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PRELIMINARY REPORT ON SUPERSTRUCTURES IN ZINC-DOLOMITE

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Abstract. Zinc-dolomite was studied by high-resolution electron microscope imaging, selected area diffraction and electron microprobe. Electron diffraction data suggest the presence of a periodic antiphase structure (PAS) in Zn-dolomite. Its unit cell probably consists of three units: $\text{CaMg}(\text{CO}_3)_2$ as a basal unit, $\text{CaZn}(\text{CO}_3)_2$, and CaCO_3 . The periodic array of PAS domains is parallel to $\bar{1}\bar{2}0$ and probably has a stair-like structure. The upper limit of $\text{CaZn}(\text{CO}_3)_2$ domain size is about 100 Å according to dark-field image study.

Other rhombohedral dicarbonates probably also have domain structures. The size of the domains is controlled by the value of misfit of the domain lattice to the host lattice.

INTRODUCTION

Zinc-dolomite was reported from Bleiberg Carinthia (Gintl 1877 see Hurlbut 1957) and plumbo-dolomite from Kreuth, Carinthia (Siegl 1936, see Hurlbut 1957). In 1957, Zn—Pb dolomite from Tsumeb was described (Hurlbut 1957). It contained 3.23—8.47 wt.% ZnO and 0.58—4.96 wt.% PbO and its chemical formula was $(\text{Ca}, \text{Pb})(\text{Mg}, \text{Zn}, \text{Fe}, \text{Mn})(\text{CO}_3)_2$. In the Cracow-Silesian deposits zinc-dolomite with the Zn:Mg ratio of 1:1 was reported on the basis of microprobe studies (Jasińska, Żabiński 1972).

Thermal analysis (Hurlbut 1957, Żabiński 1959) provides the strongest evidence of the existence of zinc-dolomite. The available X-ray powder data are far less conclusive because of the close similarities between rhombohedral dicarbonates (Graff 1961).

The failure to synthesize Zn-dolomite aroused doubts as to its stability (Goldsmith, Northrup 1965), although very extensive solid solution towards $\text{CaZn}(\text{CO}_3)_2$ is believed to exist (Rosenberg, Foit 1979).

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MATERIALS AND METHODS

Investigations were carried out on Zn-dolomite samples from strata-bound Zn—Pb deposits, Cracow-Silesian ore district, Poland. Samples C-1, C-2 and C-4 were collected from the "Dąbrówka" mine (near Bytom) in the 625-P drift (galmei ore). All the samples contain fine-grained dolomite as the main component and goethite as an associated mineral. Sample C-5 was taken from the "Grot 10" mine working in the "Trzebionka" mine and consists of laminated dolomite.

Chemical analyses of the specimens showed variable, but always significant, Zn admixtures (up to 7.6 wt.% ZnO in sample C-2). Infrared, thermal, and X-ray measurements revealed the presence of dolomite, goethite and trace calcite in sample C-1. No zinc minerals were detected in these samples. This suggested the presence of Zn-dolomite. To confirm this assumption, the samples were subjected to electron probe and electron microscopic studies.

Zn-dolomite within the Cracow-Silesian Zn—Pb ore deposits was described earlier by Ważewska-Riesenkampf (1959), Żabiński (1959), Gruszczyk and Ważewska-Riesenkampf (1960), Zawiślak (1971) and Jasieńska and Żabiński (1972).

Electron microscope investigations were performed with a JEM 100B electron microscope at 100 kV. Standard specimen was gold on a separately prepared carbon film, applied to one side of the main specimen. The measurement accuracy of sharp spots in diffraction patterns is 0.75—1 relative % in these conditions (Hirsh et al., 1965). Particles for investigations were taken under microscopic control from areas previously analysed with electron probe (defined even to $10 \times 10 \mu\text{m}$ if required).

Chemical compositions were determined with an ARL SEMQ probe at 20 kV, sample current $\sim 15 \text{ nA}$, using the following X-ray lines, synthetic compounds and pure standards: Mg K α , Si K α (SiO_2), S K α (FeS_2), Ca K α (CaF_2), Mn K α , Fe K α , Zn K α , Pb M α (PbS). The X-ray data were corrected for radiation absorption (Philibert 1965), fluorescence effects (Reed 1965) and atomic number difference (Philibert, Tixier 1968). The difference to 100% was assumed to be CO_2 .

RESULTS

Chemical composition.

