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ScienceDirect
Trans. Nonferrous Met. Soc. China 20(2010) 2303−2308
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Microstructure and electrical properties of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics

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Received 16 October 2010; accepted 25 November 2010

Abstract: Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples were prepared by a conventional mixed oxide route and sintered at temperatures in the range of 900−1 000 °C, and the microstructures of the varistor ceramics samples were characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM); at the same time, the electrical properties and *V*—*I* characteristics of the varistor ceramics samples were investigated by a DC parameter instrument for varistors. The results show that the ZnO-Bi_2O_3-based varistor ceramics with 0.3% Lu_2O_3 (molar fraction) sintered at 950 °C exhibit comparatively ideal comprehensive electrical properties. The XRD analysis of the samples shows the presence of ZnO, Bi-rich, spinel $Zn_7Sb_2O_{12}$ and Lu_2O_3-based phases.

Key words: ZnO-Bi_2O_3 ceramics; varistor; rare earth; electrical properties

1 Introduction

Zinc oxide varistors are polycrystalline semi-conducting ceramic devices, which are widely used for voltage stabilization and transient surge suppression in electric power systems and electronic circuits[1−3]. The non-linear current—voltage characteristics of ZnO varistor ceramics results from the formation of double Schottky barriers at the grain boundaries, and non-ohmic conduction in ZnO varistors is a grain-boundary phenomenon, which has been explained by thermionic emission enhanced by lowering barrier at low fields with a combination of other mechanisms at high fields[4]. These non-ohmic ZnO-ZnO grain boundaries have a break-down voltage of 3 V, and so the overall break-down voltage of the varistor builds up from the non-ohmic grain boundaries between the electrodes of the varistor and can be controlled either by the varistor thickness or the ZnO grain size. To increase the breakdown voltage, it is necessary to decrease the average size of the ZnO grains[5−7].

Recently, many studies have been made in order to understand the influence of different rare earth oxides on the microstructure and electrical properties of the ZnO varistor ceramics. BERNIK et al[8−9] reported the microstructural and electrical characteristics of ZnO-Bi_2O_3-based varistor ceramics samples doped with Y_2O_3 in the molar fraction range of 0−0.9%. The addition of Y_2O_3 resulted in the formation of a fine-grained Bi-Zn-Sb-Y-O phase along the grain boundaries of the ZnO grains, which inhibits the grain growth. The mean ZnO grain size decreased from 11.3 to 5.4 mm with increasing amount of Y_2O_3. The threshold voltage of the ceramics samples increased from 150 to 274 V/mm, the non-linear coefficient was not influenced and remained at approximately 40, and the leakage current also increased with the amount of Y_2O_3 added. LIU et al[10] investigated ZnO-Bi_2O_3-based varistor ceramics samples doped with 0−3% (molar fraction)

Foundation item: Project(50902061) supported by the National Natural Science Foundation of China; Project(2011-22) supported by the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University, China; Project(20100471380) supported by the China Postdoctoral Science Foundation; Project(J50102) supported by the Leading Academic Discipline Program of Shanghai Municipal Education Commission, China; Project(10KJD430002) supported by the Universities Natural Science Research Program of Jiangsu Province, China; Project(2010002) supported by the Jiangsu University Undergraduate Practice-Innovation Training Program, China
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DOI: 10.1016/S1003-6326(10)60645-0

Y_2O_3. They discovered that the average grain size of the varistor ceramics samples decreased from about 9.2 μm to 4.5 μm, and the corresponding varistor's voltage gradient markedly increased from 462 to 2340 V/mm, while the nonlinear coefficient decreased from 22.3 to 11.5. ASHRAF et al[7] reported the microstructure and electrical properties of Ho_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics. The bulk density varied between 5.41 and 5.47 g/cm^3 with the maximum value of 5.47 g/cm^3 for 0.50% (molar fraction) Ho_2O_3-doped ZnO-Bi_2O_3-based. The average grain sizes for all the samples were calculated from the scanning electron micrographs to be between 5.1 and 7.1 μm. The nonlinear coefficient obtained from electric field—current density plots had a maximum value of 78 for the ceramics with 0.50% Ho_2O_3. The leakage current had a minimum value of 1.30 μA for 0.50% Ho_2O_3-doped ZnO varistor ceramics. The breakdown field was found to increase with the increase of Ho_2O_3 content.

