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Microstructure and Phase Transition of ZnO Varistor Ceramics

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ZnO바리스터 세라믹스의 미세구조와 상전이

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ABSTRACT

Microstructure and phase changes during the sintering of ZnO varistors were studied in $ZnO-Bi_2O_3-CoO-Sb_2O_3$ and $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$ systems using scanning electron microscopy (SEM) with an energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD) and differential thermal analysis (DTA).

The spinel phase and the Bi_2O_3 phase were formed by the decomposition of the pyrochlore phase during heating. The spinel particles (2-4μm), which were formed both along the grain boundaries and within the ZnO grain, were always found near the pyrochlore phase. Intergranular phases (Bi_2O_3 and pyrochlore) were precipitated from the liquid phase during cooling The Bi_2O_3 phases were located at the triple (or multiple) point of the ZnO grains Cr_2O_3 played a role in decreasing the formation temperature of the spinel phase and Bi_2O_3 phase during sintering, and inhibited the grain growth.

요 약

ZnO 바리스터의 소결과정에서 상변화와 미세구조는 여러분석기기(SEM/EDAX, XRD와 DTA)를 이용하여 $ZnO-Bi_2O_3-CoO-Sb_2O_3$와 $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$계에서 조사하였다.

Spinel상과 Bi_2O_3상은 소결과정에서 pyrochlore상의 분해에 의해 형성되었다. Spinel입자(2-4μm)들은 ZnO입자들 사이와 ZnO입자내에 놓여 있었으며, 항상 pyrochlore상과 인접하게 위치하고 있었다. Intergranular(Bi_2O_3, pyrochlore)상들은 고온에서 냉각동안 액상에 의해 나타나며, Bi_2O_3상은 ZnO입자들의 triple(또는 multiple) point에 위치한다. Cr_2O_3는 소결 과정에서 spinel과 Bi_2O_3상의 생성온도를 낮추하며, 입자성장을 억제하였다

1. INTRODUCTION

Zinc oxide ceramics with a small addition of Bi_2O_3 and several other oxides show a highly non-ohmic behavior in the current-voltage characteristics[1]. They have been widely used as surge arrestors and stabilizers in electric power system and electronic circuits[2,3]

The microstructure of ZnO varistor which was composed of ZnO grains, spinel and Bi-rich intergranular phases (Fig.1) is known to have an important effect on the non-ohmic characteristics and other electrical properties.

In the early studies[1,2,5] of ZnO varistors, it was believed that continuous intergranular layers of high-resistivity (Bi_2O_3[6], $\rho \simeq 10^{13}\Omega \cdot cm$), which isolate the ZnO grains completely, were responsible for the non-ohmic behavior. However, later investigations[7] using direct observation in the transmission electron microscope have shown that the intergranular phase was not continuous but isolated at triple points of the ZnO grains

The spinel phase ($Zn_7Sb_2O_{12}$) in the $ZnO-Bi_2O_3-Sb_2O_3$ system was formed by the decomposition of the pyrochlore ($Bi_2(Zn_{1/3}Sb_{2/3})O_6$[8], $Bi_{3/2}ZnSb_{3/2}O_7$[9]) phase according to the following reaction.

$$2Zn_2Bi_3Sb_3O_{11}+17ZnO \rightarrow 3Zn_7Sb_2O_{12}+3Bi_2O_3$$

Wong[8] first reported that the ratio of the spinel to pyrochlore increases with the sintering temperature., Inada[9] has proposed that the phases present in ZnO varistors varied with cooling rate and amount of the transition metal oxide. Also, the spinel and pyrochlore phase have been identified in the ZnO varistors by the several investigators[8-10] during the last decade. Very little published work has been done, however, on the studies of the reaction between the spinel and pyrochlore phase during sintering of the ZnO varistors. The spinel and pyrochlore phase may affect the electrical properties through their effects on the microstructure development during sintering. So, it is desirable to have a better understanding of the formation reactions of spinel and pyrochlore phase.

