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METHODS FOR DIOPSIDE SYNTHESIS

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ABSTRACT

Diopside $CaMgSi_2O_6$, like wollastonite $Ca_3Si_3O_9$, can find application as a new synthetic raw material in the fine ceramic industry.

Diopside synthesis is accomplished via petrurgical method using crystallization from meltings and glass; after sintering from fine grinded compositions at temperature lower than diopside melting temperature; sol-gel method on the base of colloid solutions of silicic acid and water soluble salts of calcium and magnesium and by hydrothermal method from fresh prepared calcium and magnesium hydroxides and fine grinded silica gel.

Keywords: diopside, synthesis.

INTRODUCTION

Diopside $CaMgSi_2O_6$ contains theoretically (in mass %): 18,51MgO, 25,93 CaO and 55,55 SiO_2. Its structure is axial, built out of silicic–oxygen chains Si_2O_6 along c-axis, laterally connected with magnesium (M1-places) and calcium (M2-places) atoms in octahedral coordination and each calcium atom has two more oxygen atoms on larger distances [1]. Diopside as magmagenic and contact metasomatic mineral takes part in the composition of magmatic and contact metasomatic rocks. It is a main component of the white molded stone, and diopside solid solution – of the pyroxene glassceramics [2]. At a quick cooling of meltings from1400 to 1000°C the quantity of pyroxene on the base of diopside reaches 90 – 95 % [3].

The following methods are known for wollastonite synthesis, which can be used for diopside synthesis too: synthesis after crystallization out of meltings; synthesis in solid phase reaction; synthesis at sintering; hydrothermal method [4] and sol-gel methods [5].

EXPERIMENTAL

Batches for petrurgical and sintering methods are prepared on the base of dolomite or limestone and magnetite, on the one side and quartz sand or silicit on the other side. When diopside is prepared via a sol-gel method and hydrothermal one the raw materials - silica gel $SiO_2.nH_2O$, $Na_2SiO_3.9H_2O$, $(OC_2H_5)_4Si$, carbonates, chlorides and nitrates of calcium and magnesium - have qualification **p** and **pa.**

Laboratory drier 150°C, electrical furnace M-12, silit furnace 1350-1400°C and furnace "Naber" 1700°C are used for thermal treatment of samples. Optic investigations have been done with the help of polarization microscope MIN-8 and MIN-9, while the electron

microscope studies are done on scanning electronic microscope Tesla BS 340. The thermal curves DTA, TG and DTG are registered on Derivatograph-Q, X-ray investigations – on IRIS apparatus with goniometer URD – 6 at CuK_{α} emission with Ni filter. The infrared spectra are recorded on spectrophotometer Specord 75 IR with tabletting method in the range 4000 – 400 cm^{-1}. A program complex for the rentgenograms indexing and for specifying the element cell parameters was used.

RESULTS AND DISCUSSION

Petrurgical method

Diopside synthesis via petrurgical method has been done by crystallization from meltings (crystallization from above) and by glass crystallization (crystallization from bottom). For this method fine grinded batch, containing (in mass %):38 quartz sand and 62 dolomite or 40 silicite and 60 dolomite, is exposed to melting in corundum crucible at 1450°C -1 h, aerial atmosphere. The meltings crystallize under cooling with retention at 950°C – 1h. The crystal melting structure is dendritic, and the texture – compact. Diopside quantity is ~ 100 %. Its relative density is 3,265. It is identified by the following characteristic inter surface distances (9-460): 2,98 (100) - 3,23 (80) - 2,94 (70).

Glasses obtained via quenching after straight cooling of the meltings over a steel plate in air environment, have relative density 2,846 and beam refraction 1,600 ± 0,002. Infrared spectra of diopside glass are distinguished by their two wide adsorption bands at 1290-780 cm^{-1} and 650-400 cm^{-1}, connected correspondingly with vibrations of bonds Si-O-Si and Si-O [6]. DTA – glass curve has one exoeffect at 880°C, due to diopside crystallization and one small endoeffect at 750°C, connected with incipient crystallization. In order to establish glass tendency to crystallization, they have been exposed to isothermal crystallization in the range 600 to 1200°C each 50(100)°C for 1h. At 900 - 950°C the glasses show surface crystallization, in the range 1000 - 1200°C - mass crystallization with deformation. Infrared spectra of crystallized glasses, as well as the crystallized meltings, have four intensive adsorption bands at 1063, 970, 865 and 470 cm^{-1}, which have to be considered typical for diopside.

