Concerted Rattling in CsAg₃Te₃ Leading to Ultralow Thermal Conductivity and High Thermoelectric Performance

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Abstract: Thermoelectric (TE) materials convert heat energy directly into electricity, and introducing new materials with high conversion efficiency is a great challenge because of the rare combination of interdependent electrical and thermal transport properties required to be present in a single material. The TE efficiency is defined by the figure of merit \( ZT = (S^2\alpha/\kappa) T/\kappa \), where \( S \) is the Seebeck coefficient, \( \alpha \) is the electrical conductivity, \( \kappa \) is the total thermal conductivity, and \( T \) is the absolute temperature. A new p-type thermoelectric material, CsAg₃Te₃, is presented that exhibits ultralow lattice thermal conductivity (ca. 0.18 Wm⁻¹K⁻¹) and a high figure of merit of about 1.5 at 727 K. The lattice thermal conductivity is the lowest among state-of-the-art thermoelectrics; it is attributed to a previously unrecognized phonon scattering mechanism that involves the concerted rattling of a group of Ag ions that strongly raises the Grüneisen parameters of the material.

Thermoelectrics (TE) are important functional materials that are able to directly convert thermal energy to electricity and can enable power generation from many heat sources including waste heat.[1,2] The efficiency of thermoelectric materials (ZT) can be enhanced by various strategies of increasing the power factor \( (PF = S^2\alpha) \) and/or reducing the thermal conductivity, such as band engineering,[3] resonant states,[4] energy barrier filtering,[5] and all-scale nanostructuring.[6] Another strategy is to explore materials possessing intrinsically low thermal conductivities.[7–11] Recent studies reveal that highly disordered or layered compounds exhibit low thermal conductivities and high ZT values, such as Cu₃S, Cu₃Se, AgSbSe₂, and tetrahedrites, with thermal conductivities ranging from 0.35 and 0.60 Wm⁻¹K⁻¹.[12–15] Two examples that do not exhibit structural disorder but still possess very low thermal conductivities are the highly anisotropic In₃Se₅[9] and SnSe.[16,17] The former shows ZT values of 1.4 along the bc plane with very low thermal conductivity (0.70 Wm⁻¹K⁻¹) at 700 K,[18] and the latter ZT values of 2.6, or 2.3 along the b or c axis, respectively, at 973 K with ultra-low thermal conductivity (ca. 0.45 Wm⁻¹K⁻¹ at 973 K).[16,17] Therefore, materials with intrinsically very low thermal conductivity are highly desirable in the search for high TE performance. Herein we present CsAg₃Te₃, a new exceptional TE material with an even lower thermal conductivity than SnSe. This thermal behavior is achieved by a new phonon scattering mechanism that we call concerted rattling, which enables CsAg₃Te₃ to reach a ZT of 1.5 at 727 K without any extrinsic doping.

The synthesis and single crystal structure of CsAg₃Te₃ was first reported in 1995 by Li et al.[18] In this work, we study the thermoelectric properties of this compound and, surprisingly, find that CsAg₃Te₃ exhibits intrinsically ultralow lattice thermal conductivity (0.18–0.14 Wm⁻¹K⁻¹). We explain this on the basis of the special phonon band structure that involves peculiar low frequency rattling modes in the Ag sublattice. These Ag atoms give rise to very large Grüneisen parameters, and hence, anharmonic vibrations. As a result, CsAg₃Te₃ exhibits a figure of merit of about 1.5 at 727 K (Figure 1A), among the highest for any single-phase compound, distinguishing itself as a new promising mid-temperature TE material.

Pure polycrystalline CsAg₃Te₃ samples were prepared by melting Ag, Te elements and Cs₂Te₃ with stoichiometric ratio in a fused silica tube at 1073 K for 2 h and then cooled to room temperature. The ingot was ground into fine powders, and then densified by spark plasma sintering method (SPS-211LX, Fuji Electronic Industrial Co. Ltd.) at 723 K under a pressure of 50 MPa for 10 min. The obtained pellets had mass densities of >97% of the theoretical value (7.117 gcm⁻³) and were cut with a diamond blade saw to suitable sized specimens for measurements (Figure 1A, inset).

