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An empirical formula for the calculation of lattice parameters of the huntite-borate crystals

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Huntite-borate결정의 격자상수 산출을 위한 계산식의 도출

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Abstract An empirical relationship which can be calculated to the lattice constants a_0 and c_0 for the borate crystals with huntite structure were determined. Different compositions of twenty-eight were used for the calculations. These empirical formulas can be used to predict lattice parameters of unknown compositions as a function of the average ionic radii in the trigonal and octahedral sites of the huntite structure.

요 약 Huntite구조를 갖는 borate결정의 격자상수 (a_0 및 c_0) 산출을 위해 특정관계를 갖는 계산식을 도출하였다. 이를 위해 서로 다른 28종류의 조성을 갖고 있는 결정을 사용하였다. 이와 같은 계산식은 huntite구조내에 위치하는 이온의 평균 반경을 함수로 하여 미지의 조성을 갖고 있는 결정으로부터 격자상수를 예상하는데 사용될 수 있다.

Single crystal rare-earth aluminum and gallium huntite-borates are important nonlinear optical material for frequency conversation and laser applications [1-3].

Structure of these materials is similar to natural huntite mineral $CaMg_3(CO_3)_4$. The crystallographic and optical properties of these materials are markedly dependent on their compositions. Thus, the values of lattice constants can be used as an indication and/or as a reference of many other physical parameters.

The huntite structure consists of three kinds of cation sites : trigonal prisms (p), octahedras (o) and oxygen triangles (t). The change of each site promotes the alteration of the lattice constants. There are some reports devoting to the investigation of this effect [4,5]. However, there is no literature about the estimation of the exact mathematical dependence between the size of cations in the all sites of huntite structure and the values of the lattice constants. It can be predicted the physical parameters of the huntite-borate crystals to know the dependence proceeding from the type of cations in the structure. Also, it is possible to determine the kind of ion distribution among sites and their distribution coefficients using the difference between the measured and the calculated value of the lattice constants. In this paper the search of such dependence using two grown crystals of huntite-borate will be studied.

The p-site of huntite-borate crystals can be occupied by all rare-earth ions and Bi^{3+}, Y^{3+}, Sc^{3+}, In^{3+}, La^{3+} ions. Al^{3+}, Ga^{3+}, Fe^{3+} and Cr^{3+} ions can occupy the o-site, and B^{3+} ion can occupy t-site. Moreover, one type of site can be occupied by the different ions simultaneously. Al- and Fe- series of huntite-borate crystals were selected for the calculations, and also two mixed compositions with Al^{3+} and Ga^{3+} ions in the o-site were used for the calculations [5-8]. These crystals were grown by the flux method using Bi_2O_3-B_2O_3 flux and has been described in Ref. [9] in detail. These two compositions fill in the "free space" of the lattice constant values between Al^{3+} and Fe^{3+} series.

However, the data of lattice constants in Ref. [5-8] have not sufficient accuracy of measurements for the Ga^{3+} series of huntite-borate crystals [10]. Therefore, the Ga^{3+} series were not taken into consideration. Different compositions of twenty-eight were selected for the calculations.

The effective ionic radii R_6 calculated by R.D. Shannon [11] for the coordination number n=6 were used, because either p-site or o-site is surrounded by six oxygen anions. The average cation radii of p- and o-sites were in the range of 0.880 Å-1.032 Å and 0.535 Å-0.645 Å, respectively. Table 1 shows the chemical formula, cation radii and lattice constants of all compositions used for the calculations.

The dependence is considered as following :

$$a_0 = k_1 r_p + k_2 r_o + k_3 r_p r_o + k_4 \quad (1)$$

$$c_0 = k_5 r_p + k_6 r_o + k_7 r_p r_o + k_8 \quad (2)$$

where the average ionic radii of p- and

o-sites (rp and ro, respectively) and the unknown coefficients (k_1... k_8) were selected for the calculations. This kind of equation indicates the possibility of size modification in both p- and o- crystallographic sites for huntite-borate structure as a result of alteration of the another one. This effect (site-size effect) takes place in some crystal structures, for example such as garnet crystals [12]. The $k_3r_pr_o$ and $k_7r_pr_o$ terms in equations (1) and (2) represents this kind of influence.

The determination of k_1 ... k_4 and k_4 ... k_8 coefficients was carried out by the least square method for the multiple regression analysis. The best results of analysis has been achieved by the following values of coefficients : $k_1 = 0.1790$, $k_2 = 1.4400$, $k_3 = 0.6816$, $k_4 = 8.0322$, $k_5 = 1.9598$, $k_6 = 4.6779$, $k_7 = -2.0196$, $k_8 = 3.9336$. The calculated values using equations (1) and (2), the measured values of the lattice constants, and the deviation compared to these values for all compositions of Table 1 are shown in Table 2.

