JOURNAL OF MATERIALS SCIENCE 19 (1984) 2775–2780

Solubility limit of La in $SrZrO_3$

N. SURIYAYOTHIN, N. G. EROR
Oregon Graduate Center, Beaverton, Oregon, USA

X-ray fluorescence, X-ray diffraction and scanning electron microscopy were used to determine the solubility limit of lanthanum in $SrZrO_3$. The solubility limit was reached at approximately 6 at% La addition, with acicular $La_2Zr_2O_7$ precipitates forming at higher amounts. The lattice parameter of $SrZrO_3$ decreased linearly from 0.580 28 to 0.580 00 nm with increasing lanthanum content up to the solubility limit.

1. Introduction

The $SrO–ZrO_2$ system has been investigated in recent years for such uses as conductors, especially in MHD flow [1, 2] and as a dielectric material [3]. The addition of lanthanum, in particular, has been shown to have pronounced effects on both the electrical conductivity and the dielectric properties in similar systems, such as $SrO–TiO_2$ [4], $PbO–TiO_2$ [5], $BaO–TiO_2$ [6], and $Pb(Zr, Ti)O_3$ [7] through the creation of A-site vacancies. By analogy, it would be possible to produce similar effects when lanthanum is added to $SrZrO_3$, wherein lanthanum has been substituted on some A sites. We have previously proposed [8, 9] that the creation of A-site vacancies can be achieved through an ordered structural accommodation. The existence of a perovskite phase of composition $Sr_{1-3x/2}La_xTiO_3$ in the ternary system $SrO–TiO_2–La_2O_3$ has been reported by Tien and Hummel [4]. In all their samples, the large-cation to small-cation ratio was less than unity. Similar results were found in lanthanum-substituted lead titanate [10], in which perovskite phases of the composition $Pb_{1-3x/2}La_xTiO_3$ were produced. These perovskite phases in $(La, Sr)ZrO_3$ can be analogously considered as a series of mixed-crystals of $SrZrO_3–La_{2/3}\square_{1/3}ZrO_3$, where $\square$ represents a vacant lanthanum site. In this investigation, X-ray fluorescence, diffraction and scanning electron microscopy techniques were used to determine the range of existence of the homogeneous perovskite phase $SrO–La_2O_3–ZrO_2$ in the quasi-ternary system.

2. Experimental procedure

A liquid mix technique (LMT) [12, 16] was used to prepare thermodynamically defined compounds to make meaningful analysis of electronic and ionic disorder phenomena. By this technique it was possible to estimate the nonvolatile cationic stoichiometries of the major and minor constituents to within a few parts per million precision. Samples were prepared by dissolving appropriate amounts of $Zr(CO_3)_2$ (Electronic Space Product, Inc, spec. pure), $SrCO_3$ (Johnsen Mathey Corp, spec. pure), and $La_2(CO_3)_3$ (Rare-Earth Division, spec. pure) in an ethylene glycol–citric acid solution. The preparation stoichiometry was $Sr_{1-x}La_xZrO_3$. The mixed solutions were evaporated to a rigid polymeric state as revealed by the formation of a uniformly coloured transparent glass and then calcined at 750° C in an oxidizing atmosphere for a period of 24 h.

Specimens for scanning electron microscopy were prepared by pressing the powders made by the liquid mix technique into small discs and sintering at 1350° C for a period of 40 h. These samples were examined in a JEOL JSM-35 scanning electron microscope under a secondary electron accelerating voltage of 25 kV. Heated powders were used as such for X-ray analysis. For X-ray diffraction, a 57.3 mm Debye–Scherrer camera in a Siemens Kristalloflex-2 diffraction unit and a Norelco diffractometer and Geiger counter and Cu*Kα* radiation with a Ni-filter were used. The diffractometer unit had computerized output capabilities for plotting intensity curves and also to print out angle, intensity and *d*-spacing data.