Because of the remarkably low lattice thermal conductivity, we wanted to take a more detailed look at its crystal structure and particularly the atomic displacement parameters (ADPs), seeking useful insights. We collected accurate single crystal X-ray diffraction data for CsAg₃Te₃ at room temperature in the Ewald sphere using the SuperNova crystallographic X-ray diffractometer at beamline 7.0.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory. The model was refined using the SHELXL-2014 program. The single crystal X-ray diffraction data for CsAg₃Te₃ are presented that exhibits ultralow lattice thermal conductivity (ca. 0.18 Wm⁻¹K⁻¹) and a high figure of merit of about 1.5 at 727 K. The lattice thermal conductivity is the lowest among state-of-the-art thermoelectrics; it is attributed to a previously unrecognized phonon scattering mechanism that involves the concerted rattling of a group of Ag ions that strongly raises the Grüneisen parameters of the material.

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No phase transitions were observed in this temperature range. \( \text{CsAg}_5\text{Te}_3 \) crystallizes in the tetragonal space group \( P4_{2}2_{1}/nm \) with \( a = b = 14.645(2) \) Å, \( c = 4.5907(9) \) Å (at RT), and \( a = b = 14.567(2) \) Å, \( c = 4.5501(9) \) Å (at 100 K; Supporting Information, Table S1). The phase purity for both as-synthesized and spark plasma sintered (SPSed) samples were confirmed by powder X-ray diffraction data (Supporting Information, Figure S1). Several peaks in the difference curve indicate some deviation of the diffraction intensity, which may come from the crystallite orientation preference. According to the subsequent property measurement results, this seems to show no obvious effect on the TE properties. Field emission scanning electron microscopy (FESEM) via back-scattered electron (BSE) imaging shows clean surfaces with no visible pores and the BSE image confirms uniformity with no contrast difference, which confirms the pure phases (Supporting Information, Figure S2). The special structural feature of \( \text{CsAg}_5\text{Te}_3 \) is the open tunnels, Figure 1B, constructed by infinite parallel \( \text{AgTe}_4 \)-chains, Figure 1C. These \( \text{AgTe}_4 \) chains create two types of tunnels within the Ag-Te covalent network that run parallel to the \( c \) axis: the large-size-tunnels located at the center (0.5, 0.5, 0.5) and the origin (0, 0, 0) of the unit cell, and the small-size tunnels at each side of the unit cell. The Ag1, Ag3 atoms adopt a common tetrahedral coordination with Te atoms and with Ag-Te bonds of 2.743–3.058 Å (Figure 1C, top). In contrast, the Ag2 atoms adopt the less common coplanar triangle coordination geometry with Ag-Te bonds of 2.789–2.886 Å. Such Ag2Te triangles form the \([\text{AgTe}_4^–] \) column by sharing vertexes (Figure 1C, bottom). Each of the \([\text{AgTe}_4^–] \) columns fills in the small-size-tunnel (Figure 1D) while the large tunnels in the structure accommodate the Cs atoms (Figure 1D). Notably, the Ag atoms have large anisotropic thermal parameters, the largest among all the atoms in the unit cell (Supporting Information, Tables S2,S3), which are implicated in the strong phonon scattering of the material. The optical diffuse reflectance spectroscopy reveals a direct band gap of 0.67 eV (Figure 1E).

\( \text{CsAg}_5\text{Te}_3 \) is a semiconductor with electrical conductivity \( \sigma \) gradually increasing from about 0.17 Scm\(^{-1} \) at RT to about 49 Scm\(^{-1} \) at 727 K (Figure 2A). Above 730 K, a phase transition occurs and \( \sigma \) drops sharply (Supporting Information, Figure S3). The Hall measurements indicate holes are the dominant charge carriers with a carrier concentration...
is not really $m_s$ and Hall mobility ($\mu_H$) of about $1 \times 10^{17}$ cm$^{-3}$ and 14 cm$^2$V$^{-1}$s$^{-1}$ at 300 K, respectively (Figure 2E,F). Such a carrier concentration is 2–3 orders lower than state-of-the-art thermoelectrics (10$^{14}$–10$^{17}$ cm$^{-3}$)\cite{[19]} The Seebeck coefficients of CsAg$_2$Te$_3$ are shown as a function of temperature in Figure 2B. The material exhibits positive Seebeck coefficients from 600 to 300 µV/K$^{-1}$, in agreement with the p-type behavior of the Hall data.

