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Raman scattering of single-crystal SrZrO₃

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Received 24 March 1999

Abstract. Single-crystal SrZrO₃ with perovskite-type structure was grown by a floating-zone method. The polarized Raman scattering spectra were measured at room temperature. The observed Raman spectra were interpreted on the basis of a factor group analysis for the group D_{2h}. Although 24 Raman active modes were expected, 15 bands were observed and the mode assignments were made by using D_{2h} symmetry. Vibrational mode frequencies calculated using a rigid-ion model were helpful for the assignment of B_{1g} and B_{3g} modes and the interatomic potentials were estimated.

1. Introduction

Perovskite-type strontium zirconate (SrZrO₃) is a typical proton-conductor material when a few mol% of trivalent cations are substituted for Zr⁴⁺ ions [1, 2]. There is increasing interest, both as regards basic science and applications, in SrZrO₃-based protonic conductors at high temperatures. In particular, materials doped with some trivalent ions such as those of Yb, Y and Sc show a remarkably high chemical stability and could find application in fuel cells and hydrogen sensors. Considerable experimental effort has been devoted to achieving an understanding of the properties of the proton storage and proton dynamics in these materials. It is clear that the doped trivalent ion plays an important role in the proton-conduction mechanism and it should make the host lattice locally distort. It is suggested that a local lattice distortion should be related to proton-conductive properties. Therefore, local structural information is very important to the understanding of the protonic properties of the materials. To obtain the dynamical properties of such a local structure, a Raman scattering method is especially useful [3]. A Raman scattering study has been performed using powdered samples of SrZrO₃ [4], but an assignment of the Raman bands of SrZrO₃ has not been established. The phonon assignment is essential to the understanding of the dynamical properties associated with the local distortion.

As to the crystallographic structure of SrZrO₃, two types were reported. One is a pseudo-cubic perovskite with $Z = 8$ [5] and the other is an orthorhombic form with $Z = 4$ [6], where Z is the number of molecules included in a unit cell. Roth [7] carried out a classification of the A²⁺B⁴⁺O₃ perovskite-type oxide structures based on the ionic radii of the constituent metal ions. Following his classification, SrZrO₃ falls in the pseudo-cubic class near the boundary of the orthorhombic class. On the other hand, it had been generally believed that SrZrO₃ has an orthorhombic structure (space group D_{2h}¹⁶-*Pnma*), as was determined by neutron diffraction [6]. Recently, van Roosmalen *et al* [8] reported that at room temperature SrZrO₃ was found to crystallize with either pseudo-cubic (*P2*₁3; $Z = 8$) or orthorhombic (*Pnma*; $Z = 4$) symmetry, depending on the sintering temperature of the ceramic samples. However,

all previous structural studies were performed not with single crystals, but with powdered ceramics.

The purpose of this study is to assign the Raman bands using a SrZrO_3 single crystal, which was grown by a floating-zone method using a xenon arc-imaging furnace.

2. Experimental details

A powder sample of SrZrO_3 was prepared by solid-state reaction. After SrCO_3 (99.99%) and ZrO_2 (99.99%) were homogeneously mixed in the ratio 1:1, the mixture was air fired in an alumina crucible at temperatures of 1521–1541 K for 15 hours and then slowly cooled. The colour of the resultant powder was white. Figure 1(a) shows the x-ray powder diffraction pattern measured by using $\text{Cu K}\alpha$ radiation at room temperature. Even at higher angles, no splitting of the reflections could be observed except for the splitting due to $\text{Cu K}\alpha_1$ and $\text{Cu K}\alpha_2$ radiation, indicating a cubic structure. It was suggested by van Roosmalen *et al* that SrZrO_3 , which was prepared at relatively low temperatures, less than about 1700 K, tends to take on a pseudo-cubic structure [8].

