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D. W. STRICKLER, W. G. CARLSON

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PHASE RELATIONS IN A PORTION OF THE SYSTEM Sc_2O_3-ZrO_2

By

D. W. Strickler and W. G. Carlson

ABSTRACT

X-ray diffraction, differential thermal analysis, quench techniques, electrical conductivity measurements and microscopic examination have been used to determine the phase relations in the ZrO_2-rich portion of the Sc_2O_3-ZrO_2 system. Two birefringent compounds with the approximate formulae $Sc_2Zr_2O_7$ and $Sc_2Zr_7O_{17}$ were found to occur in this system. $Sc_2Zr_2O_7$ inverts to a cubic form at about 1250°C. The inversion temperature is depressed with the addition of ZrO_2 in solid solution and at the solid solution limit of 16 mole % Sc_2O_3, the inversion temperature is about 800°C. $Sc_2Zr_7O_{17}$ is rhombohedral at room temperature and inverts to cubic structure at 610°C. Up to two mole % Sc_2O_3 enters ZrO_2 in solid solution and depresses the monoclinic ZrO_2 inversion to about 750°C. The data presently available indicate little or no solid solution of Sc_2O_3 in the low temperature form of $Sc_2Zr_2O_7$.

I. INTRODUCTION

Zirconium dioxide has a melting point of approximately 2700°C and transforms from the monoclinic to tetragonal form at about 1170°C with a large, disruptive volume change. Fortunately, ZrO_2 forms solid solutions with a number of MO and M_2O_3 oxides and the undesirable phase transformation can be eliminated by producing a stable solid solution of fluorite-type structure. Since these solid solutions are of the direct substitution type, the introduction of lower valent cations into the lattice creates oxygen vacancies which give rise to a high oxygen ion mobility. Furthermore, both the cation mobility and electronic conduction are very low in these materials; hence, they are essentially pure oxygen ion conductors. Materials of high oxygen ion conductivity are of interest for galvanic and fuel cell applications. This interest is evidenced by recent work[1,2,3,4] on the electrical conductivity of ZrO_2-base solid solutions.

In order to properly interpret the electrical conductivity data obtained for these materials, an understanding of the phase relations in the system must also be obtained. At present there exists only limited data for the phase relations in MO-ZrO_2 systems. Earlier work by Duwez et al.[5,6] established the phase relations in the CaO-ZrO_2 and Y_2O_3-ZrO_2 systems. However, there is disagreement among present investigators[3,4] and these diagrams. Roth[7] proposed phase diagrams for the La_2O_3-ZrO_2 and Nd_2O_3-ZrO_2 systems. Other recent investigators[8,9,10] have made extensive studies in M_2O_3-ZrO_2 systems; however, the phase relations in some of these systems are given only for temperatures in excess of 1200°C. A rather detailed study by Lefevre[10] has been published on the inversion of pure ZrO_2 and the phase relations in the Sc_2O_3-ZrO_2 system. Unfortunately, the phase relation results were based almost entirely on quenching data with limited supporting DTA data.

In the present work the authors correlated electrical conductivity data with those data resulting from typical phase equilibria studies to arrive at a reasonable phase diagram for the system Sc_2O_3-ZrO_2. The value of electrical conductivity measurements, where applicable, as a sensitive tool in phase equilibria studies is illustrated.

II. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

The starting materials consisted of Hf-free ZrO_2* and Sc_2O_3** of 99.9% purity. Compositions containing 2 to 40 mole % Sc_2O_3 in two mole % increments, and 45 and 50 mole % Sc_2O_3 were prepared. The oxides were weighed in their proper proportions and mixed by grinding under alcohol for one hour. The powder mixtures were reacted at 1400°C for 24 hours, ground, and pressed into right circular cylinders which were sintered at 1800°C for two to four hours. Conventional resistance furnaces were used for heat treatment at 1400°C and an oxygen-propane furnace for heat treatment at 1800°C.

B. Specimen Examination

Typical petrographic and metallographic methods were used to examine the specimens. X-ray patterns were made with CuK_α radiation using a 114.6 mm Debye-Scherrer powder camera for room temperature X-rays and a Norelco diffractometer equipped with a Tem-Pres type furnace for elevated temperature X-ray patterns up to 1400°C.

Differential thermal analyses (DTA) were made using a Leeds and Northrup X-Y recorder and program control. For all samples, except pure ZrO_2, the 490°C inversion of $PbTiO_3$ was used as a standard.

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* Source - Titanium Alloy Corp.

