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Strontium iodide: technology aspects of raw material choice and crystal growth

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The technological features of SrI_2 crystals production are discussed in this paper. The main reasons of deterioration of the purity and quality of the crystals were identified. It is shown that anionic (OH-group) is the basic impurity significantly affecting the scintillation characteristics. Some methods for quality control of SrI_2 raw materials and crystals were proposed. Raw materials with pH < 3–4 are preferable for growing high-quality crystals with excellent scintillation parameters.
Keywords: scintillation materials, alkali-earth halide, crystal growth,SrI_2.

В работе рассматриваются технологические особенности получения кристаллов SrI_2. Определены основные причины, снижающие чистоту и качество кристаллов. Показано, что основной примесью, которая значительно ухудшает сцинтилляционные характеристики, являются анионы (ОН-группа). Предложены методы контроля качества сырья и кристалла SrI_2. Для выращивания кристаллов высокого качества с улучшенніми сцинтилляционными параметрами предпочтительно использавание сырья с pH < 3–4.

Стронцій йодистий: технологічні аспекти якості сировини і росту кристалів. *А.В. Гектін, С.О. Васюков, Е.П. Галенін, В.І. Таранюк, М.В. Назаренко, В.В. Романчук*
Розглянуто технологічні особливості одержання кристалів SrI_2. Визначено основні причини, що знижують чистоту і якість кристалів. Показано, що основною домішкою, яка значно погіршує сцинтиляційні характеристики є аніони (ОН-група). Запропоновано методи контролю якості сировини і кристалів SrI_2. Для вирощування кристалів високої якості з покращеними сцинтиляційними параметрами переважно використання сировини з pH < 3 - 4.

1. Introduction

Modern history of Eu^{2+} doped alkali earth scintillator has been started in 1963 from CaI_2 and CaI_2:Eu studies [1–4]. It is necessary to note that even at that time a very good energy resolution (5.19 % for ^{137}Cs source) was achieved. But difficulties at crystal growth of those crystals stimulated the search for alternative materials and resulted in invention of SrI_2:Eu scintillator, by R.Hofshtadter in 1968 [5]. High light yield (by two times higher comparing to NaI:Tl) and 6 % energy resolution gave a very optimistic perspective.

Last decade the renewed interest to new alkali earths based scintillators called the new works on SrI_2:Eu scintillator optimization, and the energy resolution about 3 % was achieved [6, 7]. But, despite these results, the industrial production are still missing owing to the lack of proper technology.

It is interesting to note, that in 1968 (see the patent [5]) R.Hofshtadter synthesized the raw material at the lab conditions providing the purity of SrI_2 not better than 99.5 %. So, it is clear that more purified raw materials are necessary to minimize carriers trapping by structure defects and to prevent excitation quenching.

Since the new announcement of SrI_2:Eu on 2008 [6, 8] and crystal growth technology development started afterwards [9] and continued for years [10] have not resulted in an industrial production till now.

The main goal of this study was evaluation of different growth conditions and raw material purity level for crystal growth of high quality SrI_2:Eu. The main attention was paid to verification of key chemical elements, which presence deteriorates scintillator performance.

2. Experimental

Undoped and Eu activated SrI_2 crystals were grown by Bridgman method in the vacuumed quartz ampoules, as well as by Czochralski method in the platinum crucibles under the argon atmosphere. To check the anionic impurities contribution to SrI_2 properties the series of undoped and Eu^{2+}-doped SrI_2 crystals, as well as crystals doped with $Sr(NO_3)_2$; $Sr(CO_3)_2$; $Sr(OH)_2$; SrO crystals were grown from the same raw material.

Optical absorption spectra in the range of 190–1100 nm were registered by a Specord M40 spectrophotometer, and absorption spectra in IR-range were measured using a Shimadzu IRAffinity-1 spectrometer. In IR spectra of undoped SrI_2 crystals were measured to identify the trace quantities of OH^-, H_2O ions and other anions.

Spectral and kinetic characteristics of photoemission were studied using a FLS920 combined steady state and fluorescence lifetime spectrometer manufactured by Edinb. Instr. Ltd. A Xe900 steady state xenon lamp was used in the continuous mode for UV spectroscopy. Kinetic measurements were made using a nF900 nanosecond flash lamp.