It can be noticed that the rare earth oxides play an important role in controlling operation parameters of these kinds of varistor devices from the review of the research work on ZnO-Bi_2O_3-based varistor ceramics. To address the influence of rare earth oxides on the ZnO varistor ceramics, in the present work, the influence of the amount of added Lu_2O_3 on the microstructure and electrical characteristics of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics was investigated. The objective of the work is also to understand how the composition controls the microstructure and electrical properties of the ZnO varistors doped with Lu_2O_3. The relation between the electrical characteristics of the Bi_2O_3-based ZnO varistor ceramics with various Lu_2O_3 content was investigated and the results were analyzed.

2 Experimental

ZnO-Bi_2O_3-based varistor ceramics samples with the nominal composition (96.5%–x) (molar fraction) ZnO+0.7%Bi_2O_3+0.8%Co_2O_3+0.5%MnO_2+0.5%Cr_2O_3+ x Lu_2O_3 for x=0, 0.1%, 0.2%, 0.3% and 0.4% (sample labeled N0, N1, N2, N3 and N4, respectively) were prepared. Reagent grade oxides were mixed and homogenized in absolute ethanol media at 250 r/min for 5 h by planetary high-energy ball milling in a polyethylene bowl with zirconia balls. The slurry was dried at 70 °C and pressed into discs with 12 mm in diameter and 2 mm in thickness. The pressed discs were sintered at three fixed sintering temperatures of 900, 950 and 1 000 °C for 2 h with heating and cooling rates of 5 °C/min in air (labeled as A, B, C, respectively). The sintered samples were all lapped and polished to 1.0 mm thick. The final samples with about 10 mm in diameter and 1.0 mm in thickness were obtained. The relative bulk densities (D) of the samples were measured in terms of their mass and volume. For the characterization of DC current—voltage, the silver paste was coated on both faces of samples and the silver electrodes were formed by heating at 600 °C for 10 min in air. The diameters of electrodes were 5 mm. The voltage — current characteristics were measured using a voltage-current source/measure unit (CJP CJ1001). The nominal varistor voltages ($V_{0.1}$, $V_{1.0}$) at 0.1 and 1.0 mA were measured, and the threshold voltage V_T ($V_T = V_{0.1}/t$, where t is the thickness of the sample in mm) and the nonlinear coefficient α ($\alpha = 1/\lg(V_{1.0}/V_{0.1})$) was determined. The leakage current (I_L) was measured at $0.75V_{1.0}$ [3, 11−15]. The surface microstructure was examined by a scanning electron microscope (SEM, JEOL JSM−7001F). The crystalline phases were identified by an X-ray diffractometer (XRD, Rigaku D/max 2500, Japan) using a Cu K_α radiation.

3 Results and discussion

The relative bulk density values of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics sintered at sintering temperatures of 900, 950 and 1 000 °C for 2 h are shown in Fig.1. The results represent that the sintered densities of the varistor ceramics samples have a little change at different sintering temperature, and the bulk densities almost increase with increasing the Lu_2O_3 molar fraction increasing and decrease with the sintering temperature of 900, 950 and 1 000 °C, respectively. Lu^{3+} ion has a larger radius (0.085 nm) than Zn^{2+} ion (0.074 nm). Molar mass of Zn (65.39 g) is less than that of Lu (174.97 g). Thus, initial addition of Lu_2O_3 affects the grain distribution and develops different phases in the ceramic matrix, increasing the bulk density initially. Further increase of the Lu_2O_3 content may mainly contribute to the change in grain size and phase distribution. So, bulk density increases with the increase of the Lu_2O_3 content and then decreases at the different temperatures. The decrease in