3. Results and discussion

The microstructure of the pure $SrZrO_3$ disc, as revealed in the scanning electron microscope, is

0022–2461/84 $03.00 + .12

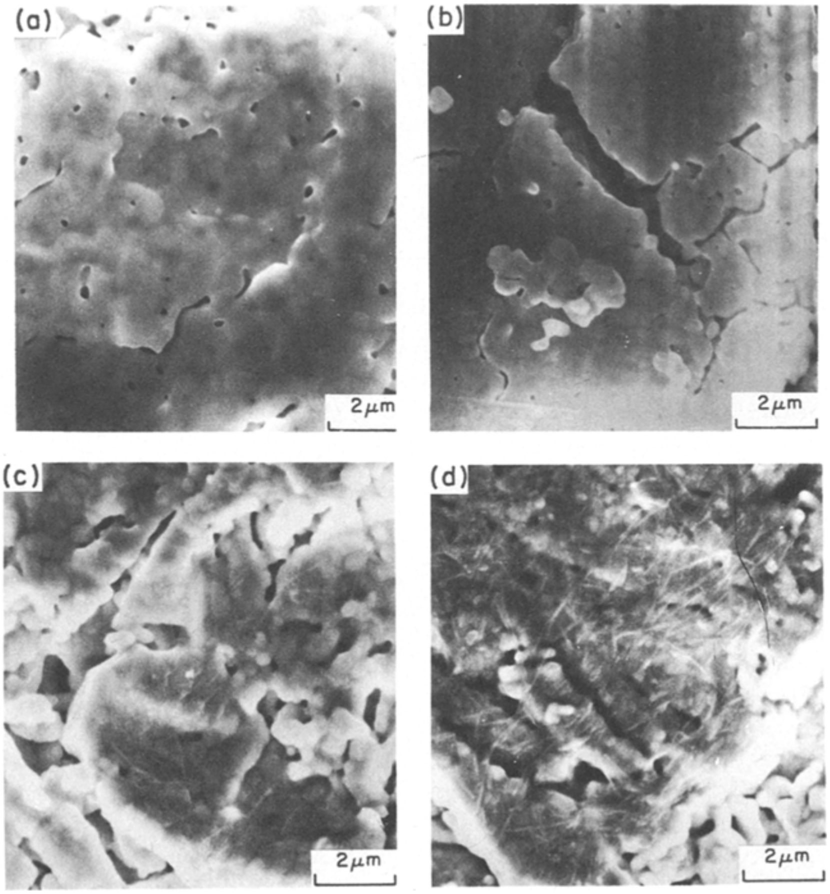
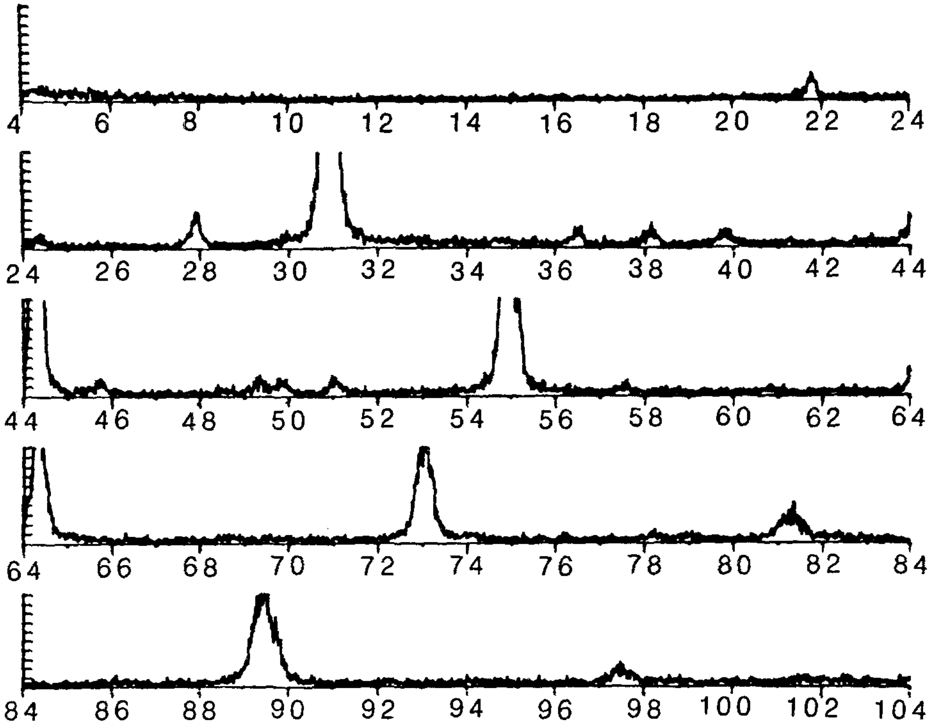