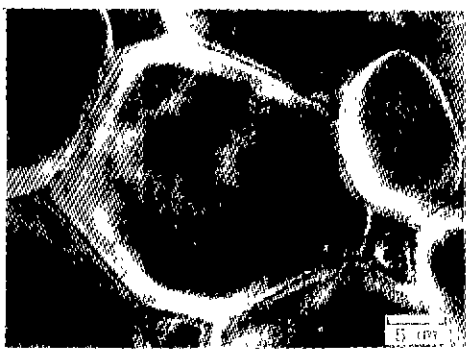

Fig.1. Scanning electron micrograph of $ZnO-Bi_2O_3-CoO-Sb_2O_3$ system sintered at 1250℃.

In this study, the microstructural features of the phases (spinel, pyrochlore) and phase transformation during heating in the $ZnO-Bi_2O_3-CoO-Sb_2O_3$ and $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$ systems are studied to understand clearly the reaction between the spinel and pyrochlore phase

2. EXPERIMENTAL PROCEDURE

Sample preparation-The raw materials used in this study were reagent-grade powders of ZnO*, Cr_2O_3**, Bi_2O_3=, CoO+ and Sb_2O_3+-. The samples were prepared by conventional ceramic process[11]. The composition of sample (a) was 97.5 ZnO containing 1.0 Bi_2O_3, 0.5 CoO, and 1.0 Sb_2O_3 in mole ratio and the composition of sample (b) was 96.5 ZnO, 1.0 Bi_2O_3, 0.5 CoO, 1.0 Sb_2O_3 and 1.0 Cr_2O_3.

The powders were ball milled with distilled water for 10 hr and were dried at 80℃ for 24 hr, and powders were granulated using 80 mesh sieve to improve the flow characteristic. These powders were formed into the disc shape with the pressure of 1000 kg/cm² and sintered by the heating schedule as shown in Fig.2. Finally the sintered specimens were quenched at the desired temperatures.

XRD-The crystal phases present in each specimen were examined by the X-ray diffraction (XRD, Philips Co. PW1710) as the powder method using Cu$K\alpha$ radiation.

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* G R grade, ** 1st grade, Junsei Chem. Co., Ltd. (Japan)

= 99.9%, Janssen Chem. Co., Ltd. (Belgium)

+ G R grade, Kanto Chem. Co., Ltd (Japan)

+- 1st grade, Kokusan Chem Co., Ltd. (Japan)

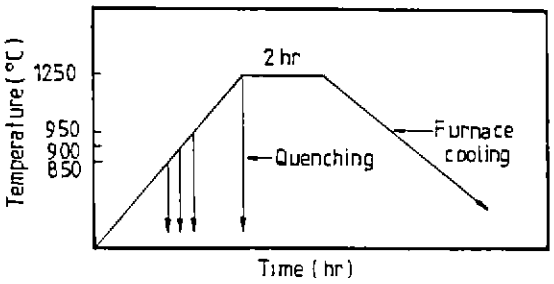

Fig.2. Thermal schedule of sintering.

SEM/EDAX—The examination of the microstructural features of the each phases was carried out using the scanning electron microscopy (SEM, Hitachi Co. X—650) with the energy dispersive X—ray analysis (EDAX).

DTA—An appropriate fine powder (320 mesh) was analyzed by the differential thermal analysis (DTA, Rigaku Co. PTC—10A). Powders were heated to 1100℃ with the heating rate of 10℃/min in an air environment. The reference material was $\alpha-Al_2O_3$.

Grain size—The average grain sizes were measured by the intercept method[13], which was calculated by counting the number of grain boundaries intercepted by the line of known length.

3. RESULTS AND DISCUSSION

3.1. PHASE CHANGE

XRD analysis—Fig.3 shows the X-ray diffraction patterns of the samples which were quenched at 850℃. Whereas phases present in the sample (a) were ZnO grains, pyrochlore and poor spinel phases, sample (b) showed Bi_2O_3 phase also. The pyrochlore

Table 1. Phase Formation in the Samples Heated at Various Temperatures.

temp / samp.	850℃	900~950℃	1250℃ (q)	1250℃ (s)
(a)	Z+P+S	Z+S+P+B	Z+S—B	Z+P+S+B
(b)	Z+P+S+B			

Z ZnO, P : pyrochlore, S : spinel, B Bi_2O_3.