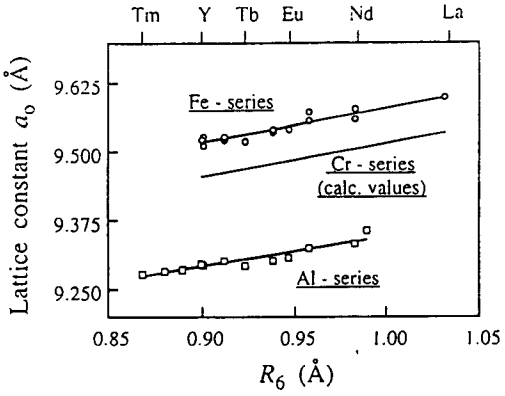

Fig. 1. Lattice constants a_0 vs. radii R_6 of cations occupied trigonal prisms (solid lines - calculated dependencies).

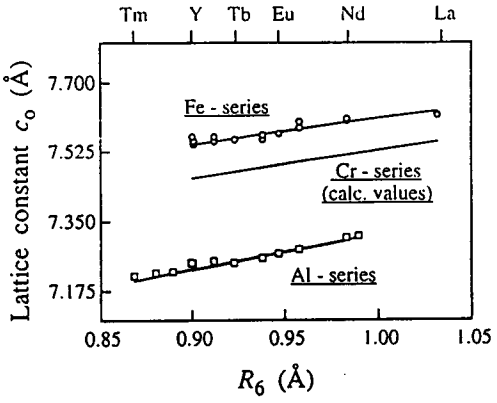

Fig. 2. Lattice constants c_0 vs. radii R_6 of cations occupied trigonal prisms (solid lines - calculated dependencies).

Figures 1 and 2 show the plots of calculated lattice constants obtained by using the empirical equations (1), (2) and the coefficients of k_1 ... k_8. All compositions used for the calculations are presented as the points. Also, the solid line representing the calculations of lattice constants for the Cr-series of huntite-borate is shown in Figs. 1 and 2, respectively, as an example of practical application of the determined dependences.

The lattice constants of $GaCr_3(BO_3)_4$ compositions, which have not used in our calculations due to the low accuracy of determination, are $a_0 = 9.49$ Å and $c_0 = 7.54$ Å [7]. In references there is no more exact information about the lattice constants of the Cr-series. However, it can be seen that the results of Figs. 1 and 2 are in good agreement with the calculated dependences.

Commonly, the limited amount of experi-

mental data can decrease the accuracy of the regression analysis. Seems to be advisable to carry out the additional experiments for using next results for the specification of the obtained coefficients k_1 ... k_8. It is necessary to note that some

Table 1

Chemical formulas, average cation radii R_6 for the positions of trigonal prisms (p) and octahedras (o), and the measured lattice constants a_0, c_0 for the compositions used for the calculations

No.	Formula	R_6(p)(Å)	R_6(o)(Å)	a_0(Å)	c_0(Å)	Ref.
1	$LaFe_3(BO_3)_4$	1.032	0.645	9.599	7.617	5
2	$NdFe_3(BO_3)_4$	0.983	0.645	9.56	7.602	5
3	$SmFe_3(BO_3)_4$	0.958	0.645	9.572	7.586	5
4	$EuFe_3(BO_3)_4$	0.947	0.645	9.54	7.568	5
5	$GdFe_3(BO_3)_4$	0.938	0.645	9.535	7.553	5
6	$TbFe_3(BO_3)_4$	0.923	0.645	9.52	7.555	5
7	$DyFe_3(BO_3)_4$	0.912	0.645	9.522	7.55	5
8	$HoFe_3(BO_3)_4$	0.901	0.645	9.51	7.542	5
9	$NdFe_3(BO_3)_4$	0.983	0.645	9.578	7.608	6
10	$SmFe_3(BO_3)_4$	0.958	0.645	9.556	7.6	6
11	$GdFe_3(BO_3)_4$	0.938	0.645	9.541	7.567	6
12	$DyFe_3(BO_3)_4$	0.912	0.645	9.528	7.56	6
13	$HoFe_3(BO_3)_4$	0.901	0.645	9.528	7.55	6
14	$YFe_3(BO_3)_4$	0.9	0.645	9.521	7.56	6
15	$YAl_3(BO_3)_4$	0.9	0.535	9.293	7.245	7
16	$NdAl_3(BO_3)_4$	0.983	0.535	9.334	7.308	7
17	$EuAl_3(BO_3)_4$	0.947	0.535	9.307	7.266	7
18	$GdAl_3(BO_3)_4$	0.938	0.535	9.302	7.257	7
19	$TbAl_3(BO_3)_4$	0.923	0.535	9.293	7.247	7
20	$SmAl_3(BO_3)_4$	0.958	0.535	9.325	7.279	8
21	$DyAl_3(BO_3)_4$	0.912	0.535	9.3	7.249	8
22	$HoAl_3(BO_3)_4$	0.901	0.535	9.293	7.24	8
23	$YbAl_3(BO_3)_4$	0.868	0.535	9.278	7.213	8
24	$PrAl_3(BO_3)_4$	0.99	0.535	9.357	7.312	8
25	$ErAl_3(BO_3)_4$	0.89	0.535	9.285	7.222	8
26	$TmAl_3(BO_3)_4$	0.88	0.535	9.282	7.218	8
27	$Ho_{0.95}Bi_{0.05}Al_{1.68}Ga_{1.32}(BO_3)_4$	0.907	0.572	9.399	7.294	This work
28	$Er_{0.95}Bi_{0.05}Al_{1.80}Ga_{1.20}(BO_3)_4$	0.897	0.571	9.365	7.282	This work

