

PRODUCTION AND STUDY OF CERIUM TRIFLUORIDE SINGLE CRYSTALS FOR IONIZING RADIATION DETECTORS

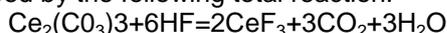
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Introduction

High quality inorganic scintillators are attracting a great attention mostly due to unprecedented demands of modern high energy physics for high quality detector materials. The main features that these materials should possess are: convenient fluorescent spectra for available commercial photodetectors, short scintillation time, high stopping power and high light yield, though the last is less urgent in applications where high energy particles should be detected. Among the traditional scintillators cerium fluoride is perhaps the material which most closely satisfies all these demands as thallium doped halides are very efficient but slow and chemically unstable, plastic scintillators are very fast but limited in stopping power, well known BGO crystal is characterized by remarkable stopping power but is still limited in speed. Cerium trifluoride is a dense (6.16 g/ccm) and rather efficient (2400 photons/MeV) scintillation material with short scintillation time (17-20 ns) which can be grown in rather large boules and what is very important - it's rather cheap.

Production of polycrystalline cerium trifluoride raw material

The proposed growing technology allows to minimize the influence of oxide impurities on the quality of grown cerium trifluoride, though it cannot help when some other trace impurities, especially containing two valent cations increasing the density of defects by offering an easy way for charge compensation are presented in the raw materials. Further progress in cerium fluoride quality should result from thorough raw materials preparation. Anhydrous gaseous hydrofluorination method of cerium trifluoride production based on treatment of cerium carbonate, hydroxide, oxalate or oxide in continuous mode apparatus at 200-550 °C was developed. The apparatus consists of a horizontal two tube screw nickel made reactor. Reaction time is varied from 2 to 6 hours the productivity of reactor defined by feed screw rotation and initial material bulk density. Hydrogen fluoride was passing the reactor opposite to solid phase. Cerium dioxide and cerium carbonate were used as raw materials. One stage process of cerium trifluoride synthesis can be described by the following total reaction:



To develop the technology, kinetics of cerium carbonate thermal decomposition resulting in cerium dioxide formation and kinetics of cerium dioxide and hydrogen fluoride reaction were

studied. In «solid-gas» reaction type solid phase should act as «active material». Reaction ability of a solid material can be quantitatively characterized by specific surface, dispersion and other parameters. Cerium carbonate used in cerium trifluoride synthesis had the following characteristics: after drying at 250 °C - density 4 g/ccm, specific surface - 26 m²/g; at 500 °C - 5.1 g/ccm, and 19 m²/g; and at 900 °C - 6.3 g/ccm and 9 m²/g respectively. The proposed anhydrous method introduces no impurities into resulting compound which is of great importance for extra pure material synthesis. Fluorination level of cerium dioxide and carbonate is up to 99.98% and final product contains no less than 99.95% of cerium trifluoride. The results on measured impurities in cerium trifluoride are collected in Table 2. According to X-ray phase analysis polycrystalline CeF₃ possesses only hexagonal structure (a=71.1 nm, c=72.7 nm) with calculated density of 6.13 g/ccm. IR spectra analysis showed that moisture content in molecular form was 0.04-0.07 mass %. At present time the continuous mode apparatus with productivity up to 50 tons/year of anhydrous polycrystalline powder of CeF₃ is developed. The cost of CeF₃ powder is estimated near 30 USD/kg. The method is protected by Russian patents. Now the process allowing to obtain 99.999% cerium trifluoride containing resulting compounds is being developed.

Table 2.

| Impurity | CeO ₂ | Ce ₂ (CO ₃) ₃ |
|---------------------------------|--------------------|---|
| Nd ₂ O ₃ | 1 10 ⁻³ | 2 10 ⁻³ |
| Pr ₆ O ₁₁ | 3 10 ⁻³ | 3 10 ⁻³ |
| Dy ₂ O ₃ | 5 10 ⁻⁴ | 5 10 ⁻⁴ |
| Er ₂ O ₃ | 5 10 ⁻⁴ | 3.10 ⁻⁴ |
| Fe | 3 10 ⁻⁴ | 1 10 ⁻³ |
| Ni | 1 10 ⁻⁴ | 2 10 ⁻³ |
| Cu | 5 10 ⁻⁵ | 1 10 ⁻⁴ |
| Co | 5 10 ⁻⁴ | 1 10 ⁻⁴ |
| Cr | 5 10 ⁻⁵ | 5 10 ⁻⁵ |
| V | 5 10 ⁻⁵ | 5 10 ⁻⁵ |
| Ti | 5 10 ⁻⁵ | 1 10 ⁻⁴ |
| Sn | 5 10 ⁻⁴ | 1 10 ⁻³ |