** Source - Fairmount Chemical Company

Electrical conductivity versus temperature measurements were made at a test frequency of 1000 cps using a General Radio model 650A impedance bridge. Specimens were heated in a platinum wound tube furnace to various temperature levels up to 1400°C. Spring loaded platinum contacts were employed to ensure good electrical contact with the specimen, and the resistance of the platinum lead wires was subtracted for each measurement. As a check on the two-probe measurement method, several specimens were also measured using the four-probe method. The results obtained using these two methods agreed within experimental error.

III. PHASE RELATIONS

The analyses, by various phase equilibrium techniques, of compositions in the ZrO_2-rich portion of the Sc_2O_3-ZrO_2 system give supporting data for the construction of the portion of the Sc_2O_3-ZrO_2 phase diagram as presented in Figure 1. The results obtained for each of the phase regions are given below.

A. Compounds

Two compounds exist in this system. One has the pyrochlore formula, $Sc_2Zr_2O_7$, and is ~~orthorhombic~~ hexagonal in symmetry. At about 1250°C a transformation from ~~orthorhombic~~ hexagonal symmetry to cubic symmetry is observed. This inversion cannot be detected by DTA and consequently may be a martensitic type transition as discussed by Wolten.[11] The melting point of the compound is greater than 2350°C, the temperature limit of our furnaces. The X-ray pattern for this compound appears in Table I.

A second compound with the formula $Sc_2Zr_7O_{17}$ possess rhombohedral symmetry and inverts to cubic symmetry at 610°C. This compound shows considerable solid solution in that the rhombhedral angle varies from about 88° 23' to 89° 49' in the compositional range 10 to 16 mole % Sc_2O_3.

B. Sc_2O_3-$Sc_2Zr_2O_7$ Phase Region

The phase diagram, Figure 1, indicates little or no solid solution in this region. Some solid solution may exist at temperatures above 1250°C, but the data are inconclusive. The eutectic temperature is about 2250°C. This temperature is based on the presence of a small amount of liquid in a 40 mole % Sc_2O_3 specimen when heated to 2300°C.

C. $Sc_2Zr_2O_7$-$Sc_2Zr_7O_{17}$ Phase Region

The addition of ZrO_2 to $Sc_2Zr_2O_7$ depresses the temperature of the hexagonal ~~orthorhombic~~ to cubic inversion. At 16 mole % Sc_2O_3, the solid solution limit of ZrO_2 in $Sc_2Zr_2O_7$, the inversion temperature is about 800°C. The evidence for this inversion is obtained from electrical conductivity data. DTA of compositions between 16 and 32 mole % Sc_2O_3 gave no peaks at the hexagonal ~~orthorhombic~~ to cubic inversion temperature. These data indicate that the transformation proceeds over a temperature range. To illustrate this, the change in conductivity with time at several temperatures is shown in Figure 2. One can conclude from these data that the inversion from hexagonal ~~orthorhombic~~ to cubic symmetry occurs over a rather wide temperature range analogous to the martensitic type inversion discussed by Wolten.[11]

D. ZrO_2-$Sc_2Zr_7O_{17}$ Phase Region

The $Sc_2Zr_7O_{17}$ phase has rhombohedral symmetry at low temperatures and inverts to a cubic structure at 610°C. The inversion temperature is depressed as ZrO_2 enters the compound in solid solution. At 10 mole per cent Sc_2O_3, the solid solution limit, the inversion occurs at about 450°C. X-ray data were obtained at elevated temperatures for those compositions containing 12 and 14 mole % Sc_2O_3. For these compositions, the low temperature rhombohedral form had transformed to the cubic phase at a temperature above 450°C. These data are summarized in Figure 3. Electrical conductivity-temperature data for 12, 16, 20 and 24 mole % Sc_2O_3 compositions are shown in Figure 4. The temperature of discontinuity in electrical conductivity is seen to increase with increasing Sc_2O_3 content. These data are indicative of a transition from a lower conductivity two-phase region to a higher conductivity single phase region. DTA of each composition lying in the region 10 to 30 mole % Sc_2O_3 showed a peak at 610°C, the inversion temperature of the rhombohedral phase.

Numerous attempts were made using quench techniques to locate this transition more precisely. The rhombohedral and cubic phases were always detected in quenched specimens by X-ray, even for those specimens quenched from temperatures well above the transition temperature. Thus, it can be concluded that this inversion is very rapid and that quench data are not reliable in this compositional region.

