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The Effects of Humidity and Pressure on the Low Field Resistivity of Zinc Oxide Based Varistor Granules

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Outline

1. Introduction
   i. Background on ZnO varistors
   ii. Motivation for studying granules

2. Experimental Procedure
   i. Fabrication and characterization of granules
   ii. Electrical measurements

3. Results and Discussion
   i. i-V characterization
   ii. Effect of humidity
   iii. Effect of compressive stress

4. Conclusions

Electrical Behavior of Varistors: Non-linear i-V Characteristic.

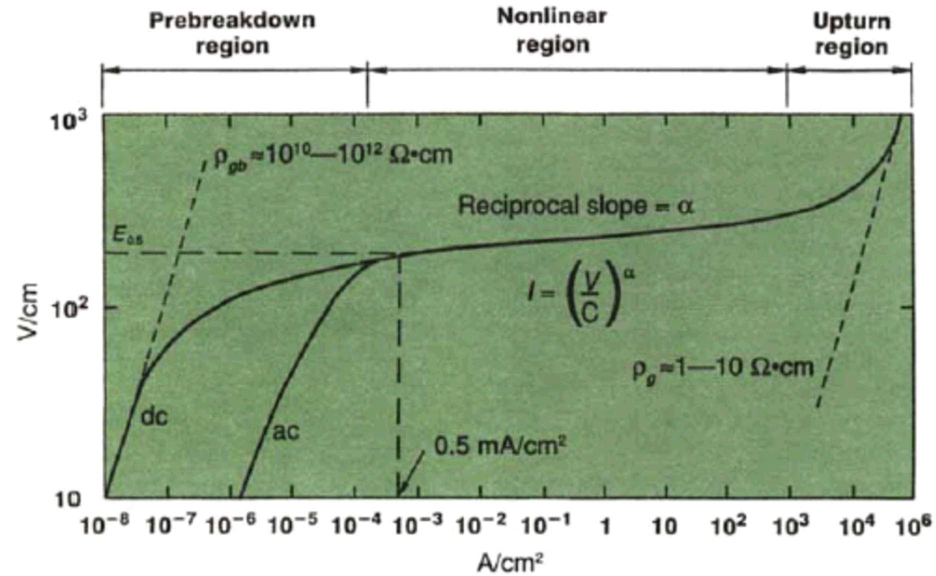
Varistors are good insulators at low E but switch to being conducting at the switching field.

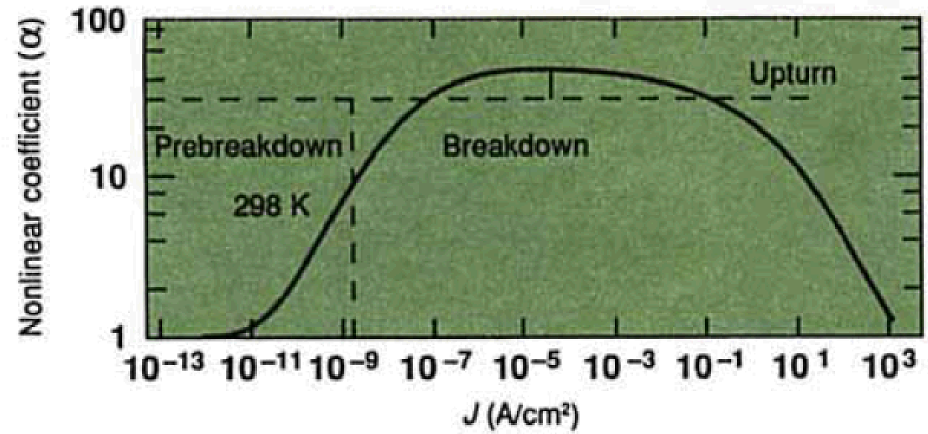
They are ohmic at very low fields.

Non-linearity increases with applied field to a maximum and then decreases.

In the breakdown region, the non-linearity, α, coefficient can be >30.

$$I = \left(\frac{V}{C} \right)^{\alpha} = KV^{\alpha}$$





T. Gupta, "Application of Zinc Oxide Varistors," *J. Am. Ceram. Soc.,* **73** (7) 1817-1840 (1990).

Origin of Varistor Effect: Voltage barriers due to segregation at ZnO grain boundaries.

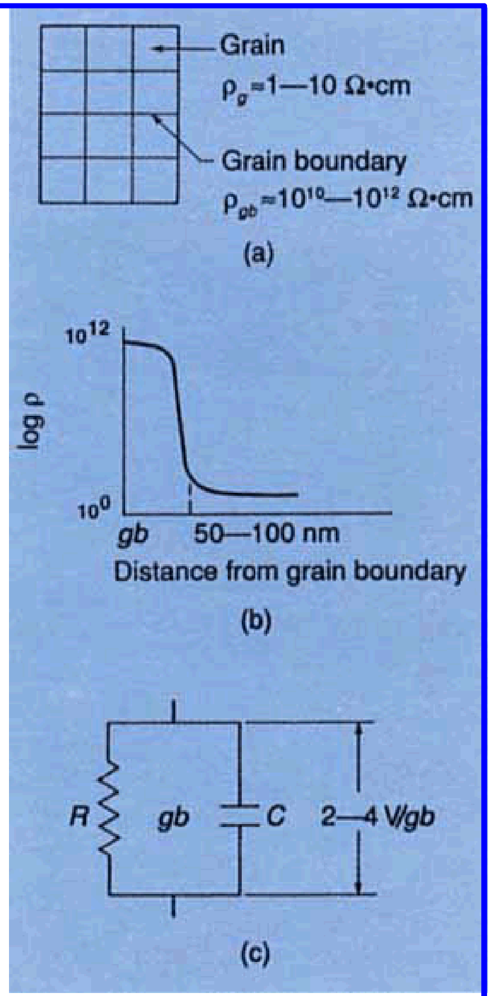
Segregation at ZnO grain boundaries results in a ~3V barrier that is ~100 nm thick.

ZnO grains are semiconducting.

