

PHYSICAL PROPERTIES
OF CRYSTALS

**Gd₃Ga₅O₁₂:Nd³⁺ Crystals for a Continuous-Wave
Diode-Pumped Laser Operating
in ⁴F_{3/2} → ⁴I_{11/2} and ⁴F_{3/2} → ⁴I_{13/2} Channels**

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Abstract—Garnet crystals of the composition Gd₃Ga₅O₁₂:Nd³⁺ (concentration series C_{Nd} = 1–10 at. %) were grown from flux. In terms of spectroscopy, these crystals, unlike those grown from melts, form a medium with a single activator center. For the first time, continuous-wave lasing was excited by diode pumping with the use of Gd₃Ga₅O₁₂:Nd³⁺ crystals at the wavelengths λ₃ = 1.3315 and λ₄ = 1.3370 μm of the ⁴F_{3/2} → ⁴I_{13/2} channel and also the simultaneous generation at two wavelengths, λ₁ = 1.0621 and λ₂ = 1.0600 μm, of the ⁴F_{3/2} → ⁴I_{11/2} channel. © 2002 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The first studies of laser generation and spectroscopy of garnets were performed on flux-grown Y₃Al₅O₁₂:Nd³⁺ crystals [1–3]. The widespread use of these materials in active elements of flashlamp-pumped lasers requires the growth of large crystals 10 cm in length and 1 cm in diameter. To grow such crystals, special methods of crystallization from melts were developed such as the Czochralski method. However, the comparison of the properties of aluminum garnets Y₃Al₅O₁₂:Ln³⁺ grown from melts (*T*_m = 1930°C) and from flux (at temperatures 1100–1200°C) showed that the latter have better spectroscopic parameters corresponding most closely to the model of a single activator center [4, 5]. Furthermore, at the crystallization of Y₃Al₅O₁₂:Nd³⁺ crystals from flux, the distribution coefficient of neodymium considerably exceeds the value *K*_{Nd} = 0.18 characteristic of the crystallization from melts. In connection with the development of semiconductor diode-laser pumping in recent years, the interest in crystals grown from flux with a volume of up to 1 cm³ is renewed (including Y₃Al₅O₁₂:Nd³⁺ with an elevated activator concentration, C_{Nd} ≥ 1.5 at. %). Such crystals are used in compact laser devices providing a high quality of radiation (a narrow spectral line, single-mode lasing, low losses, and minimum beam divergence).

Below, we report on the growth of the concentration series of Nd³⁺-doped gadolinium–gallium garnet crystals, Gd₃Ga₅O₁₂:Nd³⁺ (Nd-doped GGG), the study of their lasing properties under diode-laser pumping and also compare their laser and spectroscopic data obtained with those of crystals grown by the Czochralski method from a melt [6].

The Gd₃Ga₅O₁₂:Nd³⁺ single crystals were grown from boron–barium fluxes of the composition 56 wt % (BaO + 0.62B₂O₃) + 44 wt % Gd_{3–x}Nd_xGa₅O₁₂, where *x* = 0.03, 0.1, and 0.3. The saturation temperature of the fluxes was *T*_{sat} = 1200–1230°C; the slope of its concentration dependence was *dT*_{sat}/*dn* = 15°C/wt %. The crystals were synthesized in platinum crucibles by the group method [7] on six “prismatic” seeds with square bases of 1 mm² and heights of 10–15 mm. The lateral seed faces were formed by the equilibrium (110) and (211) planes. The seeds were cut out from selected high-quality Gd₃Ga₅O₁₂ crystals.

