

HYDROTHERMAL SYNTHESIS AND OPTICAL PROPERTIES OF CALCITE SINGLE CRYSTALS

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Calcite crystals, CaCO_3 , have been grown under hydrothermal conditions in the CaCO_3 - NH_4Br - LiCl - H_2O system doped with the In^{3+} impurity. As a result, this growth conditions allowed to grow the optical grade of this materials with variable indium impurity from 0.03 to 0.5 at %. Optical and luminescent characteristics of the crystals grown have also been studied. Analysis of reflectivity measurements at different crystal orientations revealed that the onset of strong absorption ($\geq 10^5 \text{ cm}^{-1}$) in CaCO_3 falls into the region $\sim 7\text{--}8 \text{ eV}$.

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1. Introduction

Optical calcite is one of the most important materials having high birefringence and transmission over a wide spectral range. The industrial growth technology of calcite crystals on seed plates parallel to the $\{10\text{-}11\}$ faces (split rhombohedron) has been developed in Russia for the first time in the world [1]. Serial production of polished rhombohedral cleavages up to $80 \times 80 \times 16 \text{ mm}$ became possible using steel autoclaves of a few cubic meters and vessel inserts made of a special titanium alloy. However, crystals grown on the $\{10\text{-}11\}$ oriented seeds are less useful for making polarizers because of the amount of waste that results and which increases the price of the products. The optical inhomogeneity like V-shaped defects can often occur in growth pyramids of the split rhombohedron [2]. From this point of view, the crystal growth on pinacoidal seeds provides the most economic route for machining optical calcite single crystals.

It is also found that a certain inhomogeneity of calcite crystals is caused by an intense spontaneous nucleation on $\{10\text{-}11\}$ and $\{0001\}$ faces as well as on the walls of liners [3]. Then, an addition of Li ions to starting CaCO_3 - NH_4Br - H_2O system allowed to restrict this spontaneous nucleation and to obtain calcite with strongly developed $\{10\text{-}11\}$ and $\{0001\}$ simple forms [4]. In this paper, taking into consideration the above results, a further attempt was made to improve the quality of calcite crystals using the NH_4Br - LiCl based mineralizer with the In^{3+} impurity. The optical and luminescent characteristics of the crystals grown by this method have also been studied.

2. Experimental

Steel autoclaves lined with floating type of 2-liter titanium inserts were used for the growth of calcite crystals. Hydrothermal experiments were based on the ammonium bromide solvent doped with lithium chloride and metallic indium or In_2O_3 . The starting crystalline material was prepared of

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natural CaCO_3 single crystals. This mixture was loaded in a lower part of the lining vessel (dissolution zone). Plate-like seeds of natural calcite oriented parallel to $\{10\text{-}11\}$ and $\{0001\}$ were fixed in an upper section of the liner (crystallization zone). Saturated solutions were transferred from the lower, and most heated, zone into the higher one (more cold) owing to the thermal convection. As a result of supersaturating solution in the upper section of autoclave, an excess of dissolved CaCO_3 deposited on the seeds. Experimental conditions were as follows: temperatures of 250-300 °C, $\Delta T = 5\text{-}10$ °C, pressures 50-100 Mpa, and duration of 30-85 days.

Chemical and spectral analyses of the grown crystals has been made. Optical spectra of indium doped calcite samples were measured by spectrophotometers «Specord-M40» and «SDL-1». Optical and luminescence properties of these crystals have been studied in a wide energy range 4 to 35 eV at temperatures 7 to 300 K using synchrotron radiation at the SUPERLUMI station (HASYLAB, DESY) [5].

3. Results and discussion

No spontaneous nucleation has been found in experiments with In^{3+} dopant. Normal growth rates of the faces $\{0001\}$, $\{10\text{-}11\}$ and $\{02\text{-}21\}$ were substantially reduced in comparison with the $\text{CaCO}_3\text{-NH}_4\text{Br-H}_2\text{O}$ system. Fig. 1 shows a calcite crystal grown on pinacoidal seed. No visible defects are in these crystals, but the grown up material has isometric cracks. Also, crystals grown on the seeds parallel to $\{10\text{-}11\}$ have irradiating cracks indicating In^{3+} impurity in crystal structure.