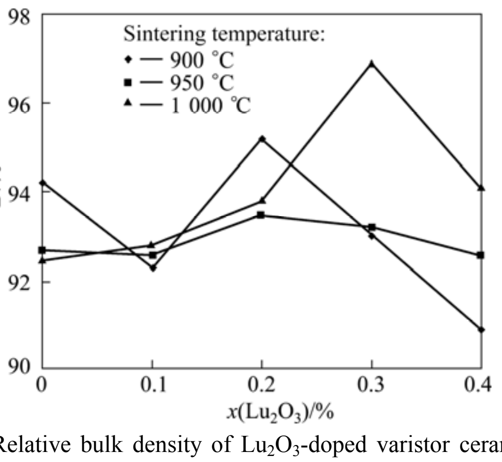

Fig.1 Relative bulk density of Lu_2O_3-doped varistor ceramics samples sintered at different temperatures

bulk density of the varistor ceramics with higher Lu_2O_3 content may be due to the increase of intragranular porosity[7].

Fig.2 shows the leakage current of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at different sintering temperatures for 2 h as a function of Lu_2O_3 molar fraction. From Fig.2 we can find that the leakage current decreases with the increase of Lu_2O_3 content, and the leakage current is not almost affected by sintering temperature in the range of 950–1 000 °C. The leakage currents of the samples with Lu_2O_3 are all lower than those without Lu_2O_3 sintered at different temperatures, indicating that Lu_2O_3 can significantly decrease the leakage current of varistor.

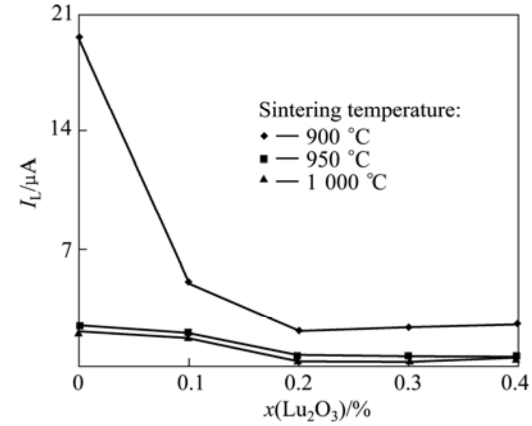

Fig.2 Leakage current of Lu_2O_3-doped varistor ceramics samples sintered at different temperatures

The variation of the threshold voltage of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at different sintering temperatures for 2 h is shown in Fig.3. It is observed that the threshold voltage firstly increases and then decreases and finally increases with the increase of Lu_2O_3 content. The changes of the threshold voltage at different sintering temperatures are similar. The threshold voltage increases as the grains size decreases. The higher the sintering temperature is, the lower the threshold voltage is, due to the growth of grain at the elevated temperatures.

As shown in Fig.4, the nonlinear coefficients of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples first decrease, then increase and last decrease at different sintering temperatures, and reach a maximum for 0.3% Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics.

As a result, for the performance index of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics (high threshold voltage, low leakage current, high nonlinear coefficient and high density), the sample with 0.3% Lu_2O_3 among Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at 950 °C is the best. The threshold voltage is 874 V/mm, the nonlinear coefficient is 20.9, and the leakage current is 0. 61 μA.

Figs.5−7 show the electric field intensity against current density (E—J) characteristics of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at three fixed sintering temperatures of 900, 950 and 1 000 °C for 2 h, respectively. As we know, the sharper the knee of the curve between the two regions is, the better the nonlinear properties are[3, 14, 16−18]. From Fig.6, we can find that the nonlinear coefficient decreases in the order of N3B→N0B→N4B→N2B→N1B and the threshold voltage decreases in the order of N4B→N1B→NB3→N2B→N0B.