A SrZrO_3 single crystal was grown from a melt of this SrZrO_3 ceramic by a floating-zone method. The growth atmosphere was a mixture of 4 Ar:1 O_2 with a flow velocity of

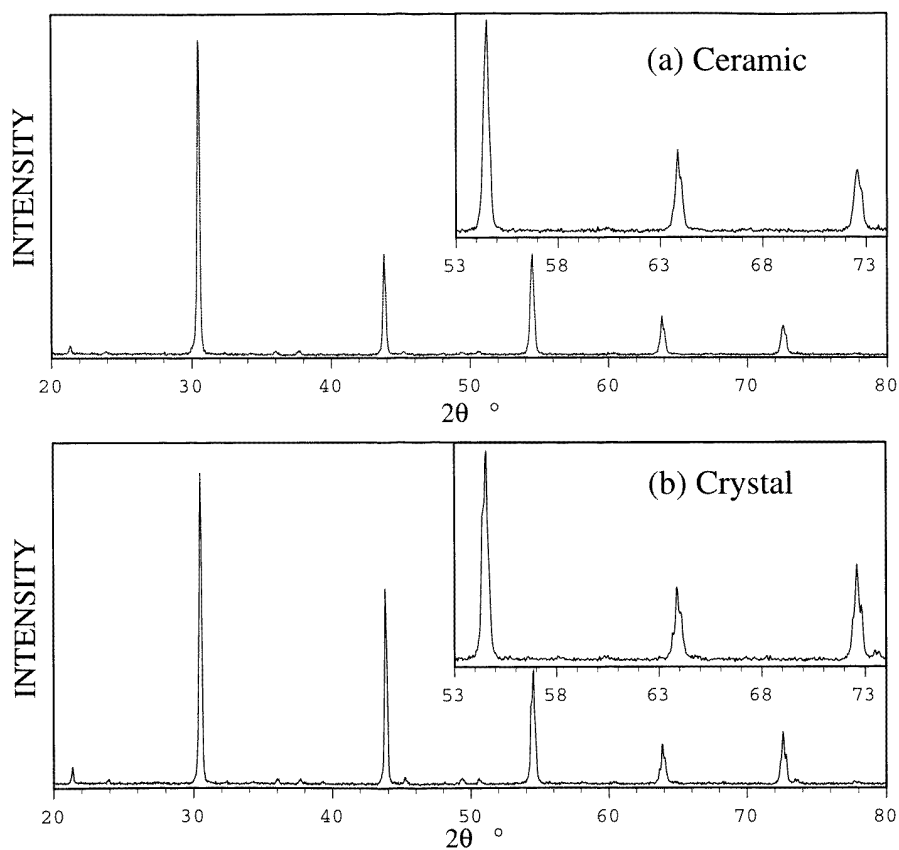


Figure 1. X-ray diffraction patterns of SrZrO_3 at room temperature; (a) ceramics and (b) crystals.

12.5 l min⁻¹. The x-ray powder diffraction of SrZrO₃ prepared by crushing a bulk crystal in an agate mortar was measured at room temperature using Cu K α radiation, as shown in figure 1(b). Figure 1(b) shows that there is a splitting of the reflections at higher angles. The crystal of SrZrO₃, which is made by melting, has been found to have an orthorhombic structure of space group *Pnma* (D_{2h}¹⁶).

The crystal was cut into a rectangular shape oriented along the crystallographic axes. The crystal was colourless, transparent and 1.0 × 0.8 × 0.3 mm³ in size. The domain structure which was observed by means of a polarizing microscope is shown in figure 2, and the Cartesian coordinates *X*, *Y*, *Z* are defined along the crystallographic axes *a*, *b* and *c*. Though the direction parallel to each crystallographic axis could be identified by the back-reflection Laue method, it was not possible to distinguish between the *a*- and *c*-axes due to the closeness of the values for the lattice constants *a* = 5.813 and *c* = 5.792 Å at room temperature [6].

