

The reduction of Eu^{3+} to Eu^{2+} in air and luminescence properties of Eu^{2+} activated $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses

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Abstract

A valence change from Eu^{3+} to Eu^{2+} was observed in the europium ion-doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses prepared at high temperature in air. The fluorescence emission spectrum of the sample consists of a broad emission band ascribed to the $5\text{d}-4\text{f}$ transition of Eu^{2+} ion and sharp emission peaks assigned to the transitions of $^5\text{D}_0-^7\text{F}_J$ ($J=0, 1, 2, 3$, and 4) of Eu^{3+} ion, indicating that part of Eu^{3+} can be reduced into Eu^{2+} in the glass. A charge compensation model is proposed. The rigid tetrahedral network structure of glasses plays an important role in stability of Eu^{2+} . The fabrication conditions are also studied.

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1. Introduction

The luminescence properties of Eu^{2+} -activated materials have been investigated for a long time because divalent europium ions (Eu^{2+}) have been widely used as activators in many kinds of commercial phosphors [1–5]. Generally, the oxide Eu_2O_3 serves as the raw material, in which Eu^{3+} is then reduced in reducing atmospheres, such as H_2 , H_2/N_2 or CO , etc.

The reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}^{2+}$ prepared in air atmosphere had been reported by Tälle et al. decades ago [6], but no further study had been done since then. Our group has systemically studied the ‘abnormal’ reduction of $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$ ($\text{RE} = \text{Sm}, \text{Eu}, \text{Tm}, \text{Yb}$) in many oxide complexes synthesized in air at high temperature [5,7–11], and proposed that nonequivalence substitution of rare earth ions into matrix ions and the rigid three-dimensional network such as BO_4 tetrahedral are necessary for reduction of trivalent rare earth in air [5]. Thereafter, Peterson’ group [12] and Machida’ group [13,14] also showed

great interest in this phenomena. Up to now, the reduction phenomena of $\text{RE}^{3+} \rightarrow \text{RE}^{2+}$ in air have been observed in borates [5,7,8], phosphates [6], borophosphates [9], aluminates [10], silicates [11] and sulfates [15]. But few researches are concerned with this phenomenon in non-crystalline materials but polycrystalline powders.

In this paper, we report the europium ions-doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses prepared at high temperature in air condition, and find that part of Eu^{3+} can be reduced into Eu^{2+} in the glass at non-reducing atmosphere. We try to optimize processing of the glasses fabrication and to discuss the possible mechanism.

2. Experiment

The chemical compositions of the host glasses used is $(1.00 - x - y) \text{ZnO-xB}_2\text{O}_3\text{-yP}_2\text{O}_5$ (in mol%) and the concentration of Eu_2O_3 is 0–1.00 mol%. The initial raw materials are reagent-grade ZnO , B_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, Eu_2O_3 . Mixed batches were melted in Pt crucibles at 1473 K for 60–120 min under an ambient atmosphere condition. The melt were then poured on

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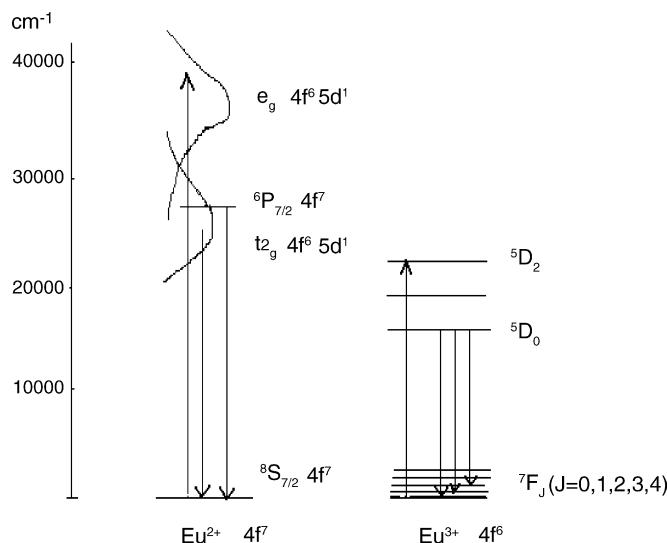


Fig. 1. Energy level scheme of europium ions (Eu²⁺ and Eu³⁺).

a stainless steel plate, annealed at 673 K for 6 h in an ambient air and cooled to room temperature naturally. The samples were cut, polished and subjected to the optical measurements.