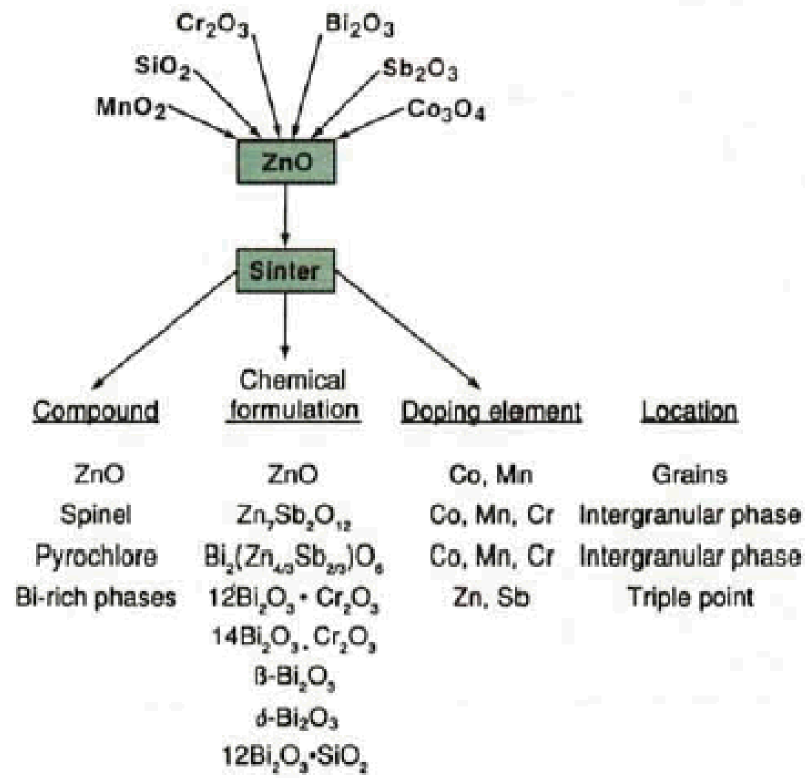
Bi or other elements at GB create barrier.

Tunneling occurs at low E.

Once applied V is enough to surpass all GB barriers, switching to high conductivity occurs.



Commercial varistors can have complex compositions and microstructures.



T. Gupta, "Application of Zinc Oxide Varistors," *J. Am. Ceram. Soc.*, **73** (7) 1817-1840 (1990).

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Motivation of Present Study

- Goal of this study: characterize varistor granule environmental performance.
    - Effect of humidity on electrical properties
    - Effect of pressure on electrical properties
- Varistor material: BaO- and Co_3O_4 -doped ZnO.
- Granules were made by pressing calcined powder into compacts that were crushed or using a droplet technique and then sintered.
- Resulting granules were typically 150 to 300 µm in size.

Granule Fabrication and Characterization

- The typical granule composition was 98.2 at% ZnO, 1.0 at% BaO and 0.8 at% Co_3O_4.

- Some samples were made by crushing a green pellet others by a droplet technique.

- Sintering was done in air at 1200°C for 3 hr followed by an anneal at 1150°C for 3 hr.

- Granules were characterized used SEM, EDS and XRF.

- Bulk samples as well as granules made by crushing bulk sintered samples were characterized electrically.

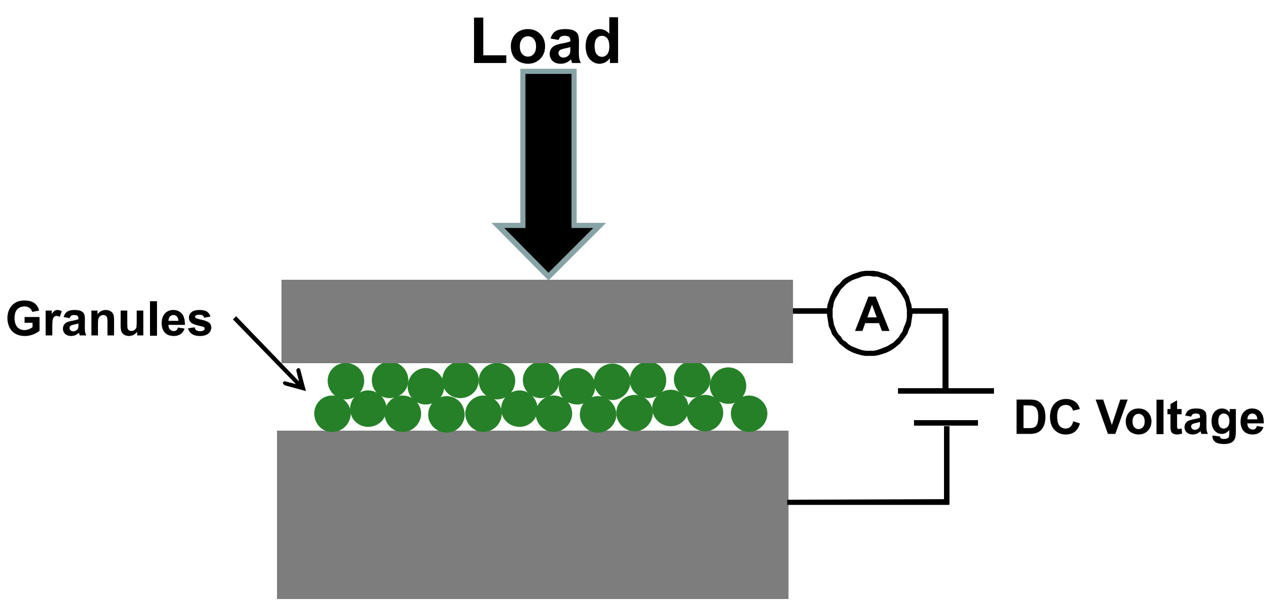
Electrical Characterization

A Keithley 237 High Voltage Source Measure Unit was used to measure the current flowing through a thin granule layer as a function of applied voltage.

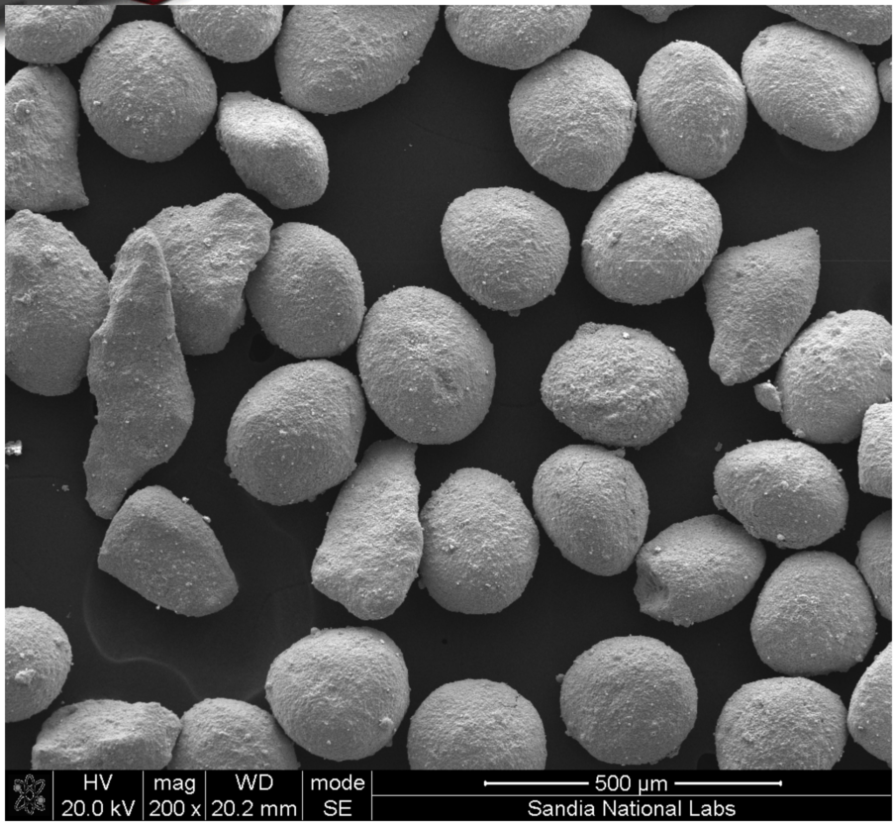
The layer was ~1 mm thick and metal (steel) plates were used as the electrodes.