The solid solution limit of Sc_2O_3 in monoclinic ZrO_2 is about two mole % and the monoclinic-tetragonal inversion temperature is depressed with increasing Sc_2O_3 additions within this range. At the solid solution limit the inversion temperature is depressed about 400°C. The four mole % Sc_2O_3 composition exhibited a DTA peak at 750°C while the six mole % Sc_2O_3 did not. Thus, the limit of the monoclinic phase is about six mole % Sc_2O_3.

In the cubic solid solution region of approximately 6 to 8 mole % Sc_2O_3, the electrical conductivity-temperature data may be expressed by an Arrhenius type equation, $\sigma = A \exp{-E/kT}$. This is typical for the electrical conductivity behavior of single phase compositions. These data are presented in Figure 5. The slight departure from linearity for the 8 mole % Sc_2O_3 composition may be due to the temperature dependence of the pre-exponential term A; however, this is of no significance in this study.

IV. DISCUSSION

The diagram for the Sc_2O_3-ZrO_2 system proposed by the present authors differs considerably from that published by Lefevre.[10] The work of Lefevre was based principally on quenching data with some DTA and dilatometric data. It has been shown in the present study that quenching results are not reliable.

Another difference is that the present authors report two compounds, $Sc_2Zr_2O_7$ and $Sc_2Zr_7O_{17}$. These compounds are necessary to explain the low symmetry lines which appear in the X-ray patterns from 10 to 50 mole % Sc_2O_3. Since all of the structures in this system are closely related, it is conceivable that the compounds observed represent only ordered structures in a complete solid solution series. Structurally, a material can progressively transform from a fluorite to a pyrochlore to a C-type rare earth simply by reducing the amount of oxygen and ordering the remaining oxygen ions.

V. SUMMARY

Phase relations have been studied in the system Sc_2O_3-ZrO_2 at temperatures above 400°C. Two compounds of composition $Sc_2Zr_2O_7$ and $Sc_2Zr_7O_{17}$ were found to exist. These compounds transform to cubic symmetry at elevated temperatures and the temperature of inversion decreases as ZrO_2 enters the structures in solid solution. At 16 mole % Sc_2O_3, the limit of a stable $Sc_2Zr_2O_7$ compound, the inversion occurs at about 800°C. At 10 mole % Sc_2O_3, the limit of stability of $Sc_2Zr_7O_{17}$, the rhombohedral to cubic inversion is depressed from 610°C to about 450°C. The addition of two mole per cent Sc_2O_3 to ZrO_2 in solid solution depresses the monoclinic to tetragonal inversion from 1170°C to 750°C. The limit of the monoclinic phase field is about six mole % Sc_2O_3.

ACKNOWLEDGEMENT

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TABLE I

X-RAY PATTERN OF THE COMPOUND $Sc_2Zr_2O_7$

d, Å	I
4.68	W
3.85	W
3.68	WW
2.89	SS
2.51	M
2.46	WW
2.18	W
2.11	W
1.978	W
1.918	W
1.758	S
1.714	W
1.566	W
1.514	S
1.486	W
1.450	M
1.386	W
1.304	W
1.276	W
1.256	W
1.191	W
1.154	M
1.125	W