Photoluminescence (PL) spectra were taken using a Hitachi F-4500 fluorescence spectrophotometer with a monochromator (resolution: 0.2 nm) and a 150 W Xe lamp.

All measurements were performed at room temperature.

3. Results and discussion

Luminescence properties of materials doped with europium ions have been systemically investigated in past decades [16,17]. Fig. 1 shows energy level of Eu²⁺ and Eu³⁺. The first excited 4f⁶5d configuration of Eu²⁺ usually lies close to the lowest excited 4f⁷ level of Eu²⁺ (⁶P_{7/2}). The transitions between the first excited 4f⁶5d configuration and 4f⁷ ground state (⁸S_{7/2}) are dipole allowed and give very intense emission. Meanwhile, the

emission spectra of f–d transition of Eu²⁺ ions are usually broad because of the large spatial extension of the 5d wave function and the lattice vibration of the surroundings [16,17]. The excited 5d level can be split into two degenerated levels by the ligand field, the energy difference between the two groups of degenerated 5d levels are highly affected by the state of chemical bonds between Eu²⁺ ions and the anions of the first coordinating sphere. So the emission wavelengths due to 5d–4f transition of Eu²⁺ ions are strongly influenced by the glasses matrixes. While the 4fⁿ valence electrons are shielded by the 5s²p⁶ electron cloud, the 4f levels of Eu³⁺ ions are hardly influenced by the ligand field, indicating that the sharp peaks due to the f–f transitions should be observed in the optical absorption and fluorescence spectra [16]. When the Eu²⁺ ions incorporated in oxide glass were excited by UV light, only a broad emission band due to the transition from 5d level to ground state of Eu²⁺ ions is observed. While, the sharp emission peak at 360 nm due to the f–f transition (⁶P_{7/2}–⁸S_{7/2}) of Eu²⁺ ions occurs when Eu²⁺ ions are located at weak crystal field and the 5d level is not splitted strongly. Generally, Eu³⁺ ions show a series of typical line emissions, locating in 570–750 nm, corresponding to their ⁵D₀–⁷F_J (J=0, 1, 2, 3, and 4) transitions [10]. In some special compounds with lower-energy phonons, Eu³⁺ ions give their emissions even from upper excitation states of ⁵D_J (J=1, 2, and 3). We could investigate what kinds of europium ions exist in these hosts based on the characters of their photoluminescence spectra.

3.1. Luminescence properties of the Eu₂O₃ doped ZnO–B₂O₃–P₂O₅ glasses

The excitation and emission spectra of Eu³⁺ are shown in Fig. 2. The excitation spectrum monitored at 613 nm consists of some sharp lines belonging to transitions within the 4f⁶ configuration of Eu³⁺ and a broad band from 200 to 270 nm with a maximum at about 232 nm due to the O^{2–}–Eu³⁺ charge–transfer (CT) transition [17]. Only sharp emission peaks at 577, 589,