Some measurements were made in a controlled humidity chamber.

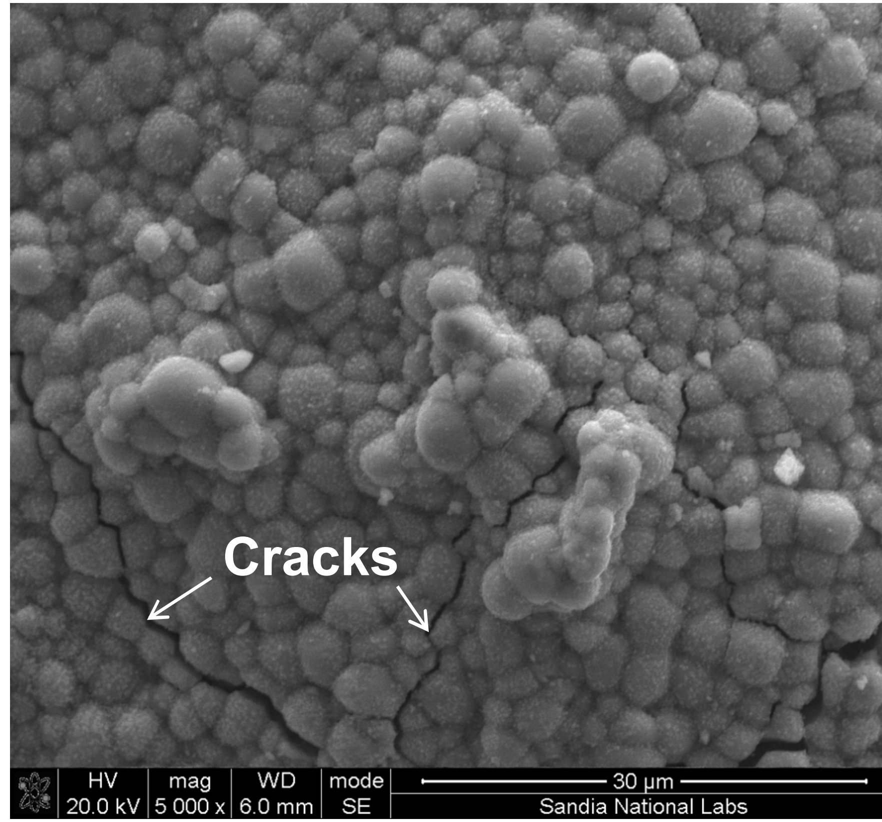
Loads were applied to the top plate electrode ranging from 0.01 to 30 bar.