Upon the attainment of the initial overcooling by 3–4°C (corresponding to the middle of the metastable zone), the flux temperature was decreased at a rate of *dT/dt* = 1–6°C/day (24 h), which corresponded to the growth rate of the crystals at the main stage of growth, up to 0.5 mm/day. The crystal holder was reversibly rotated with a period of 0.5–1 h. The crystallization temperature ranged from 80 to 100°C; the grown crys-

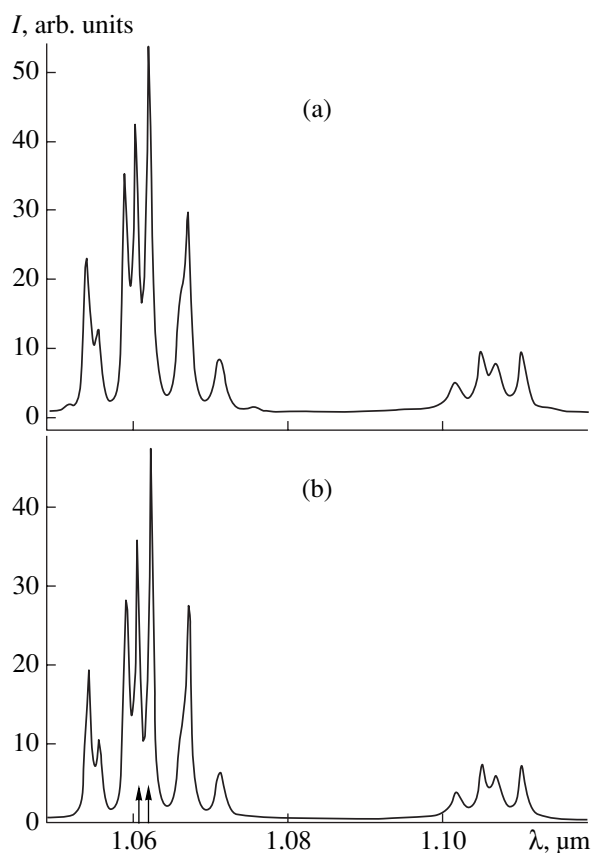


Fig. 1. Luminescence spectra of Nd³⁺ ions (concentration ~1 at. %, ⁴F_{3/2} → ⁴I_{11/2} transitions) at 300 K from gadolinium–gallium garnet crystals grown (a) from melt and (b) from flux. Arrows indicate the lasing lines.

tals weighed 100–120 g. The unit-cell parameters of the crystals were measured on a Geigerflex (Rigaku Co.) X-ray powder diffractometer (Co_{K α} -radiation, 1200, 1220, and 1222 reflections).

Gd₃Ga₅O₁₂:Nd³⁺ single crystals with a volume of up to 2 cm³ were used to prepare the samples in the shape of polished plane–parallel plates parallel to the most developed faces of the (110) rhombododecahedron with a thickness of 2–4 mm and an area of up to 50 mm². This orientation of the plates reduced the undesirable effect of growth striae on the lasing characteristics. Similar samples were also prepared from garnet crystals grown from melt. The ends of the active laser elements had no antireflection coating.

The laser experiments were performed in a 20-cm-long hemispherical cavity at 300 K. The curvature radius of the spherical (exit) mirror was 100 mm. The crystal was located close to the plane selective mirror through which the end pumping was made. This mirror had a high transmission coefficient ($T \approx 80\%$) at the pumping wavelength ($\lambda_p \approx 0.81 \mu\text{m}$) and a high reflection coefficient ($R > 99.9\%$) at the lasing wavelengths.

