

Electrical conductivity study of defects in zirconium doped yttrium aluminium garnet ceramics

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ELECTRICAL CONDUCTIVITY STUDY OF DEFECTS IN ZIRCONIUM DOPED
YTTRIUM ALUMINIUM GARNET CERAMICS

L. Schuh, R. Metselaar, G. de With

High temperature measurements of conductivity as $f(T)$ of $Y_3Al_5O_{12}$ (YAG) doped with 50 ppm Zr in CO/CO_2 and H_2/H_2O gas mixtures show a significant difference in the activation energy (3.54 resp. 1.91 eV) at constant oxygen partial pressure. The sign of the Seebeck coefficient indicates that a H_2/H_2O atmosphere introduces protons as conducting species into the garnet lattice. Impedance spectroscopy revealed that this is a bulk effect, while the grain boundaries are nearly unaffected by ambient atmosphere. Ionic and electronic conductivity as $f(pO_2)$ show that ionic conductivity dominates in the high pO_2 regime, while at low pO_2 electronic conductivity increases with $pO_2^{-1/5}$ indicating that either V_o^\cdot and V_o^\cdot or defect clusters appear as prevailing ionic defects.

INTRODUCTION

Aluminium oxide ceramics are well studied and have many applications. This material can be sintered to translucency, usually with MgO as dopant.¹ Recently it was shown that $Y_3Al_5O_{12}$ (yttrium aluminium garnet or YAG) can be sintered to a quite better translucency with SiO_2 or MgO as sintering additive than Al_2O_3 .² Moreover it is known that YAG has a higher resistance against aggressive environments (viz. hot alkali vapour) than Al_2O_3 .³ The combination of these properties make YAG ceramic a candidate material, that may be used to produce high durability envelopes for sodium discharge lamps.

Till now the mechanical, microstructural, and optical properties of YAG ceramics were investigated to some extent⁴⁻⁷. The defect chemistry is, however, also quite important for the understanding of sintering and corrosion behaviour. Some authors determined the high-temperature defect properties of single crystal $Y_3Al_5O_{12}$ ⁸⁻¹¹, because this material is an important solid state laser host crystal (Nd-YAG laser). All investigators came to the result, that YAG is a mixed ionic-electronic conductor at high temperatures. The dominating ionic defects are oxygen-vacancies. The subject of this paper is to give some information about high-temperature defect properties of zirconia-doped polycrystalline YAG-ceramics.

EXPERIMENTAL

Materials

In this work we present an investigation of YAG ceramic doped with 55 wt.-ppm Zr. The YAG powder was prepared by using the wet-chemical route (sulphate process) as described in ref. 7. Doping with zirconium was done by adding a proper amount of the nitrate. The samples were sintered at 2020 K for 4 hours in a wet H_2 -atmosphere. All samples reached a relative density higher than 98%. Microstructure of various materials was determined by SEM/EDX. The grainsize ranged from 4 - 7 μm .

Zirconium-ions have a relative high solubility in the YAG lattice (up to 700 ppm without any second phase segregation¹²). SEM/EDX observations and X-ray diffraction further showed that up to 6% Al-rich inclusions (presumably Al_2O_3) with 0.5 - 1 μm diameter are present. The presence of these inclusions was confirmed by TEM investigations.⁴

Methods

The defect-chemical investigation was done by impedance spectroscopy, ionic transport and Seebeck coefficient measurements. Our samples for electrical conductivity measurements were disc-shaped with a diameter of 10mm and a thickness of 0.7mm. The two faces of a specimen were polished down to 1 μm with diamond paste, cleaned and painted with platinum paste (Emetron Leitplatin). The electrode surface was kept small (about 3mm in diameter) in order to minimize the contribution of surface and air conduction paths.

A Solartron 1174 frequency response analyser (0.1 MHz - 1 MHz) interfaced to a Hewlett Packard HP 86 computer was used for impedance measurements. A.c.-conductivity was determined as a function of temperature (up to 1700 K) and oxygen partial pressure $p\text{O}_2$ ($10^5 - 10^{-14}$ Pa). Usually a voltage of 100mV rms was applied across the sample. After a change of $p\text{O}_2$ the system was equilibrated about 12 hours before the conductivity was measured. We used $\text{H}_2/\text{H}_2\text{O}$, CO/CO_2 and O_2/N_2 gas mixtures to establish a controlled $p\text{O}_2$. Every measurement of the frequency dispersion was checked by a determination of the d.c.-resistance. Complete impedance plots in the $Z'-Z''$ representation allow to get information about bulk (grain interior) and grain boundary conductivity.