Figure 1 Microstructure of $SrZrO_3$ as a function of lanthanum concentration: (a) 0 at % La; (b) 6 at % La; (c) 7 at % La; (d) 10 at % La.

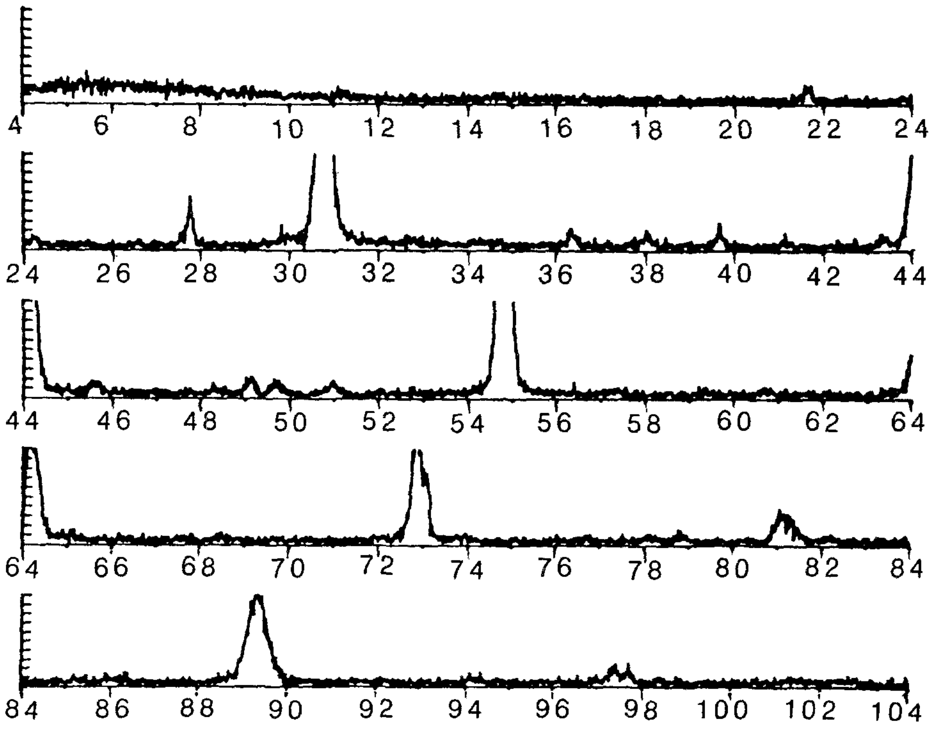
shown in Fig. 1a. With increasing lanthanum concentration, up to 6 at %, there was no significant change in this structure (Fig. 1b). When the amount of lanthanum reached 7 at %, long needle-shaped precipitates started appearing (Fig. 1c), and at 10 at % (Fig. 1d), these acicular precipitates were even more copious and readily visible. These precipitates were on an average 1 μm long and 0.1 μm thick. Energy-dispersive X-ray analysis revealed virtually no strontium counts from these precipitates, although the lanthanum and zirconium counts remained high. Similar needle-shaped precipitates in lanthanum-doped $PbTiO_3$ [5] and lanthanum-doped $SrTiO_3$ [11] have been reported and these precipitates were identified as $La_2Ti_2O_7$.

