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EFFECT OF Na_2O ADDITION ON MAGNETIC PROPERTIES OF $SrZn_2$-W TYPE HEXAGONAL FERRITE

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Abstract-An experiment was carried out to investigate the effect of Na_2O additive on the magnetic and physical properties of $SrZn_2$-W type hexagonal ferrite. The specimens were prepared by the conventional manufacturing methods without atmosphere control. It was found that the magnetic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ are considerably improved on adding 1.5wt% Na_2O. The optimum condition of making magnet with suitable properties are as follows : chemical analysis composition: $Sr^{2+}_{0.852}Zn^{2+}_{1.721}Na^{+}_{0.301}Fe^{2+}_{0.723}Fe^{3+}_{15.703}O_{27}$; semisintering condition : 1300°C x 1h in air ; sintering condition : 1250°C x 0.5h in air. The magnetic properties are : J_m= 0.390 T, J_r= 0.348 T, H_{cJ}= 133.7 kA/m, H_{cB}= 129.7 kA/m, $(BH)_{max}$ = 21.50 kJ/m^3, T_C=371°C, H_A= 1091.5kA/m, K_A = 2.13 x 10^5 J/m^3 and n_B= 31.8 μB.

I. INTRODUCTION

Many reports on the synthesis and magnetic properties of W-type hexagonal ferrites have been presented[1-19]. However, to manufacture W-type hexagonal ferrite magnets with reproducible magnetic properties, especially high coercivity, is not easy. Recently, Yamamoto et al.[14] synthesized Sr-Zn system W-type hexagonal ferrite without using any special atmosphere to achieve the considerably improved and reproducible magnetic properties. The present experiment is extended to investigate the effect of Na_2O additive on the magnetic properties of this system.

II. EXPERIMENTAL METHOD

The raw material used in this experiment were $SrCO_3$, ZnO, α-Fe_2O_3, Na_2CO_3 powders. Using these raw materials, the compound whose total weight was 0.3kg was prepared. The raw materials were homogeneously mixed by grinding under alcohol using ballmilling for 3h. The powder thus obtained was dried up at 100°C, and then was pressed at a pressure 49MPa to form a cylindrical shaped sample of 36 x 7mm^2. Those samples were semisintered at 1275 to 1325°C for 1h in air. The semisintered clinkers were pulverized to 150μm, and then Na_2O (where the contents are 0 to 2.0wt%) was added by milling the mixture under alcohol for 8h in a stainless steel vibrating mill. Here Na_2CO_3 was used to obtain Na_2O. The sample was finally compacted into a cylindrical shape of 13 x 11-13mm^2 at 294MPa under a magnetic field of 800kA/m along the pressing direction, and then sintered at 1200 to 1300°C for 0.5h in air. The magnetic properties were measured by a high sensitivity selfrecording fluxmeter, the Curie temperature and temperature dependence of the saturation magnetization and coercivity were examined by vibrating sample magnetometer(VSM). A density was measured by Archimedes principle. Microstructures of various samples were observed by SEM, and structural analysis was carried out by X-ray diffraction patterns recorded using FeKα radiation. The magnetic domains were observed by Bitter method.

III. RESULTS AND DISCUSSION

Fig.1 shows the effect of sintering temperature on magnetic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound in addition with 0 to 2.0wt% Na_2O after semisintering treatment. Here the semisintering temperature was held constant at 1300°C for 1h. The value of J_m , J_r , H_{cJ} , H_{cB} and $(BH)_{max}$ were determined from J-H curve measured by a high sensitivity selfrecording fluxmeter in the magnetic fields up to 800kA/m. In this figure, J_m is the flux density at 800kA/m, S.S.C. and S.C. are semisintering condition and sintering condition, respectively. As seen from the figure, for all the composition , both J_m and J_r increase with the increase of sintering temperature from 1200 to 1275°C , and then do not change up to 1300°C . H_{cJ} and H_{cB} decrease with the