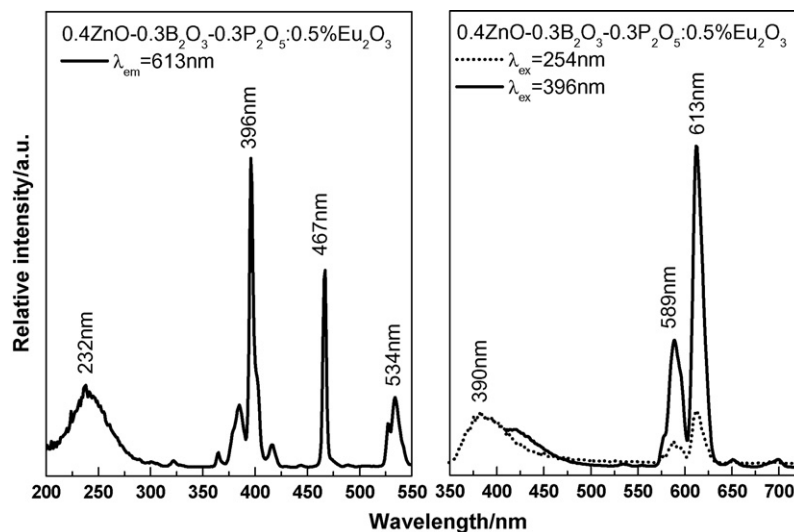


Fig. 2. The excitation and emission spectra of 0.5 mol% Eu₂O₃ doped ZnO–B₂O₃–P₂O₅ glasses prepared in air at 1473 K for a firing period of 60 min; excitation spectrum, $\lambda_{\text{ex}} = 396$ nm and $\lambda_{\text{ex}} = 254$ nm; emission spectrum, $\lambda_{\text{em}} = 613$ nm.

613, 652, and 697 nm corresponding to the $f-f$ transitions of $^5D_0-^7F_J$ ($J=0, 1, 2, 3$, and 4) transitions of Eu^{3+} were observed when the sample was excited at 396 nm. However, the emission excited at 254 nm consisted of not only the sharp emission peaks mentioned above but also a broad band from 350 to 500 nm peaking at 390 nm. The host samples of the same composite do not present any emission in the range of 350–750 nm when excited at 254 nm, so the observed emission peaking at 390 nm is correlated to the doped europium ions, which should be ascribed to the $5d-4f$ transition of Eu^{2+} ions [9,16]. We could therefore conclude that the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ occurred in Eu_2O_3 doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses prepared in air at high temperature though Eu^{3+} and Eu^{2+} ions coexist in the glasses, viz. the reduction was not conducted completely. In addition, the broad emission of Eu^{2+} overlaps the sharp excitation peaks origin from $f-f$ transition of Eu^{3+} . It is possible that energy transfer should occur from Eu^{2+} to Eu^{3+} .

Fig. 3 shows the excitation ($\lambda_{\text{ex}}=290$ nm) and emission ($\lambda_{\text{em}}=390$ nm) spectra of Eu_2O_3 ions-doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses prepared in air at high temperature. Being monitored at 390 nm, an intense and broad excitation band from 200 to 380 nm with a maximum at about 300 nm is observed, which ascribes to the $4f-5d$ transition of Eu^{2+} , and overlap the excitation band of the $\text{O}^{2+}\text{-Eu}^{3+}$ charge-transfer (CT) transition. Except the intense broad emission band from 350 to 500 nm peaking at 390 nm of Eu^{2+} , the weak and sharp emission peaks from 570 to 750 nm origin from $f-f$ transition of Eu^{3+} was observed when the sample was excited at the 290 nm, indicating that energy transfer from Eu^{2+} to Eu^{3+} occurs practically.

3.2. Dependence of the luminescence properties on the Eu_2O_3 concentration doped in $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses

We attempted to optimize processing of the glasses in terms of the luminescence of Eu^{2+} . Fig. 4 shows the emission spectra