As the result the Cs¹³⁷ γ-source (E=0.66 MeV) response of cerium fluoride crystals was measured to be not less than 4.2% of that for NaJ(Tl) crystal. The corresponding photo peak of CeF₃ sample

under γ -source excitation is shown in Fig.5. The advance in crystal quality resulted in sufficient radiation hardness improvement. The relative changes in sample's optical transmitting were observed to be less than 5% for 10^7 rad radiation dose, which is demonstrated in Fig.6. The further progress in raw material preparation should allow to obtain cheap, efficient and reliable material for high energy scintillators.

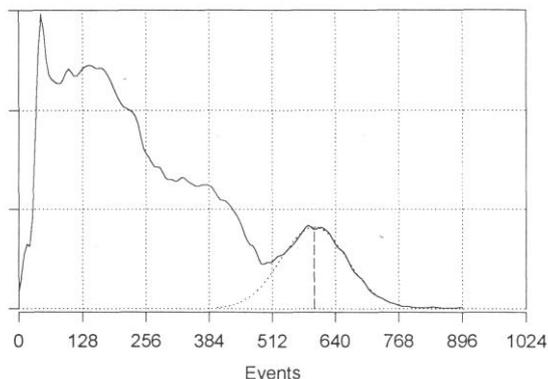


Fig.5 Photo peak of CeF_3 sample under γ -irradiation with ^{137}Cs γ -source

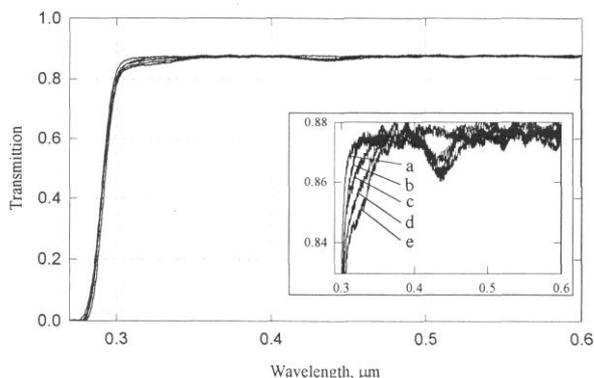


Fig.6 Changes in transmittance spectrum of CeF_3 crystal under various γ -radiation doses : a- non-irradiated, b- 10^4 rad, c- 10^5 rad, d- 10^6 rad, e- 10^7 rad

Luminescent properties of CeF_3 optical centers.

The luminescent properties of CeF_3 are due to parity allowed interconfigurational 5d-4f transitions. Unlike 4f electrons the 5d electrons are weakly shielded by outer electronic shells and are significantly influenced by the crystal field resulting in large Stark splitting. Such strong dependence of 5d electrons state on crystal field cause the spectroscopy of cerium fluoride to be to a large degree determined by the presence of two types of cerium centers, the so-called regular cerium centers, with spectroscopic properties characteristic for Ce^{3+} ions in regular sites, and perturbed cerium centers with local environment distorted by defects in the first coordination sphere the most probable defects being anion vacancies and vicinity of oxygen. The presence of defects strengthens the local crystal field diminishing the energy gap

between 4f and 5d states resulting in red shift of UV absorption edge and broad fluorescent band peaking at 340 nm. These perturbed cerium centers are known to interact with regular ones modifying the decay kinetics of the last and are characterized by longer decay time which is undesirable in most applications.

Oriented CeF_3 samples were used in photoluminescent and kinetic measurements. The photoluminescence of samples was excited by unpolarized UV light of deuterium lamp. Due to rather large amount of perturbed cerium centers the absorption spectra of the CeF_3 samples demonstrated the UV absorption edge shifted to longer wavelengths, as compared to the samples grown from highly purified raw materials, and revealed clearly seen fluorescent band peaking at 340 nm under UV excitation. The samples with different orientation of optical «c» axis were observed to have different fluorescent spectra, the integral fluorescent intensity being 16% higher in case of optical «c» axis oriented perpendicular to the excitation source-detector path. As can be seen on the Fig. 1 the growth of fluorescent intensity is observed mainly at the shortest peak of regular cerium centers fluorescence as well as at 340 nm peak corresponding to the perturbed cerium center fluorescence band which behaviour reminds that for 286 nm peak of regular centers due to efficient energy transfer.