Typical Rounded Granules



150 to 300 µm Granules

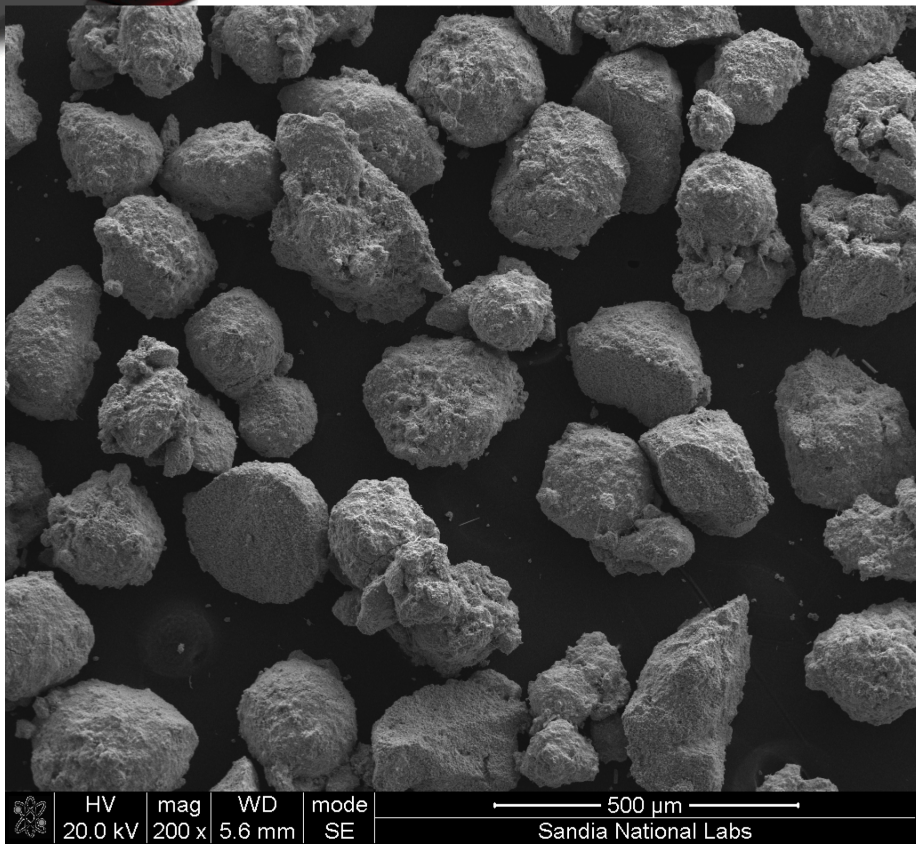


2 to 3 µm GS

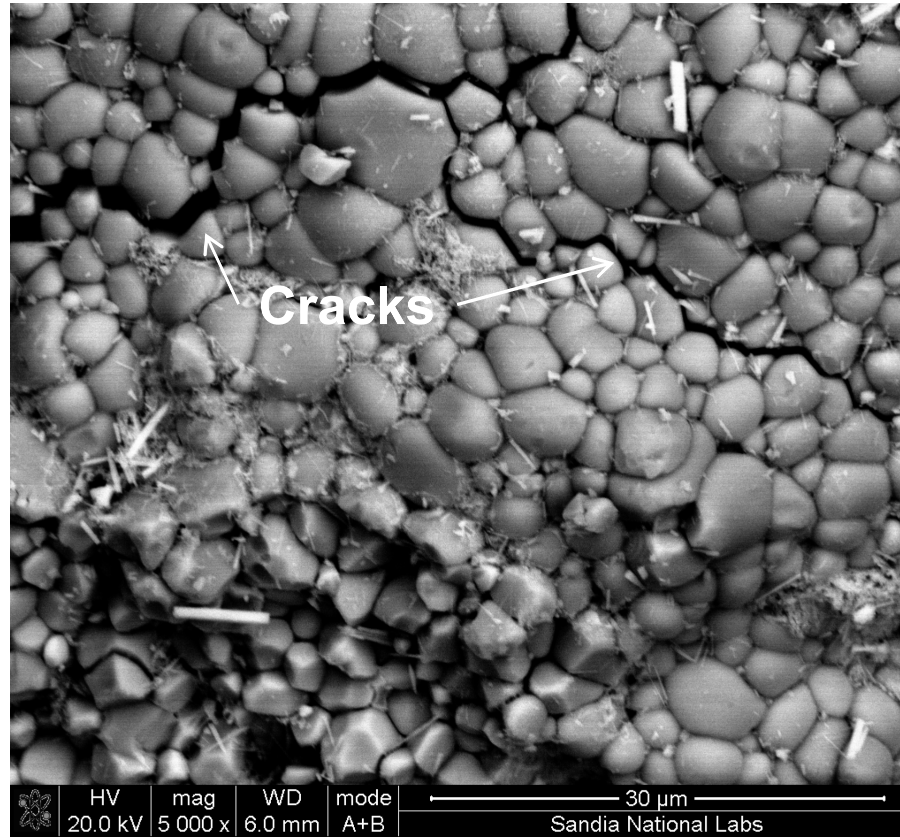
XRF Results

Element	AN	Net	norm. C. [wt.%]	Atom C. [at.%]	Error (1 Sigma) [wt.%]
Zinc	30	17129960	97.17	98.22	2.08
Cobalt	27	282023	0.66	0.74	0.00
Barium	56	208579	2.17	1.04	0.00
		Total	100.00	100.00	

Typical Crushed Granules



150 to 400 µm Granules



3 to 10 µm GS

XRF Results

Element	AN	Net	norm. C. [wt.%]	Atom C. [at.%]	Error (1 Sigma) [wt.%]
Zinc	30	17616282	97.01	98.10	2.21
Cobalt	27	316550	0.71	0.80	0.00
Barium	56	227029	2.28	1.10	0.00
		Total	100.00	100.00	

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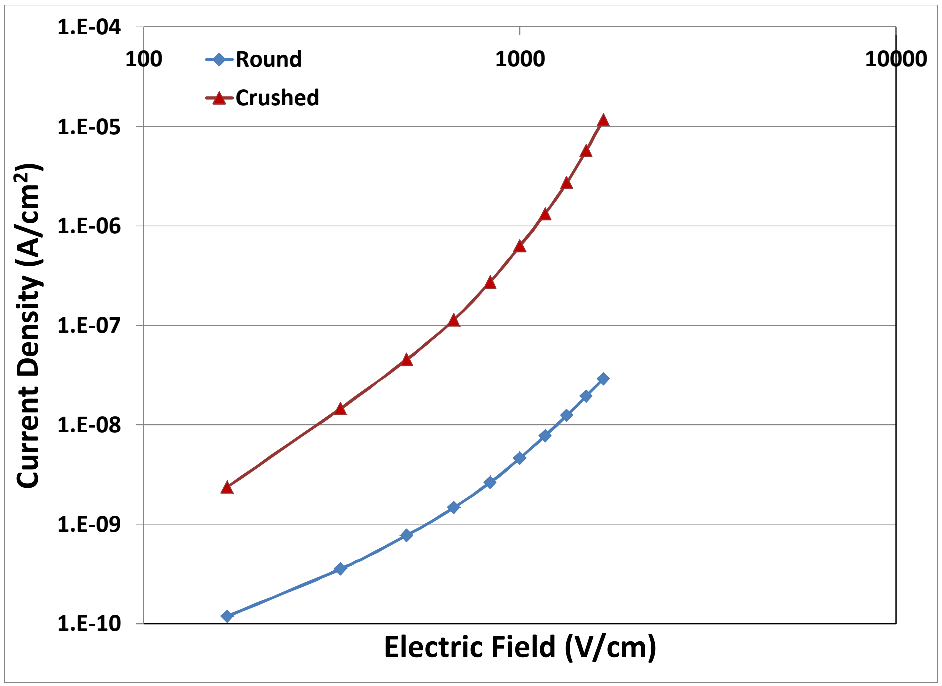
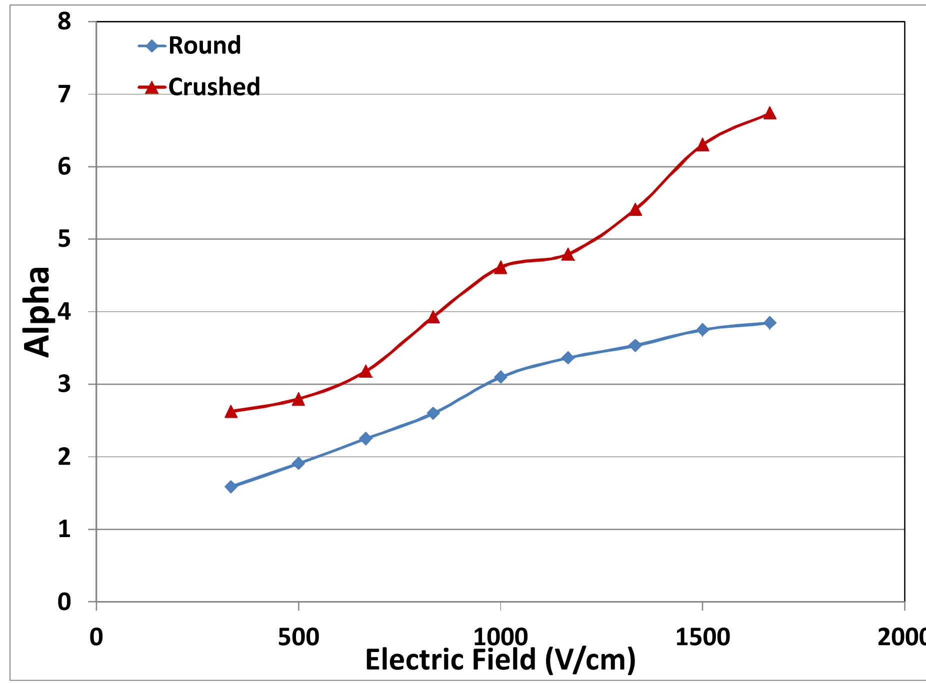
i-V characteristics for varistor granules are similar to bulk behavior.