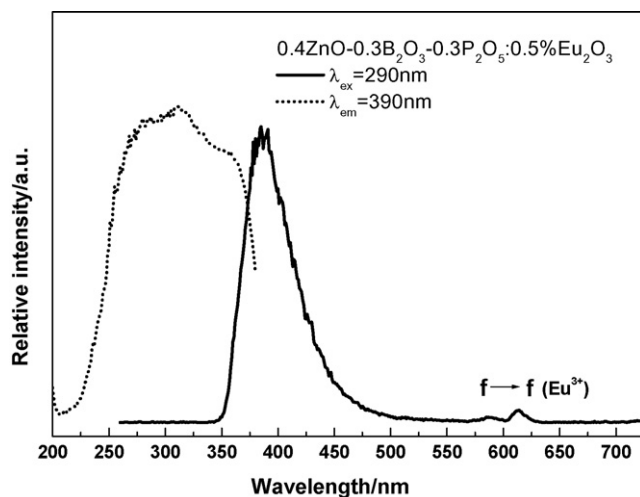


Fig. 3. The excitation and emission spectra of 0.5 mol% Eu_2O_3 doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses prepared in air at 1473 K for a firing period of 60 min; excitation spectrum, $\lambda_{\text{ex}}=290$ nm; emission spectrum, $\lambda_{\text{em}}=390$ nm.

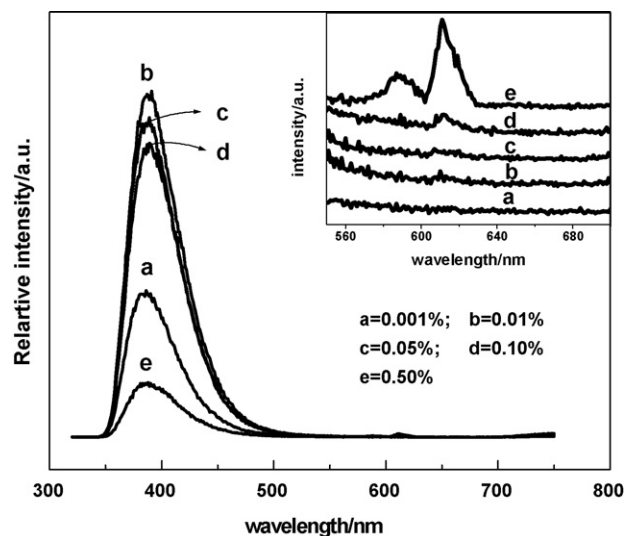


Fig. 4. Emission spectra of $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with different concentration of Eu_2O_3 prepared in air at 1473 K for a firing period of 60 min, $\lambda_{\text{ex}}=254$ nm.

of $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with different dopant concentration of Eu_2O_3 prepared in air at 1473 K. It is observed that the emission intensity of Eu^{2+} increases with the doped concentration of Eu_2O_3 increasing from 0.001 to 0.01 mol% and achieves the most intense at 0.01 mol% which presents bright violet-blue color and then decrease with increasing the doped concentration of Eu_2O_3 from 0.01 to 0.50 mol%. Whereas the emission intensity of Eu^{3+} increases continually with the doped concentration of Eu_2O_3 increasing from 0.001 to 0.50 mol% shown in insert of Fig. 4. It is possible that the concentration quenching of Eu^{2+} appears or the energy transfer happens from Eu^{2+} to Eu^{3+} when the concentration of Eu_2O_3 increases.

3.3. Effects of firing conditions on the luminescent properties

Fig. 5 shows the dependence of the emission intensity at 390 nm on the heating temperature. It is observed that the emission intensity of Eu^{2+} at 390 nm increases with increasing heating temperature from 1373 to 1523 K when the sample was prepared in air. The effects of the firing time on the reduction of Eu^{3+} into Eu^{2+} were also investigated. The results show that the emission intensity of the Eu^{2+} in the matrix presents no distinct variety as the firing time prolongs from 60 to 90 min. When the firing time prolongs further, for example 120 min, the transparent glasses become opal glasses and emit red emission of Eu^{3+} , indicating that a second phase appears in the glasses. The similar phenomenon of phase separation was also reported by Koudelka that two phases are produced when the melt of $0.50\text{ZnO-0.40B}_2\text{O}_3\text{-0.10P}_2\text{O}_5$ is cooled naturally in air, one phase is boron rich, and the other is phosphate rich, which were confirmed by Raman spectra [18]. So we hypothesize that the valence of Eu ion in borate glasses and phosphate glasses is 3.