CURVE 568462-A

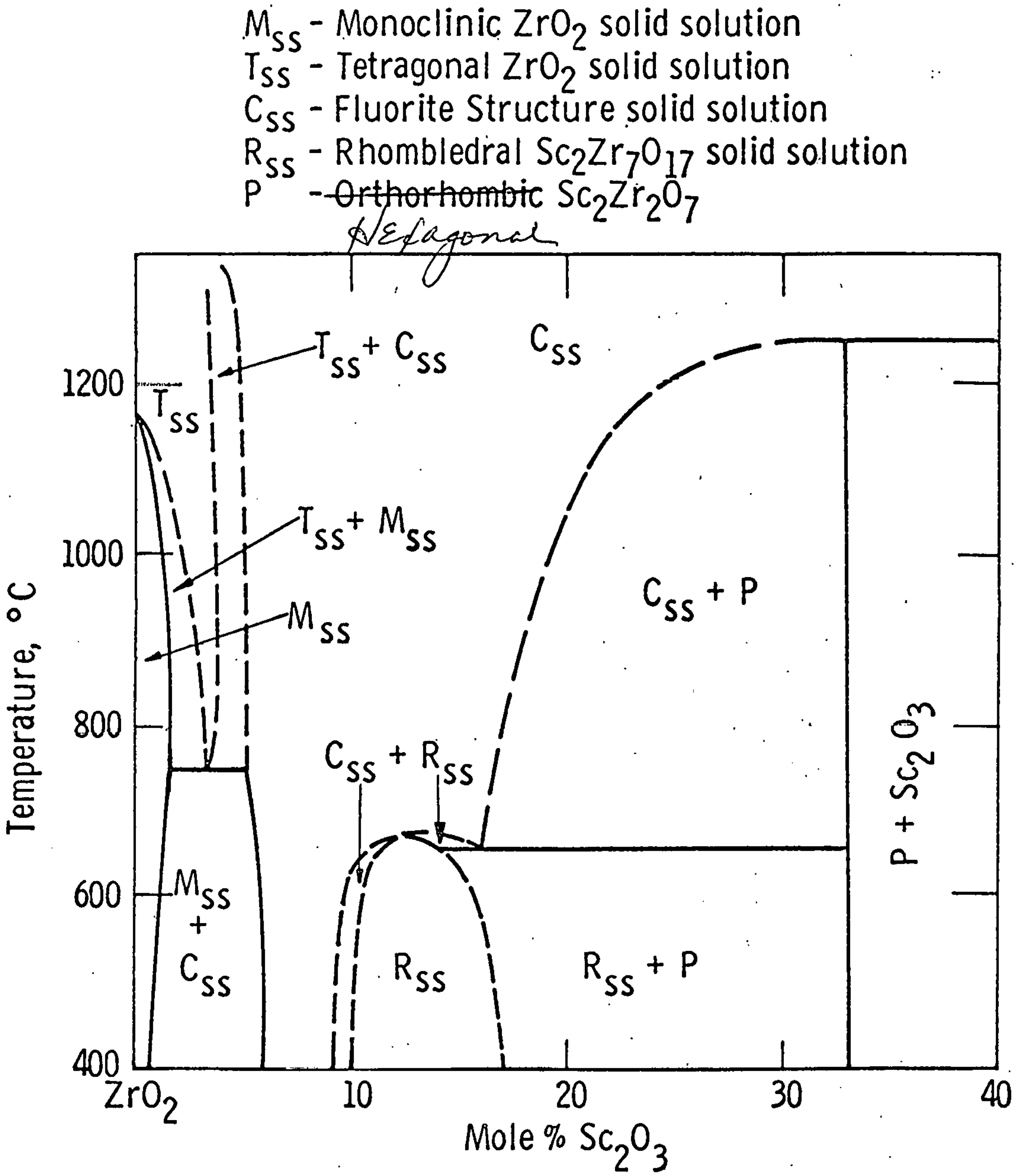

Fig. 1—Subsolidus phase relations in the ZrO_2-rich portion of the system Sc_2O_3 - ZrO_2

