

Defect Structure in Sc_2O_3 Doped with MgO

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The defect structure of the Sc_2O_3 -MgO system was investigated at low MgO compositions. Based on a comparison of measured pycnometric densities and calculated X-ray densities, it was found that the generation of anion vacancies was the predominant mode of charge compensation accompanying substitution of Mg^{2+} for Sc^{3+} in the REOC structure.

Introduction

Oxides possessing the fluorite structure, and its close derivative the rare-earth oxide type C (REOC) structure, constitute the highest-melting-temperature group of oxides available. In addition to important refractory applications, these materials also encompass a variety of properties which make them of great importance in a number of energy generation technologies including nuclear, electrochemical, and MHD.

The fluorite structure ($Fm\bar{3}m$) consists of cations in a *fcc* array with anions occupying all tetrahedral positions. Alternatively, this structure may be described as a simple cubic array of anions with cations in one-half of the cubic sites. The sesquioxide REOC structure ($Ia\bar{3}$) may be thought of as being derived from the fluorite structure dioxides by substitution of trivalent cations on all cation sites with the ordered removal of $\frac{1}{4}$ of the oxygen ions in order to maintain neutrality. The close relationship between these two structures allows extensive solid solubility to occur between them (1, 2).

A variety of electrical, optical, and mass-transport processes are controlled by defect

structure, and this, in turn, can be dominated in ionically bonded materials by the presence of aliovalent impurities. It is reasonably well established (e.g., Ref. (3)) that the principal intrinsic defect in pure fluorite materials is of the anion Frenkel type. It has been inferred from stoichiometry studies (e.g., Ref. (4)) that this type of defect also predominates in pure REOC materials. When fluorite structure materials are doped with hypervalent cations (e.g., CaF_2 doped with Y^{3+} (5) or UO_{2+x} doped with U^{6+} (6), the cation site occupancy remains essentially complete and anion interstitials are introduced for charge compensation. The same has been shown to be true for hypervalent-doped REOC materials (e.g., Er_2O_3 doped with Hf^{4+} (2) and Y_2O_3 doped with Th^{4+} (7)). It has also been clearly shown that fluorite structure oxides doped with hypovalent cations (e.g., ZrO_2 doped with Ca^{2+} (8) or HfO_2 doped with Er^{3+} (2) maintain essentially complete cation site occupancy with charge compensation being accomplished by generation of oxygen vacancies. By analogy, it might be supposed that divalent-doped REOC structures would also conform to an anion-vacancy defect model. It is the purpose of this study to test that supposition.

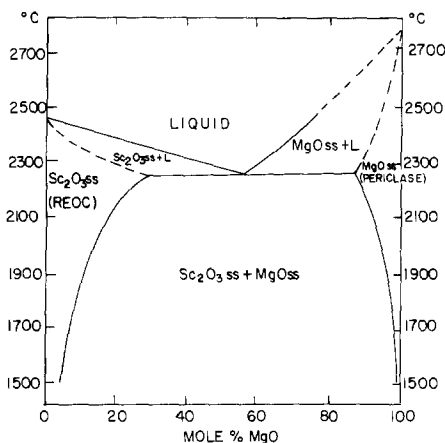
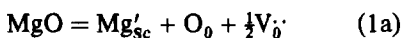


FIG. 1. The system $\text{Sc}_2\text{O}_3\text{-MgO}$ (Ref. (10)).

The materials selected for this study were Sc_2O_3 as the REOC solvent phase and MgO as the solute. This particular pair of oxides was selected because of close similarities in cation radius (0.73 Å for Sc^{3+} and 0.72 Å for Mg^{2+}) (9) which encourages formation of solid solutions. Tresvyatskii *et al.* (10) have shown that terminal solid solutions form in the $\text{Sc}_2\text{O}_3\text{-MgO}$ binary system (see Fig. 1). Lopato *et al.* (11) have investigated the defect structure of solid solutions in the periclase (MgO_{ss}) single-phase region of this system and have shown that cation vacancy formation is the predominant mode of charge compensation when Sc^{3+} substitutes for Mg^{2+} in this structure.

As divalent Mg^{2+} is substituted for trivalent Sc^{3+} in the REOC structure, charge compensation can be accomplished by generation of several different defect structures. Assuming defects to be fully ionized and that electronic compensation is nil, neutrality may be accomplished by generation of anion vacancies according to



or by introduction of additional cations interstitially according to



These two defect structures will result in different theoretical densities for the solid solu-

tions that can be expressed for the anion vacancy model (Eq. (1a)) as

$$= \frac{32}{a_0^3 A} \left[\frac{x(\text{MW MgO}) + (100-x)(\text{MW Sc}_2\text{O}_3)}{200-x} \right] \quad (2a)$$

and for the cation interstitial model (Eq. (1b)) as

$$= \frac{48}{a_0^3 A} \left[\frac{x(\text{MW MgO}) + (100-x)(\text{MW Sc}_2\text{O}_3)}{300-2x} \right] \quad (2b)$$

In these expressions, a_0 is the lattice parameter of a solid solution containing x mole% MgO , MW indicates molecular weight of the oxides, and A is Avogadro's number. A comparison of measured true densities with those calculated from Eq. (2) using lattice parameters determined by X-ray diffraction can serve to determine which of the two defect models of Eq. (1) predominates.