Zinc phosphate glasses are mainly consisted of chains of $[\text{PO}_4]$ tetrahedral confirmed by Brow and his colleagues in

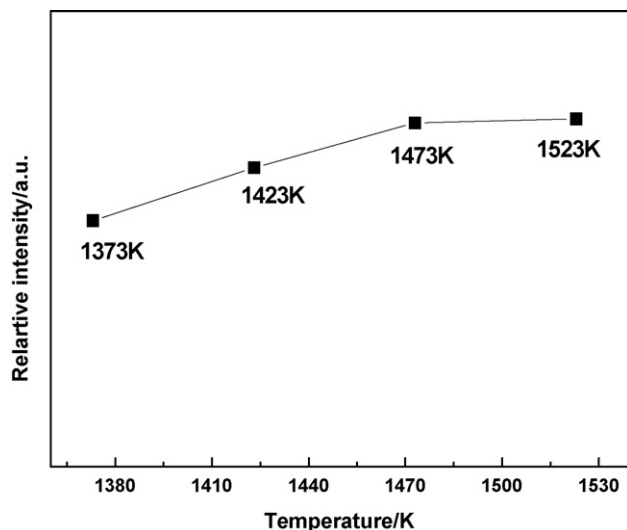


Fig. 5. The dependence of the emission intensity at 390 nm on the firing temperature.

their NMR study of the zinc phosphate glass system [19]. It is now well understood that the vitreous B_2O_3 like crystalline B_2O_3 is composed of $[BO_3]$ units which form plane boroxol rings. Bray and his colleagues have studied the structure of $M_2O-B_2O_3$ glasses ($M=Na, K$) [20] extensively and found that $[BO_4]$ unites besides $[BO_3]$ appear in the glasses as alkali metal oxides are introduced into the B_2O_3 network. Both $[BO_4]$ and $[BO_3]$ units connect each other in the borate glasses and form new network. But the glass composed mainly of crossed plane boroxol rings or boroxol chains. The structures of alkaline earth borate glasses appear to be governed by similar principles [21] so that the structures of zinc borate glasses should be composed mainly of plane boroxol rings or boroxol chains. In addition to the structural units that were found in binary borate or zinc phosphate glasses, a further type of structure unit, the borophosphate unit (BPO_4), should be taken into consideration when describing the structure of the borophosphate glasses [22,23]. The formation of borophosphate network (BPO_4) had been suggested by Yun and Bray [22] in their NMR study of the $K_2O-B_2O_3-P_2O_5$ glass system and by Scagliotti et al. [23] in their Raman study of the $Li_2O-B_2O_3-P_2O_5$ glass system. Borophosphate unit (BPO_4) consists of one $[BO_4]$ and one $[PO_4]$ unit, the two tetrahedral units are linked by a shared oxygen atom, both units having four bridging oxygens just as the basic constituents of a silica-like network. The excess of negative charge on the $[BO_4]$ unit is compensated by the excess of positive charge on the $[PO_4]$ unit. Therefore we could consider that BPO_4 units were induced when B_2O_3 is added to zinc phosphate glasses, moreover the $[BO_4]$ and $[PO_4]$ tetrahedral directly connected each other similar to $[SiO_4]$ tetrahedral units in silicate glasses and form three-dimensional network [22,23]. So we suggest that $ZnO-B_2O_3-P_2O_5$ glasses consisted mainly of the three-dimensional network, whereas one separated phase rich in boron composed mainly of plane or chains network and another separated phase with higher phosphor oxide composed mainly of chains. It indicates that the three-dimensional rigid tetrahedral network structure of homogeneous

$ZnO-B_2O_3-P_2O_5$ glasses plays an important role in stability of Eu^{2+} comparing the plane or chain structure of boron rich phase and chain structure of phosphor rich phase in phase-separated $ZnO-B_2O_3-P_2O_5$ glasses. To confirm this hypothesis, three kinds of glasses, $0.50ZnO-0.20B_2O_3-0.30P_2O_5$ (a), $0.50ZnO-0.50B_2O_3$ (b), $0.50ZnO-0.50P_2O_5$ (c) (in mol%), respectively, with 0.10 mol% Eu_2O_3 were prepared. Sample a emitted predominately violet-blue light. Samples b and c emitted red light mainly as shown in Fig. 6. It could be seen from Fig. 6 that Eu ions in borophosphate glass exist mainly in Eu^{2+} , while Eu ions in borate and phosphate glass exist mainly in Eu^{3+} .