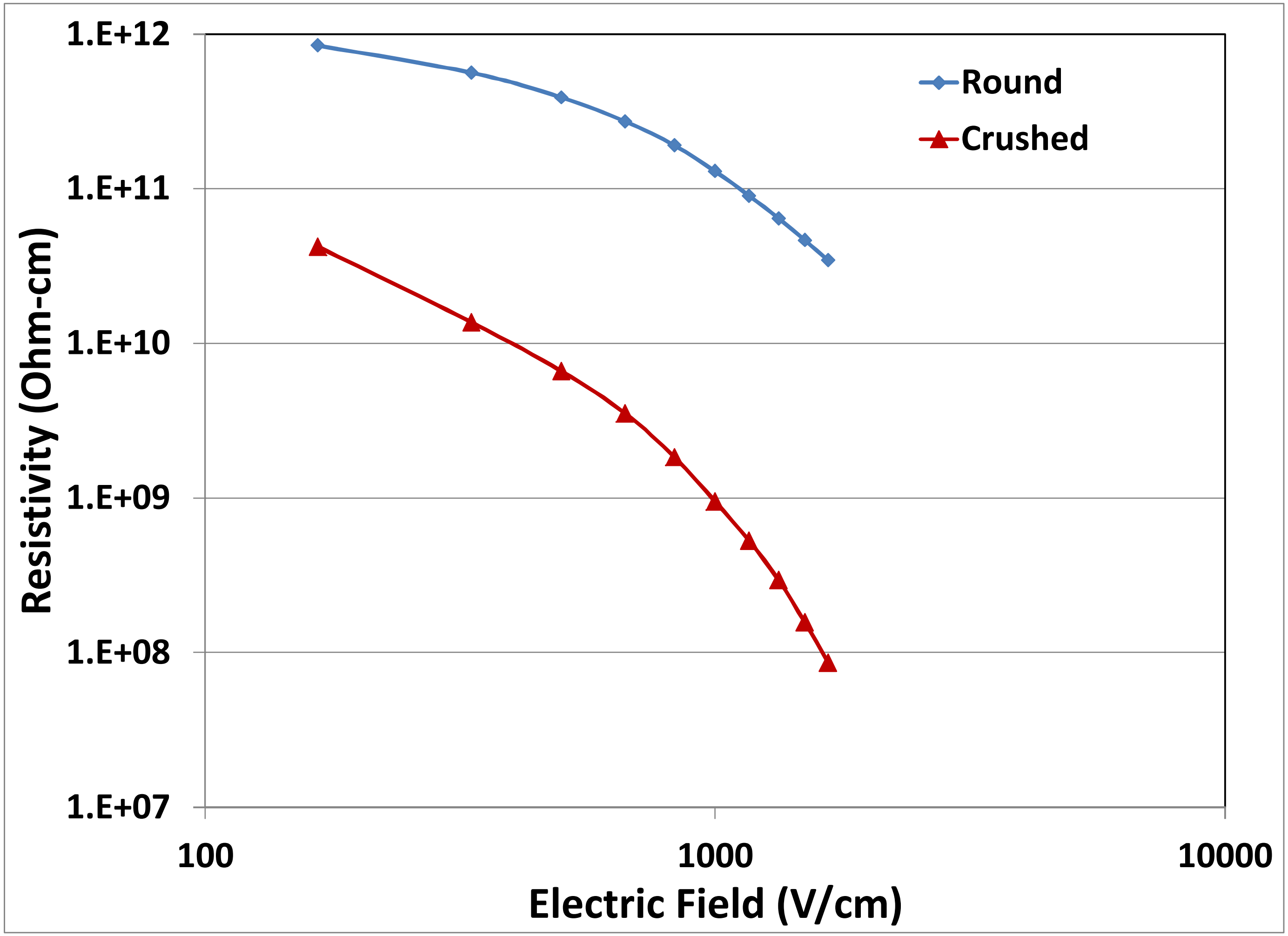
Non-linear i-V behavior



α increases with E



Granule low-field resistivity was in the expected range



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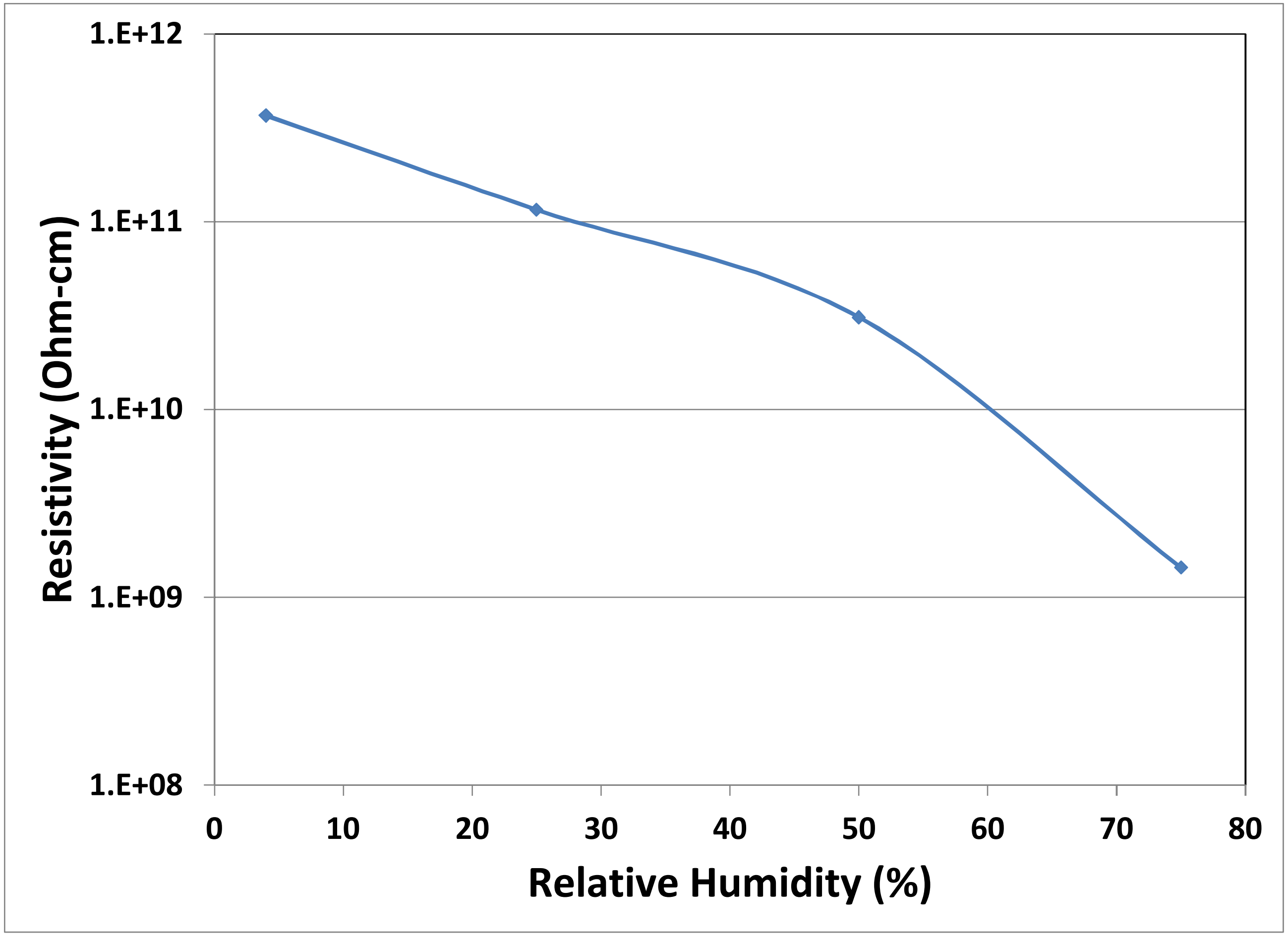
Resistivity of varistor granules decreased by several order of magnitude with increasing RH.