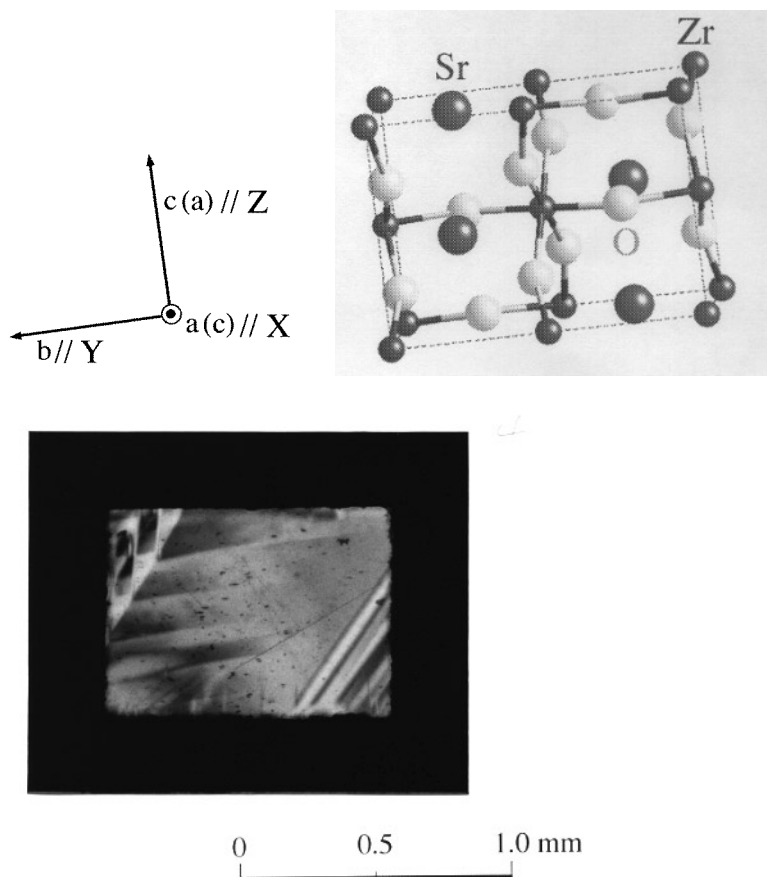


Figure 2. The cartesian coordinates *X*, *Y*, *Z* and crystallographic axes *a*, *b* and *c* of orthorhombic SrZrO₃. Also shown is the domain pattern of the SrZrO₃ single crystal at room temperature.

Polarized Raman spectra were measured at room temperature in a right-angle scattering geometry. The excitation source was the 5145 Å line of an Ar⁺-ion laser at a power level of 300 mW. The scattered light was analysed by a double monochromator having a spectral resolution of about 3 cm⁻¹. In addition to this ordinary Raman scattering measurement,

a polarized micro-Raman measurement was also carried out using a microscope objective lens ($\times 20$). The light power of the 5145 Å laser line was 100 mW. Although our micro-Raman instrument has a spectral resolution of about 6 cm^{-1} and cannot measure spectra below 120 cm^{-1} , the incident beam can be focused on the sample surface to a point of the order of a few microns in diameter, which enables us to irradiate a single domain of the crystal.

3. Results and discussion

3.1. Mode assignment

At room temperature, SrZrO₃ belongs to the space group *Pnma* containing four molecules in a unit cell as described in the previous section. The irreducible representation Γ of the phonon modes at the zone centre can be decomposed as follows by a factor group analysis:

$$\Gamma = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g} + 8A_u + 10B_{1u} + 8B_{2u} + 10B_{3u}. \quad (1)$$

Equation (1) shows that there are 24 Raman-active modes:

$$7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$$

and 25 infrared-active modes:

$$9B_{1u} + 7B_{2u} + 9B_{3u}$$

and also three translational modes:

$$B_{1u} + B_{2u} + B_{3u}$$

while the $8A_u$ modes are both Raman and infrared inactive as reported by Saine and Husson [9]. The Raman tensors are as follows:

$$\begin{pmatrix} a & & \\ & b & \\ & & c \end{pmatrix} \quad \begin{pmatrix} & d & \\ & & \\ d & & \end{pmatrix} \quad \begin{pmatrix} & & e \\ & & \\ e & & \end{pmatrix} \quad \begin{pmatrix} & & & \\ & & & \\ & & f & \\ & & & f \end{pmatrix} \quad (2)$$

A_g B_{1g} B_{2g} B_{3g}

where a, b, c, d, e and f are the independent components of the Raman tensor [10].

Figure 3 shows the polarized Raman spectra measured in a right-angle scattering geometry with various polarizations parallel to the crystallographic axes. From the scattering selection rules, it is expected that curves (a) and (b) will be irreducible components of the A_g symmetry and curve (c) an irreducible component of the B_{2g} symmetry. Although the (*XY*)- and (*YZ*)-polarized spectra are found to be different as shown by curves (d) and (e), we cannot distinguish B_{1g} and B_{3g} due to the uncertainty as regards the *a*- and *c*-axes of our crystal. It can be seen that a band at 107 cm^{-1} is only observed from curve (a) and a band at 96 cm^{-1} only from (b). Therefore, the bands at 96 and 107 cm^{-1} correspond to A_g modes. A band at 315 cm^{-1} is only observed from curve (e), indicating a B_{3g} (or B_{1g}) mode. On the other hand, bands at 169, 278 and 413 cm^{-1} are observed for all of the polarized spectra. However, it is concluded that these bands correspond to the A_g modes because of the quite strong intensities in curve (a). Bands at 117, 146, 392 and 441 cm^{-1} are also observed for all of the polarized spectra. Similarly, quite strong intensities in curve (c) yield the inference that these bands have B_{2g} character.