As shown in Figure 2C, CsAg$_2$Te$_3$ exhibits moderate power factors ($PF = S^2\sigma$) with the maximum value of 3.9 µW cm$^{-1}$K$^{-2}$ at 727 K. This value is comparable to those of other thermoelectrics that possess intrinsically low total thermal conductivities (for example, 3.9, 5.7, 6.7, 10.1, 8.2, and 12 µW cm$^{-1}$K$^{-2}$ of Ag$_2$TiTe$_2$,\cite{[20]} Yb$_4$MnSb$_6$,\cite{[21]} Tl$_2$BiTe$_2$\cite{[22]} b axis of SnSe,\cite{[19]} α-Cu$_2$Se,\cite{[15]} and β-Cu$_2$Se\cite{[22]} respectively).

The key and remarkable feature of CsAg$_2$Te$_3$ is its exceedingly low total thermal conductivity ($\kappa_{\text{tot}}$), which ranges from 0.18 W m$^{-1}$K$^{-1}$ at 296 K to 0.20 W m$^{-1}$K$^{-1}$ at 727 K (Figure 2D), agreeing well with the values of $\kappa_{\text{iso}}$ obtained using a longitudinal steady-state technique at low temperature (Supporting Information, Figure S4). According to $\kappa_{\text{iso}} = \kappa_{\text{dir}}$, the lattice thermal conductivity ($\kappa_{\text{iso}}$) can be obtained by subtracting $\kappa_{\text{dir}}$ from the $\kappa_{\text{lab}}$, and the Lorenz number ($L$) is set as $1.5 \times 10^{-8}$ V$^2$K$^{-2}$\cite{[14]} The $\kappa_{\text{dir}}/\kappa_{\text{lab}}$ ratio ranging from 1.0 to 0.73 from 300–730 K indicates that the total thermal conductivity is dominated by the phonon transport. The lattice thermal conductivity slightly decreases with increasing temperature, at 727 K reaching about 0.14 W m$^{-1}$K$^{-1}$. This is an extraordinarily low value that is even lower than those of all high performance thermoelectrics (for example, 0.5 W m$^{-1}$K$^{-1}$ in PbTe alloy nanostructured with SrTe and Na\cite{[9]}). Of course, these $\kappa_{\text{lab}}$ values are measured on polycrystalline samples, which should be lower than the corresponding values on single crystals because the grain boundaries effects should decrease the thermal conductivity.

It is interesting that the crystal structure of the title compound is anisotropic, but the TE properties are similar in different directions (the perpendicular/parallel direction of SPS pressure). Materials with anisotropic structures may not always display anisotropic TE properties. For example, when applying low SPS pressure at a relatively low SPS temperature, the anisotropy in the layered Bi$_2$Te$_3$ is not really significant\cite{[23]}

Density functional theory (DFT) was used to calculate the electronic structure and phonon properties of CsAg$_2$Te$_3$. The DFT calculated structural parameters of CsAg$_2$Te$_3$ are $a = b = 14.844$ Å, and $c = 4.639$ Å, and agree well with the experimental measurements. The DFT calculated direct band gap is 0.53 eV, which is smaller than, but comparable to, the experimental value of 0.67 eV. The band structure reveals several salient features of CsAg$_2$Te$_3$, such as flattened valence bands and degenerate band extrema at Γ points. The Cs atoms almost make no contribution around $E_F$ and act as electron donors to stabilize the structure (Figure 3).

The band effective mass $m^*$ was obtained from the electronic structure calculations (Figure 3), using the single-band-approximation and the curvature of the conduction band minimum (CBM) or the valence band maximum (VBM). The total density-of-states effective mass is as large as about 1.84 $m_e$ at the VBM, which when combined with its low hole concentration, yields a very large Seebeck coefficient. The CBM at the Γ point has a much smaller effective mass of about 0.41 $m_e$ (Supporting Information, Table S4). It is interesting to consider the origins of the ultralow lattice thermal conductivity in CsAg$_2$Te$_3$. It is only around half of the thermal conductivity of so-called phonon-limited electron-crystal (PLEC) materials α-Cu$_2$S,\cite{[13]} and β-Cu$_2$Se\cite{[12]}. Recently, theoretical studies on the thermal transport of α-Ag$_2$Te suggested that the thermal conductivity enabled by the Te–Te network interactions is more than 85% of the total thermal conductivity, whereas that associated with the Ag–Ag network is only a minor contribution.\cite{[24]} As we will show below, the Te–Te network interactions play a minor role in defining the thermal conductivity of CsAg$_2$Te$_3$. Instead we find that more important is the behavior of the Ag sublattice and the concerted rattling motions the Ag atoms undergo.