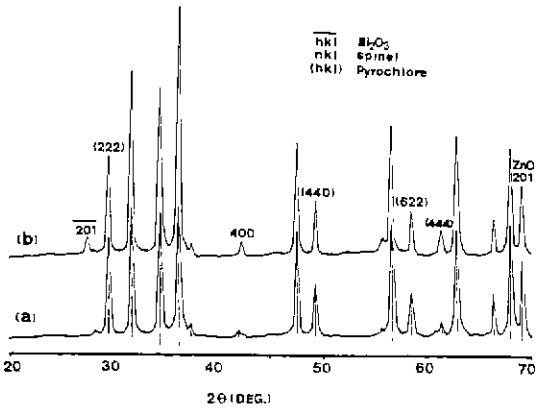

Fig.3. X—ray diffraction patterns of samples quenched at 850℃.
(a) $ZnO-Bi_2O_3-CoO-Sb_2O_3$,
(b) $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$.

phase was formed at temperatures below 850℃ in the both samples. The Bi_2O_3 and spinel phases were appeared at 850℃ in sample (b), while the poor Bi_2O_3 phases detected at 900℃ in sample (a).

Fig.4 shows ratios of the X-ray peak height Bi_2O_3 (201), spinel (400), and pyrochlore (222, 440) phase to that of ZnO (201), respectively. At 850—950℃, in the sample (a), the peak heights of the pyrochlore phase have increased. On the other hand, in the sample (b), peak heights of the pyrochlore phase have decreased, but peak heights of the spinel and Bi_2O_3 phase have increased.

In the samples sintered at 1250℃, a ZnO grains, Bi_2O_3 and spinel phase were present. It is noticeable that the samples in which were cooled slowly, pyrochlore phase was detected (Table 1). The X-ray intensities of spinel, pyrochlore and Bi_2O_3 phases were dependent on the firing temperature as well as on the additive oxides.

DTA analysis—Fig.5 shows the differential thermal analysis (DTA) patterns of the two system powders.

The endothermic peaks were observed around 910℃ in sample (a) and around 820℃ in sample (b). These temperatures almost coincide with the spinel phase formation temperatures as shown in Fig.4 (see X—ray

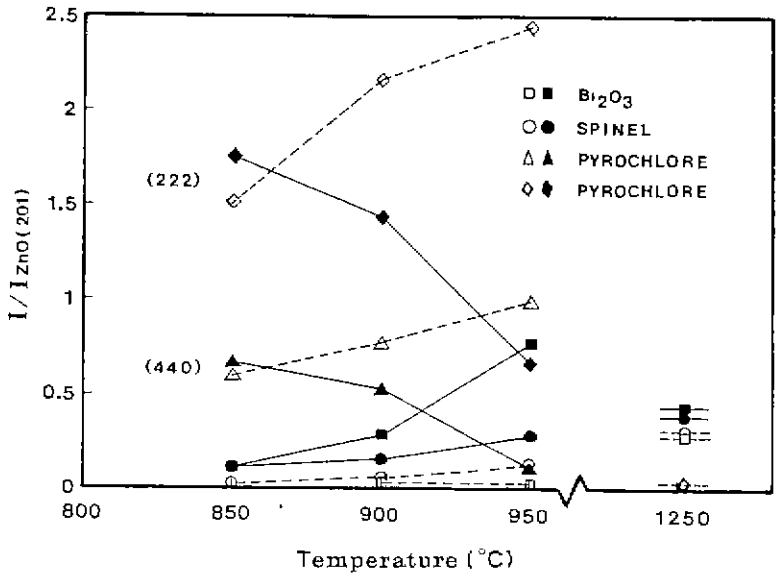

Fig.4. X-ray peak heights for Bi_2O_3(201), spinel(400) and pyrochlore(222, 440) phase as compared to ZnO(201) (— $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$ system, - - - $ZnO-Bi_2O_3-CoO-Sb_2O_3$ system).

results). The sample (a) shows sharp endothermal peak, whereas the sample (b) shows broad endothermal peak. In addition, the endothermal reaction in sample (b) starts from lower temperature than that of sample (a).