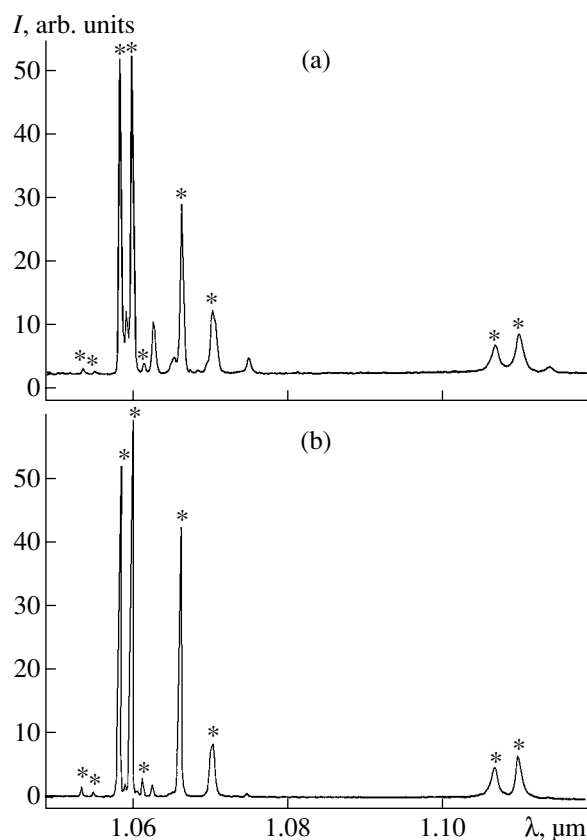


Fig. 2. Luminescence spectra of Nd³⁺ ions (concentration ~1 at. %, ⁴F_{3/2} → ⁴I_{11/2} transitions) at 15 K in the gadolinium–gallium garnet crystals (a) grown from melt and (b) grown from flux. Asterisks indicate the lines of the principal center of Nd³⁺ ions in a Gd₃Ga₅O₁₂ crystal.

A diode-laser ATS-2440 with a nominal power of 1 W thermally stabilized to 0.1°C was used as a pumping source. Absorption and luminescence spectra of Nd³⁺-doped gadolinium–gallium garnet crystals were recorded on an AM510-M1 (Action Research Co.) diffraction spectrometer by an InSbAl detector. The temperature measurements of the spectra were made on a CSW-202 (Advanced Research Systems) double-loop close-cycle helium refrigerator in the range 15–300 K.

The examination of the absorption and luminescence spectra of the Nd³⁺-doped gadolinium–gallium garnet crystals grown from melt and from flux obtained at 300 K were practically identical. The luminescence spectra consist of homogeneously broadened lines (Fig. 1) whose positions and intensities are adequately described within the approximation of a single activator center with the scheme of crystal-field splitting suggested in [6]. At the same time, the low-temperature luminescence (Figs. 2, 3) and absorption (Fig. 4) spectra were different: the number and intensities of additional lines in comparison with those of the principal activator center Nd³⁺ for crystals grown from melt were much more pronounced.

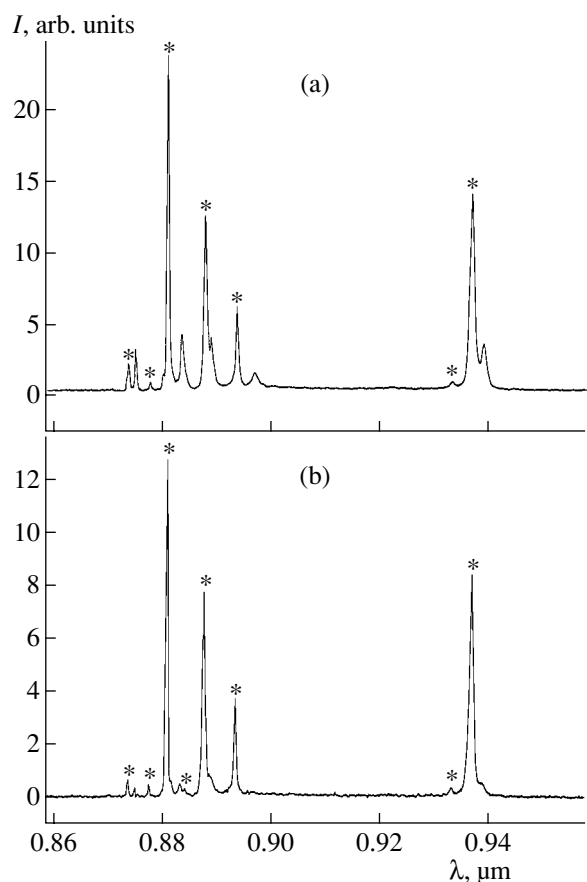


Fig. 3. Luminescence spectra of Nd^{3+} ions (concentration ~ 1 at. %, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transitions) at 15 K in the gadolinium–gallium garnet crystals (a) grown from melt and (b) grown from flux. Asterisks indicate the lines of the principal center of Nd^{3+} ions in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystal.

