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TIME-RESOLVED LUMINESCENT SPECTROMETRY OF ZINK SELENIDE CRYSTALS

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The spectral and kinetic characteristics of pulse cathodoluminescence of undoped ZnSe single-crystals grown by sublimation from the vapor phase (Davydov-Markov method) and by flux growth (Bridgman method) have been measured. Three groups of bands were found in the spectra of radiative recombination of zinc selenide: exciton, edge emission and bands due to the recombination of carriers in deep centers. The spectral-kinetic characteristics of the edge emission in ZnSe crystals with different previous history have been studied. It was found that the number of edge emission series, the ratio of their intensities and spectral position are to be determined by the previous history of crystals. It is shown that the total intensity of the edge emission reduces more than tenfold with the temperature increase in the range of 15 - 80 K. The results obtained show that the properties of the edge emission can be well described by the model of donor-acceptor pairs.

Keywords: cathodoluminescence, sublimation, single-crystals, edge emission, radiative recombination.

Introduction

$A^{II}B^{VI}$ semiconductors are considered to be promising materials in optoelectronics and infrared technology. The first information about the research of luminescent characteristics of ZnSe at low temperatures dates back to 1960. It was reported about the edge emission observed as a large number of sharp lines in ZnSe photoluminescence spectra in the temperature range 4.2 - 77 K [1, 2], and the impurity radiation observed as broad bands in longer wavelength region [3]. However, so far there is no single opinion concerning the mechanism of edge emission in ZnSe crystals. In [4] the centers of edge emission are considered to be due to the isolated oxygen O_{Se}-centers and distant O_{Se}-O_{Se} - pairs. The authors of [5] believe that this is due to the recombination of donor-acceptor pairs. The nature of the impurity luminescence also causes heated debate among researchers.

The development of luminescence centers models is constrained by the lack of information (or its complete absence) on the kinetic parameters of the observed luminescence bands radiation and their dependence on the experimental conditions. The purpose of the research is to investigate the spectral and kinetic characteristics of pulse luminescence in ZnSe crystals with different previous history grown by different technologies in irradiation by a pulsed high-current electron beam of nanosecond duration.

The practical significance of the work is defined by the possibility to use the findings for creating the model of energy transitions in ZnSe which promotes the development of new optical devices with electron excitation.

Experimental

To study the luminescence of ZnSe was used the technique of pulse luminescent spectrometry with nanosecond time resolution [6] was used. This method has several advantages compared to stationary methods of research. Additional analytical capabilities of luminescent spectral analysis by using a pulsed spectrometer are provided by the use of nanosecond high-current electron beams as well as the possibility of extracting useful information about the luminescence centers from the kinetic characteristics of luminescence decay. The spectrum and its evolution over the time after the excitation pulse are defined by the technology of the crystal growth.

The excitation source was a pulsed electron accelerator with the parameters: average electron energy in the beam of ~ 0.25 MeV, the current pulse duration FWHM of ~ 15 ns. The test sample was set at an angle of 45° to the direction of the electron flow. The samples were cooled by the industrial microcryogenic system MSMR-110N-3.2/20 which allows cooling a sample down to 12.5 K without liquid helium or nitrogen. Pulse cathodoluminescence of zinc selenide crystals was investigated in the spectral range 440 - 750 nm at 15 and 300 K. The glow of the sample was projected by a lens onto the entrance slit of the monochromator MDR-204 and detected by PMT-84 and the storage oscilloscope Tektronix TDS 2022. The time resolution of the recording channel was ~ 15 ns, the spectral resolution made ~ 0.0015 eV. The luminescence spectra were normalized by taking into account the spectral sensitivity of the spectrometer optical path. The electron beam energy was measured by radiation-chemical method.

Intentionally undoped ZnSe single-crystals with different previous history were used as samples. Samples №1 and №2 were obtained by Davydov-Markov method, sample №3 was grown by Bridgman method.

Results and Discussion

The absorption edge of the crystals may provide important information on the band gap and defects in a crystal lattice. The absorption spectra of the samples were measured by a spectrophotometer SF-256 at 300 K. As can be seen from Fig. 1, the absorption edge of the ZnSe crystals is shifted to longer wavelengths compared to fundamental absorption edge of pure ZnSe, which position is defined by free exciton FE_{ZnSe} (λ ~ 460 nm at 300 K).

