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# Preparation and Characterization of $BaMnO_3$ and $SrMnO_3$ Polytypes

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$BaMnO_3$ was found to have a two-layer hexagonal structure ($a = 5.695$ Å, $c = 4.812$ Å) at normal pressure and a nine-layer structure ($a = 5.662$ Å, $c = 20.92$ Å) at high pressures. Four-layer $BaMnO_3$ prepared at normal pressure is shown to be oxygen deficient; however, $BaMnO_3$ (4H) is very close to ideal stoichiometry when prepared at 90 kbars and 1200°C. $SrMnO_3$ has the four-layer structure at normal pressure ($a = 5.449$ Å, $c = 9.080$ Å) and the six-layer structure ($a = 5.448$ Å, $c = 13.30$ Å) at higher pressures. Magnetic susceptibility data indicated antiferromagnetic behavior for all the $BaMnO_3$ and $SrMnO_3$ polytypes; however, none of these phases exhibited well defined Néel temperatures. Electrical resistivity data indicated semiconducting behavior in all cases.

## Introduction

The structure of all $BaM^{4+}O_3$ compounds, where M is a transition metal, may be regarded as being made up of close packed $BaO_3^{4-}$ layers with $M^{4+}$ cations between the layers filling all octahedral positions which are bounded by anions only. If the $BaO_3^{4-}$ layers are cubic close packed, the perovskite structure results; all hexagonal packing gives the $CsNiF_3$ structure. Packing sequences which are a mixture of cubic and hexagonal packing also often occur (*1*).

Frequently more than one polytype of a particular $BaMO_3$ compound has been reported. In this paper these polytypes will be designated by a number, the number of $BaO_3^{4-}$ layers along the *c* direction of the hexagonal cell, and a letter indicating the symmetry. Thus, two-layer $BaMnO_3$, or $BaMnO_3$ (2H), means that the repeat unit along the hexagonal *c* axis involves only two $BaO_3^{4-}$ layers and that this particular stacking sequence leads to hexagonal symmetry.

Compounds of the type $BaMO_3$ have been reported where the transition metal is Ti, Cr, Mn, Fe, Co, Ni, Zr, Mo, Ru, Hf, or Ir. The perovskite structure is found only when the transition metal is Ti, Zr, Hf, or Mo. Pure hexagonal packing has been reported where M is Mn, Co, or Ni. However, $BaCoO_3$ and $BaNiO_3$ have apparently only been prepared as oxygen deficient phases. Intermediate packing of layers between all cubic or all hexagonal occurs in other cases. The perovskite structure is generally found for $SrMO_3$ compounds; however, $SrMnO_3$ is an interesting exception.

## Experimental

The reactants were reagent grade or better. $BaMnO_3$ was prepared by the decomposition of $BaMnO_4$ in air according to Hardy (*2*), by the reaction of $BaO/MnO_2$ mixture, or by the hydrothermal reaction of $Ba(OH)_2 \cdot 8H_2O$ with $MnO_2$. $SrMnO_3$ was prepared by the reaction of an $SrO/MnO_2$ mixture or by the hydrothermal reaction of $Sr(OH)_2$ and $MnO_2$. The hydrothermal decompositions of the Sr and Ba permanganates also yielded the $BaMnO_3$ and $SrMnO_3$ products: $BaMn_2O_6 + Ba(OH)_2$ or $SrMn_2O_6 + Sr(OH)_2$, respectively.

Hydrothermal reactions were conducted in collapsible gold ampoules, generally at 700° and 3000 atm for about eight hours. High-pressure experiments at 65 kbars were performed in a tetrahedral anvil press previously described (*3*).

X-ray powder patterns were obtained on all products at 25°C with a Hägg-Guinier camera using strictly monochromatic $CuK\alpha_1$ radiation and an internal standard of KCl ($a = 6.2931$ Å). The cell dimensions were refined by least squares. Single crystal X-ray photographs were taken with precession cameras when suitable crystals were found. Quantitative intensity data were obtained for $BaMnO_3$ (9R) with a Norelco diffractometer using $CuK\alpha$ radiation and an LiF monochromator.