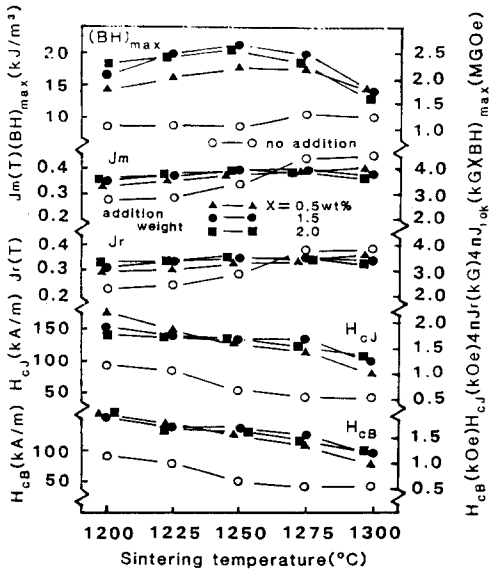

Fig.1 Effect of sintering temperature on magnetic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Xwt% Na_2O after semisintering treatment.S.S.C.:1300°Cx1h in air.

increase of sintering temperature. The values of $(BH)_{max}$ tend to increase with sintering temperature, and have the maximum values at sintering temperature of 1250 or1275°C, and then decrease up to 1300°C. As concerns Na_2O addition,

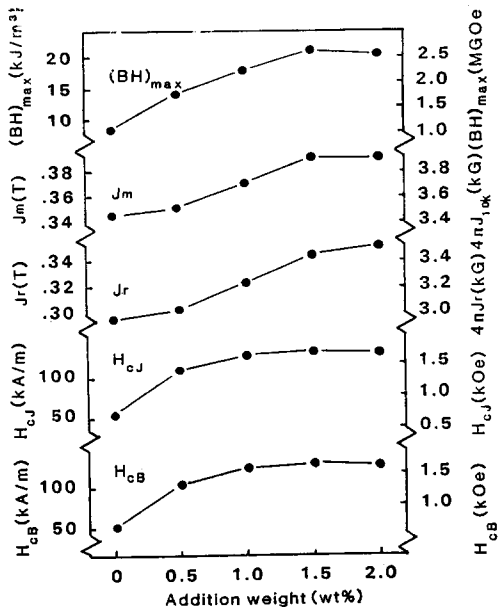

Fig.2 Effect of Na_2O addition on magnetic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Xwt% Na_2O after semisintering treatment. S.S.C. : 1300°C x1h in air.

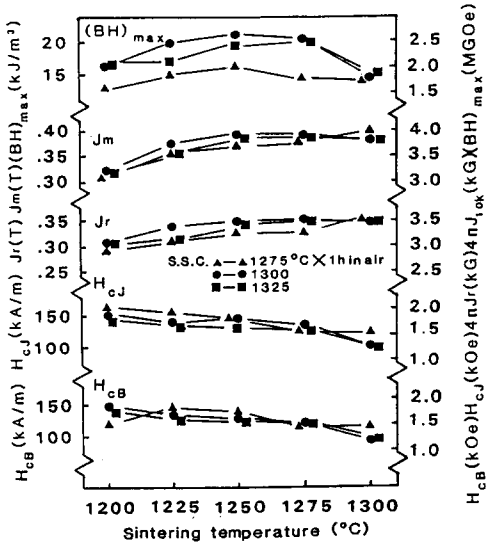

Fig.3 Effect of sintering temperature on magnetic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound in addition with 1.5wt% Na_2O at various semisintering temperatures.