The investigation of the Seebeck coefficient and transport number was done in an apparatus described elsewhere¹³.

RESULTS AND DISCUSSION

Fig.1 gives the temperature dependence of the total conductivity measured at different $p\text{O}_2$'s. Each point was determined by analysing the appertaining $Z'-Z''$ plot. Because of the difficulty to separate bulk- (R_b) and grain boundary (R_{gb}) conductivity at all temperatures we plotted ($R_b + R_{gb}$) vs. σT . The activation energies E_A were calculated by using the Arrhenius relation: $\sigma = \sigma_0/T \exp(-E_A/kT)$ with σ =conductivity, T =temperature, k =Boltzmann-constant.

TABLE 1. E_A for YAG:Zr in different gas atmospheres

Curve	Atmosphere	$p\text{O}_2$ (Pa)	E_A (eV)
1	$\text{H}_2/\text{H}_2\text{O}$	10^{-14}	1.91
2	CO/CO_2	10^{-11}	3.54
3	CO/CO_2	10^{-7}	3.38
4	O_2	10^5	3.04

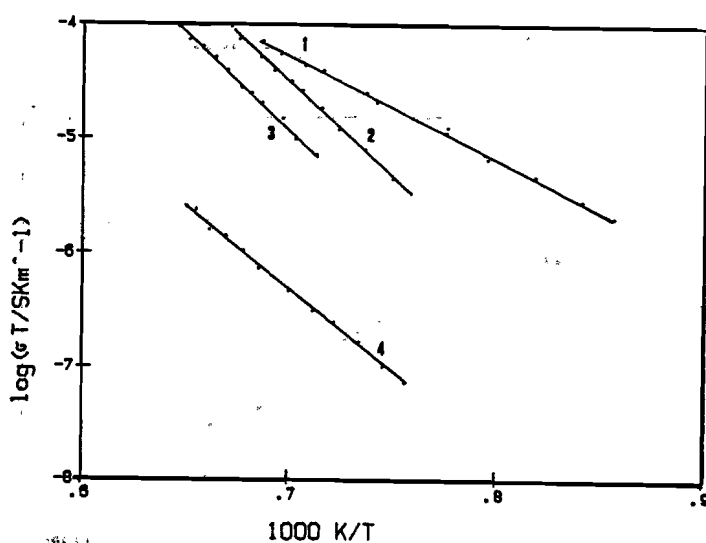


FIG.1 Temperature dependence of the volume conductivity in Zr-doped YAG. Activation energies derived from curve 1-4 are given in table 1.

E_A for the conduction process varies from 3 eV at $p_{O_2}=10^5$ Pa (pure O_2) to 3.5 eV at $p_{O_2}=10^{-11}$ Pa (CO/CO_2 mixture). In a H_2/H_2O mixture ($p_{O_2}=10^{-14}$ Pa) E_A is significantly smaller. Recently it was shown that hydrogen can enter the YAG-lattice¹⁴ forming OH-bonds. So we expect a contribution of protonic conduction in a YAG specimen that is equilibrated in a H_2/H_2O atmosphere. In order to clarify this point the thermopower in different gas mixtures was measured. The sign of the thermopower or Seebeck coefficient gives information about the sign of the dominating mobile charge carriers. Negative charge carriers are dominating in N_2/O_2 and CO/CO_2 mixtures, while positive carriers are prevailing in H_2/H_2O . N_2/O_2 and CO/CO_2 mixtures affect the conduction mechanism by a change in p_{O_2} . The E_A in both atmospheres is approximately equal. A H_2/H_2O mixture influences the conduction mechanism by introducing new positive charge carriers into the lattice. This is confirmed by IR-spectroscopic detection of OH stretch-bonds after an anneal in H_2 ¹⁴.

