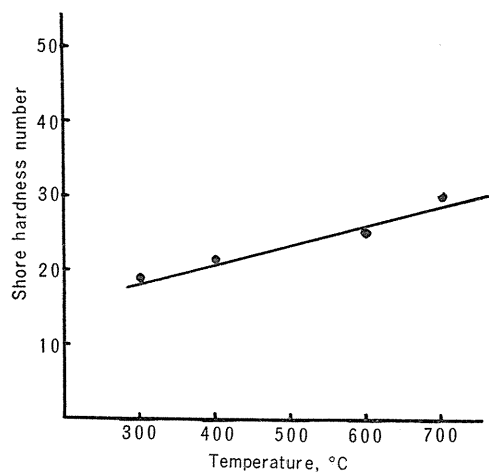
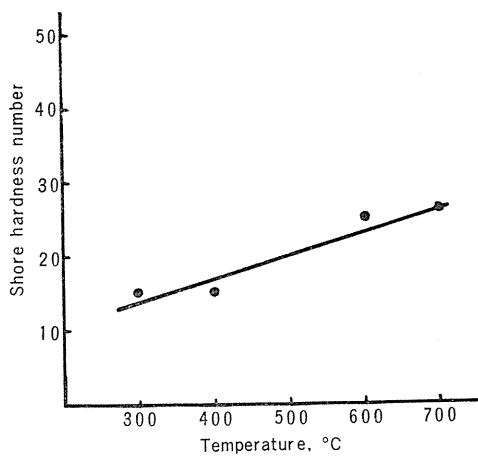


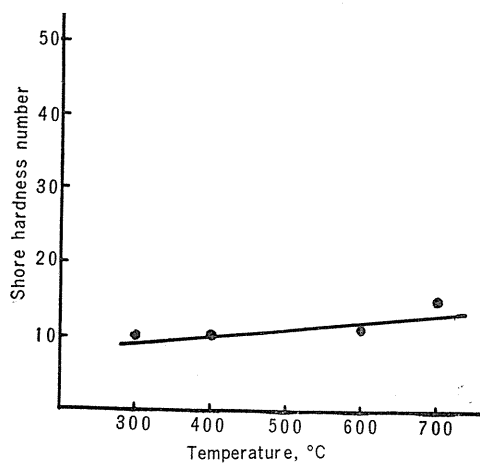
FIG. 3. Sintering in vacuum



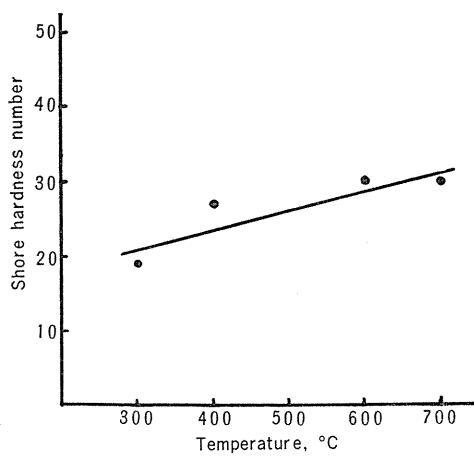
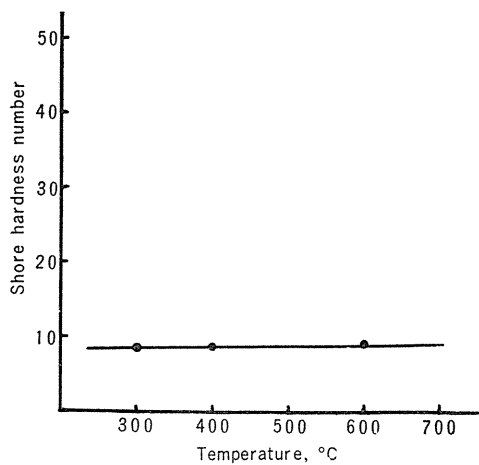
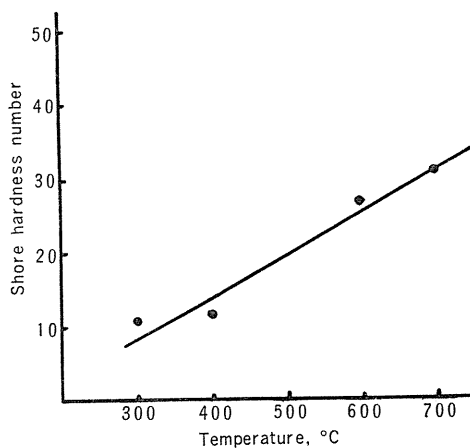
A. PbS (higher)