Figure 4 shows spectra for the various polarization configurations expected to be active for the B_{1g} and B_{3g} modes in the frequency range $100\text{--}200\text{ cm}^{-1}$. In this figure, it can be seen that the frequencies of the bands located at around 133 cm^{-1} observed for the polarization configurations (*XY*) and (*YX*) differ by about 5 cm^{-1} less than the frequencies of the bands observed for the configurations (*YZ*) and (*ZY*). Therefore, it is concluded that the two bands observed at 133 and 138 cm^{-1} belong to different irreducible representations.

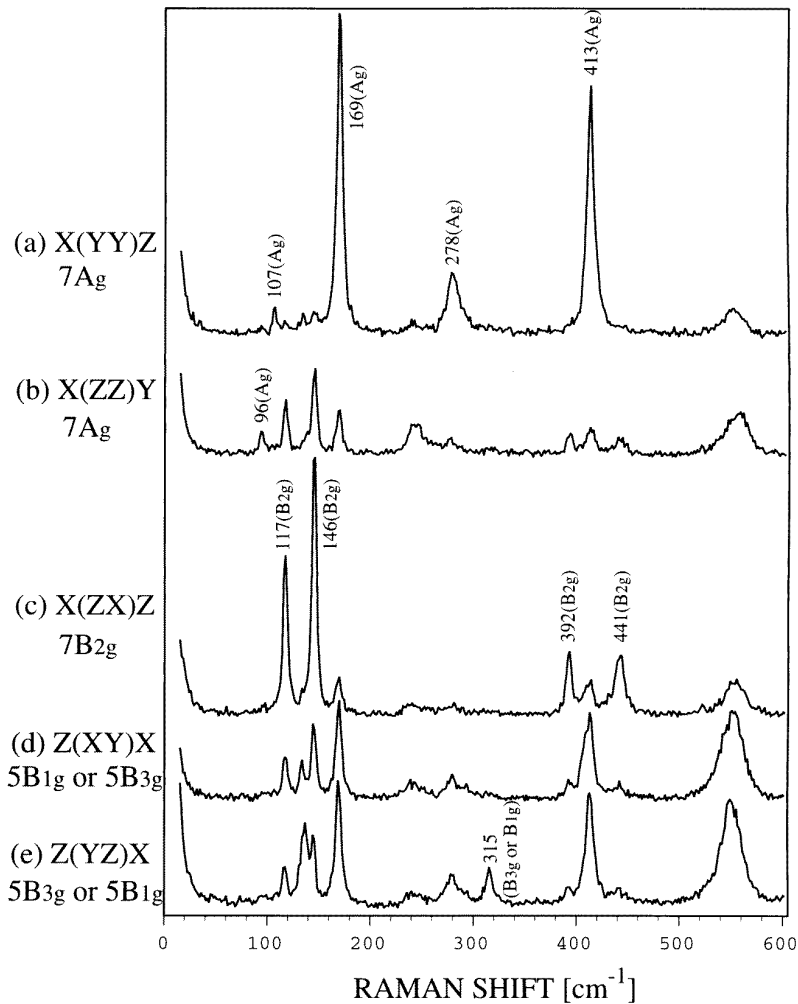


Figure 3. Raman spectra of the SrZrO₃ single crystal measured for (a) $X(YY)Z$, (b) $X(ZZ)Y$, (c) $X(ZX)Z$, (d) $Z(XY)X$ and (e) $Z(YZ)X$ polarization configurations. The experimental conditions are as follows: at room temperature; in a right-angle scattering geometry; and with 300 mW incident light.

The assignment of the two bands observed at about 240 and 550 cm^{-1} in figure 3 is difficult, because these bands are present with nearly the same intensities in all of the polarized spectra. The difficulty of the assignment could be ascribed to a strong effect from the other domains. In order to obtain scattered light only from a single domain, micro-Raman spectra were taken for an area a few micrometres in diameter in a backscattering geometry. The (YY) , (ZZ) and (ZY) polarization spectra were measured at room temperature (figure 5). The (XZ) polarization spectra for B_{2g} and the (XY) polarization spectra for B_{1g} (or B_{3g}) could not be measured, because the domain structure, as shown in figure 2, prevented us from irradiating a single domain. The 266 cm^{-1} line marked Ar in figure 5 is the 5217 Å argon emission line from the laser. Figure 5 shows that the band at 242 cm^{-1} is well defined as an A_g mode. On the other hand, the band at around 550 cm^{-1} is separated into two bands at 556 and 547 cm^{-1} .