X-ray powder diffraction patterns, from the pure $SrZiO_3$ compound exhibited strong (0 2 0, 1 1 2), (2 2 0, 0 0 4), (0 2 4, 1 3 2, 3 1 2) and (2 2 4, 4 0 0) reflections in addition to several weaker reflections. The values of the lattice constants determined for this orthorhombic structure were $a = 0.580\,28$ nm, $b = 0.820\,48$ nm, and $c = 0.582\,96$ nm, which agree well with those determined elsewhere [2, 15]. No extra lines were observed with lanthanum doping up to 6 at %. However, the lattice parameter decrease was consistent with the lower ionic size of lanthanum, compared to strontium. At 7 at % lanthanum, extra lines appeared with strong (2 2 2), (4 0 0), (4 4 0) and (6 2 2) reflections. These lines were assignable to the cubic $La_2Zr_2O_7$ structure. With further addition of lanthanum, the extra lines increased in intensity indicating a greater volume fraction of the second phase. The lattice parameter, however, remained unchanged.

The diffractometer data were also consistent with the above results. Pure $SrZrO_3$ exhibited an intensity-angle pattern as shown in Fig. 2a with primary peaks corresponding to (0 2 0, 1 1 2), 9.



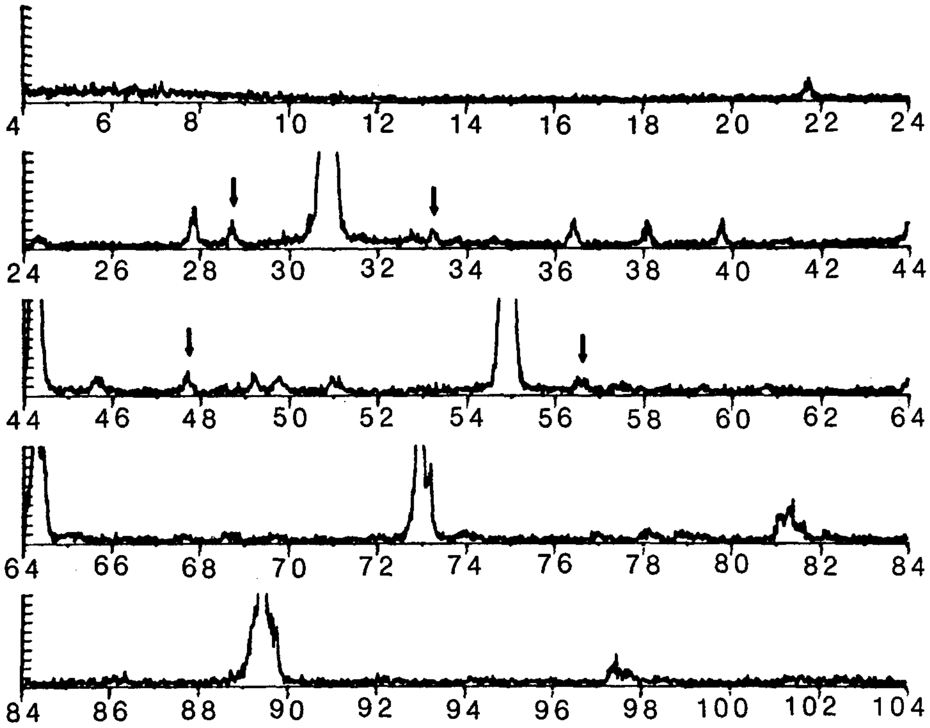
(a) Pure $SrZrO_3$



(b) 6 at % La-doped $SrZrO_3$

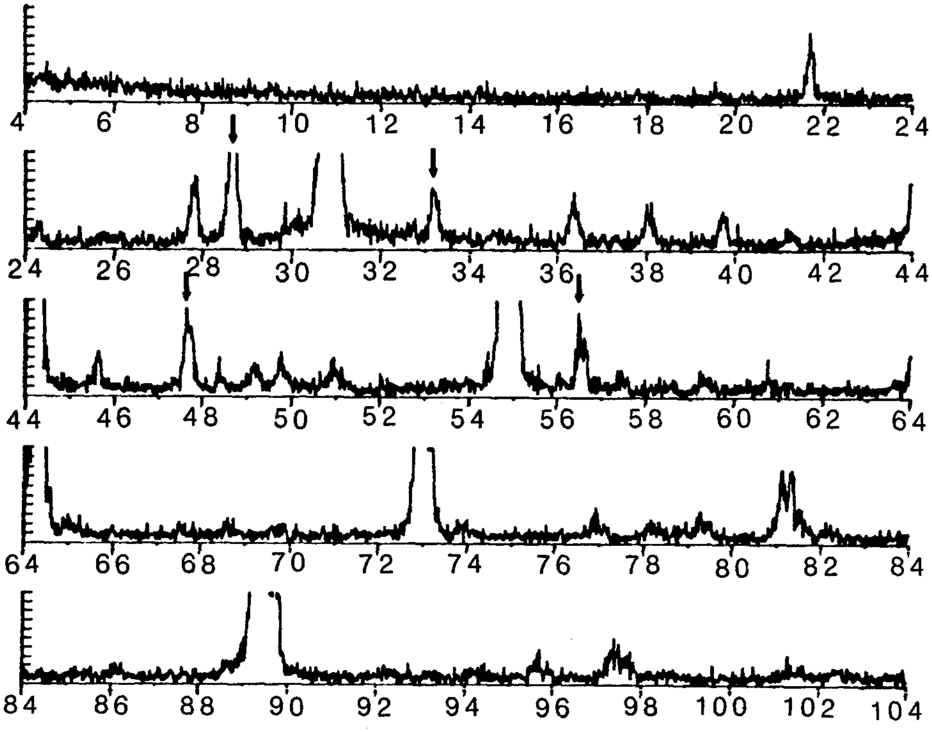
Figure 2 Diffraction patterns (intensity against Bragg angle) of $SrZrO_3$ as a function of lanthanum concentration: (a) 0 at % La; (b) 6 at % La; (c) 7 at % La; (d) 10 at % La.

10.



(c)

7 at % La-doped $SrZrO_3$



(d)

10 at % La-doped $SrZrO_3$

Figure 2 Continued

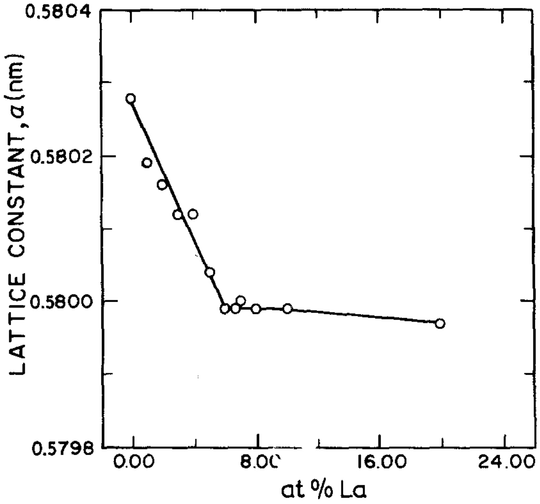


Figure 3 Lattice constant of $SrZrO_3$ as a function of lanthanum concentration.

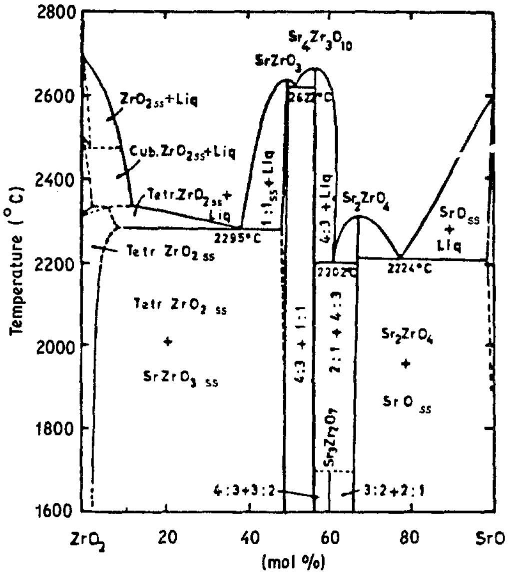


Figure 4 Tentative phase diagram of the system ZrO_2–SrO [2].