Table 2

Comparison between measured and calculated values of lattice constants a_0 and c_0 (Å), and the deviations between measured and calculated data

No	Lattice constant a_0			Lattice constant c_0		
	meas.	calc.	error	meas.	calc.	error
1	9.599	9.600041	−1.04E−03	7.617	7.629824	−1.28E−02
2	9.56	9.569698	−9.70E−03	7.602	7.597588	4.41E−03
3	9.572	9.554217	1.78E−02	7.586	7.581141	4.86E−03
4	9.54	9.547406	−7.41E−03	7.568	7.573905	−5.90E−03
5	9.535	9.541833	−6.83E−03	7.553	7.567984	−1.50E−02
6	9.52	9.532544	−1.25E−02	7.555	7.558115	−3.12E−03
7	9.522	9.525733	−3.73E−03	7.55	7.550879	−8.79E−04
8	9.51	9.518921	−8.92E−03	7.542	7.543643	−1.64E−03
9	9.578	9.569698	8.30E−03	7.608	7.597588	1.04E−02
10	9.556	9.554217	1.78E−03	7.6	7.581141	1.89E−02
11	9.541	9.541833	−8.33E−04	7.567	7.567984	−9.84E−04
12	9.528	9.525733	2.27E−03	7.56	7.550879	9.12E−03
13	9.528	9.518921	9.08E−03	7.55	7.543643	6.36E−03
14	9.521	9.518302	2.70E−03	7.56	7.542984	1.70E−02
15	9.293	9.292424	5.76E−04	7.245	7.228247	1.68E−02
16	9.334	9.337598	−3.60E−03	7.308	7.30128	6.72E−03
17	9.307	9.318005	−1.10E−02	7.266	7.269603	−3.60E−03
18	9.302	9.313016	−1.11E−02	7.257	7.261684	−4.68E−03
19	9.293	9.304942	−1.19E−02	7.247	7.248485	−1.48E−03
20	9.325	9.323992	1.01E−03	7.279	7.279283	−2.83E−04
21	9.3	9.298955	1.05E−03	7.249	7.238806	1.02E−02
22	9.293	9.292968	3.24E−05	7.24	7.229127	1.09E−02
23	9.278	9.275007	2.99E−03	7.213	7.20009	1.29E−02
24	9.357	9.341408	1.56E−02	7.312	7.30744	4.56E−03
25	9.285	9.286981	−1.98E−03	7.222	7.219448	2.55E−03
26	9.282	9.281538	4.62E−04	7.218	7.210649	7.35E−03
27	9.399	9.372387	2.66E−02	7.294	7.33975	−4.57E−02
28	9.365	9.364641	3.59E−04	7.282	7.32883	−4.68E−02

error was added to the data obtained due to the occupation of o-positions by rare-earth cations [13]. In particular, we regard this phenomena as reason of difference between calculated and measured values of lattice parameters studied.

In summary, the influence of cations type on the lattice constants for the borate crystals with the huntite structure was investigated. The empirical formulas of the lattice parameters as functions of average ionic radii of the trigonal prismatic and the octahedral sites were determined. These formulas allow to predict the values of lattice constants proceeding from the type of ions in the crystal structure. Moreover, it is possible to use the formulas obtained for the estimation of the crystal composition using lattice parameters data measured.

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