3. Results

It is well known that the functional parameters of scintillators significantly depends on material purity in general and minimization of harmful impurities in particular. The main problem relates to the possibility of these impurities verification at the first stage and their elimination from the raw material. While such impurities do not verified, an integrated criteria like total purity (amount of N for initial powder selection) can be used.

The series of SrI_2:Eu single crystal was grown using raw materials with different

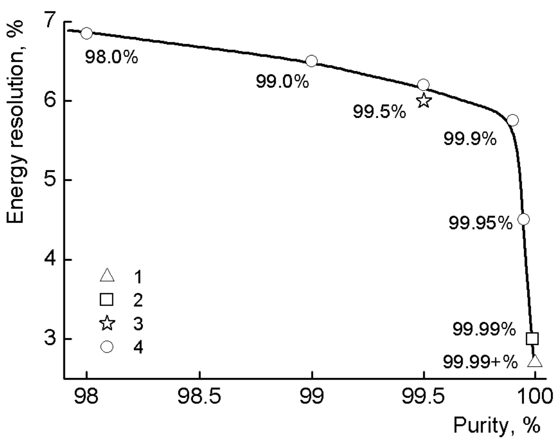

Fig. 1. Dependence of SrI_2:Eu energy resolution for different raw material purity (1 — [11]; 2 — [12] and [9]; 3 — [5]; 4 — this work).

purity. Typical anhydrous powder (total 99.99 % (4N) purity) synthesized at the laboratory scale was used, as well as raw materials from Sigma-Aldrich and Lanhit companies were used for these tests. Fig. 1 demonstrates scintillator performance improvement versus raw material purity. Additional treatments (like implemented to growth procedure [11]) are needed to provide an additional purification to the level of about 99.99+%.

This data confirm crucial importance of powder purity for scintillator performance but does not allows to justify types of harmful impurities. It is clear that at least 4-5N quality of powder and special clean growth atmosphere is needed to obtain crystals with the ~3–4 % energy resolution. In accordance with practice of growth of NaI and CsI based scintillators, 5N raw material purity is necessary to obtain good crystals. It was established that for such type of hygroscopic materials anion impurities mainly affect scintillation performance of such crystals [13, 14]. A similar tendency and similar dominating mechanisms can be assumed for the case of SrI_2:Eu. For this reason, anion impurities (oxygen containing complex anions) contribution to scintillation performance of SrI_2 was the main subject of this study.

3.1. Luminescence as the method of quality control

Figure 2 demonstrates luminescence and excitation spectra for pure and complex oxygen anions. The excitation peaks are very close to each case and lies in the ~240–255 nm range. Emission bands peaked at about 500–550 nm are much broader. It has to be

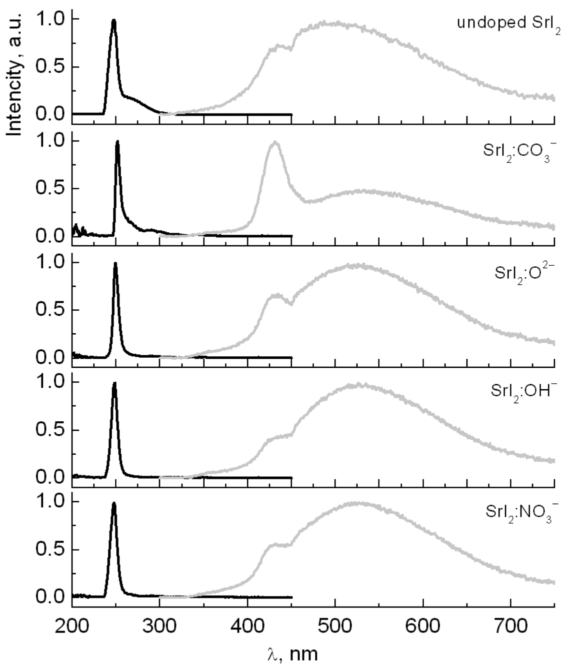

Fig. 2. Excitation (*Em* 530nm, black line) and luminescence (*Exc* 250 nm, grey line) spectra of undoped and doped by anionic impurities SrI_2 crystals. The spectra contain the peak at 425–430 nm, which is associated with divalent Europium trace.

noted that in all samples this emission is sensitive to anion impurities presence [6, 15], i.e. behavior is very closed to undoped CsI scintillators, for example. These peaks reflect purity level and can be introduced both with raw material powder, and from gaseous atmosphere during single crystal growth [16. 17].