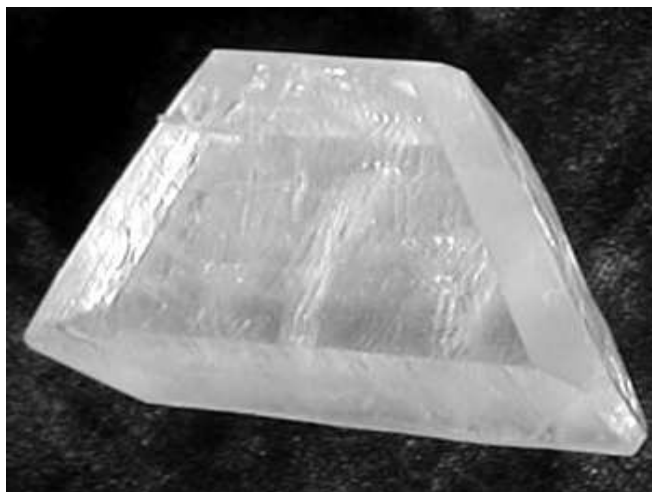


Fig. 1. 7 mm-thick calcite crystal grown in the $\text{CaCO}_3\text{-NH}_4\text{Br-LiCl-H}_2\text{O}$ system doped with In^{3+} .

As the results of chemical and spectral analyses, grown crystals have indium concentration from 0.03 to 0.5 %, in addition to the usual (and uncontrolled) impurities of Mn, Mg, Al and Fe (Table 1). It can be concluded that metallic indium and/or indium oxide differently effect on the growth kinetics. Presence of In_2O_3 reduces normal growth rates of the $\{0001\}$ face to 0.03 mm/day maximum. The faces $\{0001\}$ and $\{10\text{-}11\}$ are not twinned in these crystals and In content in the grown up layer varies from 0.1 to 0.5 %. The metallic indium effect was found rather different. The growth rate of pinacoidal crystals increases to over 0.1 mm/day, and it makes the faces less perfect. The indium concentration in crystals grown is found to be in one order lower, 0.03–0.08 %.

Table 1. The contents of impurities in grown calcite crystals.

In ³⁺ concentration in the starting mixture, mol %	(0001)/(1011) growth rate, mm/day	Impurity concentration in crystals, at %				
		In [✓]	Mn	Mg	Al [✓]	Fe
_____	0.120 / 0.125	_____	0.0460	0.0025	0.0060	0.0047
0.002*	0.039 / 0.005	0.50	0.0425	0.0054	0.0060	0.0200
_____	_____	_____	0.0415	0.0020	0.0006	0.0038
0.001	0.065 / 0.108	0.03	0.0355	0.0046	0.0006	0.0096
0.001	0.092 / 0.119	0.03	0.0470	0.0014	0.0006	0.0033
0.001*	_____	0.10	0.0320	0.0010	0.0005	0.0038
0.0015	0.080 / 0.096	0.08	0.0200	0.0011	0.0005	0.0030
_____	0.026 / 0.007	_____	_____	_____	_____	_____
_____	0.023 / 0.009	_____	_____	_____	_____	_____

*In₂O₃ used as a dopant, but metallic In was added in other experiments

✓Spectral semi-quantitative analysis

Transmission spectra of the samples prepared of In³⁺ doped material show a shift of the transmission edge towards the long wave side (from 200 to 240 nm) (Fig. 2). Fig. 3 shows reflectivity spectra of polarized synchrotron radiation from the CaCO₃ crystals with two different orientations of the c axis relative to the *E* vector of the incident radiation are shown. The angle of incidence is 17.5°. Features below 7 eV are due to the reflection from the rear surface of the crystal (this energy range corresponds to low values of the absorption coefficient and incident radiation can penetrate through the crystal). Comparison with luminescence excitation spectra of CaCO₃ pure and doped with In confirms that this range is below the threshold of fundamental absorption. Reflectivity curves in cases of c||*E* and c⊥*E* are substantially different, which was expected from the high anisotropy of the crystal. The differences are observed not only at the fundamental absorption edge but also up to 15 eV.

