Letters to the Editor

OPTICAL SCATTERING IN SYNTHETIC CaF_2 CRYSTALS

РАССЕЯНИЕ СВЕТА В СИНТЕТИЧЕСКИХ КРИСТАЛЛАХ CaF_2

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On of the main problems in the preparation of CaF_2 crystals for lasers represents the scattering of light on particles of the size of about 1 μm. Stockbarger [1] ascribed it to the presence of oxygen precipitated in the form of CaO. Already concentrations of 60 to 200 ppm added to the crystal cause the scattering of light. On the other hand, this effect does not appear upon doping by rare earths oxides until their concentration exceeds 3 mol %.

It has been confirmed that sulphur and chlorine exhibit the same effect as oxygen [2]. When added to CaF_2 in the form of CaS, $CaSO_4$, and $CaCl_2$, a detectable scattering appears already at concentrations of 20 (50) ppm. The sulphur scattering centres have the form of hexagonal plates orientated in the (111) plane. The plates have been observed also in non-doped crystals after being maintained at a constant temperature in a graphite ampoule in a vacuum. In this case the crystal was contaimnated by sulphur from graphite.

Our contribution is concerned with the scattering of light caused by CaO particles and its influence on the absorption peak at 205 nm. An almost zero light transmissivity at this wavelength is the reason why CaF_2 — made prisms cannot be used in the Uv range. In [3, 4, 5] the absorption band at 205 nm was ascribed to the $O^{2-} — \square_F$ dipole, $\square_F$ being a vacancy in the fluorine lattice motive.

The CaF_2 crystals were synthetized by the Stockbarger method in a crucible made from spectrally pure graphite. In order to prevent pyrohydrolysis, the CaF_2 raw material was dried in a vacuum at 80 °C for 48 hours and melted in products of Teflon pyrolysis. A 0.1 mol% amount of CaO was added to this material. The synthesis of CaF_2:0.1 mol% CaO crystal itself was performed in a highly pure argon atmosphere (oxygen content below 20 ppm). The cooling rate after synthesis was 20 °C/min. A strong oxygen segregation was observed on the crystal, causing CaO precipitation in its upper part. This part of the crystal had a milky colour.

From both the upper (milky) and the lower (transparent) part some samples 10 mm in diameter 1 mm thick were cut. After optical polishing a measurement by a UNICAM SP 700 C spectrometer in the wavelength range 192 to 1000 nm was performed, in a nitrogen moisture — free atmosphere under thermostable conditions. The samples were held in a special holder with a 6×6 mm^2 slit. The measurement was performed in two ranges: 0 to 110 %, and 0 to 11 % of transmission. The results are shown in Figs. 1 and 2.

In Fig. 1 the wavelength dependence of transmission is shown for a CaF_2 crystal without doping — curve 1, and for samples cut from the lower and the upper part of the CaF_2:0.1 mol% CaO crystal — curves 2 and 3, respectively. In the latter, a clear absorption in the vicinity of 205 nm is observed.

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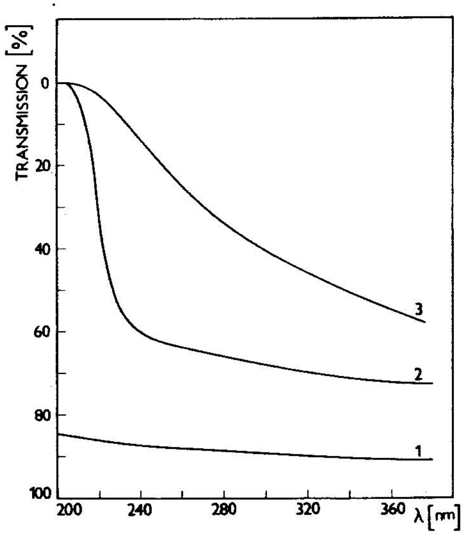

Fig. 1. Transmission spectra of CaF_2 doped by 0.1 mol % CaO in the region 200—400 nm.

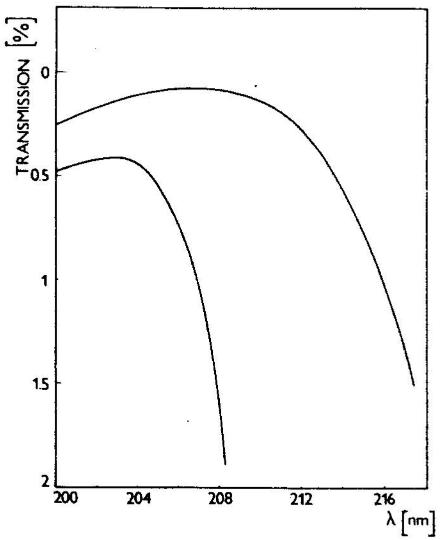

Fig. 2. The shift of the absorption maximum in vicinity 205 nm caused by the scattering.

Further, the sample with CaO precipitates shows a higher absorption. In the sample with zero oxygen content no absorption maximum within the measuring wavelength range was observed.

At temperatures where no precipitation occurs, the following quasi-chemical reaction may be considered:

$$O^{2-}_{impur.} \rightleftarrows O^{2-}_{sol.} + \square_F \rightleftarrows O^{2-} - \square_F.$$

The first reaction represents the solution of precipitated oxygen in such a way that it substitutes for the fluorine ion in the lattice, thus creating a vacancy in the location of fluorine — which compensates the excessive negative charge. The second reaction corresponds to the association of free impurity ions O^{2-}_{impur} and $\square_F$ vacancies giving $O^{2-} - \square_F$ dipoles.

The existence of absorption at 205 nm in the sample with precipitated CaO (curve 3) suggests that one part of the oxygen content is bound in $O^{2-} - \square_F$ dipoles according to the equations. The total oxygen solubility is given by the solubilities of associated and nonassociated ions.

In order to obtain a better resolution of the absorption peak, Fig. 2 presents the curves 2 and 3 measured in the range 0—11 % of transmission. It can be seen that the absorption maximum is shifted to a higher wavelength. This shift caused by the scattering on precipitates can elucidate the various values of the wavelength where absorption appears reported by various authors.

REFERENCES

[1] Stockbarger, D. C., J. opt. Soc. Am., *39* (1949), 731.
[2] Bardsley, W., Green, G. W., Brit. J. Appl. Phys., *16* (1965), xxx.
[3] Bontick, W., Physica, *22*, (1958), 650.
[4] Bontick, W., Physica 22 (1958), 639.
[5] Bruch, H., et al., phys. stat. sol., *4* (1964), 685.

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