Sintering method

The initial batch containing (in mass %): 38 quartz sand and 62 dolomite or 40 silicite and 60 dolomite is grinded in a porcelain ball mill at a ratio material: balls: water 1:3,5:1 for 10 h. The crushed material particle size is $\leq$ 2-3μm. After drying the batch is grinded, watered up to 6 % humidity and granulated by 0,5 mm sieve. When fine grinded mixtures are fired below diopside melting temperature (1391°C) at 1325-1350°C for 15-30 min a liquid phase has been formed to compensate admixtures, out of which diopside crystallizes. The crystal sizes are in the range of 5 μm.

Sol-gel method

Silicic acid colloid solutions are obtained via hydrolysis of $Na_2SiO_3.9H_2O$ and tetraethylsilicate $(OC_2H_5)_4Si$. Their hydrolysis accelerates at high water excess, at prolonged stay in the presence of hydrochloric acid as catalyst. In reaction of colloid solution with water soluble salts of calcium and magnesium (chlorides and nitrates) taken in corresponding quantities, sol turns into gel. After numerous water washings it undergoes drying at 110°C. Dried dust with crystal sizes in nanometric region after isothermal treatment at 900°C -1350 °C turns into diopside.

Hydrothermal method

For the hydrothermal method fresh prepared CaO and MgO or dolomite lime, obtained through chilling of corresponding carbonates at 1100°C - 1h, and fine pulverized silica gel $SiO_2.nH_2O$ are used. The raw materials, taken in corresponding quantities, after thorough homogeneizing in high water excess and temperature 80-90°C are constantly stirred for 24 h. After decanting and drying the mixtures undergo isothermal crystal-

Table 1. Diopside diffractograms (**1**-petrurgical method; **2** - hydrothermal method, after calcinations at 1325-1350°C – 30 min.).

1			2			Diopside JCPDS(9-460)	
d.10, nm	I / I_1, %	hkl	d.10, nm	I / I_1, %	hkl	d, Å	I / I_1, %
4,43	10	0 2 0	4,38	5	0 2 0	4,4	5
3,32	10	0 2 1	3,33	16	0 2 1	3,3	5
3,22	80	2 2 0	3,21	32	2 2 0	3,23	80
2,98	100	2 2-1	2,97	100	2 2-1	2,98	100
2,94	75	3 1 0	2,93	41	3 1 0	2,94	70
2,88	45	3 1-1	2,89	43	3 1-1	2,89	10
2,56	35	3 2 0	2,54	32	3 2 0	2,56	10
2,53	35	0 0 2	2,52	62	0 0 2	2,53	40
2,29	15	1 0 2	2,29	16	1 0 2	2,29	10
2,143	25	3 3 0	2,143	9	3 3 0	2,146	20
2,123	25	3 3-1	2,117	11	3 3-1	2,124	20
2,097	10	4 2-1	2,100	19	4 2-1	2,101	30
2,029	15	3 2-2	2,003	22	3 2-2	2,006	30
1,823	20	3 4 0	1,821	8	3 4 0	1,830	5
1,746	35	5 0-2	1,745	14	5 0-2	1,748	40
1,620	30	1 3 2	1,616	22	1 3 2	1,622	20
1,546	5	3 5 0	1,540	7	3 5 0	1,548	5

lization in 900-1350°C after each 50(100)°C for 15-30 min. DTA curve of the dried mixtures has three endo thermal effects with maximum at 116, 430, 676°C and one exoeffect at 861°C. Diopside is formed at heating of mixtures even at 900°C. This method is hydrothermal, because water suspensions of $Ca(OH)_2$, $Mg(OH)_2$ and $SiO_2.nH_2O$ are treated at normal pressure and temperature 80-90°C, and calcinations – at higher temperature (900-1350°C).

The results from the diffractometric investigations are given in Table 1. As number 1 is the diopside obtained after petrurgical method (melting at 1450°C – 1 h and crystallization at 950 °C - 1 h), and as number 2 - after hydrothermal method (hydrothermal treatment at 80-90°C and calcination at 1325-1350°C – 30 min.). With a computer program the diffractograms of the synthesized diopside are indexed and the elementary cell parameters are specified: a_o 0,9750 nm, b_o 0,8926 nm, c_o 0,5252 nm, β 105,55°, V 0,44 nm^3.

CONCLUSIONS

Diopside has been obtained following petrurgical as well as sintering methods from batches with composition (in mass %): 38 quartz sand and 62 dolomite or 40 silicite and 60 dolomite; for sol-gel method – from colloid solutions of silicic acid and water soluble salts of calcium and magnesium; and for hydrothermal method, at 80-90°C, in a large excess of water, from silica gel and from calcium and magnesium hydroxides.

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