(220, 004), (024, 132, 312) and (224, 400). This pattern was unchanged up to 6 at% lanthanum addition (Fig. 2b). Extra peaks started appearing when the lanthanum added was 7 at%. These are indicated in Fig. 2c and correspond to (222), (400), (440), and (622) reflections of $La_2Zr_2O_7$. The intensity of these peaks increased at higher amounts of lanthanum (Fig. 2d). A standard parametric method was also used for determining the solubility limit of lanthanum in $SrZrO_3$. For this, the lattice parameter *a* of $SrZrO_3$ was obtained by measuring diffraction lines and extrapolating by the method of Nelson and Riley [13]. The lattice constant of $SrZrO_3$ thus determined was plotted as a function of lanthanum concentration (Fig. 3). The resulting curve exhibited a change in slope at approximately 6 at% lanthanum. Up to 6 at% lanthanum there was a linear relationship between lattice parameter and at% lanthanum, consistent with a Vegard's law dependence. Above 6 at% lanthanum, the lattice constant did not change due to the precipitation of a second phase.

Figs. 4 and 5 represent the proposed equilibrium diagrams for SrO–ZrO_2 [2] and ZrO_2–La_2O_3 [14]. The partial ternary system SrO–La_2O_3–ZrO_2 that was generated by considering

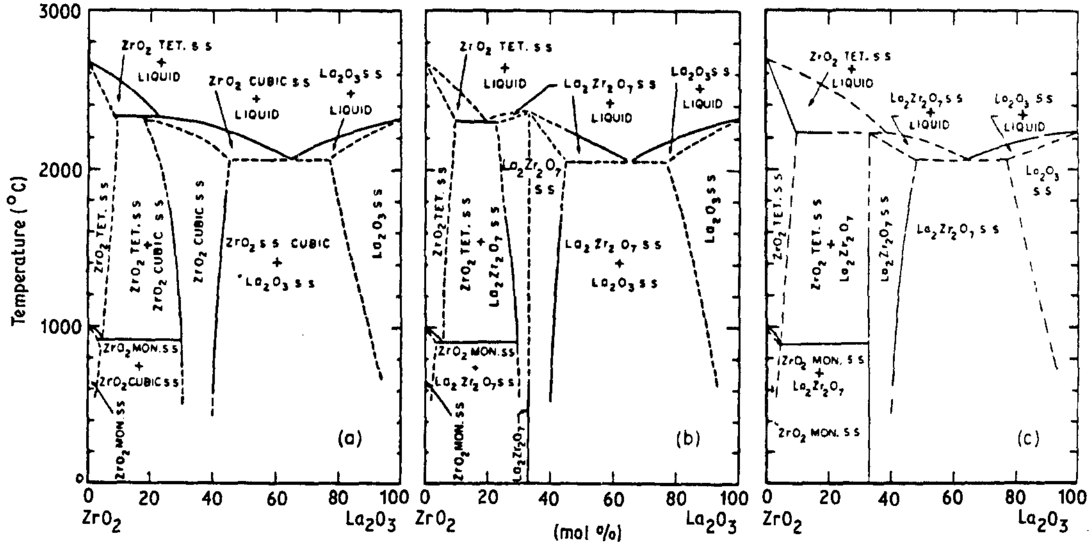


Figure 5 Possible phase equilibrium in ZrO_2–La_2O_3 system [14].

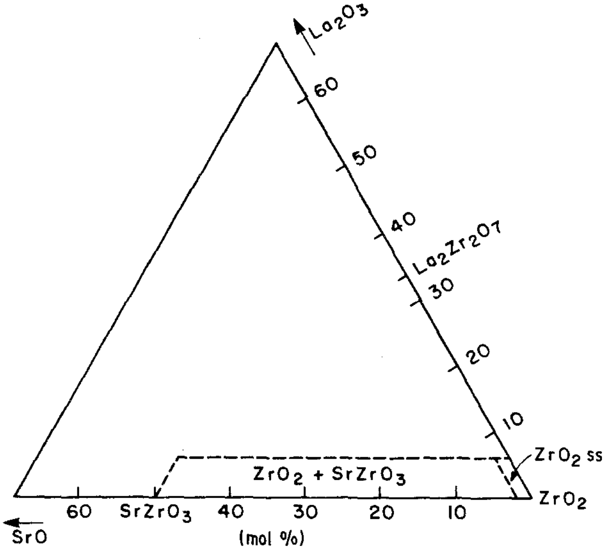


Figure 6 Proposed partial ternary diagram of the system ZrO_2–SrO–La_2O_3 at 1350° C.