All analysed dolomites and zinc-dolomites are characterized by the dominance of Ca over Mg or $(\text{Mg} + \text{Zn})$ (Table 1). Excess Ca is a characteristic feature of the ore-bearing dolomite in this area (Śliwiński 1966).

The composition of zinc-dolomites with a low Fe admixture seems to be defined by the $R_1 : R_2$ ratio close to 1:1, where $R_1 = \text{Ca} - \text{Zn}$ and $R_2 = \text{Mg} + \text{Zn} + (\text{Ca} - 0.5)$, when the $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$ formula is considered. This rule accords well with the domain structure of Zn-dolomite and is also supposed to apply to Tsumeb zinc-dolomite containing small Fe admixture (Hurlbut 1957, table 2, analyses 1, 2, 4).

Zinc-dolomite grains in samples C-1/2, C-4/7 and C-4/8 (taken from galmei ore) were found to be homogenous when studied with scanning method. Zn-dolomite of sample C-5/10 (taken from laminated dolomite) has a zonal structure (Phot. 1). The central parts of crystals were dolomitized by solutions with a high Mg:Zn ratio. In the final stage when the basal unit of Mg from solution was bound in dolomite, Zn was relatively strongly enriched and formed the external zone of Zn-dolomite. The latter feature (Phot. 1) indicates the possibility of formation of Zn-dolomite as a primary mineral.

Table 1

Chemical composition of zinc-dolomite obtained with the electron probe

No	weight %/atomic prop.										$R_1 : R_2$	size μm
	MgO	SiO_2	SO_3	CaO	MnO	FeO	ZnO	PbO	CO_2 calc.	Σ		
C-1/1 0.4811	19.40 0.26	≤ 0.02	30.90 0.5514	0.39 0.0055	0.72 0.0100	0.47 0.0058	≤ 0.04	45.80	98.18	1.0136	40	
C-1/2* 0.3487	14.05 0.12	0.10	30.10 0.5364	0.39 0.0055	1.26 0.0175	8.30 0.1017	0.25 0.0011	44.50	99.05	0.8930	30	
C-2/3 0.3824	15.50 0.88	0.05	30.60 0.5464	0.55 0.0100	1.26 0.0175	6.00 0.0918	0.32 0.0015	45.30	100.46	0.8732	50	
C-2/4 0.4317	17.40 ≤ 0.007	0.07	31.20 0.5556	0.04 0.0007	0.08 0.0014	3.15 0.0482	0.30 0.0014	45.20	97.50	0.9475	40	
C-4/7* 0.3734	15.05 0.11	≤ 0.02	30.20 0.5385	0.88 0.0124	0.77 0.0107	5.55 0.0682	0.52 0.0023	44.30	97.40	0.9796	30	
C-4/8* 0.3775	15.20 0.11	0.05	30.10 0.5379	0.98 0.0138	1.12 0.0156	5.00 0.0612	0.49 0.0022	44.40	97.45	1.0002	30	
C-5/9 0.4770	19.20 0.17	0.10	32.20 0.5738	0.03 0.0004	0.04 0.0005	0.19 0.0023	≤ 0.04	46.20	98.13	1.0333	12	
C-5/10 0.3865	15.60 0.17	0.05	29.90 0.5339	0.08 0.0010	0.05 0.0007	5.60 0.0684	2.12 0.0102	43.80	97.37	0.9523	2	

$R_1 : R_2 = \text{Ca} - \text{Zn} : [\text{Mg} + \text{Zn} + (\text{Ca} - 0.5)]$

* — grain studied by means of electron diffraction method

\leq limit of microprobe detection

Table 3

Interpretation of superstructure spots, resulting of the presence of $\text{CaZn}(\text{CO}_3)_2$ domains in zinc-dolomite. Phot. 2, superstructure system 11.1

Superstructure 11.1					
hkl	$d_{\text{meas.}}$ [Å]	$\text{CaMg}(\text{CO}_3)_2^*$	$\text{CaZn}(\text{CO}_3)_2^{**}$ calc.	Angles (in degrees)	
				00.3 meas.	00.3 calc.
10.10	1.50	1.4943	1.4976	21.50	21.00
10.13	1.20	1.1810	1.1835	17.00	16.50
10.16	0.984	0.97292	0.97500	13.50	13.50
10.19	0.838	0.82589	0.82764	11.75	11.40
10.22	0.727	0.71686	0.71838	10.00	9.90
10.23		0.71727			

Superstructure 31.1				
31.5	1.11	1.0894	70.50	70.20
31.8	1.01	1.0029	61.00	60.50
31.11	0.920	0.90700	52.00	51.60
31.14	0.822	0.81461	45.00	44.70
31.17	0.737	0.73161	40.00	39.20

* after Graff (1961),

** after Rosenberg, Foit (1979).

Electron diffraction study.