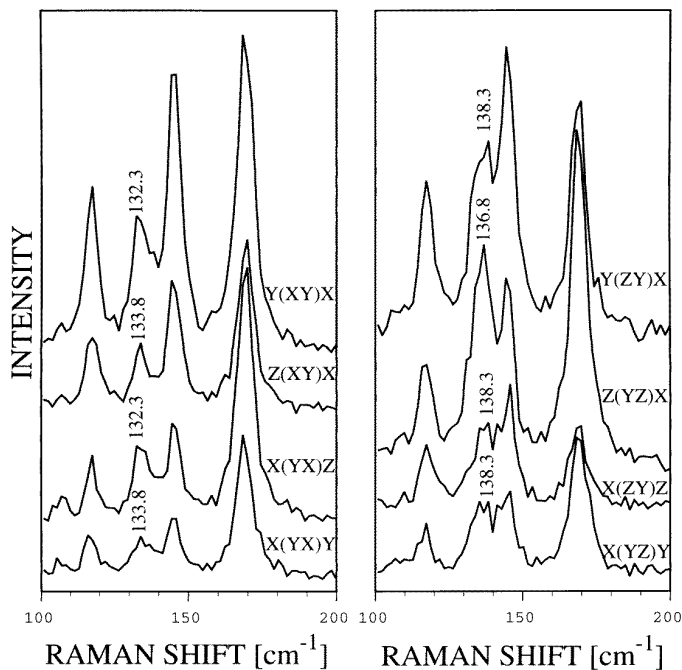


Figure 4. Polarized Raman spectra for B_{1g} and B_{3g} , for the frequency range 100–200 cm^{-1} .

The difference of 9 cm^{-1} between 556 and 547 cm^{-1} is enough to allow us to assign the band at around 550 cm^{-1} to the irreducible representations A_g and B_{3g} (or B_{1g}). As a result, 15 well resolved bands out of 24 possible Raman modes were observed below 600 cm^{-1} and assigned to the symmetry group D_{2h} , as summarized in table 1.

Table 1. Observed Raman frequencies and the symmetry assigned for SrZrO_3 . w: weak relative intensity; m: medium relative intensity; s: strong relative intensity.

Frequency (cm^{-1})	Symmetry
96 (w)	A_g
107 (w)	A_g
117 (s)	B_{2g}
133 (m)	B_{1g} or B_{3g}
138 (m)	B_{3g} or B_{1g}
146 (s)	B_{2g}
169 (s)	A_g
242 (m)	A_g
278 (s)	A_g
315 (m)	B_{3g} or B_{1g}
392 (s)	B_{2g}
413 (s)	A_g
441 (s)	B_{2g}
547 (s)	B_{3g} or B_{1g}
556 (s)	A_g