Change in ρ was rapid and reversible implying it was due to adsorption of water vapor.

Previous work* on thin-film ZnO varistors showed similar results.

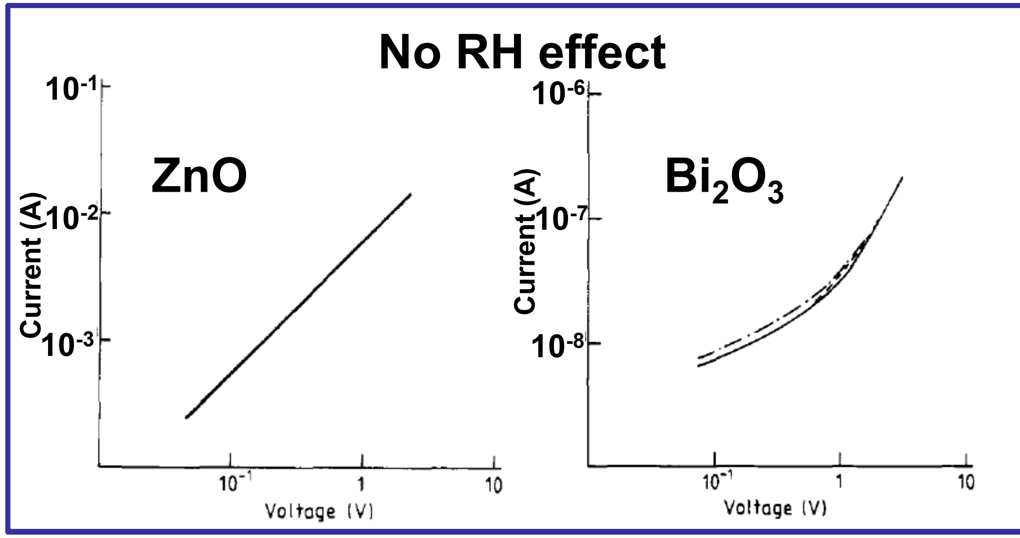
They measured I-V curves at 0%, 22%, 69% and 93% RH on individual ZnO and Bi_2O_3 layers and on a bi-layer.

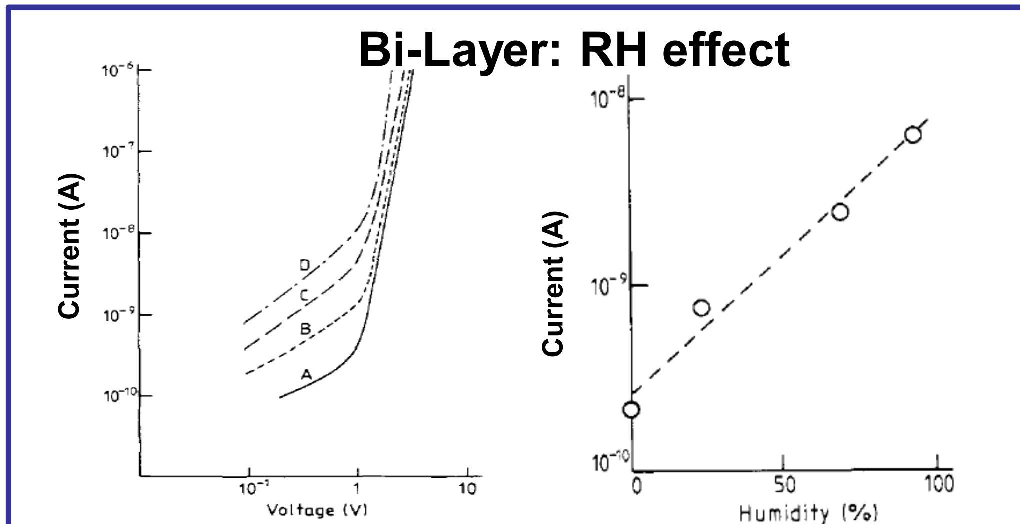
No RH effect for individual layers.

Large RH effect for bi-layer.

No effects found for other vapors including ethanol.

Explanation: Adsorption of water lowers the voltage barrier at the boundary in a reversible manner.





*Y. Suzuki, A. Ohki, T. Mizutani and M. Ieda, "Humidity Dependence of Electrical Conduction in ZnO-Bi_2O_3 Thin-Film Composites," *J. Phys. D: Appl. Phys.* **20** 518-521 (1987).