CURVE 568034

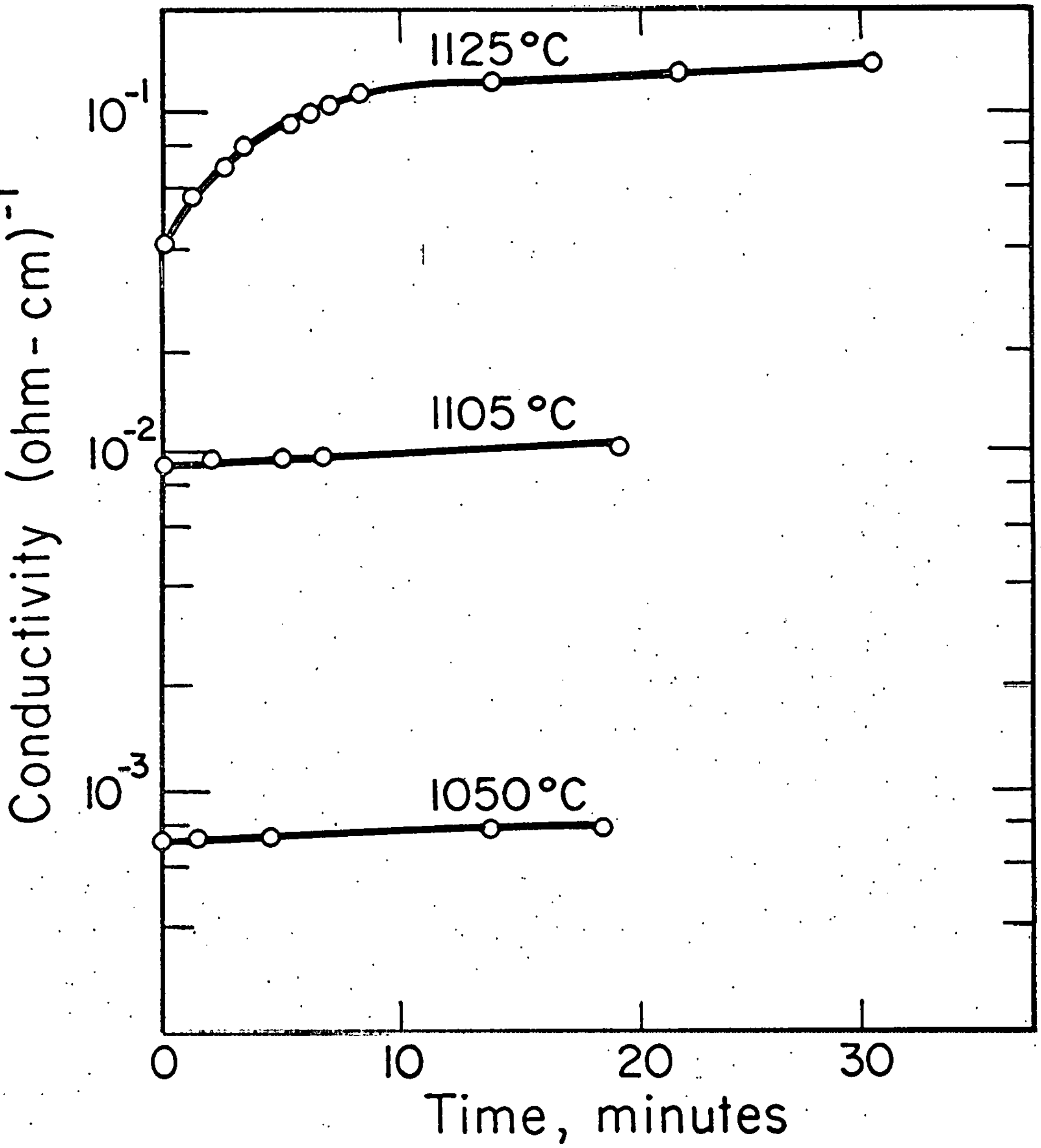

Fig. 2 - Conductivity change with time at constant temperature for a $0.20(Sc_2O_3)0.80(ZrO_2)$ composition.