So, long wavelength emission is specific one and significantly differs from the main luminescence (both STE and Eu^{2+}). The band at 530 nm (half width $H_{1/2}$ = 0.82±0.05 eV) is slightly overlapped with Eu^{2+} peak, but these peaks can be separated by analysis of each decay kinetics (see Fig. 3). Impurity-induced luminescence has decay time ~ 500±30 ns, i.e. by two times shorter comparing to Eu^{2+}. It should be noted that luminescence parameters are sensitive to SrI_2 crystal purity and could be useful for scintilator analysis. At the same time, some impurities are invisible with this excitation, i.e. no guarantee that all impurities are verified by this approach.

3.2. IR spectroscopy and main anion impurity

Another approach for harmful impurities verification is based on analysis of IR spectra. It is known that such technique can be successfully applied to impurity analysis of alkali halides with anion admixtures [18]. By the analogy, IR spectra of SrI_2 crystals in the range of 500–4000 cm^{-1} for crystals with different anions impurities were measured.

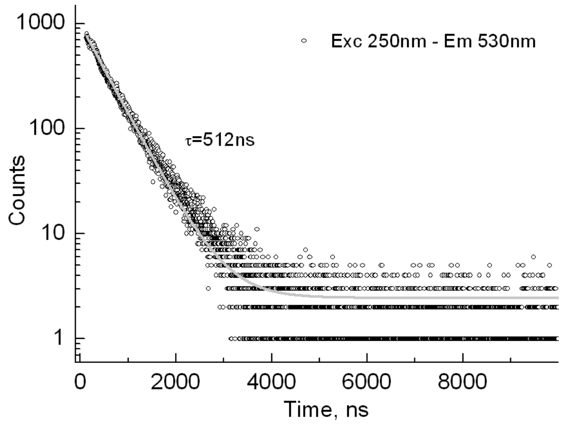

Fig. 3. Decay time of undoped SrI_2 crystal.

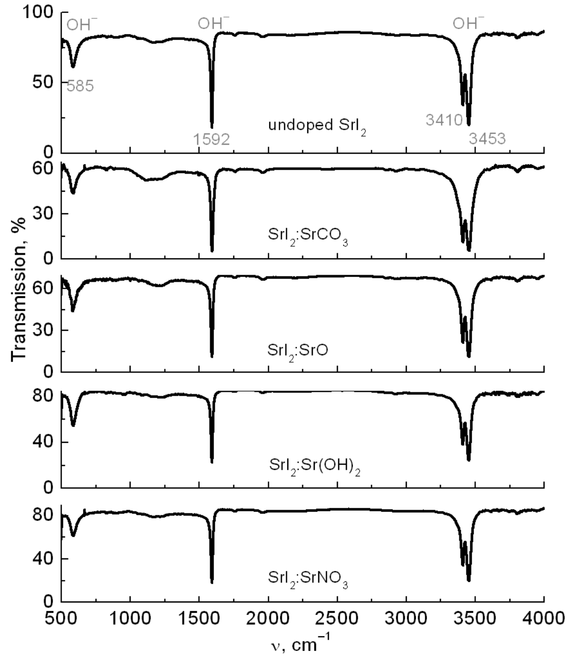

Fig. 4. IR transmission spectra of undoped SrI_2 crystals and doped with different anionic impurities.