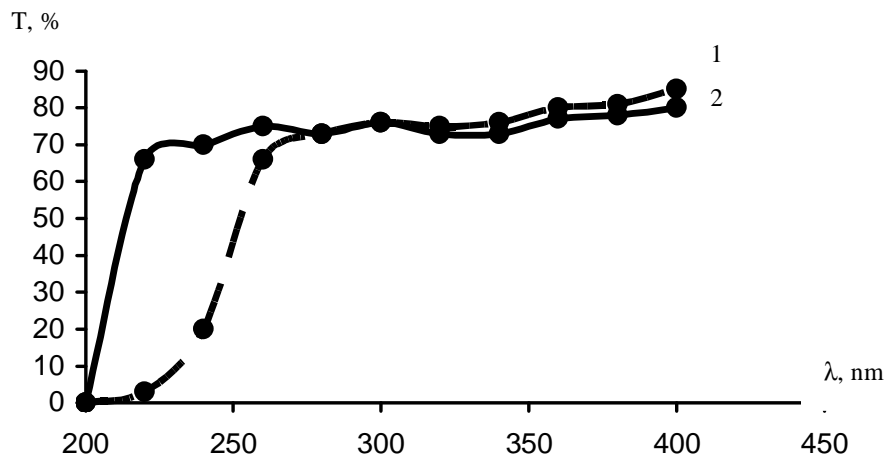


Fig. 2. Light transmission spectra of calcite grown with In^{3+} dopant (1) and without In^{3+} (2).

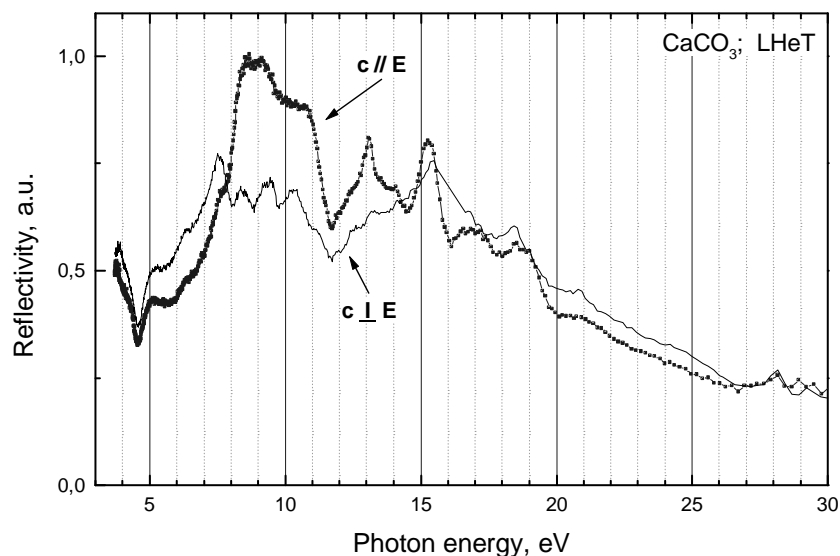


Fig. 3. Reflectivity spectra of polarized synchrotron radiation from the CaCO_3 crystals.

Excitation in the fundamental absorption range in pure CaCO_3 at LHeT results in a weak luminescence presented by a wide band peaking at ~ 400 nm. This luminescence is fast with characteristic decay time of the order of a few nanoseconds. At room temperature luminescence intensity at excitation with $h\nu > 7$ eV is at the PMT noise level. In addition to this most probably intrinsic emission, at ~ 5 eV excitation a luminescence band peaking at ~ 330 nm is observed. Similar (330 nm) bands were observed in CaCO_3 - In crystals. The origin of this luminescence is not clear at this stage. In the case of pure CaCO_3 , it is excited only in one narrow band in the matrix transparency region at ~ 5 eV. In In doped CaCO_3 crystal, the short wavelength band is comprised of two overlapping bands: fast and a slow ones are at ~ 360 nm and at ~ 330 nm with different excitation spectra respectively. Decay kinetics at 380 nm has a nice single exponential profile with characteristic decay time ~ 20 ns (Fig. 4).