Superstructure spots in zinc-dolomite electron diffraction patterns were found in $\bar{1}\bar{2}0$ orientation only. The basal pattern is that of dolomite $\text{CaMg}(\text{CO}_3)_2$ related to C-4/7 (Table 1) composition and is denoted by Miller indices hkl (Phot. 2). Rows of spots at fractional distances between dolomite lattice are connected with superstructures caused by the incorporation of Zn in the dolomite structure (hkl), the excess of Ca [hkl] and some Fe and Mn [hkl] (Phot. 2, table 2, grain C-4/7). This type of superstructure pattern seems to be specific to rhombohedral carbonates, as it was not reported in earlier studies of other kinds of solid species (Hirsh et al. 1965, Andrews et al. 1967).

One immediately sees that the series of reciprocal lattice points (hkl) and [hkl] divide the distances between dolomite matrix points into thirds (Phot. 2).

In general, such electron diffraction patterns could occur due to (Hirsh et al. 1965):

1. Twinned structure.

The twin plane (in this case 001) would coincide with the plane: dolomite — $\text{CaZn}(\text{CO}_3)_2$ domain boundary, creating additional twin points that divide the distances between matrix points into thirds. The small $\text{CaZn}(\text{CO}_3)_2$ domain size would limit the extent of twin rows to observed values (Phot. 2, (hkl) and [hkl]). However the superstructure pattern in Fe-dolomite and ankerite (being investigated at present), qualitatively similar to that of Zn-dolomite but quantitatively different, makes the twinned structure concept less probable as the complete solution.

2. Particles of a second phase.

If the domain structure of Zn-dolomite is considered, one immediately sees that the $\text{CaZn}(\text{CO}_3)_2$ and CaCO_3 domains would be typical, partially coherent

Table 2

Interpretation of superstructure spots, resulting of the presence of $\text{CaZn}(\text{CO}_3)_2$ domains in zinc-dolomite. Phot. 2, superstructure system (10.1) and (31.1)

Superstructure 10.1					
hkl	$d_{\text{meas.}}$ [Å]	$\text{CaMg}(\text{CO}_3)_2^*$	$\text{CaZn}(\text{CO}_3)_2^{**}$ calc.	Angles (in degrees)	
				00.3 meas.	00.3 calc.
10.10	1.50	1.4943	1.4976	21.50	21.00
10.13	1.20	1.1810	1.1835	17.00	16.50
10.16	0.984	0.97292	0.97500	13.50	13.50
10.19	0.838	0.82589	0.82764	11.75	11.40
10.22	0.727	0.71686	0.71838	10.00	9.90
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31.17	0.737	0.73161	40.00	39.20

between angles and d spacings is not attained for any of the considered rhombohedral carbonates. This difference in l addition may be accounted for by the significantly larger CaCO_3 unit-cell (Table 4).

DISCUSSION

The postulated domain structure of Zn-dolomite explains several difficulties connected with the classical concept of solid solution in rhombohedral carbonates. The Zn-dolomite is apparently unstable (Goldsmith, Northrup 1965). However, the extensive substitution of Zn for Mg was reported in natural dolomite (even $\text{Mg:Zn} = 1:1$, Jasieńska, Żabiński 1972).

These two facts would account for the domain structure concept in Zn-dolomite. $\text{CaZn}(\text{CO}_3)_2$ still remains unstable but its domains are stabilized by the external dolomite lattice. A positive misfit of the $\text{CaZn}(\text{CO}_3)_2$ domain to the host dolomite lattice (Table 4) limits the size of the $\text{CaZn}(\text{CO}_3)_2$ domains. The threshold is 100 Å, which equals $21 a_0$ and produces ~ 0.3 Å of total misfit. This is probably sufficient to destroy the dolomite- $\text{CaZn}(\text{CO}_3)_2$ domain boundary and to cause simultaneously the splitting of unstable $\text{CaZn}(\text{CO}_3)_2$ into two independent phases: CaCO_3 and $\text{ZnCO}_3 \cdot \text{CaZn}(\text{CO}_3)_2$. Domains are usually less than 100 Å, being therefore too small to be observed by means of X-ray methods.