B. PbS (middle)



C. PbS (lower)

D. FeS₂(higher-lower)E. FeS₂ (lower-higher)

F. ZnS (higher)

FIG. 4. Sintering in argon gas atmosphere.

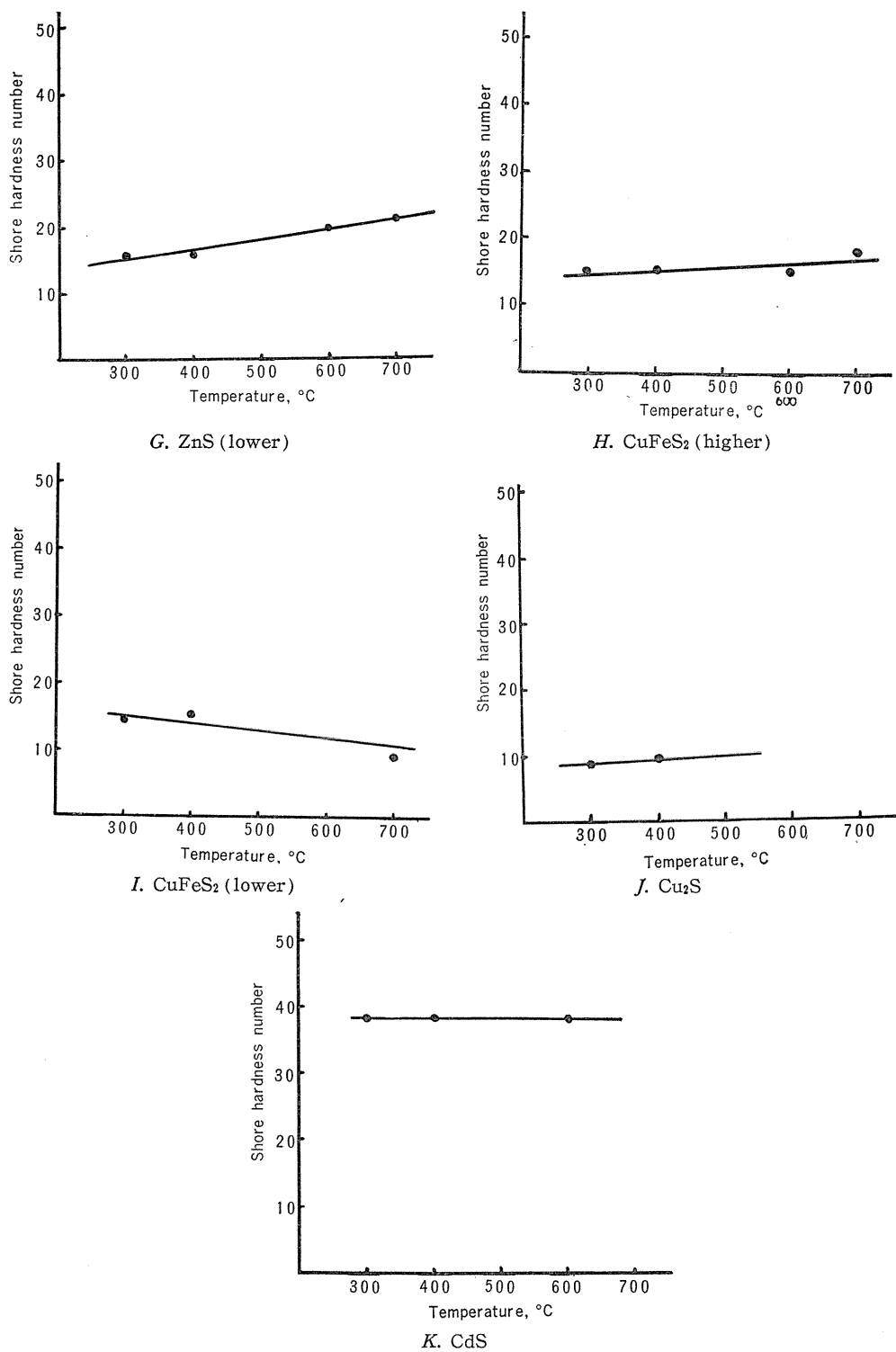