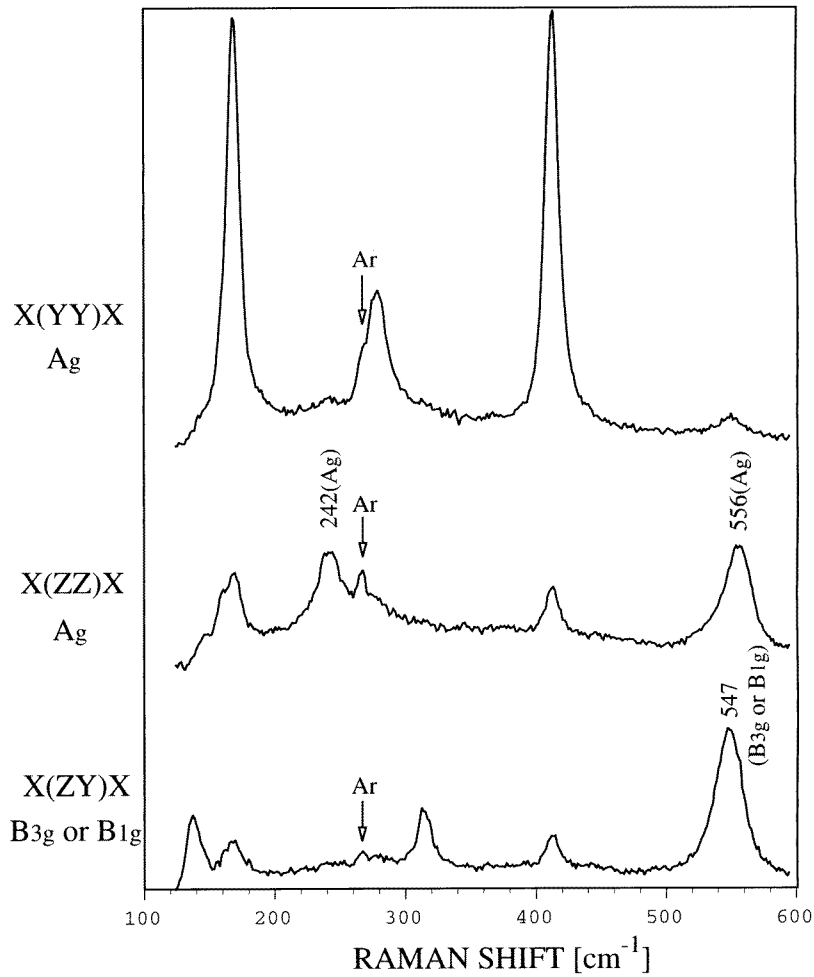


Figure 5. Micro-Raman spectra of the SrZrO₃ single crystal measured in $X(YY)X$, $X(ZZ)X$ and $X(ZY)X$ polarization configurations. The experimental conditions are as follows: at room temperature; in a backscattering geometry; and with 100 mW incident light.

3.2. The rigid-ion model

In order to assign the B_{1g} or B_{3g} Raman bands observed at 133, 138, 315 and 547 cm⁻¹, we have performed a calculation of the vibrational modes at the zone centre using a rigid-ion model. The interaction energy $V(R_{ij})$ of two ions i and j separated by a distance R_{ij} is assumed to be as follows:

$$V(R_{ij}) = \xi_{ij} \exp\left[-\frac{R_{ij}}{\sigma_{ij}}\right] + \frac{eZ_i^*eZ_j^*}{R_{ij}} \quad (3)$$

where the first term is the repulsive energy usually approximated by the Born–Mayer potential [11] and the second term is the Coulomb energy. The Pauling coefficient ξ_{ij} is defined by [12]

$$\xi_{ij} = b \left(1 + \frac{z_i}{N_i} + \frac{z_j}{N_j}\right) \exp\left[\frac{r_i + r_j}{\sigma_{ij}}\right] \quad (4)$$

where z_i , N_i and r_i are the valence, the number of electrons in the last closed shell and the Pauling ionic radius of the i th ion, respectively. These characteristic values are listed for each ion in table 2.

Table 2. The characteristic values for each ion in SrZrO₃.

	z	N	r (Å)
Sr ²⁺	+2	8	1.13
Zr ⁴⁺	+4	8	0.80
O ²⁻	-2	8	1.40

The coefficients b and σ_{ij} are adjustable parameters. The effective charge eZ^* for the long-range Coulomb force is described by

$$Z_i^* = \alpha(z_i + \Delta_i) \quad (5)$$

where α is the fraction of the charge for the all of the ions and Δ_i is the shift from the valence of the i th ion. α and Δ_i are also adjustable parameters under the condition of charge neutrality. We dealt with the long-range force by using Ewald's method [13], setting up 125 cells in both r -space and k -space, composed of 500 Sr²⁺, 500 Zr⁴⁺ and 1500 O²⁻ ions. The lattice constants