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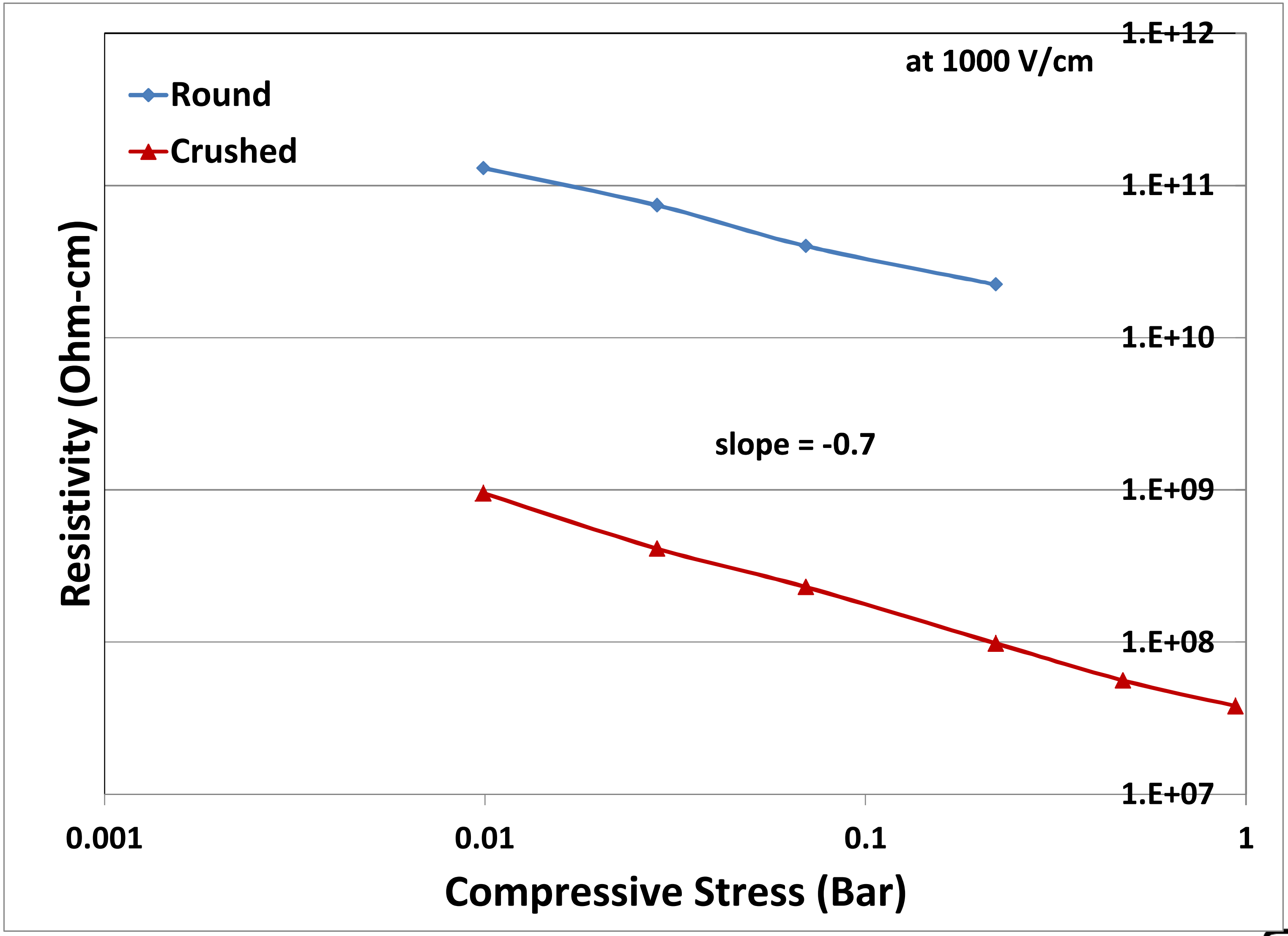
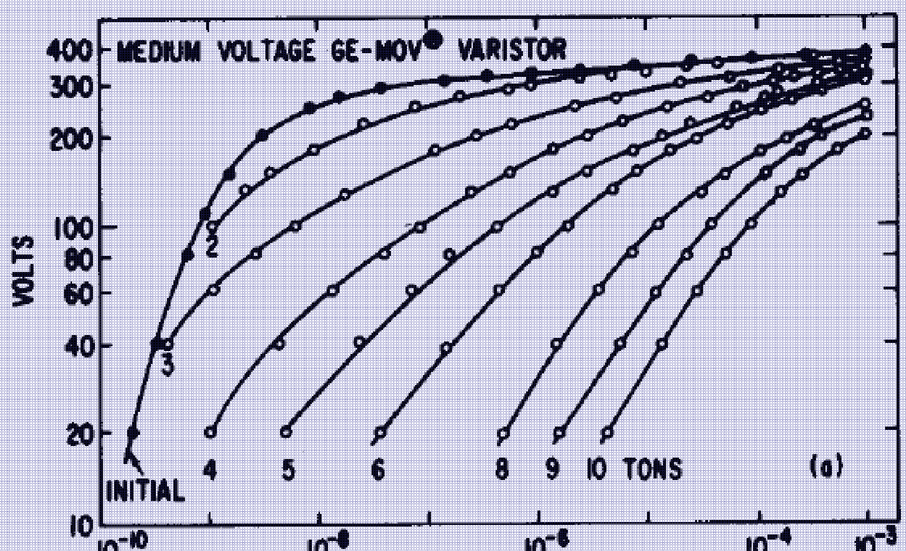
The granule resistivity decreased strongly with compressive stress at low stress levels.

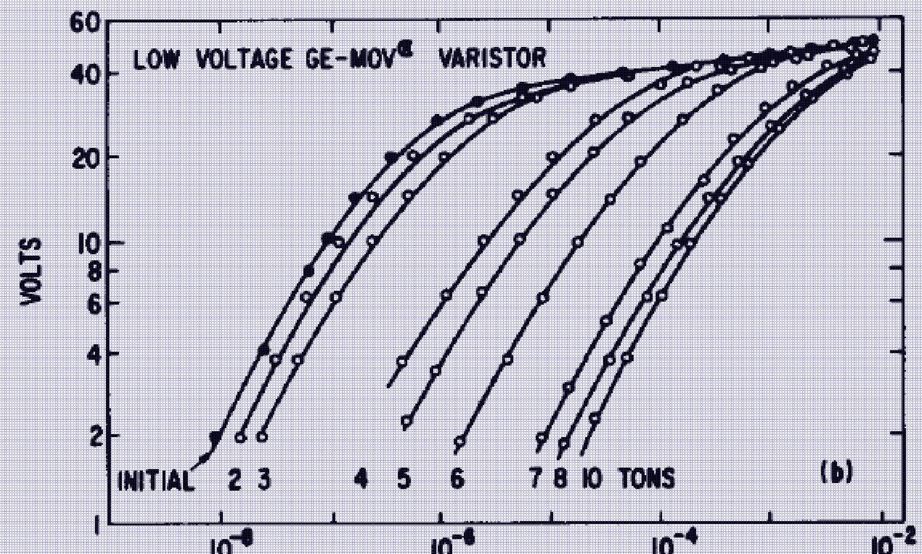


Work in the 1970's showed that compressive stress decreases low-field resistivity of bulk ZnO varistors.

i-V curves for two types of commercial varistors.



Current (Amperes)



Current (Amperes)

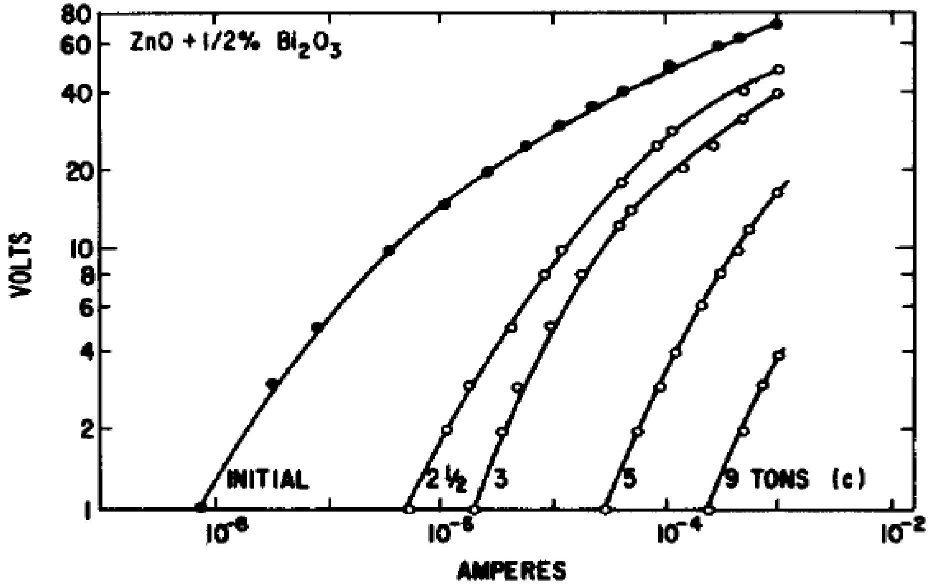
Note: 1 ton of load equaled 550 Bar of stress.