3.4. Study on the mechanism of $Eu^{3+} \rightarrow Eu^{2+}$ reduction

We are trying to explain the reduction phenomenon of $Eu^{3+} \rightarrow Eu^{2+}$ prepared in air condition with a charge compensation model as follow. When trivalent Eu^{3+} ions were doped into $ZnO-B_2O_3-P_2O_5$ glasses, they would replace the Zn^{2+} ions of these glasses. In order to keep the charge balance, two Eu^{3+} ions should be needed to substitute for three Zn^{2+} ions (the total charge of two trivalent Eu^{3+} ions is equal to that of the three Zn^{2+} ions). Hence, one vacancy defect represented as V''_{Zn} with two negative charges and two positive defects of Eu_{Zn}^{\bullet} would be created by each substitution of every two Eu^{3+} ions in the $ZnO-B_2O_3-P_2O_5$ glasses. The vacancy of V''_{Zn} then acted as a donor of electrons, while the two Eu_{Zn}^{\bullet} defects became acceptors of the electrons. Consequently, by thermal stimulation, the elections in the vacancy defects of V''_{Zn} would be transferred to Eu_{Zn}^{\bullet} sites and reduced Eu^{3+} to Eu^{2+} form. The whole progress could be presented in the following equation:

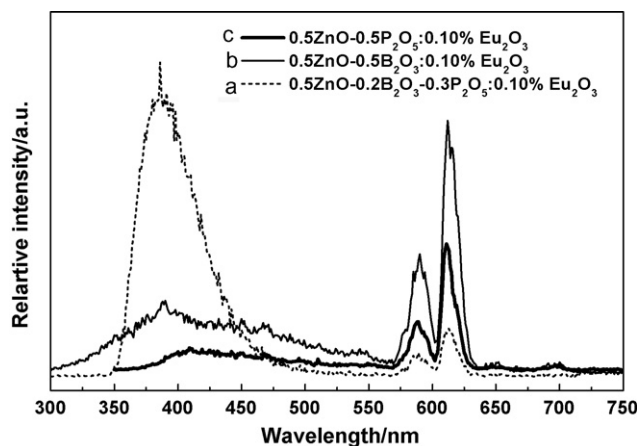


Fig. 6. The dependence of the emission properties of Eu on the composition and structure of glass matrix. (a) 0.10 mol% Eu_2O_3 doped $0.50ZnO-0.20B_2O_3-0.30P_2O_5$ glasses; (b) 0.10 mol% Eu_2O_3 doped $0.50ZnO-0.50B_2O_3$ glasses; (c) 0.10 mol% Eu_2O_3 doped $0.50ZnO-0.50P_2O_5$ glasses.

By adding Eqs. (1)–(3):



The Eu^{2+} ions in a three-dimensional (3D) network such as corner sharing of $[\text{BO}_4]$ and $[\text{PO}_4]$ in borophosphate glasses are less likely to be attacked by oxygen. While the plane rings or chains structure make the structure less stiff and the Eu^{2+} ions are loosely surrounded by the anion groups. Therefore, in this case the Eu^{2+} ions in zinc borate and zinc phosphate glasses are easily attacked by oxygen in the air and transformed into trivalent state.

4. Conclusion

We prepared the europium ion-doped $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses and found that some of Eu ions exist in the divalent state without reducing treatment. The influence of the composition and structure of the glasses on the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in air had been investigated. Two reasons, we think, are responsible for the reduction of Eu^{3+} to Eu^{2+} in $\text{ZnO-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses. Firstly, nonequivalent substitution results in reduction of Eu^{3+} . Secondly, the rigid three-dimensional tetrahedron network structure prevents Eu^{2+} ions from being re-oxidized in air at high temperature.

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