As already 2 mm thick sample demonstrated reabsorption of the short wavelength fluorescence of CeF_3 samples the surface excited fluorescence spectra of thin CeF_3 plates were recorded and also demonstrated nonequal spectra as can be seen from Fig.2. One can notice that the difference in fluorescent spectra is more pronounced the integral intensity increase being observed at the same fluorescent peaks of regular and perturbed cerium centers.

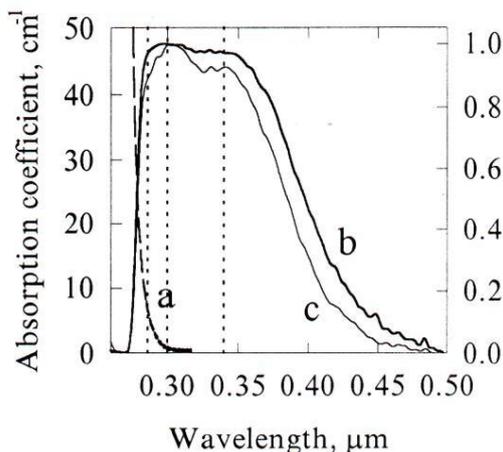


Fig.1 Absorption (a) and fluorescence spectra measured in 180° excitation scheme for CeF_3 samples with optical (c) axis parallel (b) and perpendicular (d) to sample surface

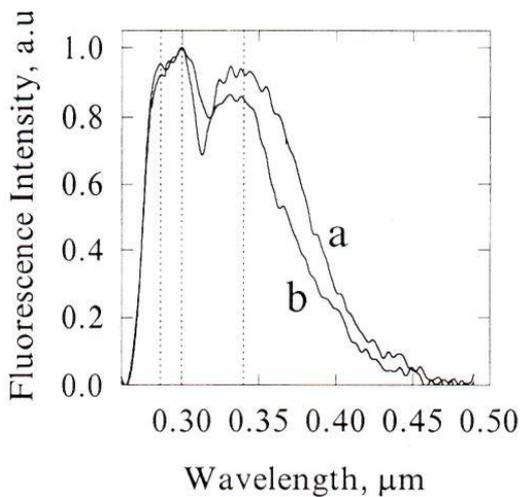


Fig.2 Fluorescence spectra measured in 45° excitation scheme for CeF₃ samples with optical (c) axis parallel (b) and perpendicular (d) to sample surface

Kinetic measurements

The decay curves of regular and perturbed cerium centers were measured under excitation by fourth harmonics of tunable LiF:F₂ color center laser at 268, 280, 290 and 300 nm for both thin plates and surface excitation and bulk crystals with volume excitation. The examples of decay curves are shown in Fig. 3 the regular centers kinetics being single exponential while perturbed centers displaying pronounced risetime. As regular centers (donors) decay Table 1. Decay time of CeF₃ sample under UV excitation reveals no nonexponentiality, the radiative by fourth harmonics of tuneable LiF:F₂-laser energy transfer mechanism should prevail in energy transfer process between regular and perturbed centers in case of relatively large concentration of the last. The results of measurements are collected in Table 1.

Table 1.

| Excitation wavelength, nm | 268 | 280 | 290 | 300 |
|---|-----|------|------|------|
| Registration, wavelength, nm | | | | |
| The decay times for surface excitation of thin plates | | | | |
| 285 | 8.9 | 9.0 | 9.1 | 9.4 |
| 305 | 9.6 | 9.8 | 10.0 | 11.2 |
| 340 | 23 | 23 | 25 | 26 |
| The decay times for volume excitation of bulk crystals | | | | |
| 285 | 27 | 29 | 29.4 | 30 |
| 305 | 27 | 29 | 30 | 30 |
| 340 | 29 | 29.4 | 32 | 32 |

As can be seen the decay time occurs to be excitation wavelength dependent and has the tendency for growth when longer excitation wavelengths are used.

