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Lattice vibrations and bulk properties of ceramics-forming materials: Piezoeffect in SiC and elasticity of ZrO_2

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The role of lattice vibrations in the crystal properties related to the homogeneous strains is discussed. Such properties depend on the individual phonon characteristics measurable by vibrational spectroscopy. So, being applicable to powderlike samples, it can provide an *indirect* information on those bulk characteristics which cannot be directly measured for such samples. The piezoelectricity of cubic SiC, and the elasticity of tetragonal ZrO_2 are considered along with the phonon spectra. Thus the mechanism of the polarization of sphalerite-like materials is elucidated; a contradiction between the elastic properties of the *t*-ZrO_2 lattice and the conventional interpretation of its Raman spectra is revealed. © *1999 Kluwer Academic Publishers*

1. Introduction

Most ceramics-forming crystalline compounds are only accessible in the form of powder. This hinders the investigations of their bulk properties requiring single crystals. Therefore, special attention is paid to the techniques applicable to the powderlike and low-quality crystal samples. Vibrational spectroscopy belongs to that category: it is routinely used to study the behavior of ceramic materials during processing and application. However, as a rule, those studies do not concern *the elastic and piezoelectric bulk properties* which very frequently remain poorly determined (if not completely unknown). In this paper, we wish to discuss some indirect facilities of the vibrational spectroscopy in this field, and to gain an insight into the microscopic nature of the properties under consideration. In turn, when dealing with powder-like samples, vibrational spectroscopy cannot provide objective data on the symmetry of vibrations, which poses heavy tasks for their interpretation. Therefore, we also wish to discuss the situations where the information on the above mentioned bulk properties can serve the solution of the spectroscopic problems.

For such a discussion, the *microscopic* mechanisms of the coupling between the lattice vibrations and the *macroscopic* strains of the crystal must be clarified. Although the information on this coupling lies outside the conventional area of the direct experimental observations, a great deal of the understanding can be derived from lattice-dynamical treatments based on a simple and physically transparent theory.

Within the harmonic approximation, customarily used in the theory, the vibrating lattice can be regarded as a set of the normal coordinates (normal vibrations) each being specified by the frequency, eigenvector (shape), and by the dipole and polarizability derivatives. The normal coordinates form a space of internal degrees of freedom of the crystal [1]. Those of them which are Raman-active participate in the internal relaxation processes induced by the macroscopic strains of the complex crystals [2], and thus influence the microscopic mechanism of those strains. So, such bulk characteristics of the crystals as the elastic and piezoelectric tensors would depend on the individual characteristics of the normal vibrations.

Being a tool to study the normal coordinates, vibrational spectroscopy can be a virtual source of the information on the elastic and electromechanical properties of crystalline materials if the role of the lattice vibrations in these properties is understood and quantitatively estimated. The present paper is aimed to consider the relationships between the above properties of crystals and the longwave vibration characteristics measurable by the standard routines of the Raman and infrared spectrometries. The fundamentals were developed in works [1–4], but it seems that their applied aspects related to the concrete materials science problems were not elaborated in detail.

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Below we provide some theoretical basis in which the properties in question are considered in the least complicated form (Section 2). Then, jointly with experimental data and the results of the quantitative model treatments, it is applied to the sphalerite-, and fluorite-like ceramics-forming crystals, SiC and ZrO_2 respectively, with emphasis on the piezoelectric effect in the former structure (Section 3), and on the elastic behavior of the latter (Section 4). Concluding remarks are made in Section 5.

2. General consideration

Vibrational, elastic, and piezoelectric properties of a lattice can be naturally joined together within the framework of the lattice-dynamical theory of homogeneous strains of crystals [1]. Along this theory, the initial instant strain U_i ($i = 1$–6 are Voigt's indices; $1 = xx$, $2 = yy, \ldots, 6 = xy$) is generally followed by the two processes: (i) an internal structural relaxation occurring in the space of normal coordinates Q_λ; (ii) the variation of the lattice polarization ΔP which produces the macroscopic electric field E within the lattice. These processes minimize potential energy density V and provide the stationary conditions $dV/dQ_\lambda = 0$, and $dV/dE_\alpha = 0$. Within the harmonic approximation, the V value can be written as a quadratic form of variables U_i, Q_λ and E_α (normalization to a unit volume and summation on repeated indices are assumed hereafter):

$$V = 1/2 U_k C^0_{ik} U_i + 1/2 Q_\lambda \omega^2_\lambda Q_\lambda + U_i F_{\lambda i} Q_\lambda - 1/2 E_\beta \varepsilon_0 \varepsilon^e_{\alpha\beta} E_\alpha - U_i e^0_{\alpha i} E_\alpha - Q_\lambda Z_{\alpha\lambda} E_\alpha \quad (1)$$