TABLE 2. Sign of the Seebeck-coefficient in different gas-mixtures

Gas-mixture	p_{O_2} (Pa)	Sign of the Seebeck-coefficient
N_2/O_2	10^5	-
CO/CO_2	10^{-11}	-
H_2/H_2O	10^{-13}	+

Fig. 2 and 3 give two impedance spectra of Zr-doped YAG measured in N_2/O_2 ($p_{O_2}=10^5$ Pa) at 1650 K and in H_2/H_2O ($p_{O_2}=10^{-13}$ Pa) at 1450 K. Fig.2 shows a wide semi-circle that could be extrapolated to zero-resistance. This arc is caused by bulk conduction. The intersection of that circle with the Z' -axis gives the bulk-resistance as 360 k Ω . At frequencies lower than 20 kHz begins a distortion of the arc which is caused by an influence of the grain boundaries. The resistance of the grain boundaries can be estimated as 20 k Ω . That means that highly resistive YAG

grains are covered by a much better conducting boundary layer.

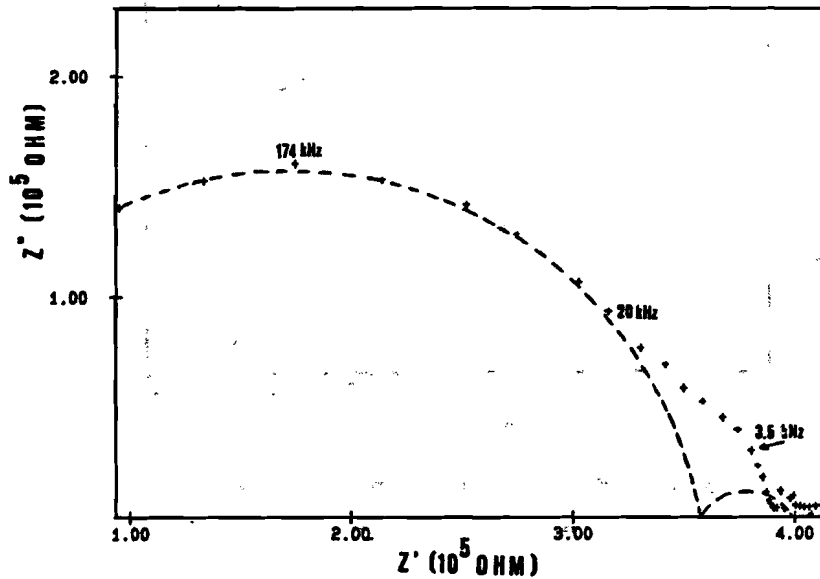


FIG. 2 Impedance plot for Zr-doped YAG at 1650 K and $p_{O_2} = 10$ Pa (N_2/O_2 mixture)

Fig. 3 gives the impedance plot for the same sort of sample, measured in a H_2/H_2O atmosphere. The relaxation times of the two conduction processes are now well separated. The bulk resistance can be derived as 40.5 k Ω and the grain boundary resistance is 18 k Ω . A low frequency dispersion, which is typically observed, is of no further interest here.

Comparing both spectra one can conclude that the grain boundary resistance is hardly influenced by ambient gas atmosphere (note that fig. 3 is recorded at a lower temperature than fig. 2 to get well formed arcs). The bulk resistance changes significantly with the gas mixture. An interpretation of the impedance

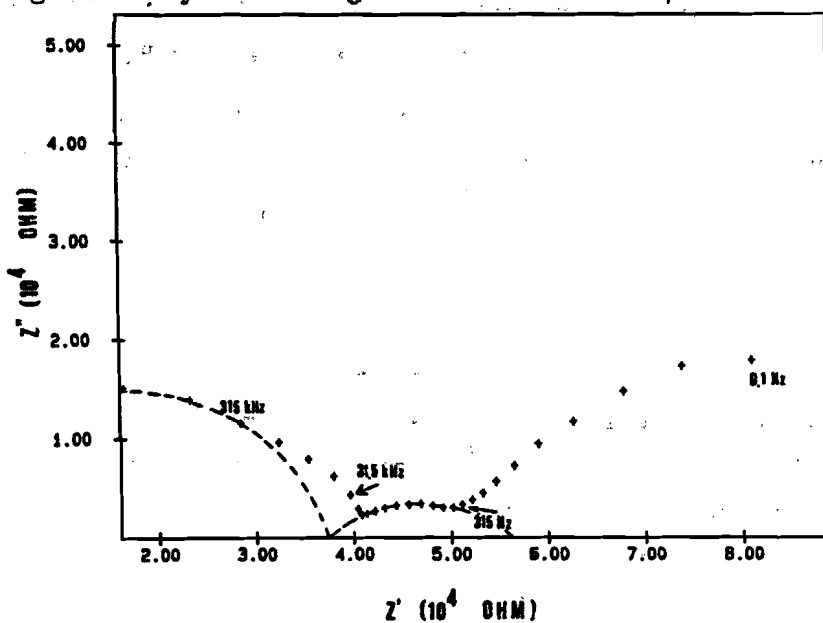


FIG. 3 Impedance plot for Zr-doped YAG at 1450 K and $p_{O_2} = 10^{-13}$ Pa (H_2/H_2O mixture)