These differences can be interpreted based on the crystal chemistry of garnets. It is well known that in the quasi-binary Gd_2O_3 – Ga_2O_3 system, the gadolinium–gallium garnet has a range of existence of $\text{Gd}_{3+x}\text{Ga}_{5-x}\text{O}_{12}$ solid solutions enriched in gadolinium oxide (Gd_2O_3) in comparison with the stoichiometric composition $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. The formation of these solid solutions is interpreted as a partial replacement of Gd^{3+} by Ga^{3+} ions in the octahedral positions of the structure [8, 9]; the unit-cell parameter of these solid solutions is described by the following formula [10]:

$$a_{s.s} = a_0 \left[1 + \left(\frac{r(\text{Gd}^{3+})}{r(\text{Ga}^{3+})} - 1 \right) \times 0.0268x \right], \quad (1)$$

where $a_0 = 12.375 \text{ \AA}$ is the unit-cell parameter of the stoichiometric garnet, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, and r are the octahedral ionic radii of the ions. The existence range of solid solutions is rather large (up to $x \approx 0.3$). The most homogeneous crystals are grown from a congruent melt of the composition $\text{Gd}_{3.05}\text{Ga}_{4.95}\text{O}_{12}$ [10].

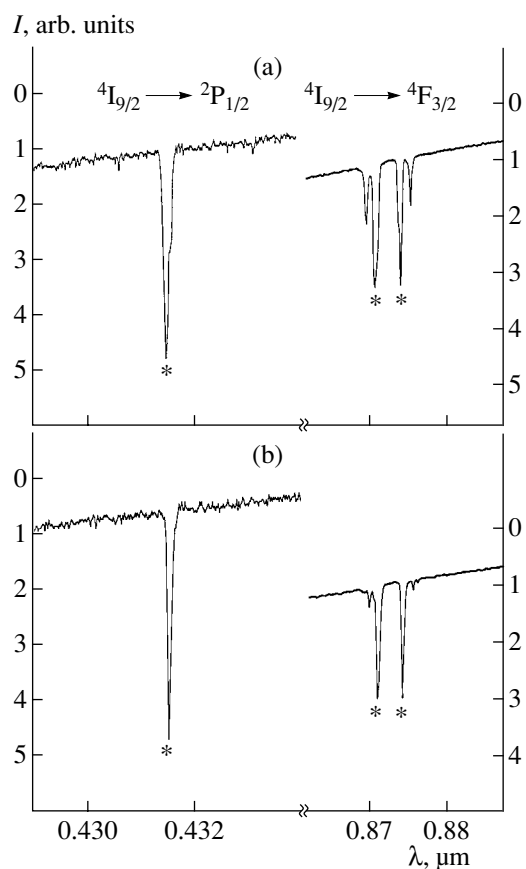


Fig. 4. Luminescence spectra of Nd^{3+} ions (concentration ~ 1 at. %, ${}^4\text{I}_{9/2} \rightarrow {}^2\text{P}_{1/2}$ and ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$ transitions) at 15 K from the gadolinium–gallium garnet crystals (a) grown from melt and (b) grown from flux. Asterisks indicate the lines of the principal center of Nd^{3+} ions in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ crystal.

All the absorption and luminescence spectral lines should be attributed to the activator centers of Nd^{3+} ions replacing the Gd^{3+} ions in the c -positions of the structure (the concentration of large Nd^{3+} ions in the octahedral positions of the garnet is very low even in the $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ crystals [11]). The structure of Nd^{3+} activator centers in the gadolinium–gallium garnet is determined to a large extent by the distribution of the cations from the second coordination sphere located in four distorted cubes, four octahedra, and six (2 + 4) tetrahedra sharing edges and vertices with a distorted NdO_8 cube (see table).

