



A new nonlinear optical silicate carbonate $K_2Ca[Si_2O_5](CO_3)$ with a hybrid structure of kalsilite and soda-like layered fragments



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ABSTRACT

Single crystals of a new silicate carbonate, $K_2Ca[Si_2O_5](CO_3)$, have been synthesized in a multi-components hydrothermal solution with a pH value close to neutral and a high concentration of a carbonate mineralizer. The new compound has an axial structure (s.g. $P6_322$) with unit cell parameters $a = 5.04789$ (15), $c = 17.8668$ (6) Å. Pseudosymmetry of the structure corresponds to s.g. $P6_3/mmc$ which is broken only by one oxygen position. The structure consists of two layered fragments: one of the type of the mineral kalsilite ($KAlSiO_4$) and the other of the high-temperature soda-like α - Na_2CO_3 , Ca substituting for Na. The electro-neutral layer $K_2[Si_2O_5]$ (denoted K) as well as the layer $Ca(CO_3)$ (denoted S) may separately correspond to individual structures. In $K_2Ca[Si_2O_5](CO_3)$ the S-K layers are connected together via Ca-O interactions between Ca atoms from the carbonate layer and apical O atoms from the silicate one, and also via K-O interlayer interactions. A hypothetical acentric structure, sp.gr. $P-62c$, is predicted on the basis of the order-disorder theory. It presents another symmetrical option for the arrangement of K-layers relative to S-layers. The K,Ca-silicate-carbonate powder produces a moderate SHG signal that is two times larger than that of the α -quartz powder standard and close to other silicates with acentric structures and low electronic polarizability.

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1. Introduction

The chemical class of silicate-carbonate is defined by the presence of major proportions of silicate and carbonate anionic groups [1]. Other mixed combinations of anionic groups are known for natural and synthetic compounds, namely aluminate-silicates [2], borate-silicates [3], borate-phosphates [3–5] and borate-carbonates [6]. The search for new representatives of more complex compositions is now widely carried out in order to produce crystals with unusual acentric structures and meaningful properties. The following Ca silicate-carbonate minerals are currently known: spurrite, $Ca_5[SiO_4]_2(CO_3)$ [1], tilleyite, $Ca_5[Si_2O_7](CO_3)_2$ [1], scawtite, $Ca_7[Si_6O_{18}](CO_3) \cdot H_2O$ [1], deferenite $Ca_6(CO_3)_{1.58}(-Si_2O_7)_{0.21}(OH)_7Cl_{0.5}(OH)_{0.08}(H_2O)_{0.42}$ [7] and fukalite, $Ca_4Si_2O_6(-CO_3)(OH)_2$ [8]. The compounds containing different metals have been found, such as tundrite, $Na_2Ce_2TiO_2[SiO_4](CO_3)_2$ [9], iimorite, $(Y_{1.44}Er_{0.56})[SiO_4](CO_3)$ [10], bussenite, $Na_2Ba_2FeTi[Si_2O_7](CO_3)$

$(OH)_3F$ [11], biraite, $Ce_2Fe^{2+}[Si_2O_7](CO_3)$ [12], ashburtonite, $Cu_4Pb_4[SiO_3](HCO_3)_4(OH)_4Cl$ [13], kainosite, $Ca_2Y_2[SiO_3]_4(CO_3) \cdot H_2O$ [14], fencooperite, $Ba_6Fe_3[Si_8O_{23}](CO_3)_2Cl_3 \cdot H_2O$ [15], ashcroftite, $K_5Na_5Y_{12}[Si_2O_5]_{14}(CO_3)_8(OH)_2 \cdot 8H_2O$ [16], caysichite $Ca_4Y_4[Si_2O_5]_4(CO_3)_6 \cdot 7H_2O$ [17] and carletonite, $KNa_4Ca_4[Si_8O_{18}](-CO_3)_4F \cdot H_2O$ [18]. In all these examples the silicate component is represented by isolated or condensed Si-tetrahedra, up to complicated sheets [1]. Until now the existence of separate silicate and carbonate parts that are similar to the structures of individual compounds were not found in one structure.