Fig. 4 demonstrates the lines at 585 cm^{-1}, 1592 cm^{-1} and double peak at 3410 cm^{-1} and 3453 cm^{-1} indicating the presence of oxygen-containing impurities. The main absorption peaks are associated with OH-group in all samples studied regardless of the type of activator. It can be supposed that segregation coefficient of OH-group is higher than those of the other anionic impurities

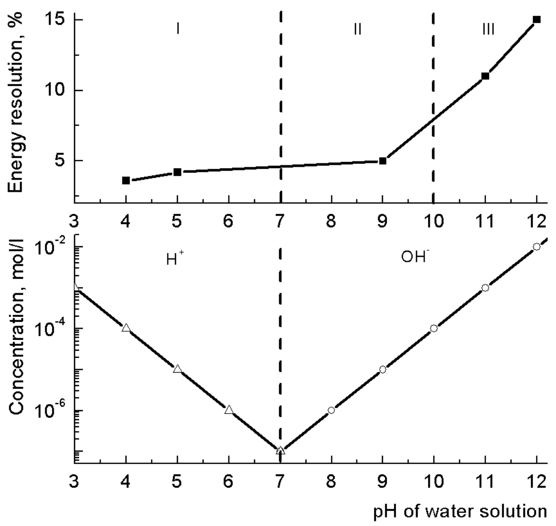

Fig. 5. Dependence of SrI_2:Eu crystal energy resolution (^{137}Cs, 662 keV) on pH of raw material water solution (Top). Concentration of H^+ and OH^- in water solutions (Bottom).

(NO_3^-, CO_3^{2-} etc). OH-group contamination can take place at all stages of the experiment: from raw materials preparation, crystal growth, and spectral measurements. Since material is highly hygroscopic, surface contamination is possible. Anyway, OH-group is the principal impurity and can be successfully detected by IR spectroscopy as well as other anionic impurities.

It has to be noted that spectroscopy analysis allows to verify anion impurities (like OH^-, NO_3^-, CO_3^{2-} and etc.) in SrI_2 scintillator and it was used as purity criteria at development of such type of scintillator [18, 20].

4. Criteria for high quality raw material selection for growth of high-quality crystals

Experimental data demonstrate that OH-group is the main potential impurity in alkali-earth halides. All processes in activated (Eu^{2+} and anionic impurities) and non-activated crystals occur in the presence of large amounts of this impurity. The simplest and most accessible way to identify the OH-group in the raw material and the crystal is the pH determination in the water solution, i.e.control of solution pH can be used as a criterion of grown crystal or raw material quality.

We have not succeed to grow the crystals with the energy resolution <5 % under the pH > 5 without additional purification. It is impossible to grow single crystals under pH > 9. The correlation between pH and quality of SrI_2 crystals (energy reolution was taken as the quality criterion) is presented in Fig. 5. According to pH values, the plot can be conditionally divided into the following sections: I — crystals with high scintillation quality; II — crystals with parameters similar to classic NaI:Tl and CsI:Tl; III — low quality crystals, polycrystalline ceramics.

As one can see from Fig. 5, the concentration of OH-groups is very high at pH > 10–12 and constitute $10^{-2} - 10^{-4}$ mol/L. This amount of impurity is sufficient to the crystallization disrupt. There is a high probability of polycrystal growth under these conditions.

The OH concentration decreases from 10^{-4} mol/L down to 10^{-7} mol/L in the range of pH = 7–10. This level of purity is normal for SrI_2 with parameters similar to alkali-halide scintillators and not allows to reveal the full potential of the material. The excitations transport to luminescence centers is hampered due to the impurity presence. Thus it is shown, that the alkaline reaction of water solution (pH > 7) is suitable to estimate the concentration of OH-groups, and evaluate the quality of both the SrI_2 powder and crystal.

It was shown that the acid reaction (pH < 7) of the strontium iodide water solution is typical for crystals with good scintillation parameters. The most optimal and desirable pH value is <3–4. There is a high probability to grow high quality scintillator with top parameters from raw materials with pH < 3.

5. Conclusions

Scintillation parameters of different quality SrI_2 crystals vary in a wide range. Experimental data demonstrate the correlations between luminescence, IR-transmittance and pH value and the quality of nominally pure raw materials and crystals.

Model experiment demonstrate that, similar to alkali halide scintillators, even minimal traces of OH-group ions can lead to creation of defects quenching scintillation emission. Impurities play a crucial role in the formation of scintillation properties of SrI_2 crystals. Some ways for revealing of such impurities are described. The method has been proposed to control the quality of SrI_2 raw materials and crystal by the pH value of the water solution. The practical criterion for raw material acidity preliminary check-in is proposed and can be useful for industrial technology development.

Raw materials with pH < 3–4 desirable for growing high-quality crystals with excellent scintillation parameters.

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