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TABLE I

CRYSTALLOGRAPHIC AND ANALYTICAL DATA[a]

| Compound | a, Å | c, Å | % Å | % Mn | % O |
|---|---|---|---|---|---|
| $SrMnO_3$ (4H) | 5.449 | 9.080 | 45.0(46.0) | 28.5(28.8) | 25.6(25.2) |
| $SrMnO_3$ (6H) | 5.448 | 13.30 | | | 24.5(25.2) |
| $BaMnO_3$ (2H) | 5.695 | 4.812 | 57.1(57.2) | 22.6(22.9) | 20.6(20.0) |
| $BaMnO_3$ (9R) | 5.662 | 20.92 | 57.5(57.2) | 22.6(22.9) | 20.5(20.0) |
| $BaMnO_{2.85}$ (4H) | 5.706 | 9.370 | 58.2(57.7) | 22.7(23.1) | 19.1(19.2) |

[a] Theoretical analytical values are given in parentheses.

The magnetic susceptiblities were measured by the conventional Faraday method using a Cahn RG microbalance, a field gradient ($H\delta H/\delta x$) of the order of $10^7$ $Oe^2/cm$ at 8000 Oe, and $HgCo(CNS)_4$ as a calibrant.

Differential thermal analyses (dta) and thermogravometric analyses (tga) employed a Du Pont 900 thermal analyzer.

## Results

Analytical and crystallographic data are given in Table I. The magnetic susceptibility results are shown in Figs. 1 and 2.

### $SrMnO_3$

This compound prepared at 3 kbars and 700°C was found to possess the four-layer structure. However, when either $SrMnO_3$ (4H) or an $SrO/MnO_2$ mixture was treated at 65 kbars and 1000°, the six-layer structure resulted.

Several single crystals picked from a 3-kbar-700°C hydrothermal run were found to have the two-layer structure. The possible space groups are $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$, and the cell dimensions are $a = 5.467$ Å and $c = 4.536$ Å. No evidence for a larger $c$ axis could be found in the single crystal photographs, yet the powder photographs could only be completely indexed when $c$ was doubled. It would appear, therefore, that the 3-kbar-700°C hydrothermal runs produced a mixture of $SrMnO_3$ (2H) and $SrMnO_3$ (4H). The predominant phase was $SrMnO_3$ (4H), but the larger crystals were $SrMnO_3$ (2H).

The magnetic susceptibility of $SrMnO_3$ (6H) showed some field dependence at low temperatures. Therefore, the susceptibilities were extrapolated to infinite field, and these corrected values were found to be in reasonable agreement with the Curie–Weiss Law. The squares in Fig. 1 are the corrected values, and the triangles are for a field of 8000 Oe. The intercepts with the temperature axis, $\theta$, are −508°K (squares) and −280°K (triangles). The effective moments calculated from the slopes are $2.74 \pm 0.50$ $\mu B$ (triangles) and $3.4 \pm 0.4$ $\mu B$ (squares). It appears likely that $SrMnO_3$ (6H) is basically antiferromagnetic and becomes magnetically ordered at about 90°K. Below this temperature it would be a parasitic ferromagnetic. However, the possibility of a small amount of a ferromagnetic impurity cannot be excluded.

The magnetic susceptibility of $SrMnO_3$ (4H) was dramatically different than that of $SrMnO_3$ (6H), and it did not clearly obey the Curie–Weiss Law up to 800°K. Nonetheless, it appears likely that $SrMnO_3$ (4H) is approaching Curie–Weiss behavior at high temperatures (Fig. 1). Thus, the very broad maximum in the susceptibility at about 350°K may represent the Néel temperature. The line drawn asymptotically to this data gives a $\mu_{eff}$ of $4.6 \pm 0.4$ $\mu B$ and a $\theta$ of −1210°K. There was no field dependence for the susceptibility of $SrMnO_3$ (4H).

### $BaMnO_3$

At 65 kbars and 400–1000°C, and usually at 3 kbars and 700°C, the nine-layer structure was found. Some products contained crystals large enough for crystallographic and electrical studies. Four-probe electrical measurements on single crystals of $BaMnO_3$ from 4.2–298°K indicated semiconducting behavior ($\rho_{25°K} = 5.6 \times 10^5$ $\Omega$ cm and $E_a = 0.4$ eV). Measurements in directions both parallel and perpendicular to the $c$ axis gave the same results within experimental error. High-temperature X-ray, dta, and tga experiments in air show $BaMnO_3$ (9R) to be very stable. The first dta peak (endotherm) is at 994°C and up to this temperature a weight loss of only 0.2% was observed by tga. Furthermore, $BaMnO_3$ (9R) is not attacked by dilute hydrochloric acid.