Our systematic search for technically promising compounds obtained from hydrothermal solutions led us to discover a new K,Ca-silicate-carbonate with an acentric structure and channels occupied by K-atoms. The most interesting feature of this substance is a hybrid character of its structure with alternate layered structural moieties of silicate and carbonate, which may be characterized as individual compounds. The work includes the synthesis of crystals, examination of their nonlinear-optical properties, chemical and single crystal structure analyses, as well as discussion of possible structural modifications and structure-properties relations.

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2. Experimental

2.1. Synthesis and characterization

In our attempts to model natural processes, a new K,Ca-silicate-carbonate was crystallized in a hydrothermal solution containing carbonate, oxide and borate components in the ratio $\text{K}_2\text{CO}_3:\text{CaO}:\text{SiO}_2:\text{B}_2\text{O}_3 = 3:1:2:1$ that corresponds to 3.0 g (~0.026 mol) K_2CO_3 , 1.0 g (~0.013 mol) CaO, 2.0 g (~0.023 mol) SiO_2 , 1.0 g (~0.022 mol) B_2O_3 . All the reagents were of analytical grade. The presence of boron oxide in the system increased viscosity of the solution and retained pH value close to neutral. The ratio of solid and liquid phases was 1:5. K_2CO_3 at high concentration of 20% in the solution acted as a mineralizer. The synthesis was performed at temperature between 270 and 290 °C and pressures of 70–100 atm in standard autoclaves (volume 5–6 cm³) lined with teflon. The lowest and highest temperatures of the experiments were restricted by kinetics of hydrothermal reactions and the instrumental capabilities, respectively. The duration of the experiments (18–20 days) corresponded to the completion of the reactions. After synthesis, final cooling to room temperature was done in 24 h.

New crystals (total 40% of the yield) contain K, Ca and Si atoms (Jeol JSM-6480LV analytical scanning electronic microscope). Grown crystals were isolated by filtration of stock solution and washed with hot water. Crystals were colorless, lustrous, and usually in the form of hexagonal thin plates. Larger crystals up to ~0.6 mm in size often had defects in the centers; smaller ones were transparent and more perfect.

Experimental powder XRD pattern (powder diffractometer DRON-UM, $\lambda_{\text{Cu-K}\alpha}$, Fig. S1a) generally exhibited a small assembly of strong reflections (Fig. S1a), thus indicating both texturing and the high symmetry of the structure. No analogues of this pattern were found in the ICDD data base [19]. After crystal structure determination (see below), a theoretical powder pattern (Fig. S1b) was calculated on the base of .cif file using program STOE XPow [20]. The calculated pattern matches well with the experimental one, except for the intensities. Obviously, the influence of strong texturing led to an increasing of basal (004) and (008) reflections which prevailed over all other in the experimental pattern. So, the use of the theoretical powder pattern is severely impeded for phase determination. In identifying this compound by powder XRD methods the experimental powder pattern is preferred and should be used in the database.

2.2. Nonlinear optical properties

The second harmonic generation (SHG) measurement was carried out on the polycrystalline samples according to the Kurtz and Perry scheme [21]. A minilite-I Nd:YAG laser operating at Q-switched mode at the repetition rate of 10 Hz produced frequency doubling from $\lambda_{\omega} = 1064$ nm to the second harmonics, $\lambda_{2\omega} = 532$ nm in the sample. The green light of the second harmonics was collected with the lens and then directed to the photomultiplier tube. To detect the light only at 532 nm, a narrow band-pass interference filter was attached to the photomultiplier. The measured signal intensity ($I_{2\omega}$) from the sample was calibrated in relation to α -quartz powder standard with the grain size of 3 μm . $Q = I_{2\omega}/I_{2\omega}(\text{SiO}_2)$ presents quantitatively the SHG activity of the sample.