We can estimate the Debye temperature from the ADPs from the following function:\cite{[25,26]}

$$\frac{\Delta(U_{\text{tot}})}{\Delta T} = \frac{3\hbar^2}{m_{\text{lab}}}$$

where $U_{\text{tot}}$ is the ADP, $\hbar = h/2\pi$ is the reduced Planck constant, $(m_{\text{lab}})$ is the average atomic weight, $k_B$ is the Boltzmann constant, $\Theta_D$ is the Debye temperature, and $T$ is the absolute temperature. The $U_{\text{tot}}$ value was determined from the single crystal (Supporting Information, Table S2). The average $U_{\text{tot}}$ value of CsAg$_2$Te$_3$ is calculated to be 0.0306 Å$^2$ for room temperature and 0.0129 Å$^2$ for 100 K, and the average atomic weight mass is 117 amu. These values give a Debye temperature of 118 K for CsAg$_2$Te$_3$.\cite{[11,16]}
The Debye temperature was also estimated from the $C_p$ data, which were measured from 2–300 K (Supporting Information, Figure S5). At low temperatures, the heat capacity $C_p$ can be expressed as:

$$C_p = \alpha T + \beta T^3$$

Here the two terms represent the electron and lattice contributions, respectively. From low temperature, $\alpha$ and $\beta$ could be obtained by plotting $C_p/T$ as a function of $T^2$. The intercept value is $\alpha$ and the slope value is $\beta$, and, for CsAg$_5$Te$_3$, these values are 0.01505 J mol$^{-1}$ K$^{-2}$ and 0.01254 J mol$^{-1}$ K$^{-4}$ respectively (Supporting Information, Figure S5). Then the Debye temperature $\Theta_D$ could be calculated through the formula:

$$\Theta_D = \left(\frac{12\pi^2 N R}{5p}\right)^{1/3}$$

where $N$ and $R$ denote the number of atoms in the compound formula and the gas constant. The calculated $\Theta_D = 111.7$ K, which is close to the result estimated from ADP.

To quantitatively confirm the above analysis and explore the origin of this low thermal conductivity at the atomic level, we utilize DFT phonon calculations and the Slack model\cite{27} as introduced in the calculations section to more quantitatively evaluate the lattice thermal conductivity of CsAg$_5$Te$_3$. It is known that the Grüneisen parameters, which characterize the relationship between phonon frequency and crystal volume change, are useful to estimate the lattice anharmonicity and thus helpful to interpret the physical nature of the lattice thermal conductivity behavior.\cite{16,28} Thus the phonon and Grüneisen dispersions were calculated using first-principles DFT phonon calculations within the quasi-harmonic approximation. The CsAg$_5$Te$_3$ phonon dispersions are calculated using a 144 atom supercell at two volumes, the equilibrium volume $V_0$ and an isotropically expanded volume 1.015 $V_0$ (Supporting Information, Figure S6).

The phonon dispersions and Grüneisen dispersions are plotted in Figure 4A,B. To quantitatively evaluate the anharmonicity, we plot the dispersion of the Grüneisen parameters of acoustic modes in CsAg$_5$Te$_3$ (Figure 4B), and find that they are all very large. The average Grüneisen parameter (\(\bar{\gamma}\)) of each acoustic dispersion are, respectively \(\bar{\gamma}_x = 3.9\), \(\bar{\gamma}_y = 4.8\) (Supporting Information, Table S5). These values are even larger than the average Grüneisen parameter of SnSe \(\bar{\gamma} = 4.1\), a compound which has an ultralow lattice thermal conductivity (ca. 0.64 W m$^{-1}$ K$^{-1}$ at 300 K).\cite{29} On the basis of the Slack model, the calculated lattice thermal conductivities ($\kappa_L$) are shown in Figure 4C. The calculated values of 0.034–0.013 W m$^{-1}$ K$^{-1}$ in the temperature range of 300–800 K are close of our experimental values of about 0.2 W m$^{-1}$ K$^{-1}$. Besides the rattling model and large Grüneisen parameters, the complex crystal structure of the materials and its large number of atoms (36 per unit cell), also contributes to the low lattice thermal conductivity on the basis of the Slack model.\cite{28}