The principal center (type 1 in table) is formed by distorted NdO_8 cubes built by ten Ga and four Gd atoms from the second coordination sphere, which corresponds to the stoichiometric garnet of the composition $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and a low concentration of Nd^{3+} activator ions. The additional activator center (type 2) observed in the spectroscopic experiment is, most likely, formed in the case where nine Ga atoms and five Gd atoms are

within the second coordination sphere around a Nd³⁺ ion. Since the octahedral ionic radius of Gd³⁺ (0.94 Å) substantially exceeds that of Ga³⁺ (0.62 Å), this replacement strongly distorts the oxygen environment of a Nd³⁺ ion (since the NdO₈ polyhedron and the nearest octahedron share an edge). The calculation shows that in a gadolinium–gallium garnet of the congruent composition Gd_{3.05}Ga_{4.95}O₁₂ grown from melt, the centers of type 2 would comprise up to 8% of the total number of the Nd³⁺ activator centers even if one ignores possible correlations characteristic of the garnet structure (the structure with large Ln atoms in *c*-positions is stabilized by the ions larger than Ga³⁺ located in the octahedral *a*-positions, e.g., by Sc, Lu, and Yb ions [12]).

The gadolinium–gallium garnet crystals grown from melt studied have the unit-cell parameter $a_{Cz} = 12.385 \pm 0.001$ Å; their composition estimated by Eq. (1) is Gd_{3.06}Ga_{4.94}O₁₂. Our garnet crystals grown from flux have the unit-cell parameter $a_{flux} = 12.377 \pm 0.001$ Å, their composition is close to stoichiometric, Gd₃Ga₅O₁₂, which is typical of crystals grown from flux [13]. This explains a considerably lower concentration of the second activator center (type 2) in our Gd₃Ga₅O₁₂:Nd³⁺ crystals grown from flux in comparison with its concentration in the crystals grown from melt.

The pair centers (type 3)—a pair of Nd³⁺ ions in the adjacent distorted cubes—can evidently be formed in crystals grown from both melt and flux depending on the activator concentration in the crystal. However, the spectra obtained show that, at the activator content of about 1 at. % in Nd³⁺-doped gadolinium–garnet crystals, the concentration of these centers is lower than the concentration of type 2 centers.

In laser experiments, a continuous-wave lasing was excited in Gd₃Ga₅O₁₂:Nd³⁺ crystals grown from flux. With no selective elements in the cavity, lasing occurred simultaneously at the wavelengths $\lambda_1 = 1.0621$ and $\lambda_2 = 1.0600$ μm of the ⁴F_{3/2} → ⁴I_{11/2} channel. The lasing threshold for Gd₃Ga₅O₁₂:Nd³⁺ crystals grown from flux was somewhat (by ~20%) lower than that of crystals grown from melt. The use of selective mirrors with high reflection coefficients in the vicinity of 1.33 μm highly transparent in the range 1.05–1.06 μm in the cavity provided generation at the wavelengths $\lambda_3 = 1.3315$ and $\lambda_4 = 1.3370$ μm of the ⁴F_{3/2} → ⁴I_{13/2} channel. The accuracy of the photoelectric record of the lasing wavelength was ±0.0005 μm. The output power for the Gd₃Ga₅O₁₂:Nd³⁺ lasers emitting in the vicinity of 1.06 and 1.33 μm as a function of the pumping power is shown in Fig. 5. In a crystal with the concentration $C_{Nd} \approx 10\%$, lasing in both spectral ranges was also excited, which shows that one can use highly concentrated Gd₃Ga₅O₁₂:Nd³⁺ crystals to design minilasers. These high concentrations provide the com-

Cation distribution around distorted NdO₈ cubes within the second coordination sphere in Nd³⁺-doped gadolinium–gallium garnet

Type of center	<i>c</i> -positions (distorted cube)	<i>a</i> -positions (octahedron)	<i>d</i> -positions (tetrahedron)
1	4Gd	4Ga	6Ga
2	4Gd	3Ga + 1Gd	6Ga
3	3Gd + 1Nd	4Ga	6Ga

plete absorption of the pumping energy at a wavelength of the active element of about 2–3 mm.