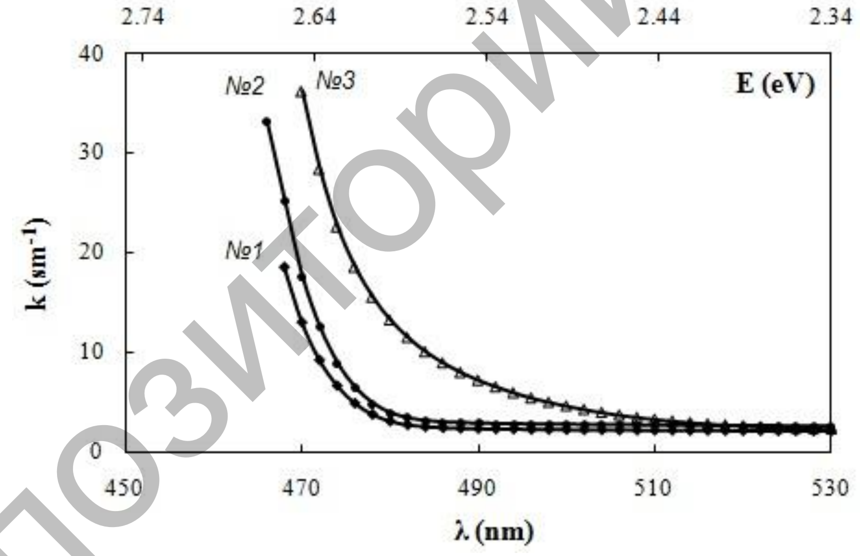

Fig.1. Absorption spectra of ZnSe crystals at 300 K.

The absorption spectra of the samples №1 and №2 are close to each other, this may be caused by the same nature of the defects responsible for the absorption edge in these crystals. The spectrum of the sample №3 is shifted to longer wavelengths by ~ 10 nm compared to the absorption spectra of the samples №1 and №2 and has no sharp edges, indicating high concentration of both shallow and deep levels in the band gap of the crystal.

The spectral and kinetic characteristics of the pulse cathodoluminescence in ZnSe was measured at the electron beam energy density 0.02 J/cm^2 (G = 10^{26} cm^{-3} s^{-1}). In the luminescence spectra of the samples №1 and №2 measured at 300 K we observed one band with the maxima at λ = 470 nm and λ = 468 nm, respectively. Its decay time was τ ≤ 15 ns. The spectrum of the sample №3 is distinguished by the band in the long wavelength region with the peak at λ = 550 nm. The study of the kinetic characteristics of this band showed that it consists of three components with the relaxation time τ_1 = 2 µs, τ_2 = 15 µs, and τ_3 = 50 µs.

After 2.5 µs after the excitation pulse in the spectrum of the sample №3 only one broad ($\Delta E_{1/2}$ ~ 0.32 eV) band could be observed with the peak at λ = 600 nm and decay time τ_1 = 15 µs and τ_2 = 50 µs. The authors in [3] explain this band as one caused by Cu impurity ~ $5{\cdot}10^{-6}$ % in ZnSe crystals. In [7] the interpretation of the bands of about 600 nm based on the theory of band anticrossing, which determines the initiated by oxygen splitting of the conduction band, is proposed.

At 15 K the emission lines of bound excitons I_1 at λ = 448 nm with a relaxation time $\tau \leq 15$ ns and phonon replicas I_1 - LO (Fig. 2-4) can be observed in the pulse cathodoluminescence spectra of ZnSe crystals measured at the time of the excitation pulse.

All the samples along with the exciton spectrum are characterized by multi-band edge emission in the region of 460-490 nm. In this case, there are series of equidistant bands with the step between the components equal to longitudinal optical phonons.

The comparative analysis of the luminescence spectra in zinc selenide crystals measured at different times after the excitation pulse shows that the edge emission can be observed in all the samples. The number of series and intensity of the bands is determined by the previous history of the crystals.

Figures 2-4 show the spectra of edge emission of zinc selenide crystals measured at various times after the excitation pulse. We can see that the spectrum of sample №1 (Fig. 2) contains one series of equidistant bands with a maximum phonon line at λ = 462 nm and its repetitions with the maxima at 467, 472 and 478 nm.