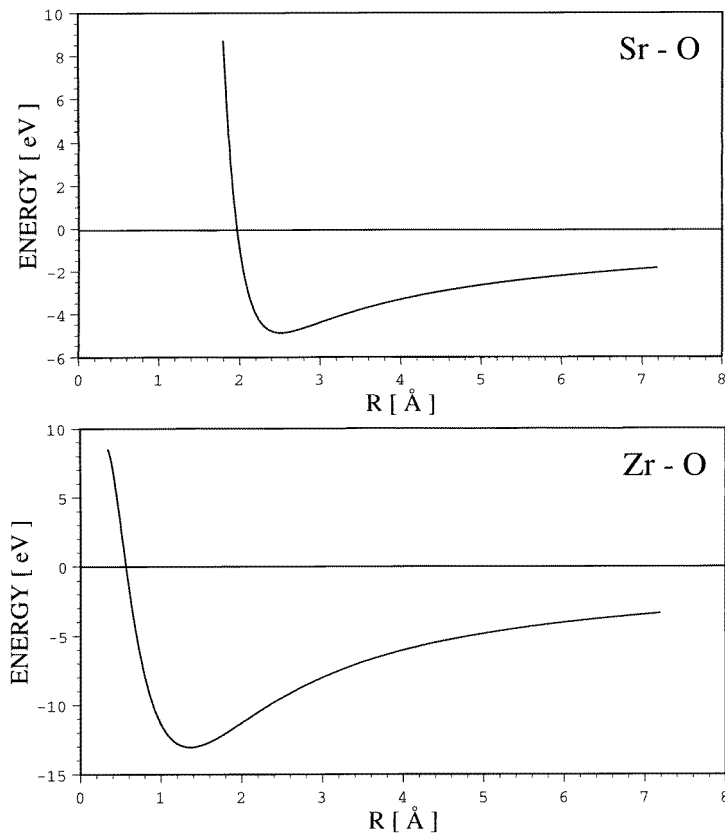


Figure 6. The Sr-O and Zr-O interatomic potentials evaluated by substituting the fitting values from table 3 into equation (3).

and atomic coordinates presented by Ahtee *et al* [6] were used. In a non-linear least-squares fitting procedure, the distances between the metal ions are so large that the short-range-force parameters $\sigma_{\text{Sr-Sr}}$, $\sigma_{\text{Zr-Zr}}$ and $\sigma_{\text{Sr-Zr}}$ are given the same values. The best set of parameters in the fitting procedure is given in table 3. There are Zr-O, Sr-O, O-O, Zr-Zr, Sr-Sr and Sr-Zr interatomic potentials.

Table 3. Values of the rigid-ion model parameters fitted to the Raman frequencies of SrZrO₃. The symbol ZSr-ZSr in $\sigma_{\text{ZSr-ZSr}}$ denotes the three kinds of ionic pair: Sr-Sr, Zr-Zr and Sr-Zr.

$\sigma_{\text{Sr-O}}$ (Å)	$\sigma_{\text{Zr-O}}$ (Å)	$\sigma_{\text{O-O}}$ (Å)	$\sigma_{\text{ZSr-ZSr}}$ (Å)	b (eV)	α	Δ_{Sr}	Δ_{Zr}
0.1933	0.3613	0.3806	0.5103	0.3701	0.4628	0.1415	-0.1052

The Zr-O and Sr-O potentials are displayed in figure 6. The mean interatomic distances of the first-nearest Zr-O and Sr-O distances were determined by neutron diffraction to be