in which the coefficients can be specified as follows: C^0_{ik} is a "bare" (nonrelaxed) elastic constant, ω_λ is a frequency of λth phonon, $F_{\lambda i}$ is a so-called elastic-optic coupling constant describing the "mechanical" force on coordinate Q_λ induced by instant strain U_i (nonzero $F_{\lambda i}$ means that the λth vibration is Raman active [2]); $\varepsilon_0 \varepsilon^e_{\alpha\beta}$ is an electronic dielectric constant (here ε_0 is permitivity of vacuum; $\alpha, \beta = 1, 2, 3$ are indices of the Cartesian axis), $e^0_{\alpha i}$ is a "bare" piezoelectric constant describing the instant polarization of the strained lattice, and $Z_{\alpha\lambda}$ is the effective dynamical charge which describes the polarization properties of coordinate Q_λ.

Condition $dV/dQ_\lambda = 0$ leads to

$$Q_\lambda \omega^2_\lambda + U_i F_{\lambda i} - Z_{\alpha\lambda} E_\alpha = 0 \quad (2)$$

By excluding Q_λ in Equation 1, one obtains expression

$$V = 1/2 U_k C_{ik} U_i - 1/2 E_\beta \varepsilon_0 \varepsilon^{\mathrm{st}}_{\alpha\beta} E_\alpha - U_i e_{\alpha i} E_\alpha \quad (3)$$

in which the coefficients have the following physical sense:

$$C_{ik} = C^0_{ik} - F_{\lambda i} F_{\lambda k} \big/ \omega^2_\lambda \quad (4)$$

is an element of the elastic tensor at a constant electric field;

$$\varepsilon_0 \varepsilon^{\mathrm{st}}_{\alpha\beta} = \varepsilon_0 \varepsilon^{\mathrm{e}}_{\alpha\beta} + Z_{\alpha\lambda} Z_{\beta\lambda} \big/ \omega^2_\lambda \quad (5)$$

represents the static dielectric tensor, and

$$e_{\alpha i} = e^0_{\alpha i} - Z_{\alpha\lambda} F_{\lambda i} \big/ \omega^2_\lambda \quad (6)$$

is the element of the piezoelectric tensor.

By applying condition $dV/dE_\alpha = 0$ to expression (3), one gets

$$V = 1/2 U_i \Gamma_{ik} U_k \quad (7)$$

where

$$\Gamma_{ik} = C_{ik} + \left(e_{\alpha i} e_{\beta k} \big/ \varepsilon_0 \varepsilon^{\mathrm{st}}_{\alpha\beta} \right) \quad (8)$$

is a piezoelectrically stiffened elastic constant, which can be rewritten as

$$\Gamma_{ik} = C_{ik}(1 + k^2) \quad (9)$$

where the k^2 value describes the electromechanical coupling. Its components for $\alpha = \beta$ and $i = k$ are electromechanical coefficients squared, widely used in practice:

$$k^2_{\alpha i} = e^2_{\alpha i} \big/ \varepsilon_0 \varepsilon^{\mathrm{st}}_{\alpha\alpha} C_{ii} \quad (10)$$

Equations 4–6 show that the elastic, dielectric and piezoelectric characteristics of solids generally include two contributions: the first terms in the right-hand sides of Equations 4–6 specify the instant response of the lattice to the change of parameters U_i and E_α, whereas the second terms relate to the relevant relaxation processes arising in the phonon subsystem.

The coefficient ω^2_λ in (1) determines the "mechanical" stiffness of the λth phonon. The $Z_{\alpha\lambda}$ and $F_{\lambda i}$ values are the phonon characteristics describing the coupling of the phonon to the macroscopic field E_α (a first-rank tensor) and to the strains U_i (a second-rank tensor) respectively. The $Z^2_{\alpha\lambda}$ value specifies the oscillator strength of the λth mode. This value can be estimated from the IR-reflection spectra, or from the TO-LO splitting in Raman spectra. The $F_{\lambda i}$ is not straightforwardly accessible from the experiment. For any Raman-active vibration participating in the relaxation processes, the symmetry rules dictate the following properties: the vibration which changes the $\alpha\beta$ element of the polarizability tensor is coupled to the macroscopic strain U_i having the same cartesian index ($i = \alpha\beta$). In particular, a totally symmetric mode would provide contributions to the U_i ($i = 1, 2, 3$) strains.