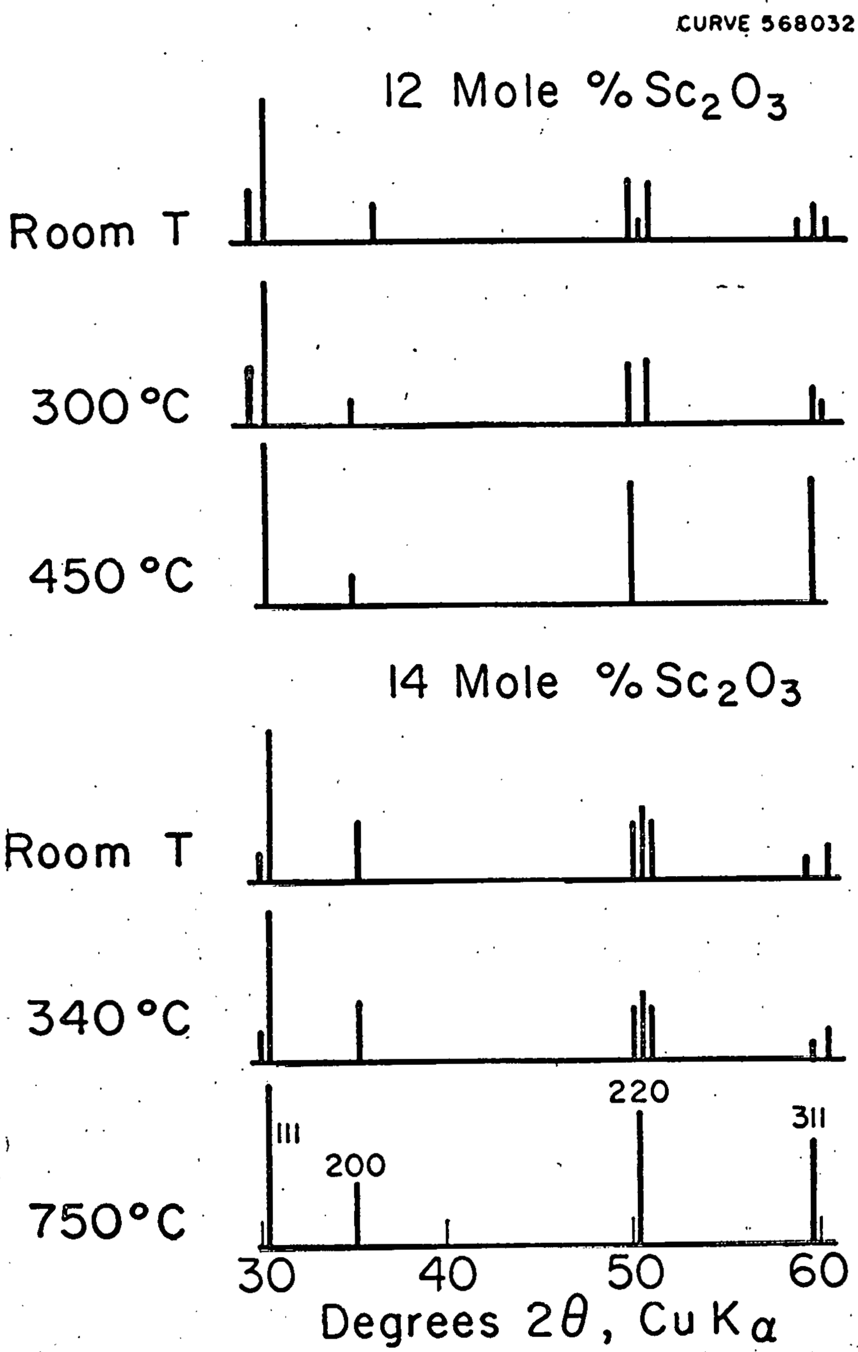

Fig. 3 - High temperature X-Ray data for two Sc_2O_3 - ZrO_2 compositions.