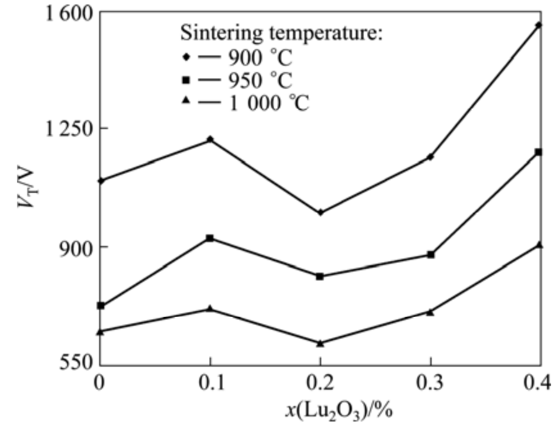

Fig.3 Threshold voltage of Lu_2O_3-doped varistor ceramics samples sintered at different temperatures

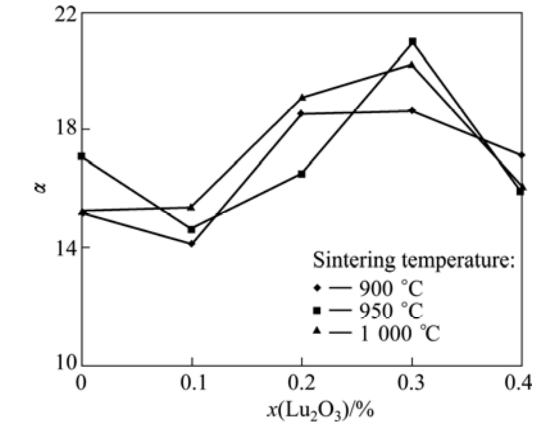

Fig.4 Nonlinear coefficient of Lu_2O_3-doped varistor ceramics samples sintered at different temperatures

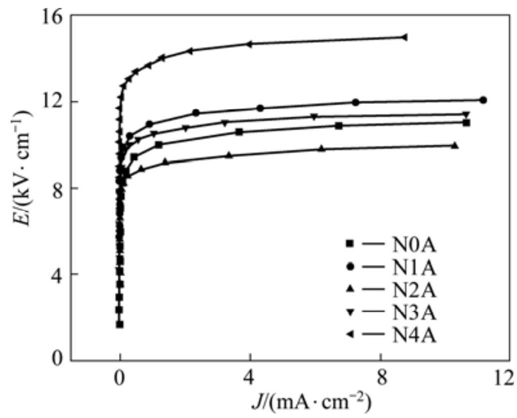

Fig.5 E—J curves of Lu_2O_3-doped varistor ceramics samples sintered at 900 °C

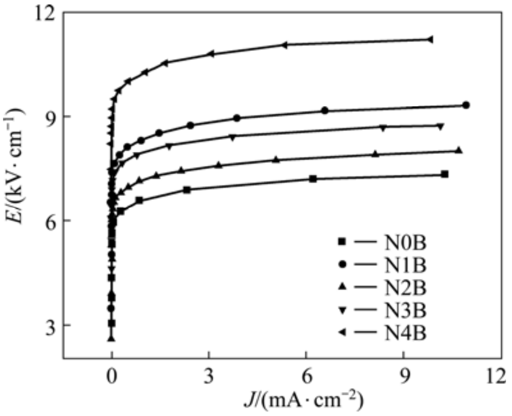

Fig.6 E—J curves of Lu_2O_3-doped varistor ceramics samples sintered at 950 °C

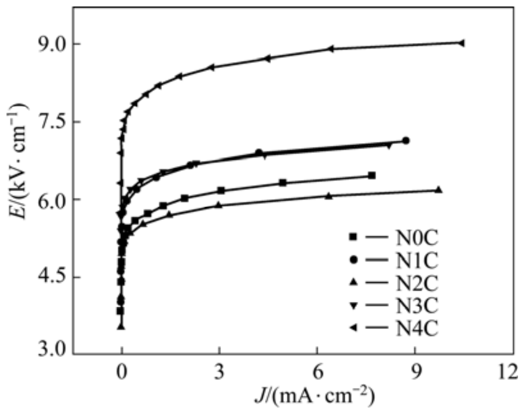

Fig.7 E—J curves of Lu_2O_3-doped varistor ceramics samples sintered at 1 000 °C

The SEM images of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at 950 °C for 2 h are shown in Fig.8. Those varistor ceramics samples are composed of ZnO phase, Bi_2O_3-rich phase, $Zn_7Sb_2O_{12}$ spinel-type phase and Lu_2O_3 phase, as determined by XRD analysis (Fig.9). From Fig.8, we can find that the grains size is fine when the amount of Lu_2O_3 added is 0.1%, then it increases with increasing the molar fraction of Lu_2O_3 to 0.2%.