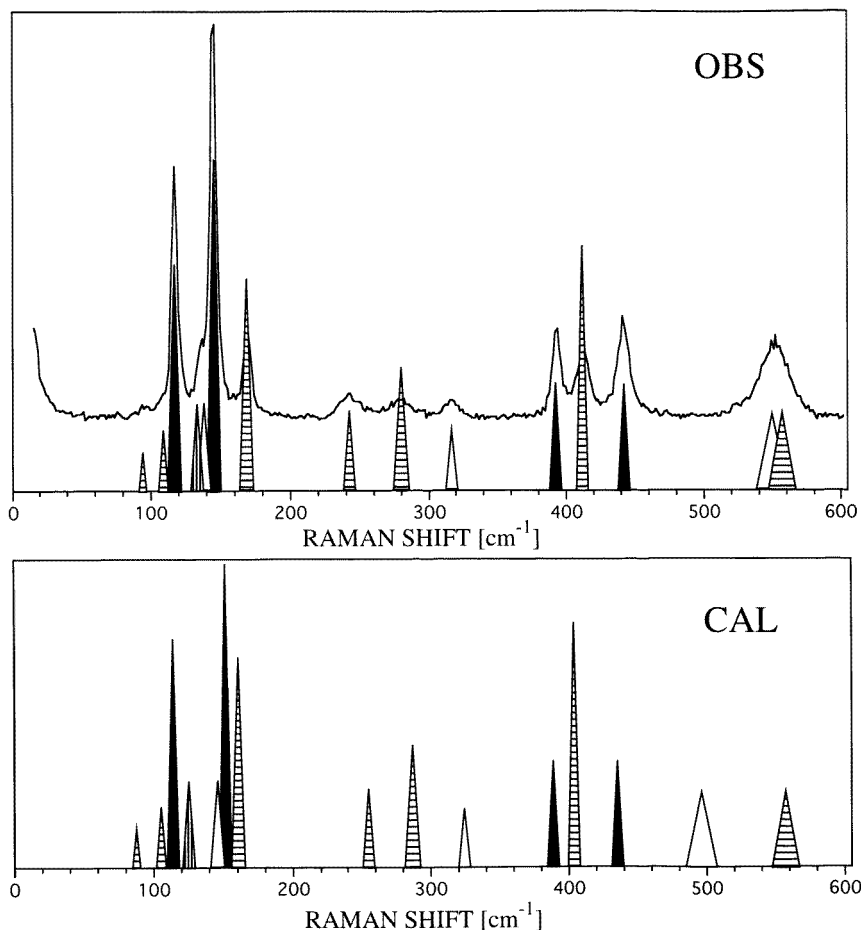


Figure 7. Comparison of the observed and calculated mode frequencies; horizontal shading: A_g modes; vertical shading: B_{1g} modes; fully shaded areas: B_{2g} modes; and unshaded areas: B_{3g} modes.

2.084–2.095 Å and 2.490–3.386 Å at room temperature, respectively [6]. It is reasonable that the minimum position of the present Zr–O potential is at lower R than that of the Sr–O potential, as shown in figure 6. The comparison of observed and calculated mode frequencies is described in figure 7 and the numerical results are given in table 4. The mode frequencies calculated by the rigid-ion model are helpful for assigning the observed B_{1g} and B_{3g} modes, and for determining the a - and c -axes of our crystal. The agreement of the calculated frequencies with the experimental values is very good except for a 547 cm^{-1} band. The observed 547 cm^{-1} band is quite different from the calculated one (494.7 cm^{-1}) assigned as B_{3g} . It was previously reported by Orera *et al* that the Raman spectra of CaZrO_3 , which belongs to the same space group as SrZrO_3 , had a similar broad band at the highest wavenumber [14]. They concluded that the band could be assigned as A_g , B_{2g} and B_{3g} by taking polarized Raman spectra and by performing a vibrational calculation using a first-nearest-neighbour interaction model. In this model, only stretching Ca–O, Zr–O and O–O and bending O–Ca–O and O–Zr–O were considered. Like our result for the B_{3g} band, their calculation result was also a poor fit, in which the discrepancy was 52 cm^{-1} . The present rigid-ion model has no non-central forces for all ions and the model adopted by Orera *et al* did not consider bending O–O–O, Ca–O–Ca and Zr–O–Zr. It is found from our analysis of the eigenvectors that the B_{3g} band, which is calculated to be at 494.7 cm^{-1} , is mainly due to displacement along the a -axis on the oxygen sublattice located at 8d sites. This would suggest that the non-central force around the oxygen plays an important role as regards the B_{3g} band observed at 547 cm^{-1} . In this respect, it will be necessary to carry out further study.

Table 4. Raman frequencies observed and calculated on the basis of a rigid-ion model, and symmetry assignments.

Observed (cm^{-1})	Calculated (cm^{-1})	Symmetry
96	85.8	A_g
107	107.7	A_g
169	160.0	A_g
242	255.1	A_g
278	287.3	A_g
413	404.6	A_g
556	554.4	A_g
—	100.2	B_{1g}
133	123.8	B_{1g}
—	236.6	B_{1g}
—	300.9	B_{1g}
—	436.7	B_{1g}
117	113.5	B_{2g}
146	155.9	B_{2g}
—	236.6	B_{2g}
392	388.6	B_{2g}
441	435.5	B_{2g}
—	515.3	B_{2g}
—	533.7	B_{2g}
—	85.8	B_{3g}
138	149.6	B_{3g}
315	324.1	B_{3g}
—	460.2	B_{3g}
547	494.7*	B_{3g}

*Poor fitting.

4. Conclusions

A SrZrO₃ single crystal was grown by the floating-zone method using a xenon arc-imaging furnace. It was determined by x-ray powder diffraction that the SrZrO₃ crystal, which is made by melting, has not pseudo-cubic but orthorhombic structure. Polarized Raman spectra of the SrZrO₃ single crystal in right-angle and backscattering geometries were measured at room temperature. The numerical calculation using a rigid-ion model made clear the assignment of B_{1g} and B_{3g}, and provided the interatomic potentials. Fifteen well resolved Raman bands were observed and interpreted as corresponding to the symmetry group D_{2h}.

Acknowledgments

We wish to acknowledge the contributions of Mr K Yanagi in the procedure of polishing the crystal. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No 260).

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