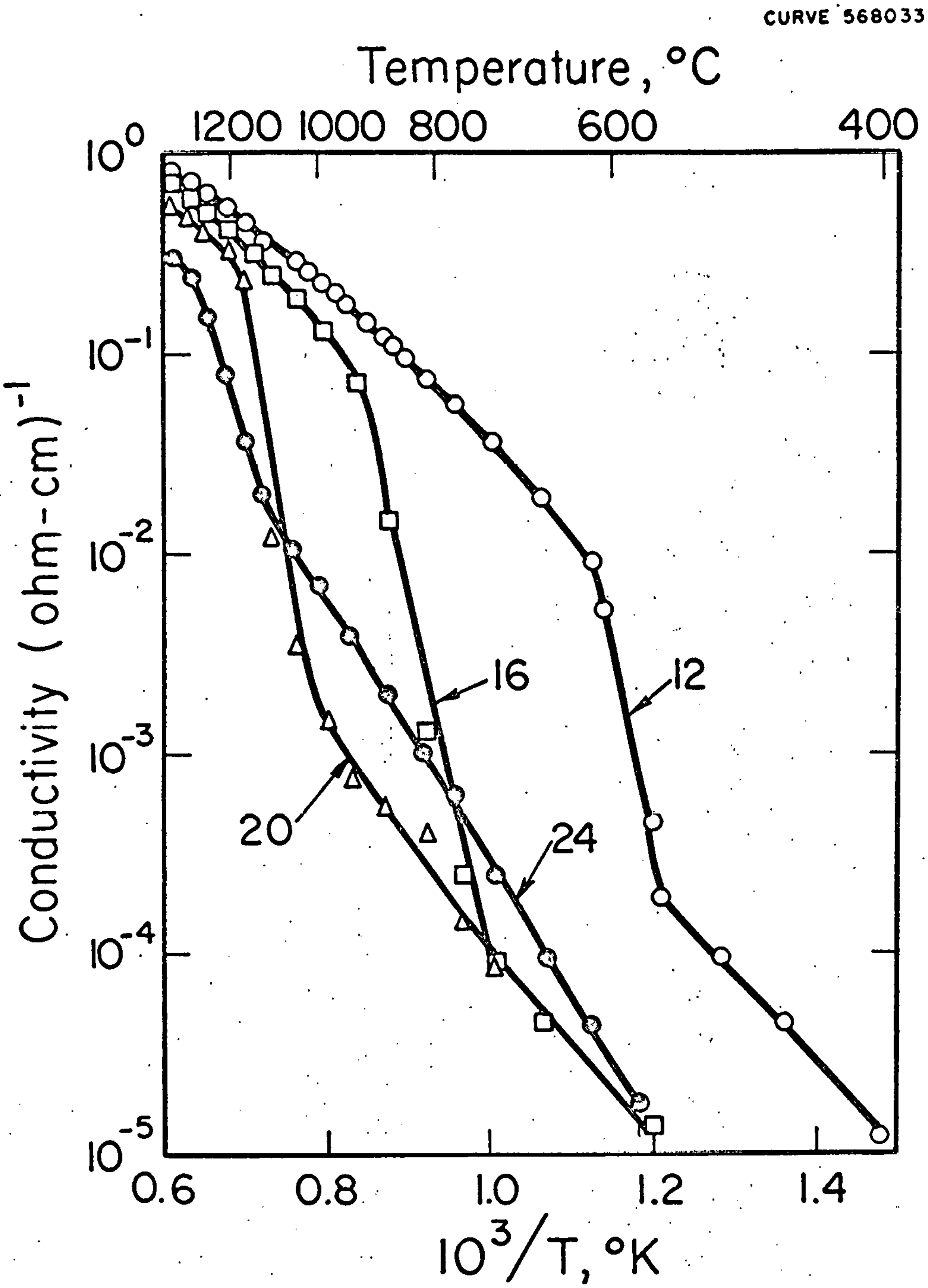

Fig. 4- Conductivity - temperature data for compositions in the two-phase region, cubic solid solution and $\alpha\, Sc_2Zr_2O_7$. The number on each curve denotes mole % Sc_2O_3.

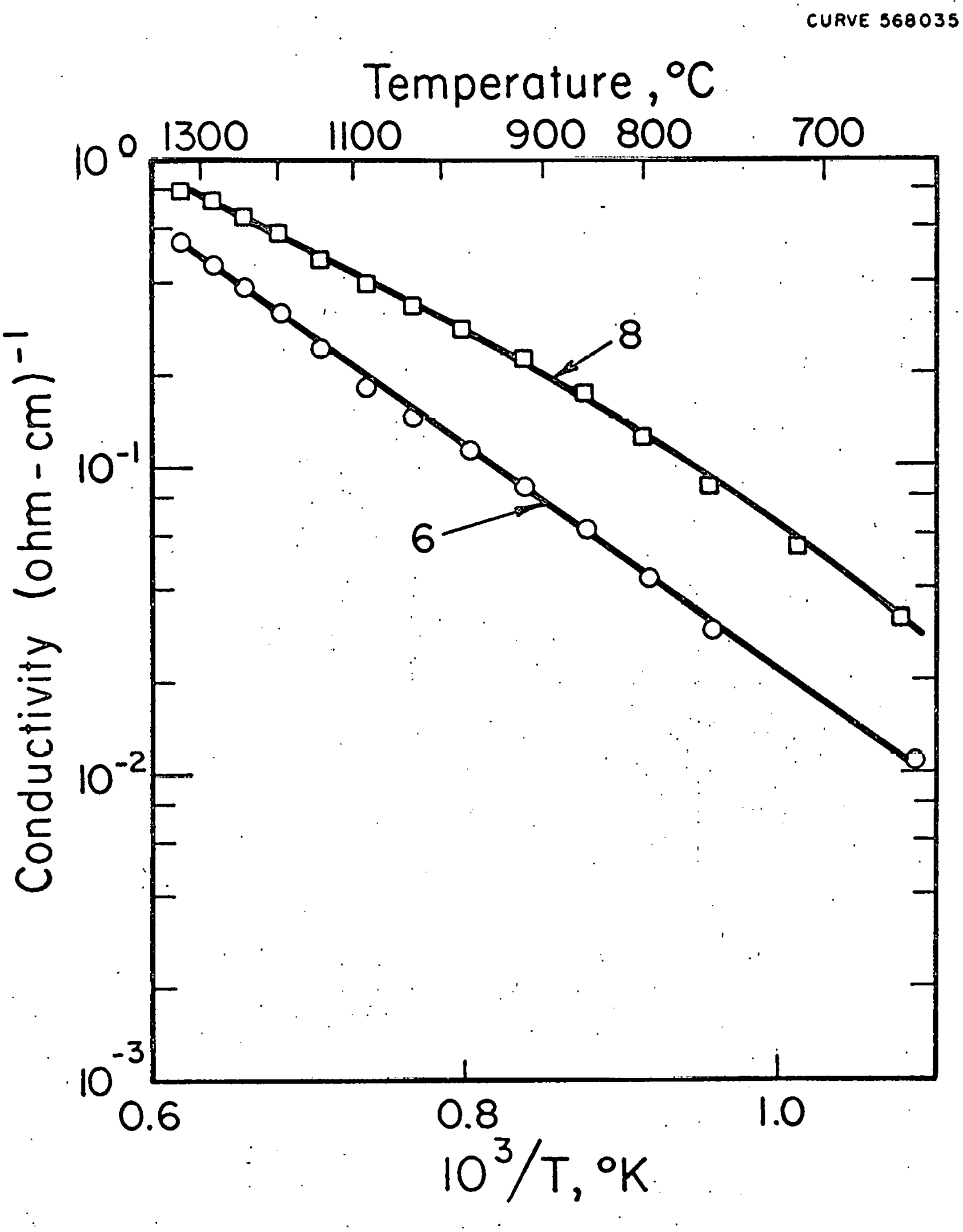

Fig. 5 - Typical conductivity - temperature data for Sc_2O_3-ZrO_2 compositions in the cubic solid solution region. The number on each curve denotes Sc_2O_3 content in mole percent.