J_m , J_r , H_{cJ} , H_{cB} increase with the increase of Na_2O contents various sintering temperature. Especially, in these compounds added with 2–3wt% Na_2O, the value of H_{cJ} was obtained 2 to 3 times larger than that of without Na_2O addition. It was also found that the highest $(BH)_{max}$ was obtained at a Na_2O contents of 1.5wt% and a sintering temperature of 1250°C for 0.5h. (Fig.2)

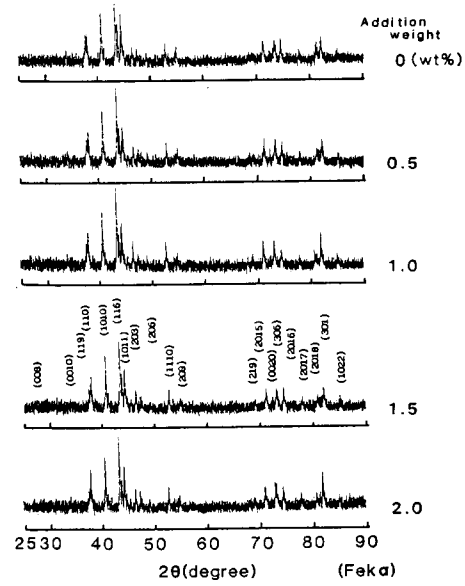

Fig.4 X-ray diffraction patterns of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Na_2O after semisintering treatment.
S.S.C.:1300°Cx1.0h in air, S.C.:1250°Cx0.5h in air.

The magnetic properties of resulting when the semisintering temperature of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ added with 1.5wt% Na_2O was varied between 1275 and 1325 °C appear in Fig.3. As a result, it was found that the best magnetic properties were obtained by semisintering at 1300°C for 1h followed by final sintering at 1250°C for 0.5 h. The resulting magnetic properties are : J_m=0.390T, J_r=0.348T, H_{cJ}=133.7kA/m, H_{cB}=129.7kA/m, and $(BH)_{max}$ = 21.50kJ/m^3

Fig.4 shows X-ray diffraction patterns for samples sintered at 1250°C, with the Na_2O content varied between 0 and 2.0. Fig.5 shows X-ray diffraction patterns of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ added with 1.5wt% Na_2O, with the sintering temperature varied in the range 1200 to 1300°C. As seen in these figures, the diffraction patterns reveal that samples consist of a single phase after sintering at all compositions and temperatures.

Table1 shows the relation between the sintering temperature and crystal phases for $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound added with 0 to 2.0wt% Na_2O. As seen in this table, it was found that adding Na_2O in the the form of Na_2Co_3 powder during crushing after semisintering, resulted in stable single W-phase samples starting from lower temperatures compared with samples without Na_2O added.

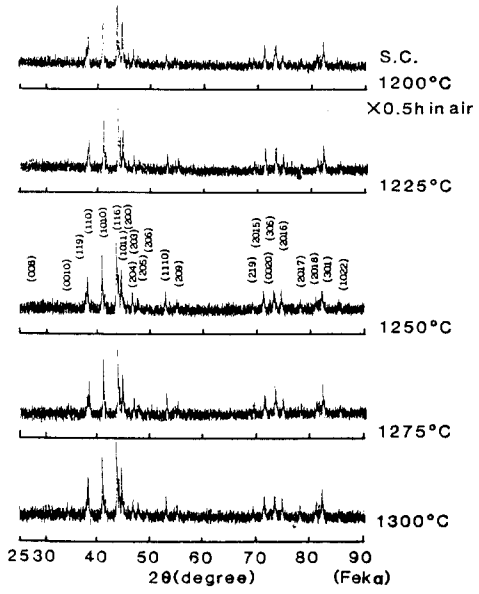

Fig.5 X-ray diffraction patterns of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound in addition with 1.5wt% Na_2O after semisintering treatment. S.S.C.:1300°Cx1h in air.

Table 1 Phases of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Na_2O after semisintering treatment.

W:W-phase, α-αFe_2O_3-phase, S.S.C.:1300Cx1.0h in air.