The magnetic behavior of $BaMnO_3$ (9R) in some ways resembles that of $SrMnO_3$ (4H). Curie–Weiss behavior is not observed up to 700°K, but it appears

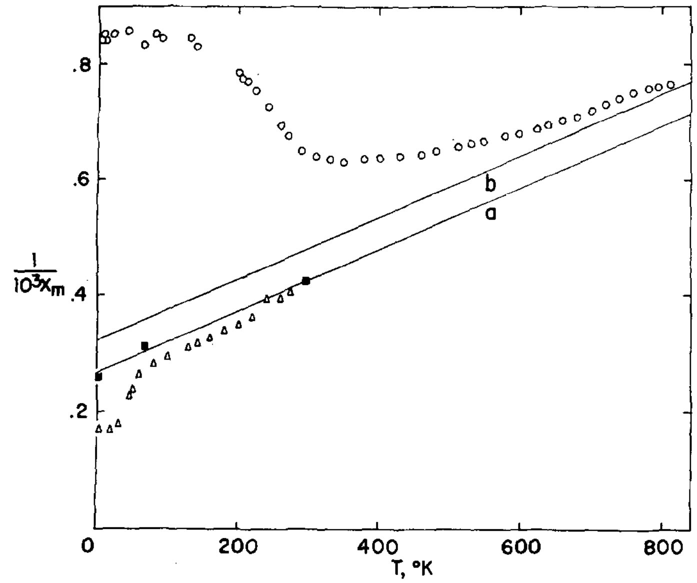

FIG. 1. Magnetic susceptibility of $SrMnO_3$ (6H), *a*, and $SrMnO_3$ (4H), *b*.

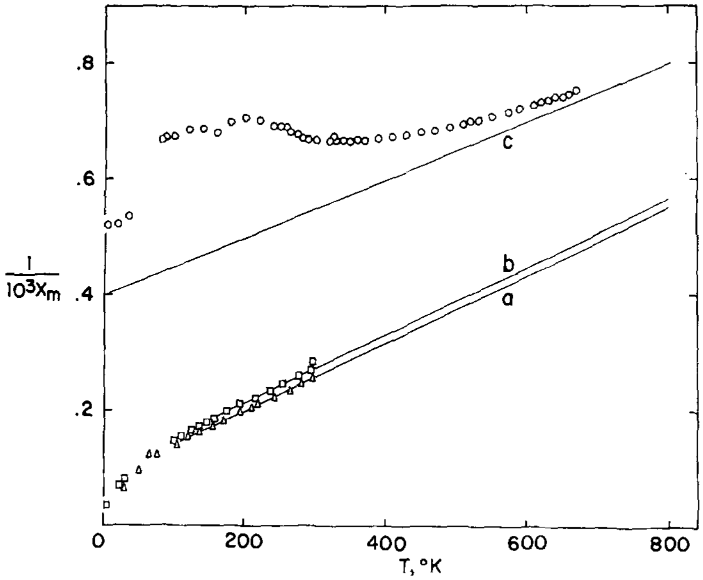

FIG. 2. Magnetic susceptibility of $BaMnO_3$ (2H), *a*; $BaMnO_{2.85}$ (4H), *b*; and $BaMnO_3$ (9R), *c*.

that such behavior is being approached at the higher temperatures. The broad maximum in the susceptibility at about 350°K presumably represents a Néel temperature. The line drawn asymptotically to the data (Fig. 2) gives an effective moment of 4.0 $\mu$B and a $\theta$ of $-804$°K. It is probable that extending the susceptibility measurements to higher temperatures would lead to a somewhat lower $\mu_{eff}$ and a less negative $\theta$. No field dependence of susceptibility was detected for $BaMnO_3$ (9R).