XRD patterns of Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples sintered at 950 °C for 2 h are presented in Fig.9. The samples consist typically of three phases: ZnO phase, Bi-rich phase and spinel phase; ZnO is the predominant phase. However, for the samples doped with Lu_2O_3, additional peaks are evident due to the formation of Lu-based phases in the ceramic and their intensity increases with increasing Lu_2O_3 molar fraction in the starting composition. They may mainly

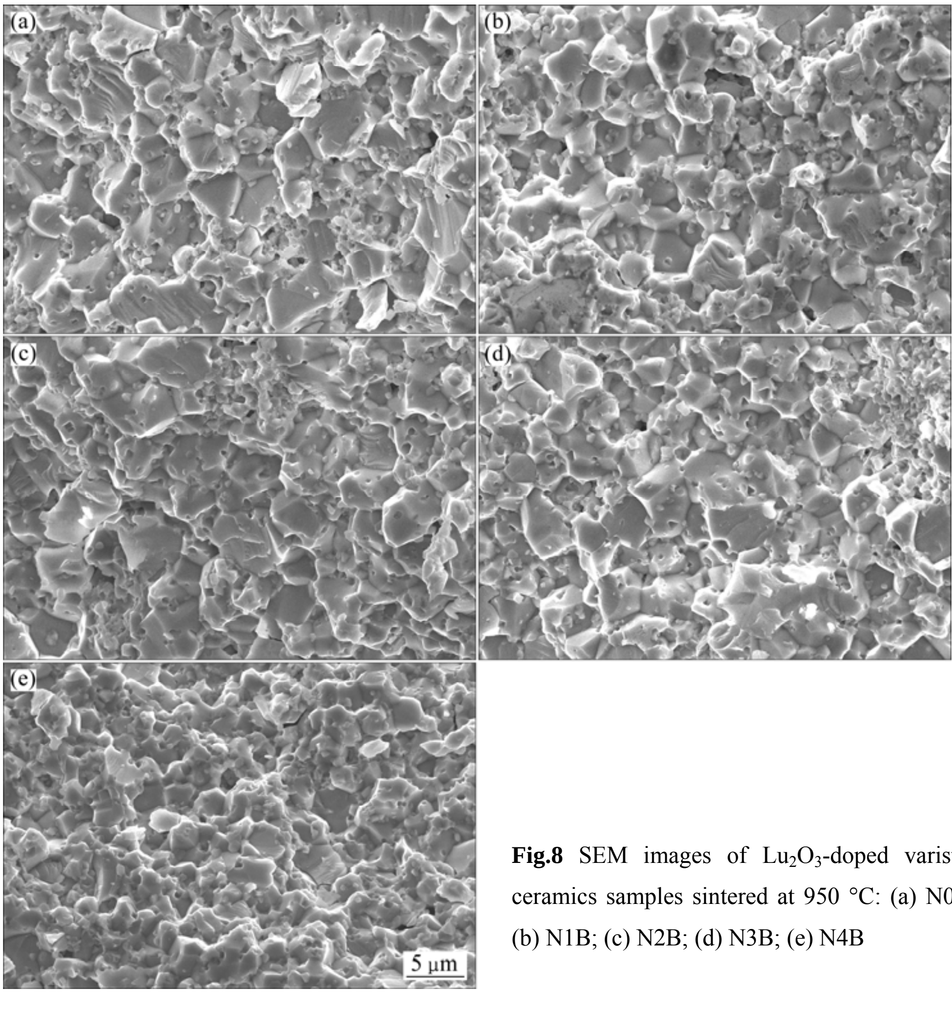

Fig.8 SEM images of Lu_2O_3-doped varistor ceramics samples sintered at 950 °C: (a) N0B; (b) N1B; (c) N2B; (d) N3B; (e) N4B