The concept of three-component periodic antiphase domains defines the upper limit of Zn in dolomite as 0.1667 atomic Zn (for $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$ formula). Jasieńska, Żabiński (1972) found values as high as 0.25. However they did not report complete analytical data, which precludes a discussion in terms of the domain concept. In their case, the two-component periodic antiphase (without CaCO_3) is possible.

To summarize, it seems feasible, that most binary rhombohedral carbonates possess domain structures, i.e. they cannot be considered as classical solid solutions. The size of domains seems to be controlled by the value of the misfit of the domain lattice to the host lattice, and by the value of octahedral distortion, i.e. the less the misfit and octahedral distortion, the larger the domain size. When the misfit and distortion are insignificant the classical continuous solid solution series is obtained. These rules are more important when metastable or unstable carbonates enter into the dolomite structure.

REMARKS ON DOLOMITE FORMATION

Dolomite with $\text{Ca:Mg} > 1$ possesses probably also a domain structure consisting of CaCO_3 domains in dolomite matrix with the ideal $\text{Ca:Mg} = 1$. This seems to be fairly well justified because dolomite $\text{CaMg}(\text{CO}_3)_2$ is the most ideal and stable carbonate structure (Althoff 1977).

If the domain concept is applied to dolomitization, some difficulties in understanding the process (Althoff 1977) will be smoothed away. Dolomitization starts with Mg-calcite as the initial product (op.cit.). It is the most distorted carbonate of those investigated and is metastable (op.cit.). So pressure is an essential contributor to the transformation of metastable Mg-calcite into the most ideal dolomite structure (op.cit.).

In the domain concept of dolomitization in the growth of domains there exists probably a critical size threshold above which the domains change the distorted

Mg-calcite structure into an ideal dolomite and initiate the growth of dolomite crystals. The external rim on a growing dolomite crystal has probably higher distortion than the central part of the crystal. This facilitates the incorporation of Zn in the dolomite structure at the final stage of crystal growth, also because of the high distortion predicted for $\text{CaZn}(\text{CO}_3)_2$. During maturation (temperature, pressure) also the external zones of dolomite crystals solidify, assuming a domain structure. This would explain the presence of Zn-dolomite as a primary mineral in the course of dolomitization (Phot. 1).

The growth of domains is also possible in all discontinuities in the calcite lattice acting as the initial centres, if Mg is supplied.

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WSTĘPNE DANE O WYSTĘPOWANIU NADSTRUKTURY
W DOLOMICIE CYNKOWYM

Streszczenie

W pracy przedstawiono wyniki interpretacji dyfrakcji elektronów uzyskanych dla próbek, które na podstawie wcześniejszych dokładnych analiz uznano za dolomit cynkowe. Materiał do dyfrakcji pobrano pod kontrolą mikroskopu z obszaru, w którym skład chemiczny określono za pomocą mikroanalizatora rentgenowskiego.

Dyfrakcja elektronowa wskazuje na obecność w badanym dolomicie cynkowym uporządkowanej, domenowej, struktury antyfazowej. Komórka elementarna dolomitu cynkowego z okresową strukturą antyfazową składa się prawdopodobnie z trzech części: $\text{CaMg}(\text{CO}_3)_2$ — jako podstawowej sieci goszczącej, $\text{CaZn}(\text{CO}_3)_2$ i CaCO_3 . Zgodnie z tą koncepcją Zn^{2+} i nadmiar Ca^{2+} wydają się być wprowadzone do sieci goszczącej dolomitu $\text{CaMg}(\text{CO}_3)_2$ w formie domen $\text{CaZn}(\text{CO}_3)_2$ i CaCO_3 jednolicie rozmieszczenych, a nie wprost na miejsca Mg^{2+} , z regularną okresowością kontrolowaną przez średnią zawartość Zn^{2+} w dolomicie, jak to się przyjmuje dla klasycznego roztworu stałego. Proponowana struktura domenowa dobrze zgadza się ze składem chemicznym dolomitów cynkowych określonym przez stosunek $R_1 : R_2$ (tabela 1).

Niedopuszczanie sieci domenowej $\text{CaZn}(\text{CO}_3)_2$ w stosunku do sieci goszczącej dolomitu oraz dystorsja oktaedryczna ograniczają wielkość domen $\text{CaZn}(\text{CO}_3)_2$ do 100 Å, a zatem są one za małe, aby je obserwować metodami rentgenowskimi lub za pomocą mikrosondy elektronowej. Dane z dyfrakcji elektronowej nie są niezgodne z dotychczasowymi wiadomościami o budowie podwójnych węglanów romboedrycznych, prezentują jedynie ich nową interpretację. Inne podwójne węglany romboedryczne mają prawdopodobnie także strukturę domenową, o czym świadczą wyniki dyfrakcji elektronowych uzyskanych na dolomitach ankerytowych i ankerytach.