Single crystal X-ray photographs of $BaMnO_3$ (9R) were consistent with space group $R\bar{3}m$ as expected. Intensity data collected from the powder were refined to an $R$ of 8.5%

$$(R = \Sigma|F_{obs} - F_{calc}|/\Sigma F_{obs}).$$

The final $F^2_{obs}$ and $F^2_{calc}$ are given in Table II, and the refined parameters are given in Table III. The positional parameter errors are rather large, mainly due to the unfavorable parameter-to-observation ratio. Temperature factors were not refined since they tended to go slightly negative. The most

TABLE II

OBSERVED AND CALCULATED SQUARED STRUCTURE FACTORS

| $h$ | $k$ | $l$ | $F^2_{obs}$ | $F^2_{calc}$ |
|---|---|---|---|---|
| 1 | 0 | 4 | 170 | 191 |
| 0 | 1 | 5 | 376 | 411 |
| 1 | 1 | 0 | 885 | 920 |
| 1 | 0 | 7 | 133 | 172 |
| 0 | 2 | 1 | 76 | 51 |
| 2 | 0 | 2 | 59 | 31 |
| 0 | 0 | 9 |  | 171 |
| 0 | 1 | 8 |  | 267 |
|  |  |  | 570[a] | 438 |
| 0 | 2 | 4 | 651 | 475 |
| 2 | 0 | 5 | 953 | 791 |
| 1 | 0 | 10 | 381 | 230 |
| 0 | 2 | 7 | 238 | 224 |
| 1 | 1 | 9 |  | 235 |
| 2 | 0 | 8 |  | 312 |
|  |  |  | 383[a] | 547 |
| 2 | 1 | 4 | 386 | 309 |
| 1 | 2 | 5 | 626 | 631 |
| 3 | 0 | 0 | 868 | 674 |
| 0 | 2 | 10 | 326 | 340 |
| 2 | 1 | 7 | 244 | 246 |
| 1 | 0 | 13 | 238 | 223 |
| 1 | 2 | 8 | 405 | 367 |
| 0 | 1 | 14 | 337 | 275 |
| 2 | 2 | 0 | 950 | 942 |
| 2 | 1 | 10 | 484 | 342 |
| 0 | 2 | 13 |  | 336 |
| 3 | 0 | 9 |  | 103 |
|  |  |  | 373[a] | 439 |
| 1 | 3 | 4 | 223 | 250 |
| 3 | 1 | 5 | 570 | 504 |

[a] These values of $F^2_{obs}$ are compared with the sum of two $F^2_{calc}$ values from unresolved reflections.

TABLE III

CRYSTALLOGRAPHIC PARAMETERS FOR $BaMnO_3$ (9R)

| Atom | $x$ | $y$ | $z$ | B |
|---|---|---|---|---|
| Ba1 | 0.0 | 0.0 | 0.0 | 0.0 |
| Ba2 | 0.0 | 0.0 | 0.220(2) | 0.0 |
| Mn1 | 0.0 | 0.0 | 0.5 | 0.0 |
| Mn2 | 0.0 | 0.0 | 0.386(6) | 0.0 |
| O1 | 0.5 | 0.0 | 0.0 | 1.0 |
| O2 | 0.171(15) | −0.171 | 0.546(7) | 1.0 |

accurate interatomic distances of interest are the Mn–Mn distances in the Mn–Mn–Mn linear cluster which were found to be 2.5 ± 0.1 Å. The twelve oxygen to Ba 1 distances range from 2.8–2.9 Å, and the twelve oxygen to Ba 2 distances from 2.7–2.9 Å. The six oxygen to Mn 1 distances are 2.0 Å, and the oxygen to Mn 2 distances range from 1.9-2.2 Å. Such distances are not unreasonable since the errors involved are all somewhat greater than 0.1 Å. Thus, although this refinement of $BaMnO_3$ (9R) provides reasonably good proof of structure type, no great significance can be ascribed to the values of the refined parameters.

Two-layer $BaMnO_3$ was most readily prepared after the method of Hardy (*2*). The decomposition of $BaMn_2O_8$ at 700°C and 3000 atm also appeared to give $BaMnO_3$ (2H) instead of $BaMnO_3$ (9R). However, the $BaMnO_3$ (2H) so prepared could not be purified, so all the data on $BaMnO_3$ (2H) in this paper refer to the decomposition product of $BaMnO_4$ at 450°C.