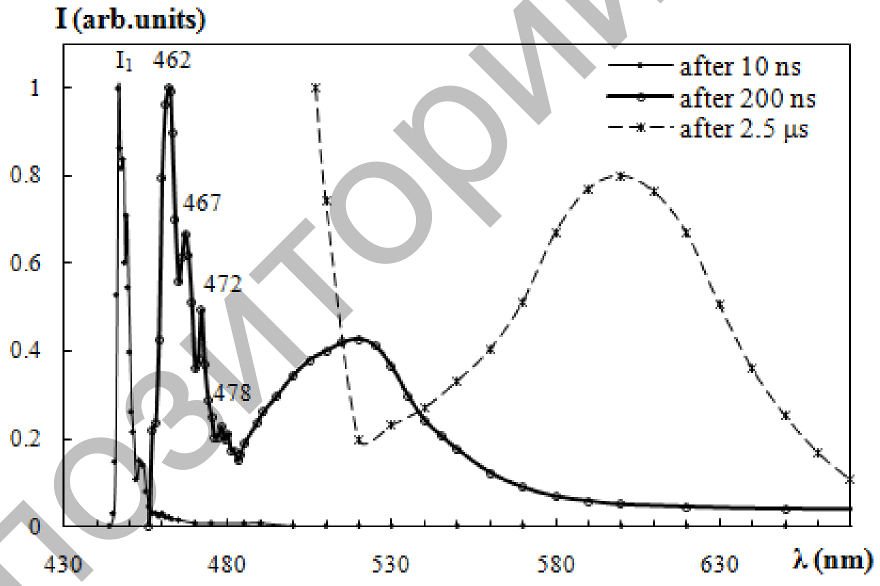

Fig. 2. Pulse cathodoluminescence spectra of ZnSe sample №1 measured at various times after excitation pulse at 15 K.

There are two series of edge emission in the spectrum of the crystal №2 (Fig. 3). It was established that only short-wave series (λ ~ 462, 467, 472 nm) can be observed in the spectrum measured after 100 ns after the excitation pulse.

Over the time the situation changed. First, the emission lines of the short-wave series shifted to lower energies, and their form changed. At the initial time the width of the edge emission lines was 0.02 eV, and over the time it decreased to 0.009 eV. Secondly, along with a short-wave series (λ ~ 463.5; 468.5; 474.5; 480 nm), the long-wave series of edge emission (λ ~ 465.5, 471, 476.5, 482.5 nm) appeared in the emission spectrum measured after 200 µs (Fig. 3, b).

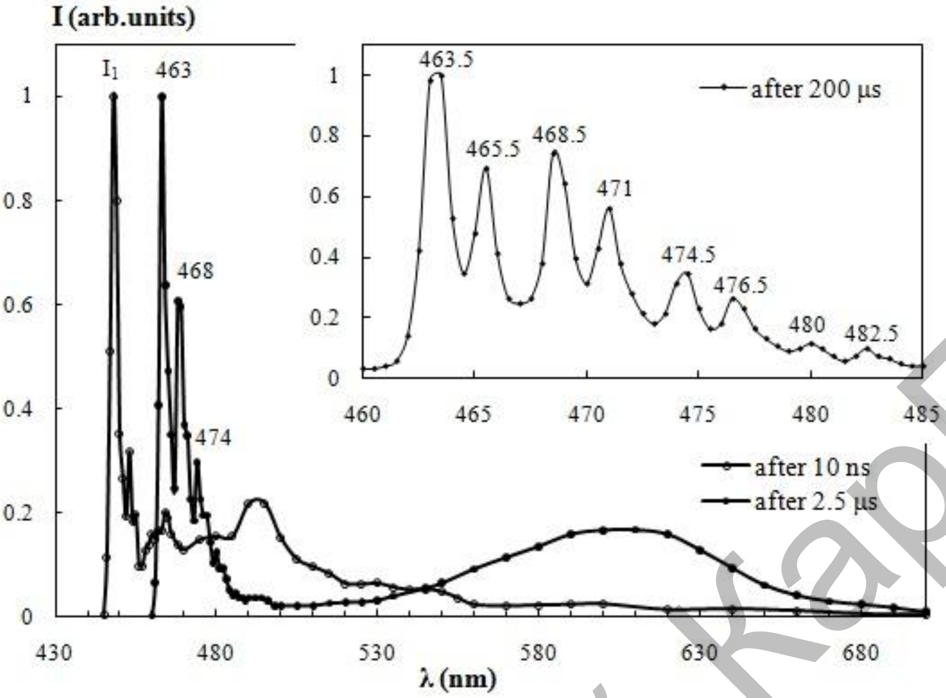

Fig. 3. Pulse cathodoluminescence spectra of ZnSe sample №2 measured at various times after excitation pulse at 15 K.