the isothermal section at 1350° C in Figs. 4 and 5 is given in Fig. 6. From this ternary diagram, the range of existence of the perovskite phase can be inferred to be small. This prediction is in agreement with the experimental results.

4. Conclusions

The solubility limit of lanthanum in $SrZrO_3$ was determined to be approximately 6 at %. Beyond 6 at % lanthanum, $La_2Zr_2O_7$, in the form of long needle-shaped precipitates, was identified. Second-phase formation above 6 at % lanthanum was also confirmed by the observation of extra reflections in the X-ray powder patterns and extra peaks in the X-ray diffractometer plots that were all assignable to $La_2Zr_2O_7$.

The structure of pure $SrZrO_3$ was established as orthorhombic with the lattice parameters $a = 0.58028$ nm, $b = 0.82048$ nm, and $c = 0.58236$ nm. With increasing lanthanum concentration, the lattice parameter of $SrZrO_3$ decreased linearly up to the solubility limit with the amount of lanthanum, consistent with a Vegard's law dependence. Above the solubility limit, the lattice constant remained unchanged. A partial ternary diagram for the system SrO–La_2O_3–ZrO_2 was generated and this indicated a small range of existence of the homogeneous perovskite phase, consistent with the experimental results.

Acknowledgement

This work was supported by a grant from the Gas Research Institute.

References

1. A. M. ANTHONY and M. FOEX, in "Proceedings of the Symposium on Magnetic Hydrodynamic Electrical Power", Salzburg, Austria, July 1966 (National Agency for International Publication Inc., New York, 1966) Vol. 3, p. 265.
2. T. NOGUCHI, T. OKUBO and O. YONEMOCHI, *J. Amer. Ceram. Soc.* **52** (1969) 178.
3. H. STETSON and B. SCHWARTZ, *ibid.* **44** (1961) 420.
4. T. Y. TIEN and A. HUMMEL, *Trans. Brit. Ceram. Soc.* **66** (1967) 233.
5. D. HENNINGS, *Mat. Res. Bull.* **6** (1971) 329.
6. G. H. JONKER, *Solid State Electronics* **7** (1964) 895.
7. K. H. HARDTL and D. HENNINGS, *J. Amer. Ceram. Soc.* **55** (1972) 230.
8. N. G. EROR and D. M. SMYTH, in "Proceedings of the Institute for Advanced Study on the Chemistry of Extended Defects in Non-Metallic Solids", Scottsdale, Arizona, April 1969, edited by L. Eyring and M. O. Keeffe (North-Holland, Amsterdam, 1970) p. 62.
9. N. G. EROR and U. BALACHANDRAN, *J. Solid State Chem.* **40** (1981) 55.
10. D. HENNINGS and K. H. HARDTL, *Phys. Status Solidi (a)* **3** (1970) 465.
11. U. BALACHANDRAN and N. G. EROR, *Comm. Amer. Ceram. Soc.* April (1981) C-75.
12. M. PECHINI, US Pat. 3330 697, July (1967).
13. J. B. NELSON and D. P. RILEY, *Proc. Phys. Soc. (London)* **57** (1945) 16.
14. R. S. ROTH, *J. Res. Nat. Bur. Stand.* **56** (1956) 17.
15. G. TILLOCA and P. Y. JORBA, *Rev. Hautes Temp. Ref.* **1** (1964) 331.
16. N. G. EROR and T. M. LOEHR, *Solid State Chem.* **12** (1975) 319.

Received 30 August
and accepted 22 September 1983