The results presented in Fig.3, 4(XRD) and Fig. 5(DTA) can be explained as follows. The pyrochlore phase was formed during heating. The spinel and Bi_2O_3 phase were formed by the decomposition of the pyrochlore phase. The Bi_2O_3 phase were formed at 850℃ in sample (b) and at 900℃ in sample (a), respectively. The Cr_2O_3 seemed to lower the formation temperature of the spinel and Bi_2O_3 phase.

These results are similiar to the previous researchers[9,10] which showed the DTA results of the varistor materials Inada[9] also showed that a pyrochlore was formed at 900℃ during heating and the additions of the transition metal oxides decreased the formation temperature of spinel and Bi_2O_3 phase.

Imai[10] reported that because the pyrochlore phase has a defective structure, the additive oxides(SiO_2 and

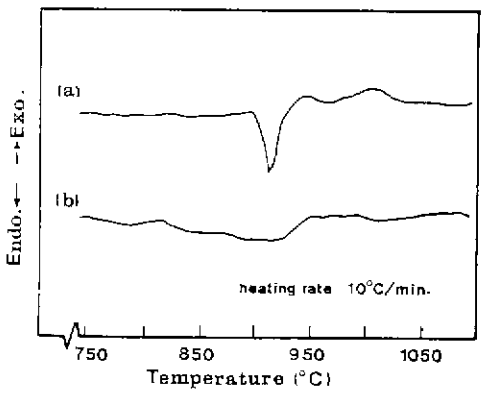

Fig.5. Differential thermal analysis curves for starting powders.
(a) $ZnO-Bi_2O_3-CoO-Sb_2O_3$,
(b) $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$.

Cr_2O_3) could be dissolved into the pyrochlore, their dissolution would make the structure unstable.

3.2. MICROSTRUCTURE

SEM/EDAX analysis—Fig.1 shows the microstructure of the sample (a) which was sintered at 1250℃

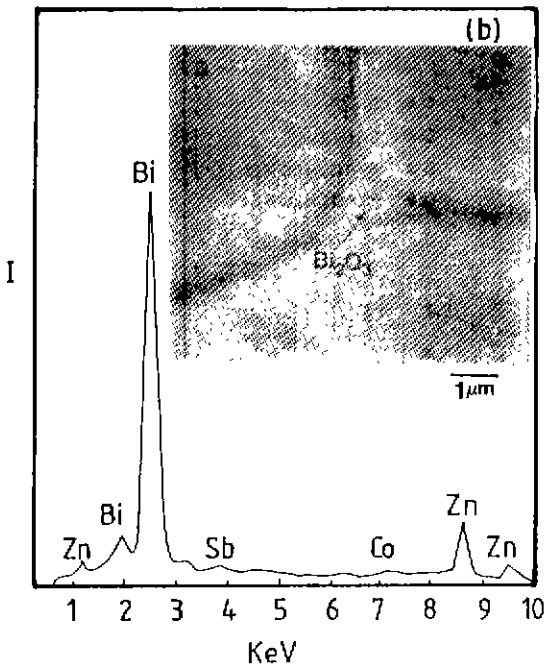

Fig.6. (a) Morphology of the Bi_2O_3 phase in Fig.1. (b) EDAX spectrum of Bi_2O_3 phase taken from the triple junction.

and slow cooled. The microstructure consisted of ZnO. grains Bi_2O_3, pyrochlore (Bi-rich phase) and spinel grains. The spinel grains were surrounded by the pyrochlore phase. Some of the spinel particles were also present within the ZnO grains. Intergranular phases (Bi_2O_3, pyrochlore) were precipitated from the liquid phase during cooling. The pyrochlore phase was found both at the triple(or multiple) points of ZnO grains and at the grain boundaries, and Bi_2O_3 phases were surrounded by ZnO grains.

Fig.6 shows the EDAX pattern of the Bi_2O_3 phase (Fig.1). The Bi_2O_3 phase located at the triple point of the ZnO grains shows that it contains zinc, cobalt and antimony.