The edge emission spectrum of the sample №3 measured after 1 µs after the exciting pulse (Fig. 4) differs from the edge emission spectra of the samples №1 and №2.

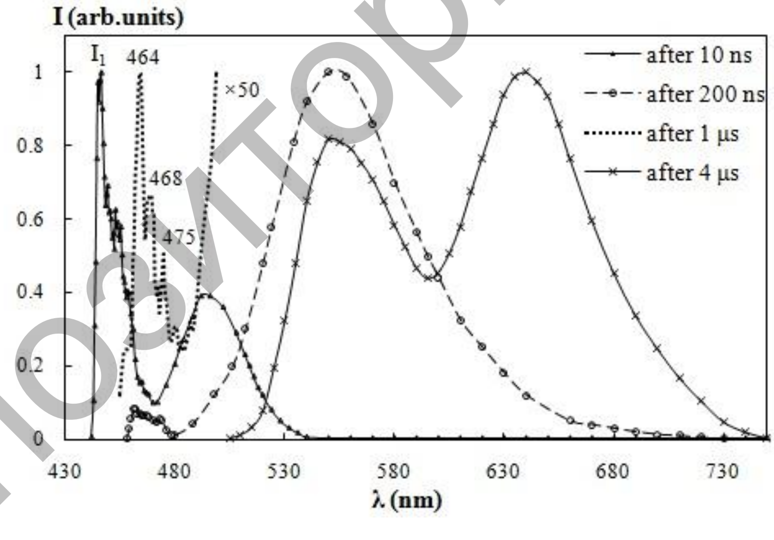

Fig. 4. Pulse cathodoluminescence spectra of ZnSe sample №3 measured at various times after excitation pulse at 15 K.

Its intensity is an order of magnitude smaller than the intensity of the defect - impurity luminescence band peaking at λ = 550 nm, which indicates a very high degree of crystal defectiveness compared with crystals №1 and №2.

The decay kinetics of the pulse cathodoluminescence at λ = 463 nm is described by a hyperbolic law of electrons and holes concentration reducing, which is typical for recombination luminescence. The emission intensity decreases over the time in accordance with the law $I \sim t^{-1}$ (Fig. 5a)

Table 1. The spectral characteristics of ZnSe edge emission measured at different time intervals after the pulse high-current electron beam at 15 K

Sample №1			
Measuring point	After 200 ns	After 1 µs	After 25 µs
λ, nm (E, eV)	462 (2.684 eV) 467 (2.655 eV) 472 (2.627 eV) 478 (2.594 eV)	462.5 (2.681 eV) 467.5 (2.652 eV) 474 (2.616 eV)	463 (2.678 eV) 468.5 (2.647 eV) 474 (2.616 eV)

Sample №2				
Measuring point	After 200 ns	After 2.5 µs	After 20 µs	After 200 µs
λ, nm (E, eV)	462 (2.684 eV) 467.5 (2.652 eV) 473 (2.622 eV)	463 (2.678 eV) 468 (2.650 eV) 474 (2.616 eV)	463 (2.678 eV) 465 (2.667 eV) 468.5 (2.647 eV) 470.5 (2.635 eV) 474 (2.616 eV) 476 (2.606 eV) 479.5 (2.586 eV)	463.5 (2.675 eV) 465.5 (2.664 eV) 468.5 (2.647 eV) 471 (2.633 eV) 474.5 (2.613 eV) 476.5 (2.602 eV) 480 (2.583 eV) 482.5 (2.570 eV)

Sample №3		
Measuring point	After 200 ns	After 1 µs
λ, nm (E, eV)	461.5 (2.687 eV) 473 (2.622 eV)	464 (2.672 eV) 468 (2.650 eV) 475 (2.611 eV)