$BaMnO_3$ (2H) is not nearly as stable as $BaMnO_3$ (9R). It is readily attacked by dilute hydrochloric acid, whereas $BaMnO_3$ (9R) is not. It also loses oxygen much more readily, and by 1000°C the weight loss corresponds to 1.2%. This oxygen loss is accompanied by a transition of $BaMnO_3$ (2) to $BaMnO_{3-x}$ (4H), which may be oxidized and converted back to $BaMnO_3$ (2H) by annealing the $BaMnO_{2.85}$ (4H) under 1000 atm of oxygen at 500°C.

Crystals of $BaMnO_3$ (2H) and $BaMnO_{2.85}$ (4H) were too small for either crystallographic or electrical resistivity measurements. However, two-probe resistivity measurements on powders of these compounds showed semiconducting behavior: $BaMnO_3$ (2H); $\rho_{25^\circ} = 3 \times 10^5\ \Omega$, $E_a \sim 0.4$ eV and $BaMnO_{2.85}$ (4H); $\rho_{25^\circ} = 7 \times 10^2$, $E_a \sim 0.2$ eV.

Both $BaMnO_3$ (2H) and $BaMnO_{2.85}$ (4H) exhibit Curie–Weiss behavior from about 100°K to room temperature and higher. The lines of Fig. 2 give a $\mu_{eff}$ of 3.70 ± .05 $\mu$B and a $\theta$ of −139°K for $BaMnO_3$ (2H) and a $\mu_{eff}$ of 3.69 ± .05 $\mu$B and a $\theta$ of −164°K for $BaMnO_{2.85}$ (4H). Since $BaMnO_{2.85}$ (4H) presumably contains some $Mn^{3+}$, it might be expected to have a somewhat higher $\mu_{eff}$ than $BaMnO_3$ (2H) if the $Mn^{3+}$ is in the high spin state. However, that this is not the case is not too surprising in view of the accuracy of the data and since the two compounds do have different structures. Neither compound shows a maximum in susceptibility indicative of a Néel temperature, and there is no field dependence of the susceptibility in the low-temperature region where the Curie–Weiss Law is not obeyed.

Very recently Syono et al. (*4*) reported that $BaMnO_3$ (4H) could be prepared at 90 kbar and 1200°C. Consequently, we had our $BaMnO_3$ (9R) treated under these same conditions. The product was indeed partially transformed to $BaMnO_3$ (4H) with $a = 5.643$ Å and $c = 9.232$ Å. An oxygen analysis of the product gave 20.6% oxygen indicating that this $BaMnO_3$ (4H) was not significantly oxygen deficient.

## Discussion

The relationship of pressure, temperature, and cationic sizes to polytypism in hexagonal layer structures of the type found for $BaMnO_3$ and $SrMnO_3$ has been extensively investigated by Longo and Kafalas (*5*), (*6*). There are five commonly occurring polytypes, and in order of decreasing hexagonal character these are: 2H, 9R, 4H, 6H, and 3C. The 3C polytype is the perovskite structure with cubic packing, and the 2H type is the $CsNiF_3$ structure where the packing is completely hexagonal. All the other types have varying degrees of intermediate hexagonal character. Longo and Kafalas have shown that the amount of hexagonal character in any compound, or series of compounds, of this type decreases with pressure and the A/B cation size ratio.

Four of the five possible polytypes are found for the $BaMnO_3$ and $SrMnO_3$ systems. Low-pressure $BaMnO_3$ has the two-layer structure and is thus 100% hexagonal. Increasing pressure decreases the hexagonal character as expected, giving the nine-layer structure. Still higher pressures result in the formation of $BaMnO_3$ (4H).

The A cation size is greatly reduced on going from $BaMnO_3$ to $SrMnO_3$, and the hexagonal character decreases as expected. The four-layer form is now found at lower pressures, and at 65 kbars the six-layer polytype is produced. A perovskite form of $SrMnO_3$ could not be prepared at our highest pressure, although of course on decreasing the size of the A cation even further, i.e., $CaMnO_3$, the perovskite structure is found. $SrMnO_3$ is unique among $A^{II}B^{IV}O_3$ compounds in that it forms an undistorted hexagonal (nonperovskite) polytype where the A cation is Sr.