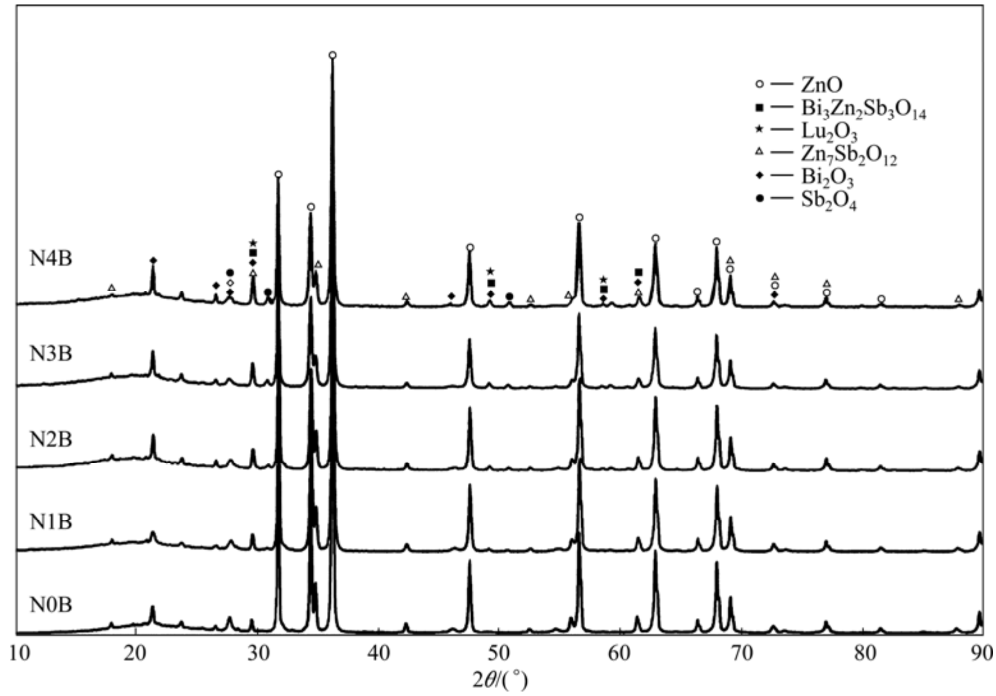

Fig.9 XRD patterns of Lu_2O_3-doped varistor ceramics samples sintered at 950 °C

disperse in the grain boundary[18]. At the same time, some of the peaks corresponding to spinel phase of $Zn_7Sb_2O_{12}$ for varistor ceramics diminish for samples with higher content of Lu_2O_3. So, 0.3% Lu_2O_3-doped ZnO-Bi_2O_3- based varistor ceramics appears to have an optimal composition of spinel phase of $Zn_7Sb_2O_{12}$ and Lu-based phase, which results in homogeneous grain size of ZnO among those samples as observed by SEM.

4 Conclusions

1) Lu_2O_3-doped ZnO-Bi_2O_3-based varistor ceramics samples were prepared by a conventional mixed oxide route and sintered in the temperatures rang of 900−1 000 °C.

2) The ZnO-Bi_2O_3-based varistor ceramics with 0.3% (molar fraction) Lu_2O_3 sintered at 950 °C exhibits comparatively ideal comprehensive electrical properties with the threshold voltage of 874 V/mm, the nonlinear coefficient of 20.9 and the leakage current of 0.61 μA.

3) The X-ray diffraction analysis of the samples show the presence of ZnO, Bi-rich, spinel $Zn_7Sb_2O_{12}$ and Lu_2O_3-based phases; at the same time, some of the peaks corresponding to spinel phase of $Zn_7Sb_2O_{12}$ diminish for samples with higher content of Lu_2O_3.

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(Edited by YANG Hua)