FIG. 4. Sintering in argon gas atmosphere

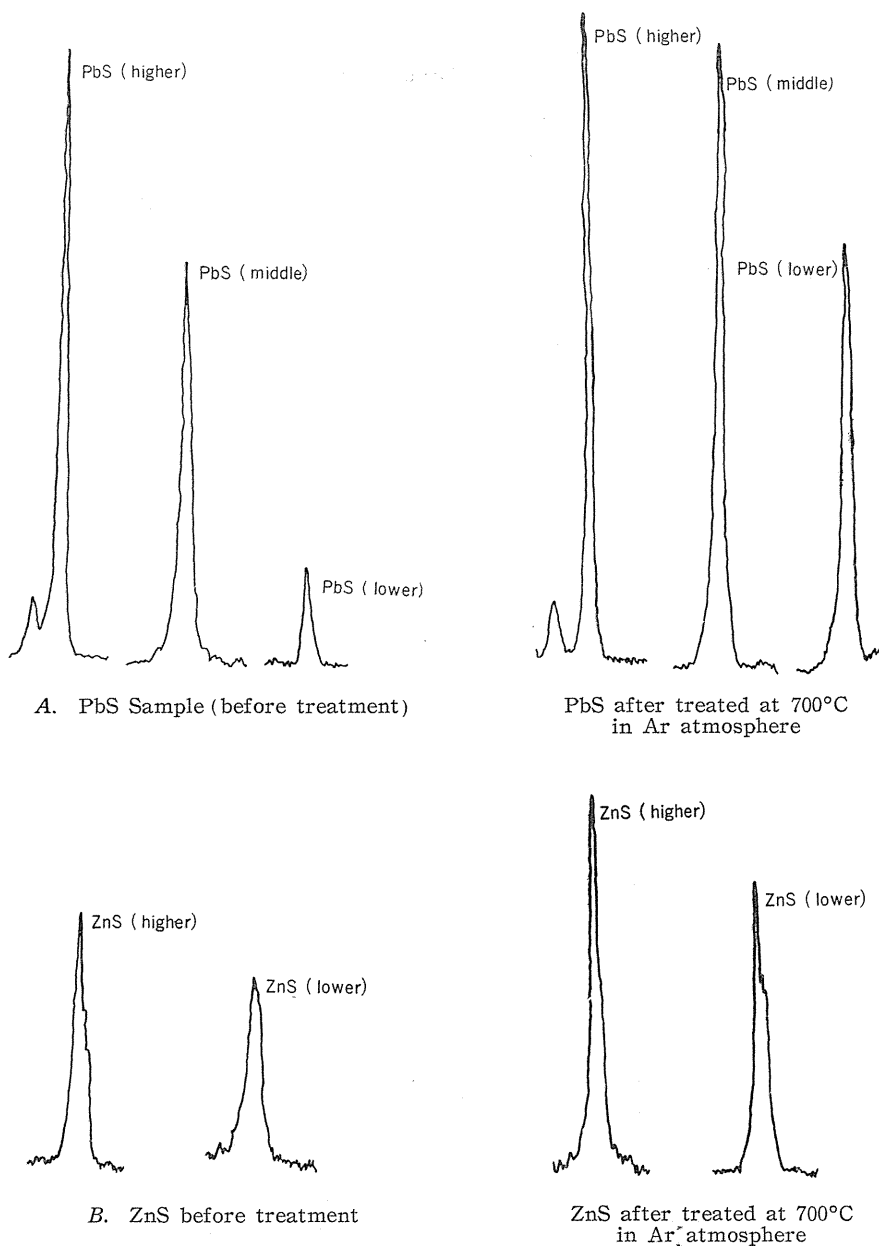


FIG. 5. Various relative crystabilities by means of diffraction X-ray intensity.