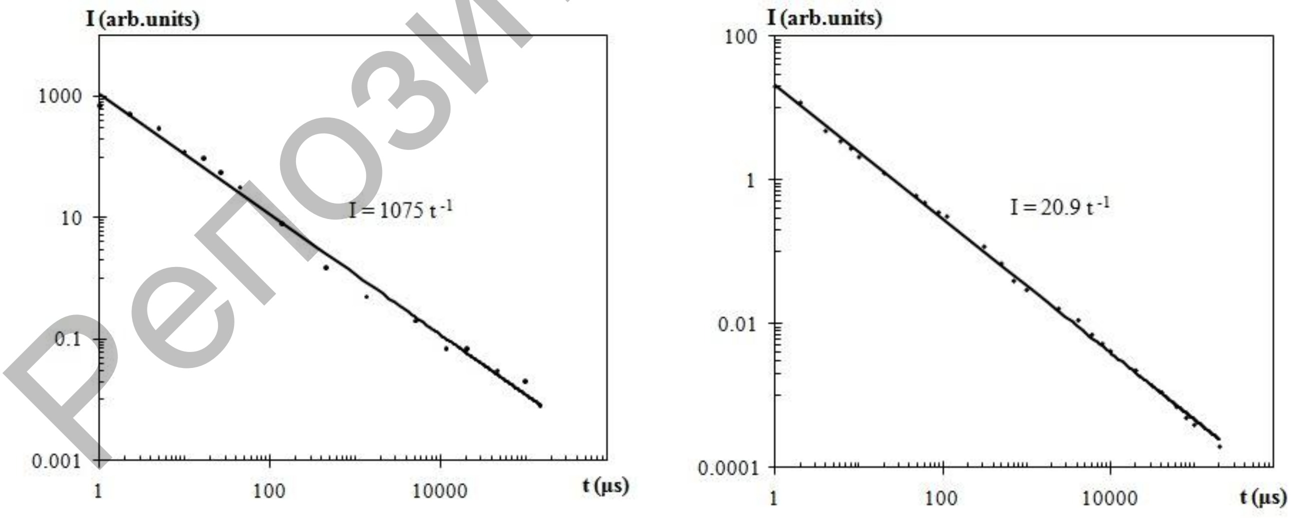

Fig. 5. Decay kinetics of pulse cathodoluminescence of ZnSe sample №2 at 15 K: a) at λ = 463 nm, b) at λ = 640 nm.

The dependence of the edge emission intensity on the temperature was researched. Edge emission was found to experience strong temperature quenching with temperature increasing (Fig. 6).

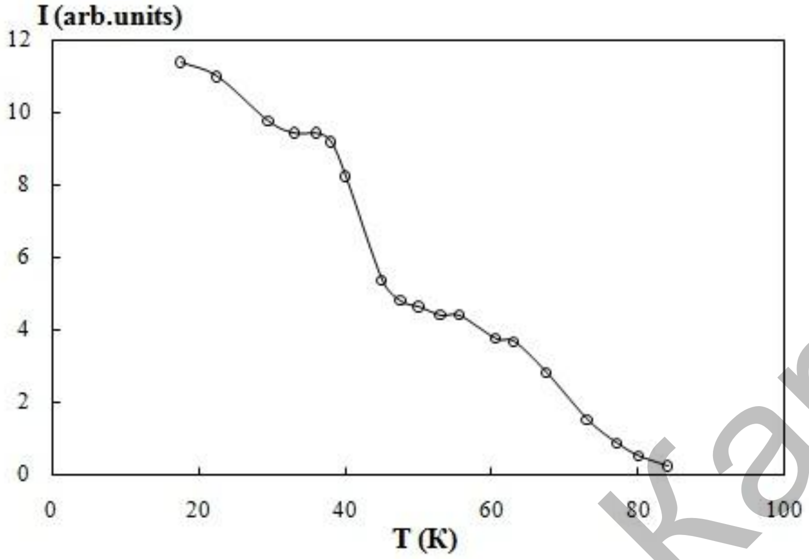

Fig. 6. Dependence of edge emission intensity (at λ = 463 nm) of ZnSe sample №2 on temperature.