- **This effect was due to the lowering of the GB barrier voltage with stress.**
- **Changes occurred at much higher stress levels and with granules.**

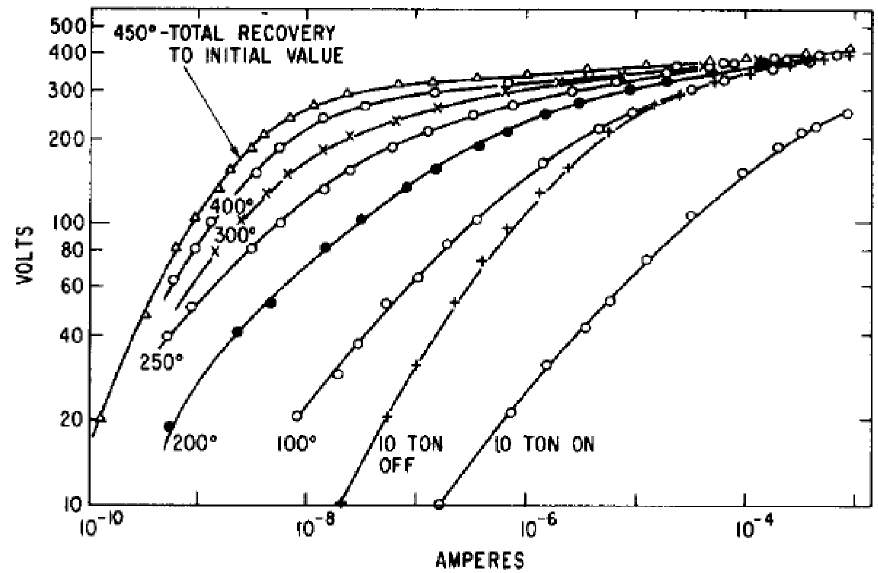
J. Wong and F.P. Bundy, "Pressure Effects on Metal Oxide Varistors," *Appl. Phys. Lett.* **29** 49-50 (1976).

High stress was required for a simple composition and stress caused an irreversible change in ρ.

Simple composition: Effect occurs at somewhat lower stress.



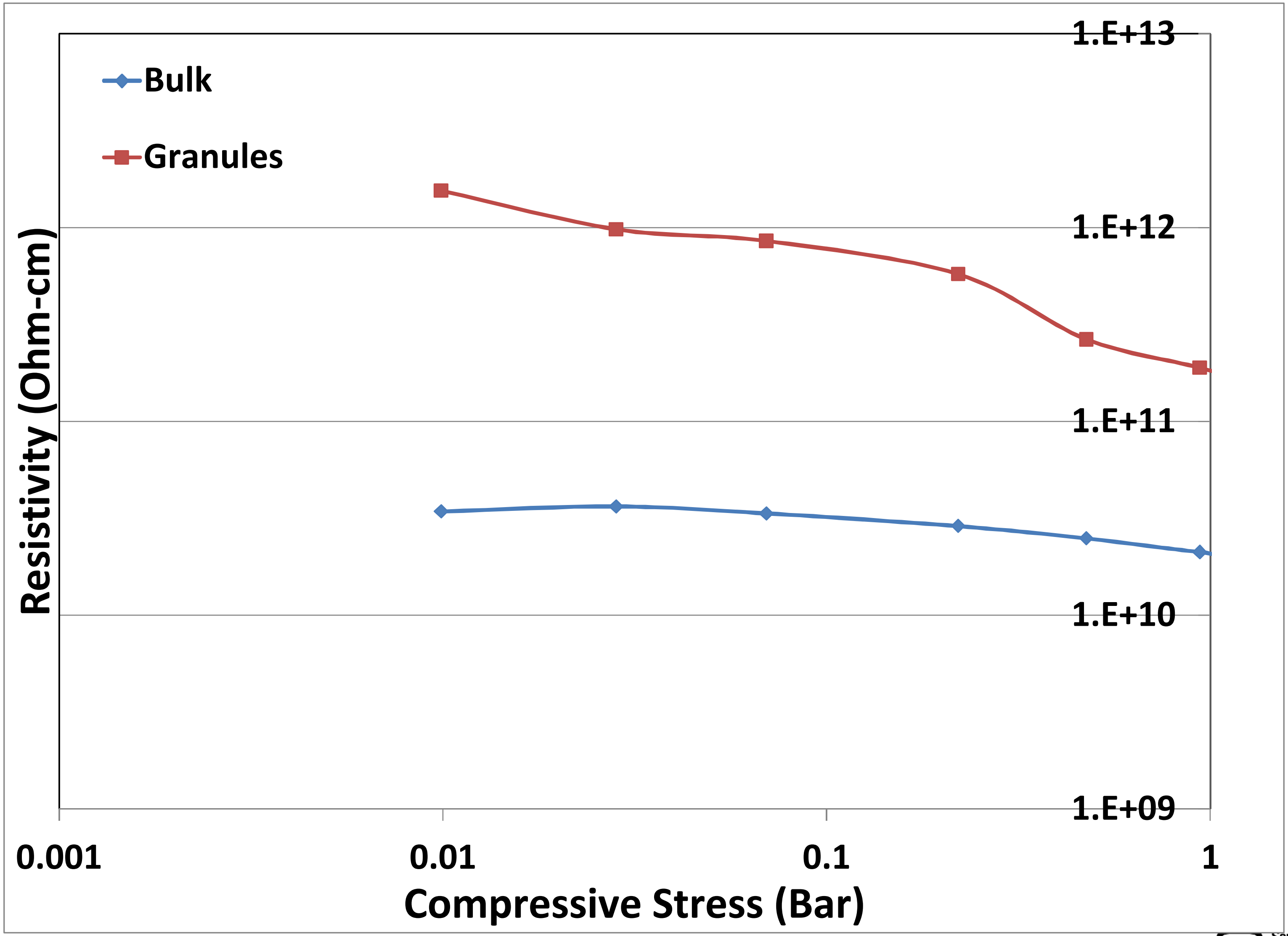
Annealing at 450C was required for total recovery.



These characteristics are not consistent with the results on varistor granules.

J. Wong and F.P. Bundy, "Pressure Effects on Metal Oxide Varistors," *Appl. Phys. Lett.* **29** 49-50 (1976).

Crushing a bulk varistor pellet increased its pressure sensitivity.



Conclusions

1. Varistor granules have low field i-V characteristics similar to bulk varistors but with increased sensitivity to humidity and compressive stress.

2. Their resistivity can decrease by over 2 orders of magnitude as the RH increases from low to high.

3. This effect is caused by the adsorption of water vapor, which lowers the grain boundary barrier near the surface.

4. The measured resistivity of varistor granules is pressure sensitive at very low pressures.

5. The pressure sensitivity is not due to the same mechanism that decreases the barrier height of bulk varistors at much higher pressure.

6. More research is needed to determine the mechanism but it appears to be caused by pressure sensitivity at the contact points that is increased in varistor materials.