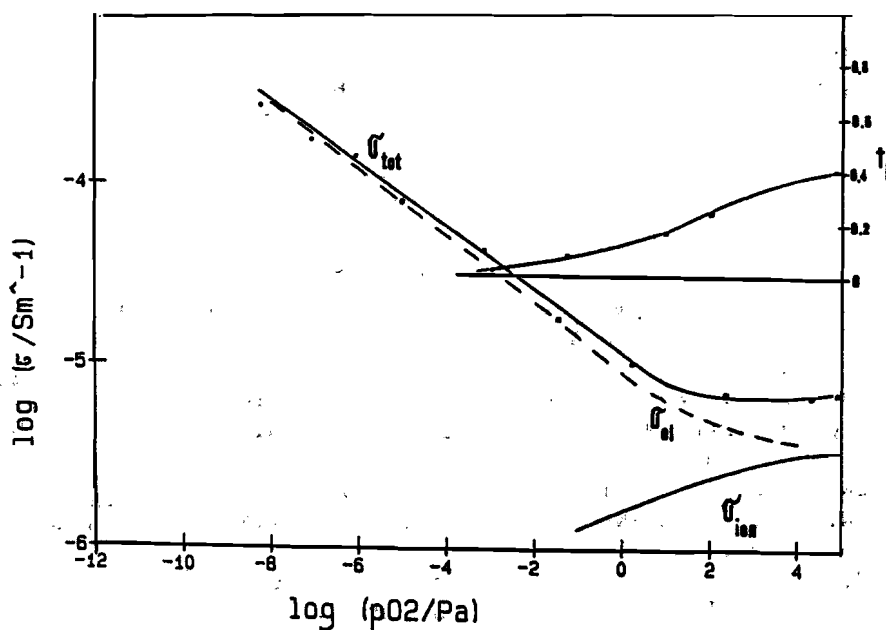


FIG. 4 Total electrical conductivity, ionic transport number t_1 , electronic σ_{el} and ionic σ_{ion} conductivity in YAG doped with 55 ppm Zr at 1670 K.

spectra indicates that a H_2 -containing gas atmosphere changes the bulk properties, while leaving the grain boundaries nearly unaffected.

The pO_2 dependence of conductivity at 1670 K is shown in fig. 4 together with the ionic transport number t_1 and the ionic and electronic contribution to the total conductivity. Zr-doped YAG shows a red colour after treatment in a reducing atmosphere and decolours upon annealing in an oxidizing atmosphere.

An interpretation of the isotherms shown in fig. 4 combined with the fact, that the sign of the Seebeck-coefficient is negative at low pO_2 (except in a H_2 -containing atmosphere), indicate that $\sigma = \sigma_{el}$ in this pO_2 regime. σ_{el} increases $\propto pO_2^n$ with $n = -1/5$. In the high oxygen pressure region conductivity is independent of pO_2 . This is the regime of ionic conductivity. Recently it was shown by several workers that the dominating defects in YAG are oxygen vacancies $V_O^{\bullet\bullet}$.⁸⁻¹¹ The electronic conduction increases with a slope of $-1/5$. This dependence is intermediate between the intrinsic conduction mechanism with a slope of $-1/6$ and a simple impurity controlled mechanism exhibiting a slope of $-1/4$. Several workers interpreted an analogous $1/5$ power oxygen pressure dependence in NiO by assuming the simultaneously presence of singly and doubly ionised nickel vacancies¹⁶. Taking over this proposition we can interpret the $1/5$ slope found in the present work by assuming singly and doubly ionised oxygen vacancies V_O^{\bullet} and $V_O^{\bullet\bullet}$. Recently it was shown by computer simulation for NiO, CoO, MnO and FeO that also cluster formation can explain a slope of $1/5$.¹⁷

FINAL REMARKS

Further investigation of an influence of other doping elements on defect related properties in YAG may enable us to decide whether V_{O}^{\bullet} and $V_{\text{O}}^{\bullet\bullet}$ or cluster formation dominates.

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