Comparing the measured spectral and laser characteristics of the Nd³⁺-doped gadolinium–gallium garnet crystals grown from melt and from flux, we see that the latter have somewhat narrower (by 10–30%) absorption and luminescence lines (Figs. 2–4). In our opinion, the high structural disorder in crystals grown from melt is explained by the following: (1) The equilibrium concentration of point defects (vacancies and atoms in interstitial and unusual positions) is high at temperatures close to 1800°C and decreases only slightly during fast cooling upon completion of growth; (2) the presence in the melt of the component Ga₂O₃ that can be evaporated and dissociated with an increase in the temperature; and (3) the pulling rate is 1–2 mm/h, which is higher by several orders of magnitude than the rate of crystallization from flux. On the other hand, growth from flux proceeds at a temperature of about 1200°C in air, with the concentration of point defects being lower and the Ga₂O₃ component more stable. Finally, the partial filling of the octahedral positions in the gadolinium–gallium garnet structure with Gd³⁺ ions also gives rise to a certain structural disorder. (Similar

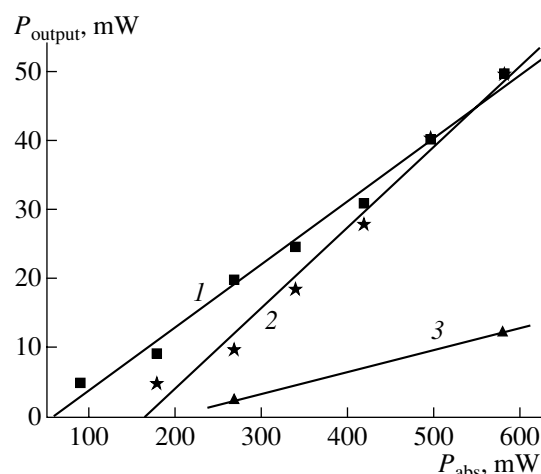


Fig. 5. The emission power (at two wavelengths) of a continuous-wave Gd₃Ga₅O₁₂:Nd³⁺ laser in the 1.06 μm range with activator concentrations (1) 3 and (2) 10 at. % and in the 1.33 μm range with activator concentration (3) 10 at. % as a function of the pumping power of a semiconductor laser ($\lambda_{pump} = 0.81$ μm).

phenomena were earlier observed when studying the crystals grown from melt in the mixed $\text{Nd}^{3+}:\text{Y}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ [14] and $\text{Nd}^{3+}:\text{Y}_3(\text{Y},\text{Ga})_2\text{Ga}_3\text{O}_{12}$ [15] systems.) However, the crystallization from melt does not allow the attainment of a high degree of gadolinium–gallium garnet matrix disorder because of the substantial divergence of the solidus and liquidus curves in the instances where the composition of the melt differs from the congruent one. Therefore, the crystallization from flux seems to be more advantageous because the range of existence of the $\text{Gd}_{3+x}\text{Ga}_{5-x}\text{O}_{12}$ solid solutions is also quite large at a temperature of 1200°C [10]. Thus, varying the $\text{Gd}_2\text{O}_3/\text{Ga}_2\text{O}_3$ ratio in the flux, it is possible to grow a disordered garnet of the composition up to $\text{Gd}_{3.3}\text{Ga}_{4.7}\text{O}_{12}$.

Thus, the concentration series of the $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Nd}^{3+}$ garnet crystals were grown from flux. It was shown that unlike crystals grown from melt, spectroscopically, these crystals can be considered as a medium with a single activation center. For the first time, continuous-wave lasing was excited in diode-pumped $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Nd}^{3+}$ crystals at wavelengths $\lambda_3 = 1.3315$ and $\lambda_4 = 1.3370$ μm of the ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$ channel and the simultaneous generation at two wavelengths $\lambda_1 = 1.0621$ and $\lambda_2 = 1.0600$ μm of the channel ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$. The power characteristics of lasing can be essentially improved by using an antireflection coating with optimum dimensions and the activator concentration or by optimizing the cavity. In the growth experiments, an interesting problem, along with the reduction in the optical inhomogeneity (growth striae and faceting) of the $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Nd}^{3+}$ crystals, is also the preparation of the $\text{Gd}_{3+x}\text{Ga}_{5-x}\text{O}_{12}:\text{Nd}^{3+}$ crystals ($x \geq 0.2$) with considerable structural disorder. The media whose absorption spectra have broadened lines provide better matching with the diode pumping whose wavelength can experience temperature drift.

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