4. Consideration

The crystability changes owing to lattice randomness, which is occurred by lattice defects, thermal vibration of lattice point element, strain of lattice and so on. In the case of the same materials, the material with lower crystability shows

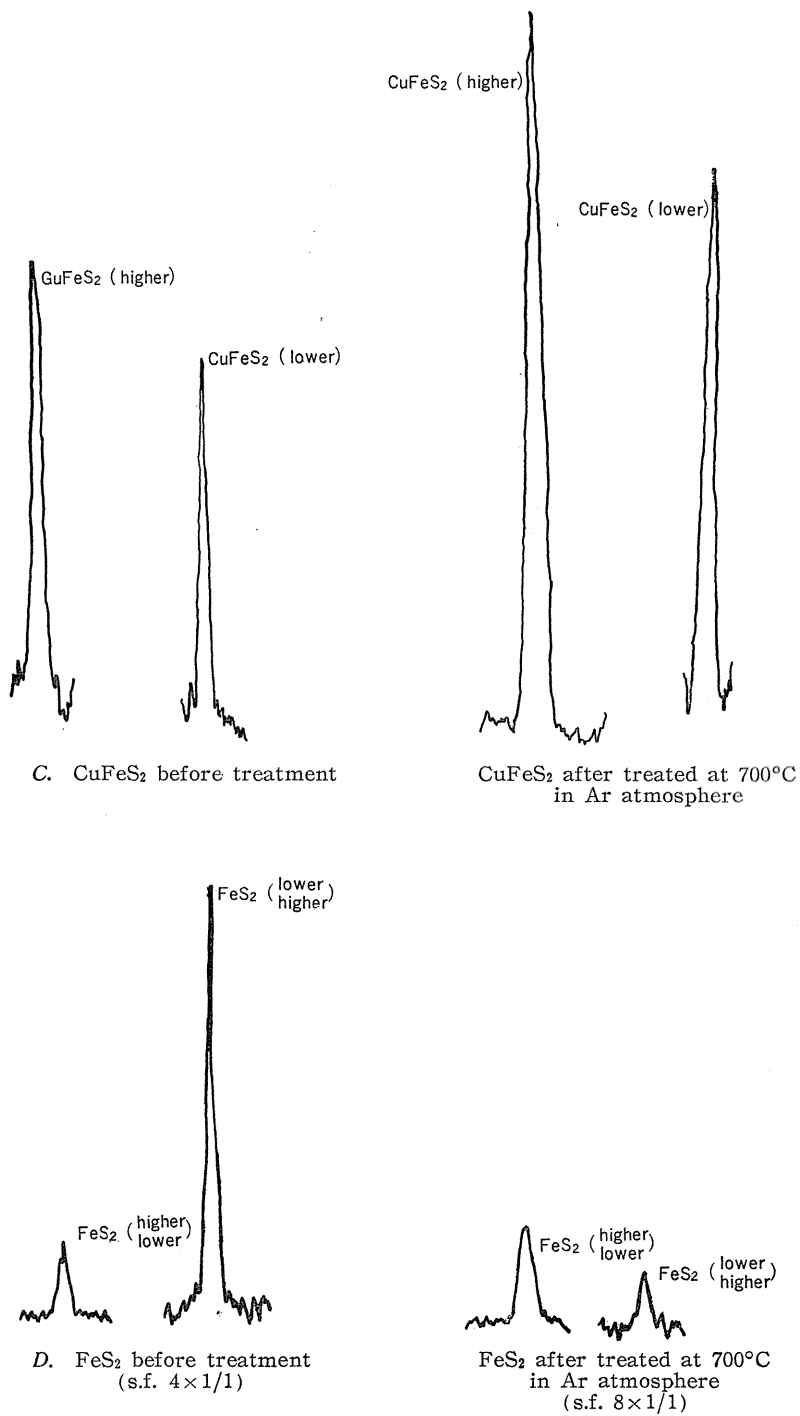


FIG. 5. Various relative crystallinities by means of diffraction X-ray intensity.