Addition weight (wt%)	Sintering Temperature(°C)				
	1200	1225	1250	1275	1300
0	W,α	W,α	W	W	W
0.5	W	W	W	W	W
1.0	W	W	W	W	W
1.5	W	W	W	W	W
2.0	W	W	W	W	W

Sintering time for 0.5h

Fig.6 shows lattice constants of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound added with 0 to 2.0wt% Na_2O. From this figure, the lattice constant c increases with the increase of Na_2O 0 and 1.5wt% addition, and does not change between 1.5 and 2.0wt% addition. The otherwise, the lattice constant a trend to decrease with 0 and 1.5wt%. This phenomenon suggest that Na_2O might be present as a substitutional solid solution. The lattice constant a and c of this sample added with 1.5wt% Na_2O is a=5.90 x 10^{-10} m and c=32.760 x 10^{-10}m.

Fig.7 shows the temperature dependence of σ_s and H_{cJ} of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound added with 1.5wt% Na_2O. The samples designed in spherical shapes were in order to make a correction of the demagnetizing factor. As the temperature decreases, the σ_s exhibits a linear increasing tendency. The H_{cJ} increases up to about 210°C followed by an abrupt decrement. This trend is very similar to that observed in M-type ferrites[20]. Extrapolation from the data in the figure indicated that the σ_s at 0K(-273°C) is 146.9 x 10^{-6} Wb·m/kg,

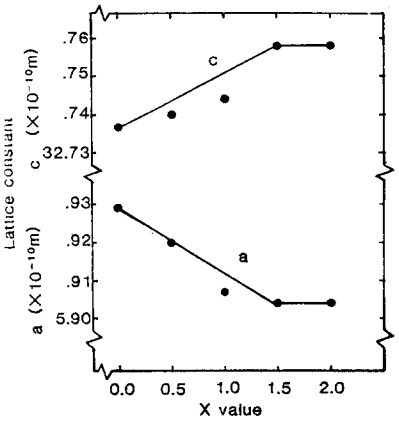

Fig.6 Effect of X value on lattice constant of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Xwt% Na_2O after semisintering treatment. S.S.C.:1300°Cx1h in air, S.C.:1250°Cx0.5h in air.

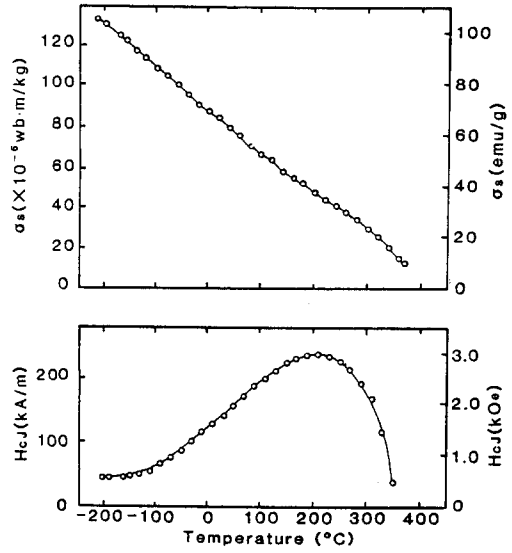

Fig.7 Temperature dependence on magneic properties of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound in addition with 1.5 wt% Na_2O after semisintering treatment.
S.S.C.:1300°C x1.0h in air, S.C.:1250°Cx 0.5h in air.