3. Silicon carbide SiC

It can be seen from Equation 6 that the λth vibration contributing to the *piezoeffect* is to be necessarily active in the Raman scattering ($F_{\lambda i} \neq 0$), and in the infrared spectra ($Z_{\alpha\lambda} \neq 0$). The simplest structures possessing such a property are the sphalerite-like lattices to which a series of ceramics forming materials belongs (3C-SiC, AlN, BN, etc). The unavailability of large single crystal is typical for these. Consequently, the measurements of the piezo-elastic properties remain beyond the facilities of the direct methods, whereas the phonon characteristics, namely, the ω_λ^2 and $Z_{\alpha\lambda}^2$ values, are accessible from the powder Raman spectra in which TO and LO phonon frequencies can be well observed. In this Section, we shall discuss the situation of the cubic silicon carbide, and focus on the bulk polarization properties of this lattice.

The longwave vibrational spectrum of a sphalerite-like structure consists of a single triply degenerate T_2 mode in which the sublattice of anions, and the sublattice of cations move in opposite directions. This mode has the properties described by a first-rank tensor (a polarization vector P), and by a second-rank tensor (a non-diagonal polarizability matrix). As a result, this vibration is coupled to the macroscopic electric field of any polarization, and to any shear strain of the lattice. Thus it contributes to the $e_{14} = e_{25} = e_{36}$ piezoelectric constants, and to $C_{44} = C_{55} = C_{66}$ elastic constants.

In Fig. 1, a fragment of the sphalerite-like structure is presented. Let us consider the effects occurring in this lattice during a positive shear strain U_i in the $\alpha\beta$ plane (which diminishes an angle between axes α and β). We shall follow the approach used for SiC [5]. That reflects the largely covalent nature of the compound in implying that the chemical bonds play the central role in the lattice dynamics and in the polarization effects. The arrows in Fig. 1 correspond to the atomic shifts relevant to the instant U_i shear strain. Due to this strain, bonds 5-1 and 5-2 would be lengthened, whereas bonds 5-4 and 5-3 would be shortened. At the same time, angle 2-5-1 enlarges, and angle 3-5-4 diminishes. The relevant restoring forces would act on anions and cations along the γ-axis in opposite directions. They form the $F_{\lambda i}$ internal "mechanical" forces (see Section 2). Concurrently, the above atomic shifts would give rise to the instant electric field $E_\gamma^0 = e_{\gamma i}^0 U_i$ which produces electrostatic forces acting on the ions together with the mechanical ones. To find a novel lattice geometry providing the energy minimum (i.e., zero net forces on ions), the two sublattices would displace in opposite directions along the γ-axis. Consequently, the Q_λ (T_2) normal coordinate and the electric field would simultaneously vary until the above mentioned stationary conditions $dV/dQ_\lambda = 0$ and $dV/dE_\gamma = 0$ be fulfilled. This corresponds to the following values:

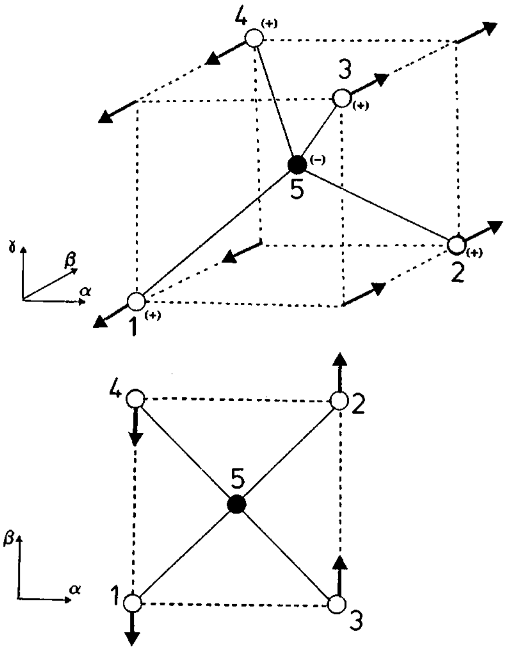

Figure 1 The atomic displacement pattern of the sphalerite-type lattice undergoing the $\alpha\beta$ shear strain. Position (0, 0, 0) is occupied by a positive ion; the position of a negative ion corresponds to (1/4, 1/4, 1/4).

$$\Delta Q_\lambda = -\left(F_{\lambda i}/\omega_\lambda^2\right)\Delta U_i + \left(Z_{\gamma\lambda}/\omega_\lambda^2\right)\Delta E_\gamma \qquad (11)$$

$$\Delta E_\gamma = \left(e_{\gamma i}/\varepsilon_0 \varepsilon_{\gamma\gamma}^{\mathrm{st}}\right)\Delta U_i \qquad (12)$$

Equation 11 shows that the Q_λ (T_2) normal coordinate can be regarded as a spring which, in the strained lattice, is loaded by the mechanical and electric forces (the first and the second terms in the right-hand side of Equation 11 respectively), and which is responsible for the equilibrium in the lattice. Equation 12 shows that the macroscopic field E results from the screened piezoeffect.