CURVE 568035

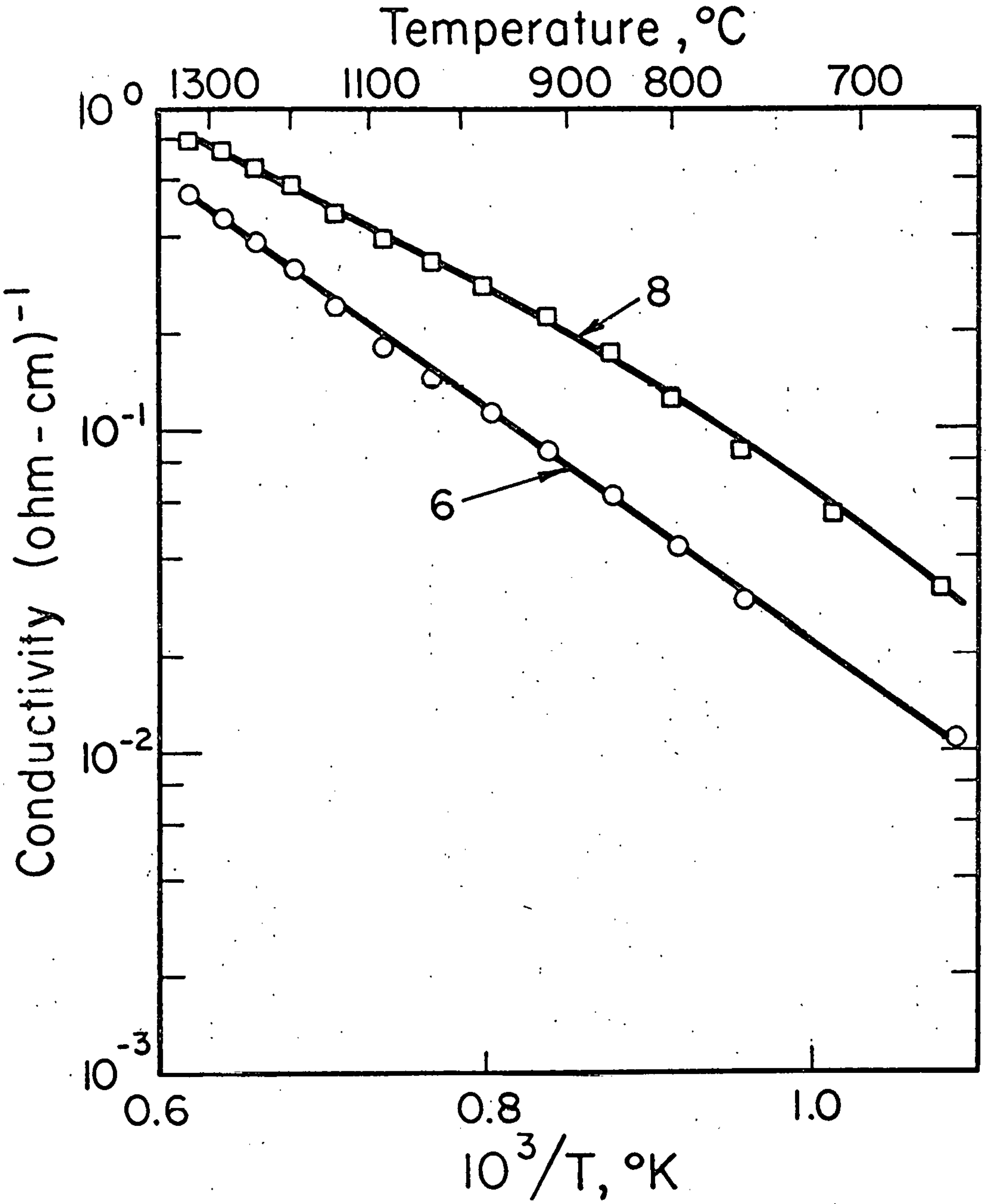

Fig. 5 - Typical conductivity - temperature data for Sc_2O_3-ZrO_2 compositions in the cubic solid solution region. The number on each curve denotes Sc_2O_3 content in mole percent.

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