correction of the demagnetizing factor. As the temperature decreases, the σ_s exhibits a linear increasing tendency. The H_{cJ} increases up to about 210°C followed by an abrupt decrement. This trend is very similar to that observed in M-type ferrites[20]. Extrapolation from the data in the figure indicated that the σ_s at 0K(-273°C) is 146.9 x 10^{-6} Wb·m/kg, and the molecular weight of this sample, MW=1543.4, was obtained from the chemical analysis($Sr^{2+}_{0.852}Zn^{2+}_{1.721}Na^{+}_{0.301}Fe^{2+}_{0.723}Fe^{3+}_{15.703}O_{27}$). As a result, the magnetic moment per formula unit of this compound was calculated to be n_B =31.8μB(without any correction for 4.5% non-magnetic impurities expected by the chemical analysis). If all of this compound was W-phase, the n_B was found to be 33.0μB from σ_s=151.4 x 10^{-6} Wb·m/kg. This value is lower 6% than 35μB reported for $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ single crystals by Graetsch.et al.[6]. This result seems to be obtained for reasons of not to be substituted Zn^{2+} for all Fe^{2+} from the results of chemical analysis. This compound was $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound added with 1.5wt% Na_2O after semisintering treatment, while by the chemical analysis, Na_2O weight only was 0.59wt%. As the melting point of Na_2CO_3 is low, Na_2O in these compounds were many sublimation loss.

Fig.8 shows the Curie temperature T_c of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds added with 0 to 2.0wt% Na_2O. As the amount of Na_2O added is increased, the Curie temperature declines. However, because it is nearly constant for Na_2O contents of 1.5wt% Na_2O and above. The T_c of the sample added with 1.5wt% Na_2O having the best properties is 371°C. It appeared that in $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ there is a range of Na_2O solubility. It seems likely that the Na_2O content affects the Zn^{2+}, Fe^{2+} or Fe^{3+} ion contents.

The sintered density and shrinkage of these samples are compared in Fig.9($SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds added with 0 to 2.0wt% Na_2O). Obviously, the sintered density and shrinkage increase up to 1.5wt% Na_2O addition, and then are nearly constant.

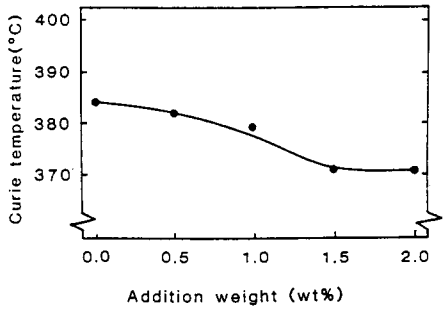

Fig.8 Curie temperature of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Na_2O after semisintering treatment.
S.S.C.:1300°C x 1.0h in air, S.C.:1250°C x 0.5h in air.

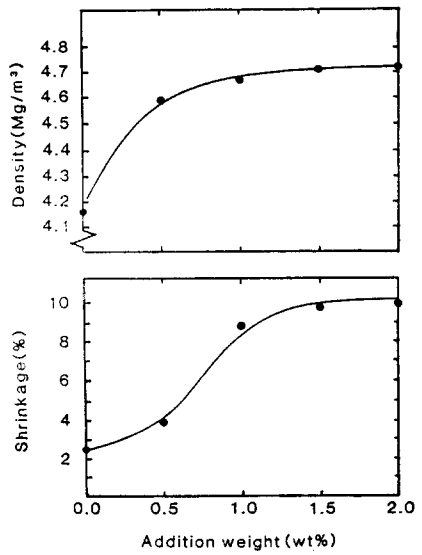

Fig.9 Density and shrinkage of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds in addition with Na_2O after semisintering treatment.
S.S.C.:1300°Cx1.0h in air, S.C.:1250°Cx0.5h in air.

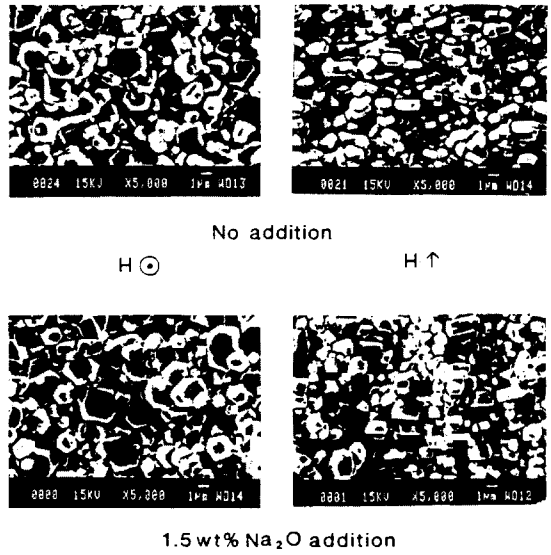

Fig.10 SEM photographs of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compound in addition with 1.5wt% Na_2O and without the additives.
S.S.C.:1300°Cx1h in air, S.C.:1250°Cx0.5h in air.