Fig.7(a) shows spinel and pyrochlore phases. In case of the samples which were sintered at 1250℃, above morphology was detected and the pyrochlore phase was always found near the spinel particle Fig. 7(b) and (c) are the EDAX patterns of the spinel and pyrochlore phase. Whereas the spinel($Zn_7Sb_2O_{12}$) particles contained only cobalt in sample (a), cobalt and chromium were detected in sample (b)

Fig.8(a) and (b) show a spinel grain located along grain boundary and a spinel grain within ZnO grain.

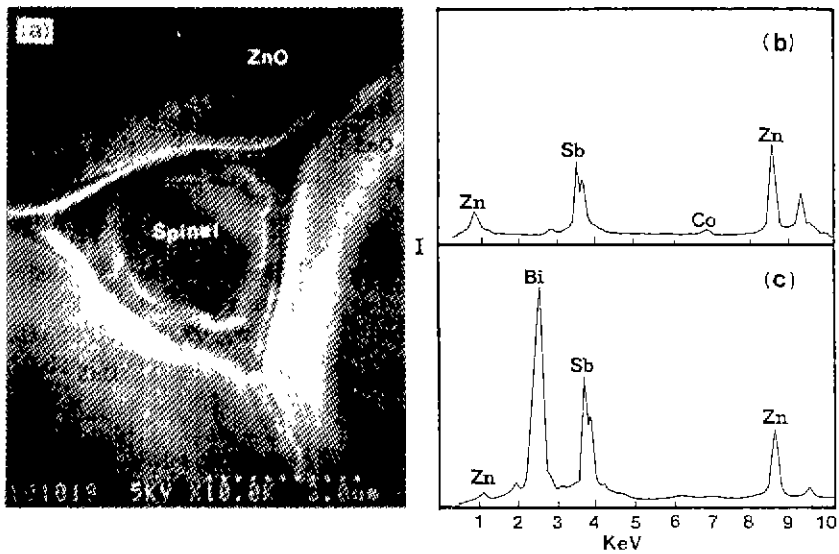

Fig.7. (a) Scanning electron micrograph of $ZnO-Bi_2O_3-CoO-Sb_2O_3$ system sintered at 1250℃, (b), (c) EDAX spectrum taken from the spinel and pyrochlore phase.