In systems where polytypism occurs, mixtures of the polytypes are common. Although in this work the products generally appeared to be one polytype only, the predominant polytype could be contaminated with small amounts of one or more other polytypes. Since the strong lines of the X-ray powder patterns have essentially the same *d* values for all the polytypes of a given composition, it would be very difficult to detect small amounts of other polytypes. Even the examination of several crystals is not a dependable check because it is likely that certain polytypes in any given mixture will be more crystalline than others.

Previously, three polytypes of $BaMnO_3$ have been reported in the literature. Hardy (*2*) reported low-temperature $BaMnO_3$ (2H) and high-temperature $BaMnO_3$ (4H). We have shown that the high-temperature phase is oxygen deficient when prepared under normal pressure. It should also be noted that the cell dimensions of this $BaMnO_{2.85}$ (4H) are considerably larger than those of $BaMnO_3$ (4H) prepared at high pressure. Two-layer $BaMnO_3$ had first been reported by Gushee, Katz, and Ward (*7*). Nine-layer $BaMnO_3$ has been reported by Donohue, Katz, and Ward (*8*); however, these authors stated that they could not reproduce their preparation of $BaMnO_3$ (9R). They did find, however, that solid solutions of $BaMnO_3$ (9R) and $BaRuO_3$ (9R) were readily prepared.

High-pressure phases are in general expected to have higher densities than corresponding low-pressure phases; thus we can expect density increases in the series 2H, 9R, 4H, 6H, and 3C. An increase in density of 4.53% is found after going from $BaMnO_3$ (2H) to $BaMnO_3$ (9R), an increase of 1.33% after going from $BaMnO_3$ (9R) to $BaMnO_3$ (4H), and an increase of 2.45% after going from $SrMnO_3$ (4H) to $SrMnO_3$ (6H). The $c/a$ ratio per layer ($c/aN$, where $N$ is the number of layers) might also be expected to change significantly in going from one polytype to another. This value must be $\sqrt{3}/3\sqrt{2}$ (0.40825) for the three-layer cubic case and is usually found to be higher in other cases. In fact, this reduced $c/a$ ratio generally increases with increasing hexagonal character in the series of polytypes. Thus, $c/aN$ is 0.4069 and 0.4166 for $SrMnO_3$ (6H) and $SrMnO_3$ (4H), respectively, and 0.4090, 0.4105, and 0.4225 for $BaMnO_3$ (4H), $BaMnO_3$ (9R) and $BaMnO_3$ (2H), respectively. For the $BaRuO_3$ polytypes (*5*) $c/aN$ is 0.4086 for 6H, 0.4145 for 4H, and 0.4174 for 9R.

Although there was considerable variation in the magnetic properties of the $AMnO_3$ compounds under study, all may be regarded as antiferromagnetic. In all cases the Curie–Weiss Law was obeyed or presumably approached at the higher temperatures, and the intercept with the temperature axis always had a large negative value. The effective moments calculated from the slopes never greatly departed from the spin only value of 3.88 $\mu$B for $Mn^{4+}$.

Hexagonal stacking of the $AO_3$ layers in $ABO_3$ compounds leads to face-shared $BO_6$ octahedra and thus to the possibility of short metal–metal distances and metal–metal bonding. It is possible that metal–metal bonding is present in $BaMnO_3$ (9R) and $SrMnO_3$ (4H) and that this is responsible for the very high Néel temperatures. Similar magnetic behavior is found (*9*) for $BaRuO_3$ (9R), and in both $BaRuO_3$ (9R) and $BaMnO_3$ (9R) the metal–metal distances are well within the range where one might expect metal–metal bonding, i.e., 2.55 Å in $BaRuO_3$ (9R) and 2.58 Å in $BaMnO_3$ (9R). Assuming that there really is metal–metal bonding in $BaMnO_3$ (9R) and $SrMnO_3$ (4H), it is somewhat surprising that this bonding is so much weaker in $BaMnO_3$ (2H) and $SrMnO_3$ (6H). In $BaMnO_3$ (2H) the Mn–Mn distance across the infinite chains of face-shared octahedra must be 2.40 Å. Detailed structural refinements of these compounds would probably be very helpful in understanding their bonding and magnetic properties.

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