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Zdjęcie w mikroobszarze pierwotnego dolomitu cynkowego tworzącego zewnętrzne obwódki na kryształach dolomitu. Próbka C-5, Kopalnia Trzebionka
a — obraz elektrynowy absorpcyjny, b — obraz rozmieszczenia Zn K_{α} , c — obraz rozmieszczenia Mg K_{α}

Fot. 2. Dyfrakcja elektronowa dolomitu cynkowego zawierającego 5,55% wag. ZnO w mikroobszarze (tabela 1, C-4/8). $uvv = \bar{1}\bar{2}\bar{0}$. Obserwowana nadstruktura jest wynikiem okresowej struktury antyfazowej

hkl — sieć podstawowa dolomitu, (hkl) — efekt od domen $\text{CaZn}(\text{CO}_3)_2$, $[hkl]$ — efekt od domen CaCO_3 , $\{hkl\}$ — niewyraźny efekt prawdopodobnie od domen $\text{CaFe}(\text{CO}_3)_2$

ПРЕДВАРИТЕЛЬНЫЕ ДАННЫЕ О ПРИСУТСТВИИ
СУПЕРСТРУКТУРЫ В ЦИНКОВОМ ДОЛОМИТЕ

Резюме

В работе представлены результаты интерпретации дифракции электронов, полученных для образцов, которые на основании более ранних детальных анализов считались цинковыми доломитами. Отбор материала для дифракции контролировался под микроскопом в микроучастке, в котором химический состав был определен с помощью микрозонда.

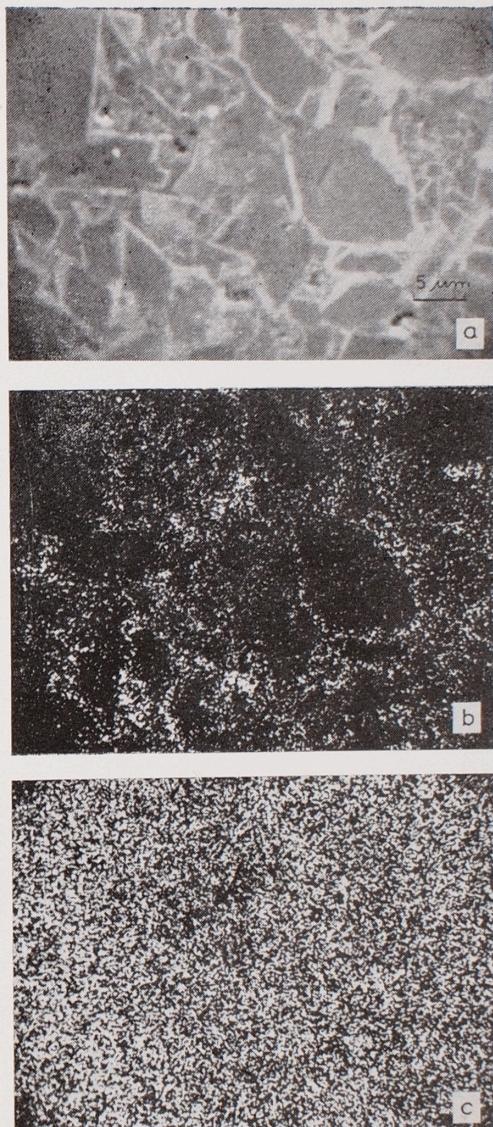
Дифракция электронов указывает на присутствие в изучаемом цинковом доломите упорядоченной доменной антифазовой структуры. Элементарная ячейка цинкового доломита с периодической антифазовой структурой, по-видимому, состоит из трех частей: $\text{CaMg}(\text{CO}_3)_2$ — как основной решетка-хозяина, $\text{CaZn}(\text{CO}_3)_2$ и CaCO_3 . Согласно этой концепции Zn^{2+} и излишек Ca^{2+} кажется введены в решетку-хозяина доломита $\text{CaMg}(\text{CO}_3)_2$ в виде доменов $\text{CaZn}(\text{CO}_3)_2$ и CaCO_3 однородно размещенных, а не прямо в места Mg^{2+} , с регулярной периодичностью, контролированной средним содержанием Zn^{2+} в доломите, как это принималось для классического твердого раствора. Предлагаемая доменная структура хорошо согласуется химическим составом цинковых доломитов, определенным через соотношение $R_1 : R_2$ (таблица 1).