$\text{K}_2\text{Ca}[\text{Si}_2\text{O}_5](\text{CO}_3)$ crystals were too small to be studied by SHG techniques individually. On the other hand, the application of the standard SHG powder technique was hampered owing to the strong anisotropy of crystal morphology that does not allow to prepare polycrystalline samples with the different crystal grain orientations. Hexagonal-like plates of $\text{K}_2\text{Ca}[\text{Si}_2\text{O}_5](\text{CO}_3)$ were put on

a glass support on their large faces, thus producing a perfect texture of crystals with their c-axes along the direction of the laser beam (sample 1). This geometry makes ineffective laser beam interaction with crystals of all hexagonal point groups except for $-6m2$, where a third-order rank non-linear tensor matrix d_{ijk} includes non-zero coefficients d_{111} (or d_{222}) [21,22]. On the other hand, a similar matrix for non-polar point group 622 includes non-zero coefficients d_{123} and d_{231} , active only in the case of oblique incidence of the laser beam relative to the c-axis of the crystal. In order to obtain suitable sample nearly isometric grains with linear dimensions of 5–10 μm were prepared by grinding single crystals in a mortar filled with alcohol. Almost non-textured powder of the grains oriented at random was used as sample 2.

Intensities for the SHG signal $Q = 0.2$ and 2.2 were measured for samples 1 and 2 respectively. The signals confirm the absence of the inversion center in the crystals under investigation. A large difference in the intensities of these signals provides evidence in favor of the point group 622 determined by X-ray structure analysis (see below). A little bit larger SHG signal output from sample 2 as compared to the output from the α - SiO_2 standard indicates close values of optical nonlinearities d_{ijk} of SiO_2 (0.36 pm/V) and $\text{K}_2\text{Ca}[\text{Si}_2\text{O}_5](\text{CO}_3)$ (nearly 0.5 pm/V), which is not surprising owing to the presence of acentric silicate layers in the crystal.

2.3. Single crystal structure determination

A transparent crystal in the form of a thin half hexagonal plate with the area dimensions of 0.2×0.14 and height 0.025 mm was chosen and glued on a glass fiber for single-crystal X-ray study. The unit cell corresponded to the hexagonal system and did not have any analogues in the ICSD data base [2]. The Xcalibur S diffractometer equipped with CCD area detector and graphite-monochromated Mo K_{α} radiation was used for the experimental data collection (Table 1) with the exposure time of 5 s per frame and with the control frames measurement during the process of data collection. The absorption of K,Ca-silicate-carbonate crystal was negligible because of small $\mu_{\text{r,max}} = 0.22$. The data were integrated by CrysAlis program. A space group suggested by CrysAlis system was $P6_3/mmc$. However, the extinctions of the reflections correspond well only to G_3 axis while the extinctions corresponding

Table 1
Crystal data and structure refinement for $\text{K}_2\text{Ca}[\text{Si}_2\text{O}_5](\text{CO}_3)$.

Formula	$\text{K}_2\text{Ca}[\text{Si}_2\text{O}_5](\text{CO}_3)$
Formula weight (g/mol)	314.87
T (K)	293
Crystal system	Hexagonal
Space group, Z	$P6_322, 2$
a (Å)	5.04789(15)
b (Å)	5.04789(15)
c (Å)	17.8668(6)
V (Å ³)	394.27(2)
Crystal size (mm)	$0.20 \times 0.14 \times 0.025$
ρ_{calc} (g/cm ³)	2.649
μ (mm ⁻¹)	2.172
F(000)	312
Wavelength (Å)	0.71073
θ range(deg.)	4.56–32.57
Limiting indices	$-7 \leq h \leq 7, -7 \leq k \leq 7, -26 \leq l \leq 26$
Refl. collected/unique	7480/471 [$R_{\text{int}} = 0.0725$]
Completeness to theta (%)	95.0
data/restraints/parameters	413/0/24
GOF	0.909
R_1, wR_2^a [$I > 2\sigma(I)$]	0.0515, 0.0974
R_1, wR_2 (all data) ^a	0.0621, 0.1034
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ (e.Å ⁻³)	0.152 and -0.67

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

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