All observed dependences, which characterize ZnSe bands near the fundamental absorption edge, are typical for the luminescence of donor-acceptor pairs. Notably: the presence of the emission spectrum equidistant structure, which characterizes the interaction with photons of the lattice; the donor-acceptor luminescence kinetic is not exponential; the luminescence spectra measured at different time intervals after the excitation pulse are different. Predominantly short-range pairs recombine at the initial time after the excitation. Distant pairs illuminate later due to the low probability of interimpurity transitions. As a result, with the time after the excitation pulse, short-wave and long-wave series bands of ZnSe crystals shift over 0.01 eV to low-energy spectral region. The edge emission intensity strongly decreases with the temperature increasing from 15 to 80 K.

Electronic transition mechanisms and the nature of the defects responsible for different series of edge emission in crystals $A^{II}B^{VI}$ are still under discussion [3 - 8]. It is considered that donors are shallow (E_D = 0.015 eV for ZnSe), and acceptors corresponding to both series are deep (E_A = 0.12 eV for ZnSe) and are of the same origin [1]. The donor-acceptor pairs' luminescence has the following mechanism. Nonequilibrium electron is nonradiatively trapped by positively charged ionized donor, a hole is trapped by ionized acceptor, and then the radiative electron transition from donor to acceptor occurs. The emitted photon energy is determined by the equation:

$$h\nu = E_g - (E_D + E_A) + e^2/4\varepsilon\varepsilon_0 R, \quad (1)$$

where E_g is a band gap, E_D and E_A are energy positions of donor and acceptor levels relative to the edges of nearest bands; R is distance between impurities; e is electron charge, ε is dielectric constant. The Equation (1) is written without taking into account a small summand, which characterizes the difference between interimpurities interaction and the Coulomb interaction of the short-range pairs.

Currently, no researches clearly point to the physicochemical nature of the defects responsible for different series of edge emission in undoped crystals of $A^{II}B^{VI}$ group. Intrinsic defects and impurity atoms are assumed to be donors and acceptors. Clarifying nature of the centers, which are responsible for the crystals edge emission, requires individual study beyond the scope of this research.

Defect-impurity luminescence bands are observed in the range 490-750 nm in the samples spectra measured at 15 K. A broad band ($\Delta E_{1/2}$ ~ 0.15 eV) with the maximum at $\lambda = 492$ nm and relaxation time τ ~ 500 ns appears in spectra of crystals №1 and №2 at the time of the excitation pulse. Its occurrence is associated with the occurrence of uncontrolled impurities of tellurium and oxygen in the crystal lattice of ZnSe [7].

A broad band ($\Delta E_{1/2}$ ~ 0.2 eV) with the maximum at $\lambda = 600$ nm appears in the spectra of samples №1 and №2 (Fig. 2, 3) measured after a few microseconds after the excitation pulse at 15 K. The luminescence intensity at $\lambda = 600$ nm decays according to the hyperbolic law $I \sim t^{-1}$ (Fig. 5 b). This band intensity decreases more than tenfold with the temperature increase in the range of 15 - 150 K.

The bands appearance, observed in the samples spectra in the range 520 - 650 nm (Fig. 3-5), measured over the time after the excitation pulse at 15 K, can be explained by the theory of band anticrossing and oxygen and copper impurities in the crystals [8] . In this case, the transitions to the Cu acceptor level take place from the narrow band of strongly localized states and extended states band, splitted by isoelectronic impurity of conduction band oxygen.

Conclusions

I. The evolution of the edge emission spectra of ZnSe crystals grown by various methods is researched in the time interval of $10^{-7} - 10^{-2}$ s using the method of pulsed spectrometry with nanosecond time resolution. The number of edge emission series, their intensities ratio and spectral position can be determined by the previous history of the crystals.

II. The edge emission time shift of ZnSe crystals after the excitation pulse is measured. It is shown that depending on the crystal type the maxima of edge emission bands shift to longer wavelengths by 0.006 - 0.014 eV.

III. The dependence of the edge emission on temperature is researched. It is shown that the total intensity of the edge emission decreases more than tenfold with the temperature increase in the range of 15 - 80 K.

IV. The results obtained confirm the donor-acceptor mechanism of the edge luminescence in zinc selenide crystals.

V. The bands found in the range of 490 - 750 nm indicate the intrinsic and extrinsic defects in the ZnSe samples.

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