Неприспособление доменной решетки $\text{CaZn}(\text{CO}_3)_2$ по отношению к решетке-хозяина доломита, а также октаэдрическая дисторсия, ограничивают размеры доменов $\text{CaZn}(\text{CO}_3)_2$ до 100 Å, следовательно они слишком небольшие, чтобы их наблюдать рентгеновскими методами, или с помощью микрозонда. Данные из дифракции электронов не противоречат прежним сведениям о строении двойных ромбоэдрических карбонатов, только представляют их новое истолкование. Другие двойные ромбоэдрические карбонаты, по-видимому, тоже имеют доменную структуру, о чем свидетельствуют результаты дифракции электронов, полученные на анкеритовых доломитах и анкеритах.

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

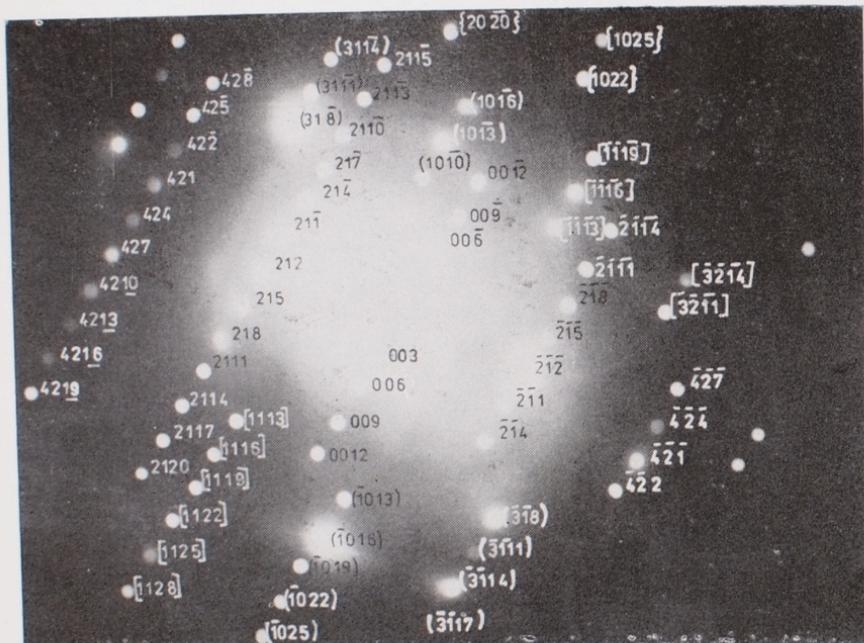
Фото. 1. Изображение в микроучастке первичного цинкового доломита, образующего каемки на кристаллах доломита. Образец C-5, рудник Тшебионка
a — абсорбционное электронное изображение, b — картина размещения Zn K_{α} , c — картина размещения Mg K_{α}

Фото. 2. Дифракция электронов цинкового доломита, содержащего 5,55 вес. % ZnO в микроучастке (таблица 1, C-4/8). $uvv = \bar{1}\bar{2}\bar{0}$. Наблюдаемая суперструктура является следствием периодической антифазовой структуры
 hkl — основная решетка доломита, (hkl) — эффект от доменов $\text{CaZn}(\text{CO}_3)_2$, $[hkl]$ — эффект от доменов CaCO_3 , $\{hkl\}$ — нечеткий эффект, вероятно, от доменов $\text{CaFe}(\text{CO}_3)_2$



Phot. 1. Microphotograph of so called primary Zn-dolomite forming rims on the dolomite crystals
Sample C-5, Trzebionka Mine.

a — EAI — electron absorption image, b — scanning picture of Zn K_{α} , c — scanning picture of Mg K_{α} .



Phot. 2. Electron diffraction pattern of Zn-dolomite containing 5.55 wt.% ZnO in microarea (Table 1, C-4/8). $uvw = \bar{1}\bar{2}0$. Observed superstructures are expected to result from periodic antiphase structure

hkl — basal dolomite lattice, (hkl) — effect of CaZn(CO₃)₂ domains, $[hkl]$ — effect of CaCO₃ domains, $\{hkl\}$ — effect unclear, may be CaFe(CO₃)₂ domain?

Henryk KUCHA, Bogusław BĄK, Andrzej WIECZOREK — Preliminary report on superstructures in zinc-dolomite