Fig.10 shows SEM photographs of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds added with 1.5wt% Na_2O and without the additives sintered at 1250°C for 0.5h after semisintered at 1300°C for 1h. For the surface perpendicular to the applied field direrction, a hexagonal-board structure is observed, and parallel to the applied field direction had a flat shape. This structure is very similar to M-type ferrites. The grain size was found to be about 2 to 3μm.

Fig.11 shows the domain structures of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ compounds added with 1.5wt% Na_2O. For ease of domain observations, the sample was sintered at 1325°C for 2h. As shown in Fig.11(a), on the surface perpendicular to easy direction(c axis) of the magnetization, a maze pattern is found. On the other hand, in Fig.11(b), on the surface parallel to the easy direction, 180 domain walls are observed in the demagnetized state. These are typical of the domains in hexagonal crystal systems with uniaxial anisotropy, and are very similar to the domain patterns of M-type ferrite[20].

(a)Surface perpendicular to the easy direction

(b)Surface parallel to the easy direction

Fig.11 Magnetic domain structures of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ magnet in addition with 1.5wt% Na_2O after semisintering treatment.

Table.2 summarized the condition and properties for the best performance obtained in the present study. The magnetic anisotropy field H_A was obtained based on two magnetization curves by applying field up to 1600kA/m parallel and perpendicular to the alignment axis(c axis) and by using an extrapolation method for ten different samples ($7x7x7mm^3$).

Table 2 Magnetic and physical properties of Sr-Zn-Na system W-type ferrite magnets. Na_2O addition : 1.5wt%. S.S.C.:1300°C x 1h in air, S.C.:1250°C x 0.5h in air.

$Sr_{0.852}Zn_{1.721}Na^{+1}_{0.301}Fe^{2+}_{0.723}Fe^{3+}_{15.703}O_{27}$		
Magnetic properties	J_m(T)	0.390
	J_r(T)	0.348
	H_{cJ}(kA/m)	133.7
	H_{cB}(kA/m)	129.7
	$(BH)_{max}$(kJ/m^3)	21.5
	K_A($\times 10^5$J/m^3)	2.13
	H_A(kA/m)	1091.5
	σ_s($\times 10^{-6}$Wb · m/kg)	82.8(23℃)
	η_B(μ_B)	31.8
	T_C(℃)	371
Density	(Mg/m^3)	4.71
Lattice constant	a($\times 10^{-10}$m)	5.904
	c($\times 10^{-10}$m)	32.76
	c/a	5.549
Molecular weight	MW	1543.4

K_A was estimated by $K_A=J_m{\cdot}H_A/2$. As a result, K_A is 2.13 x 10^5J/m^3 and H_A is 1091.5kA/m, these values are larger than those of $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ single crystals by Graetsch[6].

IV. CONCLUSION

This paper describes the effect of Na_2O additive in $SrO{\cdot}2ZnO{\cdot}8Fe_2O_3$ W-type hexagonal ferrite. From this experiment, it was found that the magnetic properties of this compounds are significantly improved by adding Na_2O. Particulary, intrinsic coercivity(H_{cJ}) is 60-87% larger than that without any additives. The best magnetic properties are obtained at a total of 1.5 wt% addition with Na_2O. The $(BH)_{max}$ was found to be increased by 84% by using of the additive. These result indicate a potential industrial use of the W-type ferrite materials.

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