Crystal growth

The cerium fluoride single crystals were grown using the directed crystallization technique in the furnace allowing to conduct the process in vacuum, fluorinating or inertial gas. During the process of single crystal synthesis using Stockbarger technique the temperature gradient of 100 °C/cm is sustained allowing to grow high optical quality CeF₃ crystals up to 40 mm in diameter at the speed of 5-10 mm/hour. As undesirable formation of perturbed centers was shown to arise from the presence of defects the most probable being anion vacancies and vicinity of oxygen ions much attention should be paid to removal of oxide admixture from source material during crystallization process. The original technique used is based on the formation of chamber's atmosphere by the products of teflon thermal decomposition. The resulting products of the process react intensively with oxygen containing admixtures forming compounds in gas phase which are further removed from the chamber. Cerium trifluoride crystals synthesized using the mentioned active fluorinating atmosphere revealed to have less than 10³ atomic % of oxygen. Such technique allows to use rather simple growing apparatus and obtain simultaneously up to four high optical quality boules up to 20 mm in diameter and 150 mm long during single synthesis. The continuous improvement of the technique allowed to increase greatly the quality of resulting product which can be characterized by observed changes in fluorescent spectra shown in Fig. 4. Here the curve 1 shows the UV excited fluorescence spectra of first generation samples which are characterized by large concentration of perturbed cerium centers and reveals practically no short wavelength fluorescence of cerium in regular sites. The curve 2 presents the analogous spectrum for samples of second generation which have clearly pronounced short wavelength fluorescence with sufficiently lower concentration of perturbed centers.

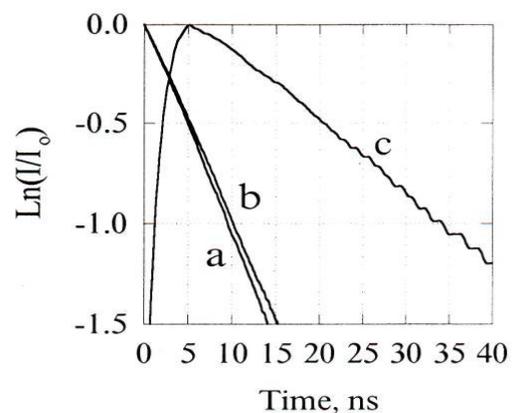


Fig.3 Decay curves of CeF₃ samples excited in 45° geometry by fourth harmonics of laser at 290 nm and registered at 285 nm (a), 305 nm (b) and 340 nm (c)

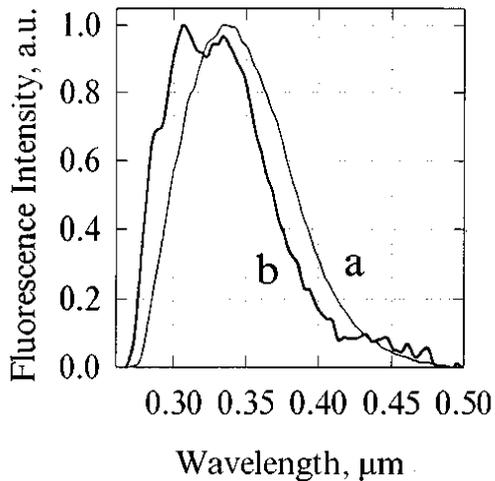


Fig.4. Fluorescence spectra of CeF_3 sample of first generation (a) with predominant fluorescence of perturbed centers and second generation sample (b) with clearly pronounced regular centers fluorescence

Conclusions

- New anhydrous gaseous hydrofluorination method was demonstrated to ensure impurity free polycrystalline cerium trifluoride as raw material for extra pure material synthesis.
- The combination of new method of raw material preparation and crystal growth technique was shown to result in further increase of light output and remarkable radiation hardness of synthesized single crystals.
- The developed original crystal growth technique was shown to improve the quality of resulting product by sufficient reduction of oxygen containing impurities by using the fluorinating atmosphere.
- The investigation of oriented samples fluorescent properties showed the 16% growth of integral fluorescent intensity in case of optical «c» axis perpendicular to excitation source - detector path.
- The radiative mechanism of energy transfer between regular and perturbed centers is shown to prevail in case of rather large perturbed cerium centers concentration.