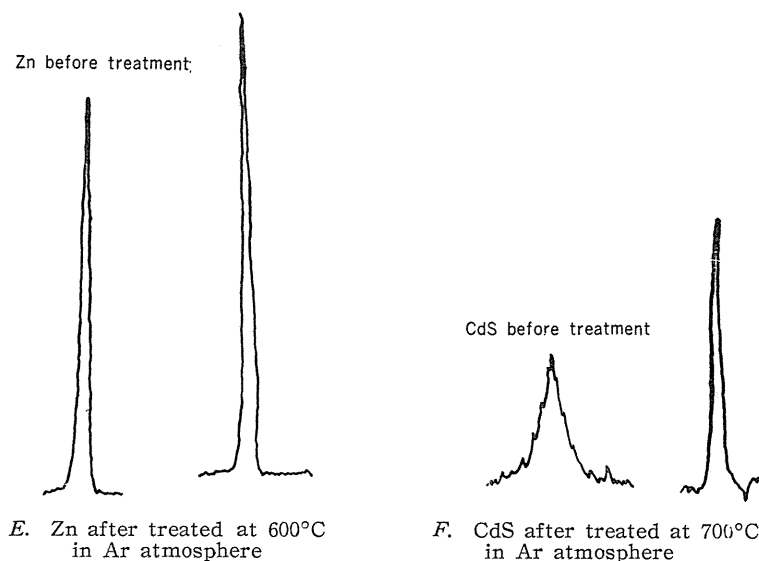


FIG. 5. Various relative crystabilities by means of diffraction X-ray intensity.

greater chemical reactivity, as it has good crystalline diffusion or ion conductivity of elements, but in mechanical properties the material with higher crystability has better properties than with lower crystability, as higher crystability shows a better ordered lattice arrangement.

The sintering characteristics consists of the sludging properties of crystallization of materials. We think that is the combination of both properties, where the better property proceeds in preference to the other. In the conditions of surface sludging enough to sinter each other, the necessary factor having an important influence upon the sintering characteristics is the mechanical properties (hardness in this case) of crystallization of materials, which has the crystability as most influential element. In a crystal, the higher crystability the crystal has, the better mechanical property it shows.

In this experiments, before the starting period of sintering there were found many various facts, *i.e.* in zinc sulphide treated at lower temperature we observed that the lower relative crystability showed a greater hardness. This phenomenon is explained as follows:

At this period the sintering did not yet occur, then the properties of sample block shows its compressibility, its contactibility and so on, but not sintering characteristics. All over these experiments except the irregular phenomena like the above, after starting sintering at the same conditions, the higher the crystability or randomness of crystalline materials is, the higher the sintering characteristics (in hardness) of the materials is.

Thus from the above facts, we consider that in sintering of crystalline materials in general, there is an important relation between the crystability (or the relative crystability) and the sintering characteristics.

5. Summary

1. There are "Temperature effect" and "Crystability effect" in sintering at oxidizing atmosphere, in vacuum and in argon gas atmosphere.

The temperature effect shows: the higher the sintering temperature is, the greater the hardness number of the specimen is. And also the crystalsbility effect shows: mechanical properties (hardness) are greater in the specimen with higher initial crystability than with lower crystability.

2. There is an important relation between the crystability and the sintering characteristics, Namely, the higher the crystalsbility or randomness of crystalline materials is, the higher the sintering characteristics of them is.

3. It is enough possible to compare the crystability of the specimen in diffraction X-ray intensity of the materials (by means of powder method), using the proportional relation of the next formula

$$y_c = kxIW$$

In conclusion, the intimate relation between the crystability and the sintering characteristics of materials is very important and valuable for sintering ore and powder metallurgy. In addition, after the result of this research we succeeded in rapid oxidizing roasting of lead sulphide ore-concentrates in fluo-solid roaster without sintering of their ore-particles and besides, we obtained lead ore-concentrates with extremely small quantities of sulphur (0.2-0.5% S).