The ultralow lattice thermal conductivity of CsAg$_5$Te$_3$ can be attributed to the very strong anharmonicity indicated by the large Grüneisen parameters. Along with the Grüneisen parameters, however, it is insightful to examine the low frequency vibration modes and the specific atoms contributing to them to further understand the physical origin of the ultralow thermal conductivity. The calculated phonon dispersion results show that there are some very low frequency modes at $\Gamma$ and $Z$ at about 14.6 and 20.2 cm$^{-1}$ that are rattling modes. We call them rattling modes because: 1) there are three rattling signatures of anticrossing points\cite{25,29} between the rattling and longitudinal acoustic modes along $\Gamma$-$X$, $\Gamma$-$M$, and $\Gamma$-$Z$, as indicated by red arrows in Figure 4A; and 2) the four Ag$_3$ atoms at the 4g site vibrate with much larger amplitudes than all other cage atoms of Cs, Te, Ag$_1$, and Ag$_2$. Note that the Ag$_3$ peak has contributions from 4 Ag atoms from the Ag$_4$g site and the Ag$_2$ peak originates from 8 Ag atoms from the 8i(a) site. As shown in the Supporting Information, Figure S8 and Table S2, the largest ADP at room temperature for Ag$_3$ is about 62% larger than Cs and 110% larger than Te. The largest ADP of Ag in CsAg$_5$Te$_3$ is regarded as an evidence of rattling modes, as in the case of La in La$_5$Te$_3$Co$_2$Se$_6$.[29] Owing to the much larger bond distances around the Ag$_3$ atoms than Ag$_1$ and Ag$_2$ sites, we see that the Ag$_3$ atoms play a key role in the proposed rattling vibrations. Furthermore, the homogeneity of the sample was assessed by averaging the compositions of 10 different grains of the SPSed sample and taking the average using an EPMA (Supporting Information, Table S6). The result (namely, Cs$_{29.0(2)}$Ag$_{50.5(3)}$Te$_{20.5(3)}$) is in agreement with the starting composition, to a certain extent, it also shows that Ag$_3$ does not in static disorder. Different from traditional rattling vibration modes, where a lone rattler atom has large oscillations (vibrations) in an oversized cage forming localized Einstein modes,\cite{28} the rattling modes in

![Figure 4](image-url)
CsAg₃Te₃ involve part or all of the Ag₃ sublattice atoms oscillating in phase in a mode we call concerted rattling.

Four representative concerted rattling modes corresponding to four frequencies labeled with circles in Figure 4A are shown as movies in Supporting Information (Figures S9–S12). As can be seen from the movies, for example, for the rattling mode at Γ at 14.6 cm⁻¹, the four Ag₃ atoms can be divided into two groups with opposite vibrations of two Ag atoms in each group. Besides the rattling modes at Γ and Z, a mode at the anticrossing point along Γ-X in the LA branch (blue line) also exhibits rattling characteristics, which can be regarded as a mixed mode between a mode at Γ and a mode at X. To quantitatively confirm the strong Ag₃ contributions to the low frequency vibrations, we also plotted the projected phonon density of states in Figure 4D. As can be seen the line defined by the red squares the Ag₃ atoms indeed exhibit a clear peak around 20 cm⁻¹, which is much higher than the other atoms of Cs, Te, Ag₁, and even Ag₂. The above analysis suggests the concerted rattling mode from Ag₃ site and the strong lattice anharmonicity play a very important role in suppressing the lattice thermal conductivity of CsAg₃Te₃.