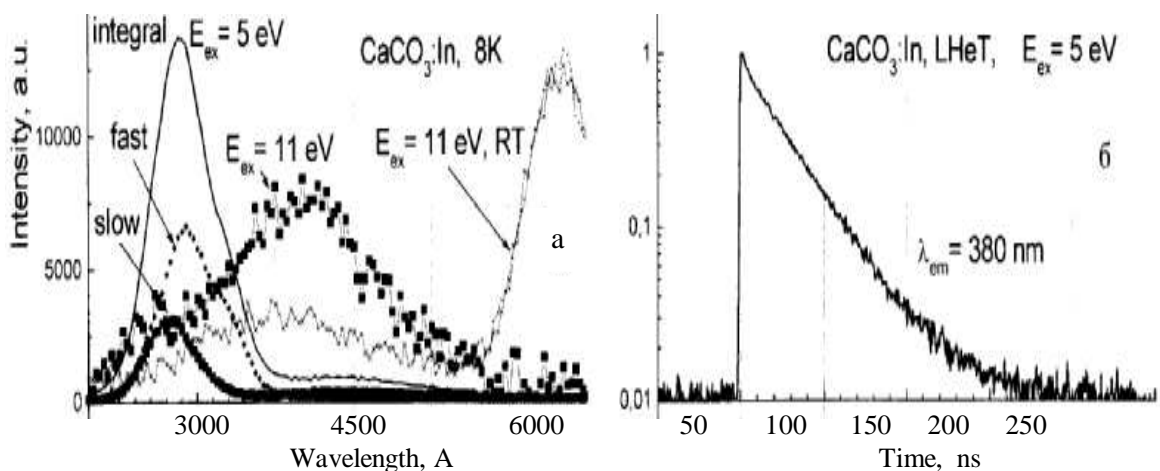


Fig. 4. Luminescence spectra and decay kinetics.

4. Conclusion

Indium impurity has a certain effect on growth mechanism of calcite crystals: the faces (0001), (10-11) and (02-21) are visibly perfect and no spontaneous crystallization is noted. Though, a certain shift of transmission band to the long wave region reduced the field use of this material in optics. Analysis of reflectivity measurements at different crystal orientations revealed that the onset of strong absorption ($\geq 10^5 \text{ cm}^{-1}$) in CaCO_3 falls into the region $\sim 7\text{--}8 \text{ eV}$. In many crystals, these can provide an estimate of the forbidden energy bandgap. These values are substantially lower than theoretical estimations presented in for absorption band gap of 8.9 and 12.0 eV [6].

References

- [1] V. L. Borodin, I. V. Nefyodova, P. P. Chvanski, X National Conference on Crystal Growth, Moscow, November 24-29, 2002, Abstracts, p. 341 (in Russian).
- [2] V. I. Lyutin, I. V. Nefyodova, *Experiment in Geosciences* **4**, N 4, 77 (1995).
- [3] I. N. Nefyodova, V. I. Lyutin, V. L. Borodin, P. P. Chvanski, N. I. Leonyuk, *J. Crystal Growth* **211**, 458 (2000).
- [4] I. N. Nefyodova, V. I. Lyutin, V. L. Borodin, P. P. Chvanski, N. I. Leonyuk, *Progr. in Cryst. Growth and Charact.* **40**, 263 (2000).
- [5] G. Zimmerer, *Nuclear and Methods in Physics Research* **A308**, 178 (1991).
- [6] G. Ghosh, *Optics Communications* **163**, 95 (1999).