Experimental Procedure

Oxide solid solutions containing 1, 2, 3, 5, and 7 mole% MgO were prepared by blending nitrate solutions of scandium and magnesium followed by drying and calcining in air at 960°C for 3 hr. The resulting powders were ground to pass a 325-mesh screen and were dry-pressed into 0.5-g pellets $\frac{3}{8}$ in. in diameter at 1200 psi followed by isostatic pressing at 30 000 psi. All compositions were sintered in vacuum at 1800°C for 1 hr. Additional specimens of 3 and 5 mol% MgO were sintered in air at 1800°C to compare with vacuum-sintered specimens for evidences of density differences due to reduction. Chemical analysis of the sintered powders showed that MgO concentrations were within 0.1 mole% of the expected values based on concentrations of the nitrate solutions. Sintered specimens were ground to pass 325 mesh and were subjected to X-ray analysis and pyrometric density measurements.

Diffraction traces using Fe radiation were generated for each oxide powder. The Nelson-Riley function using 4 to 9 reflections and extrapolated to $2\theta = 180^\circ$ was used to determine lattice parameters. Pycnometric powder densities were determined in accordance with ASTM C135-66 (12) with the exceptions that octanol at 20°C was used instead of water and with air being removed by ultrasonic treatment rather than by boiling.

Results

The results of lattice parameter measurements on the oxide solid solutions are shown in Table I. Figures in this table enclosed in parentheses refer to air-sintered materials; all other data are for vacuum-sintered materials. It is seen that there is a steady contraction of the REOC unit cell with the addition of MgO. The lattice parameters for air-sintered are slightly higher (2 parts in 10^4) than for vacuum-sintered specimens, but the magnitudes of the differences are not large enough to influence density calculations by more than 0.06%.

The densities measured on the powders and those calculated for the two defect models of Eq. (1) using measured lattice parameters are compared in Table II and Fig. 2. The measured density values decrease with increasing MgO content, and follow closely, al-

TABLE II
DENSITIES FOR VACUUM-SINTERED Sc_2O_3 -MgO SOLID SOLUTIONS

Composition	Measured density (g/cm^3)	Calculated densities (g/cm^3)	
		Anion vacancy model	Cation interstitial model
1% MgO	3.8350	3.8390	3.8455
2% MgO	3.8303	3.8345	3.8474
3% MgO	8.8219	3.8298	3.8493
5% MgO	3.8007	3.8166	3.8495
7% MgO	3.7986	3.8007	3.8473

though are slightly lower than, the theoretical values calculated for the anion vacancy model (Eq. (1a)). It is apparent from Fig. 2 that the generation of anion vacancies is the predominant mode of charge compensation accompanying substitution of Mg^{2+} for Sc^{3+} in the REOC structure. If a significant cation interstitial contribution was present, the measured curve would fall above the anion vacancy curve. Thus, the analogy between the fluorite and REOC structures is verified for the case of doping with hypovalent cations. The reason for the measured densities falling below the calculated values for the anion vacancy model is probably the presence of a small amount of closed porosity in the oxide powders, perhaps augmented by a slight loss in mass due to mild reduction during sintering.

TABLE I

LATTICE PARAMETERS FOR VACUUM-SINTERED Sc_2O_3 -MgO SOLID SOLUTIONS

Composition	a_0 (Å)	Number of diffraction peaks
Pure Sc_2O_3	9.845	a
1% MgO	9.840	8
2% MgO	9.837	9
3% MgO	9.834 (9.836) ^b	4 (7) ^b
5% MgO	9.831 (9.833) ^b	5 (5) ^b
7% MgO	9.830	6

^a From ASTM powder diffraction file.

^b Data for specimens sintered in air in parentheses.

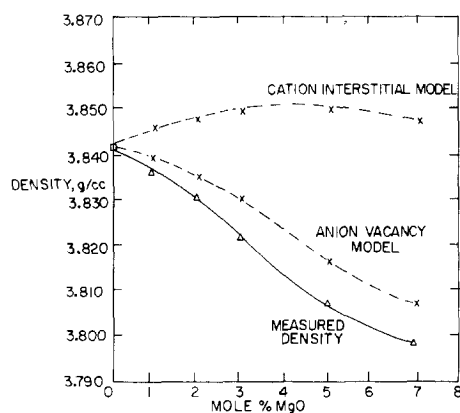


FIG. 2. Experimental and calculated densities for Sc_2O_3 -MgO solid solutions.

Acknowledgment

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