The special electronic environment of Ag ⁴g atoms induces a very strong anharmonicity, which is expressed as big Grüneisen parameters and also seems to create a rattling mode environment. The rattling modes decrease the phonon group velocity around multiple anticrossing points and reduce the phonon lifetimes due to the Umklapp process, thereby strongly reducing the mean free path.[31,33]

To conclude, CsAg₃Te₃ exhibits the lowest lattice thermal conductivity among state-of-the-art thermoelectric materials and reaches a figure of merit of about 1.5 at 727 K, which is among the highest for any single phase bulk material, distinguishing itself as a new promising mid-temperature TE material. CsAg₃Te₃, which is a ternary compound, is even more effective in inhibiting heat flow through its crystalline structure than the binary PLEC materials Ag₉Q and Cu₅Q (Q = S, Se, Te) and its low thermal conductivity appears to be different in origin from the so-called Cu/Ag sublattice melting. Instead, a new mechanism producing ultra-low lattice thermal conductivity appears to be operating in CsAg₃Te₃ that is associated with the concerted rattling of a group of Ag atoms in the structure. Based on this new insight we anticipate that other materials exist exhibiting similar modes of vibration and exceedingly low thermal conductivities.

**Experimental Section**

Polycrystalline CsAg₃Te₃ samples were prepared by melting the elements Ag (shot, 99.999 %, Alfa Aesar), and Te (shot, 99.9999 %, Alfa Aesar), and Cs₂Te₃ that was prepared by reacting stoichiometric amounts of the elements in liquid ammonia in a fused silica tube at 1,073 K for 2 h and then cooled to room temperature. Single crystals were obtained. The obtained ingot was ground into fine powders using agate mortar to reduce the grains to less than 4 μm in diameter. The powders were then put inside a 12.7 mm diameter graphite die and densified by spark plasma sintering (SPS, SPS-211XL, Fuji Electronic Industrial Co., Ltd.) at 723 K for 10 min under an axial compressive stress of 50 MPa in vacuum. Highly dense disk-shaped pellets with dimensions of 12.7 mm diameter and ca. 12 mm thickness were obtained. The obtained pellets had relative densities larger than 97 % of the theoretical value (7.117 g cm⁻³). The powder XRD patterns were taken at room temperature on a Rigaku DMAX 2500 powder X-ray diffractometer by using Cu Kα radiation (λ = 1.5418 Å) and data were analyzed using a profile fitting by a least-squares method employing the computer program GSAS implemented with EXPGUI.[39] Scanning electron microscopy (SEM) images and backscattering electron (BSE) detector modes using a field emission scanning electron microscope (FE-SEM, JSM6700-F, Japan). The chemical composition of the samples was determined using an electron probe micro-analyzer (EPMA-1600, Japan). Temperature dependent powder XRD patterns were recorded between 300 and 723 K on a Shimadzu XRD-7000. The optical diffuse reflectance spectrum of powdered sample was measured at room temperature using a PerkinElmer Lambda 950 UV/Vis spectrophotometer equipped with an integrating sphere attachment and BaSO₄ as a reference. The absorption spectrum was calculated from the reflection spectrum via the Kubelka-Munk function: aS = (1 − R)²/2R, in which a was the absorption coefficient, S was the scattering coefficient, and R was the reflectance.[39] DTA experiments were performed on a computer-controlled Shimadzu DTA-50 thermal analyzer. The electrical resistivity and Seebeck coefficient were measured simultaneously in a low pressure helium atmosphere using a ULVAC-RIKO ZEM-3 instrument system. The thermal diffusivity (D) was measured at 296–773 K by using the laser flash diffusivity method in a commercial Netzsch LFA-457 instrument and the heat capacity (C) was obtained using a NETZSCH DTA 404PC. The total thermal conductivity was calculated using the formula \( \kappa = D \times C \times d \), where \( d \) was the sample density, which was determined using the dimensions and mass of the sample and then reconfirmed by measurements using a gas pycnometer (Micromeritics AccuPyc 1340). Low temperature thermal conductivity measurements were carried out over the temperature range of 5–300 K using a longitudinal steady-state technique in a homemade cryostat (for details, see the Supporting Information). The electrical and thermal properties were measured from different parts on the same SPSed pellet with high homogeneity (Figure S2). No significant anisotropy was observed parallel or perpendicular to the sintering pressure directions (Figure 1). The Hall coefficient was measured on a K2500-5RSLP Variable Temperature Hall Measurement System under a magnetic field (up to ±1 T) perpendicular to the sample surface.

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