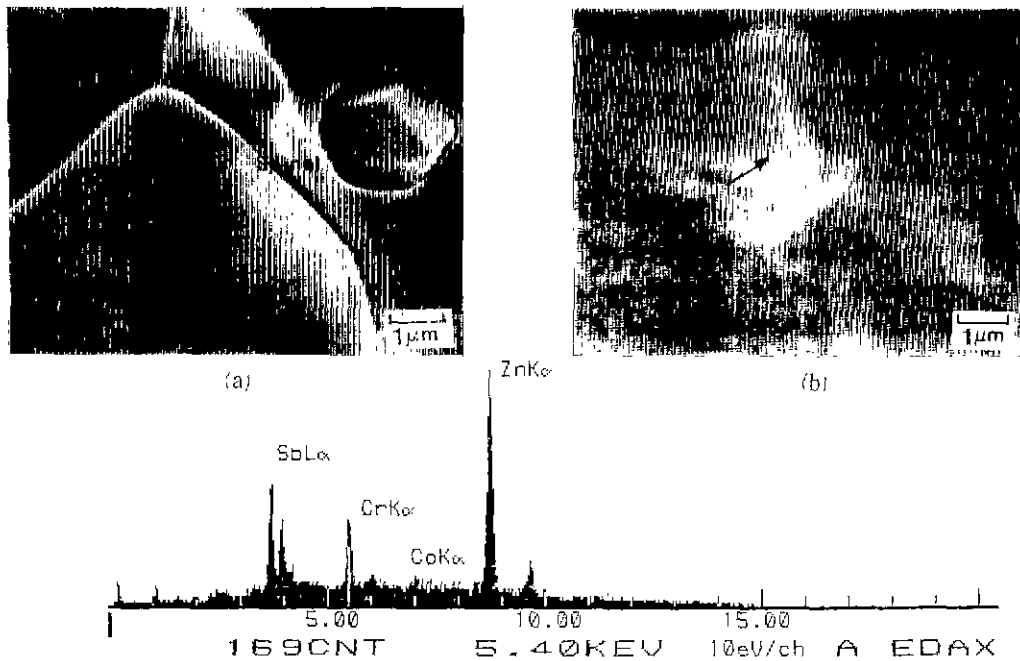

Fig.8. (a), (b) Morphology of the spinel phase taken from the $ZnO-Bi_2O_3-CoO-Sb_2O_4-Cr_2O_3$ system sintered at 1250℃. (c) EDAX spectrum taken from the spinel phase.

As shown in Fig.8(a), some spinel grains with the *pyrochlore phase were present within the ZnO grain.* Because spinel particles are too small to be effective as pinning points, spinel particles can be isolated by the migration of the ZnO grain boundaries. Their migration resulted in inclusion such as Bi-rich liquid phase within the ZnO grains. Also, The spinel grains occasionally were in contact directly with ZnO grains.

Fig 8(c) shows an EDAX pattern of the spinel particle. Only dissolved Cr was found in the spinel *particle.*

Grain growth of ZnO—Fig.9 shows the average ZnO grain sizes of the sintered samples at the various tempertures.

From the above results, the ZnO grain size increased with the sintering temperature. The grain sizes of ZnO in sample (b) were smaller than those of the sample (a).

In the previous observations[11,12], ZnO varistor material *which contained only* Bi_2O_3 *as an additive* showed that more addition of Bi_2O_3(0.5~5mol%) results in decrease of the grain sizes. From our present research, it shows that grain growth was

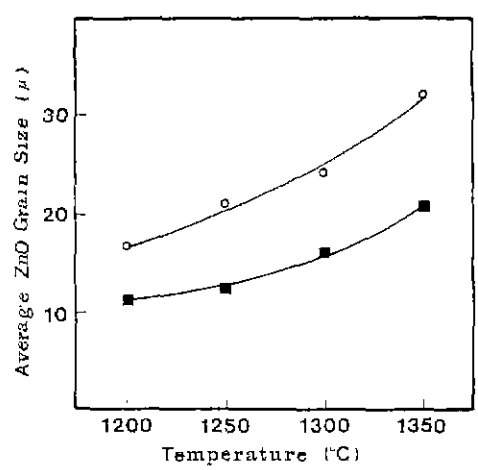

Fig.9. Average ZnO grain size of samples sintered at various temperatures.
○ $ZnO-Bi_2O_3-CoO-Sb_2O_3$,
■ $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$.

influenced by the spinel and liquid phase Bi_2O_3 which were formed by the decomposition of pyrochlore at the early stage of sintering. The growth of the ZnO grains was controlled by the spinel particles during sintering, because ZnO grain boundaries were pinned by the spinel particles. Thus, the ZnO grain growth occurred coincidently with the spinel formation. From the results presented in XRD and DTA, because the Cr_2O_3 seemed to lower the formation temperature of the spinel phase, the ZnO grain growth in sample (a) was happened easier than that of in sample (b).

4. CONCLUSION

From the discussion on the microstructure as well as on the phase change in the systems $ZnO-Bi_2O_3-CoO-Sb_2O_3$ and $ZnO-Bi_2O_3-CoO-Sb_2O_3-Cr_2O_3$, the following conclusions can be obtained:

1) During the heating, the spinel ($Zn_7Sb_2O_{12}$) and Bi_2O_3 phase appeared at around 850℃. The spinel phase which was formed both in the junctions of the ZnO grains and within the ZnO grain, was found to be always adjacent to a pyrochlore.

2) The intergranular phases (Bi_2O_3 and pyrochlore) were precipitated from the liquid phase during cooling. The Bi_2O_3 phase was located at the triple(or multiple) points of the ZnO grains.

3) The formations of spinel and Bi_2O_3 phase resulted in the decrease of the volume fraction of pyrochlore phase. Cr_2O_3 played a role in decreasing the formation temperature of the spinel phase and Bi_2O_3 phase, and prevented the grain growth.

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