The above considerations show that a polarization mechanism of a strained lattice includes a number of changeable factors. This makes the piezoelectric effect a very subtle phenomenon. Actually, its magnitude and sign depend on those of parameters $F_{\lambda i}$, $e_{\alpha i}^0$ and $Z_{\alpha\lambda}$ which are not predictable from the "common sense". Of course, the first two values, as well as the sign of the third one, are not measurable. Therefore their model considerations can be instructive.

The origin of the $F_{\lambda i}$ value in the sphalerites was discussed above, and the lattice-dynamical studies [3, 5] shows that $F_{\lambda i}$ is *negative* in those structures. The origin of the $e_{\alpha i}^0$ and $Z_{\alpha\lambda}$ values depends on the mechanisms of the lattice polarization. By using the simplest description of the dipole moment density, $P = z_s R_s$ (here R_s is the position vector of the sth ion, and z_s specifies the ionic charge), one can describe the α-component of polarization ΔP as follows

$$\Delta P_\alpha = z_s \Delta R_{s\alpha} + \Delta z_s R_{s\alpha} \qquad (13)$$

The first term in the right-hand side of (13) corresponds to the displacements of the ionic charges, and the second one describes the *purely electronic effect*, namely, the redistribution of the intrabond electron density, which results in the charge variations Δz_s. Within our approach [5], this is associated with the changes of bond lengths L.

Being negligible in a mainly ionic lattice, the role of the electronic term in (13) would increase with increasing covalency of the interatomic bonds, but consequences of this effect are ambiguous. Actually, for a given atomic displacement pattern related to a macroscopic strain, the relevant electron redistribution would either *decrease* the ionic charges magnitudes, thus cancelling the first term in the right-hand side of (13), or *increase* them, thus adding to the ionic contribution. To clarify the situation of the sphalerite-like compounds, let us analyse the dependences of the $Z_{\alpha\beta}$ and $e_{\gamma i}$ values in these structures on the character of the chemical bonding. The signs of those values are of importance for this analysis. However, neither dielectric characteristics (Equation 5), nor electromechanical ones (Equation 10) can give such an information, since they contain those values squared. Therefore, we concentrate on the Equation 6, and firstly concern the $e^0_{\gamma i}$ value, i.e., the "instant" lattice polarization along the γ-axis, induced by the unit $\alpha\beta$ ($=U_i$) nonrelaxed shear strain. Since such a strain does not displace any atom in the γ direction (see Fig. 1), the ionic term in (13) is identical to zero, and the relevant polarization (and thus a nonzero value of $e^0_{\gamma i}$) can result from the electron flow only. This is negligible for a mainly ionic lattice CuCl. Therefore, the *positive* sign of the piezoeffect ($e_{\gamma i} = 0.16\,\mathrm{C/m^2}$) observed for CuCl (experimental data from Refs. [4, 5] will be used hereafter) must be associated with the second term in the right hand of Equation 6. Consequently, since $F_{\lambda i} < 0$, one can conclude that $Z_{\alpha\lambda} > 0$ in this compound.

The sphalerite family includes many members ranging from the presumably ionic I–VII such as CuCl ($|Z_{\alpha\lambda}| = 1.12\,e$), through the II–VIs such as ZnS ($|Z_{\alpha\lambda}| = 2.15\,e$), through the III–Vs such as InSb ($|Z_{\alpha\lambda}| = 2.43\,e$), to the single IV–IV-cubic SiC ($|Z_{\alpha\lambda}| = 2.7\,e$). A monotonous increase of the absolute magnitudes of the $Z_{\alpha\lambda} = dP_\alpha/dQ_\lambda$ value in this series correlates with the increasing covalency of the bonds, i.e., with an increasing role of the electronic term in Equation 13. So, it is highly likely that, for all the sphalerite-like structures, the sign of the electronic contribution to $Z_{\alpha\lambda}$ is the same as that of the ionic one. Thus, the $Z_{\alpha\lambda}$ value also keeps this sign. Since it is positive for CuCl lattice, it would remain positive for all the structures under consideration.

According to the bond polarization mechanism [5], the positiveness of the both terms in the $Z_{\alpha\lambda}$ value means that the magnitudes of the ionic charges increase as the bonds lengthen, and they decrease as the bonds shorten. A bond elongation would cause the electron charge to flow from the positive ion to the negative one, and the bond shortening would move this charge in the opposite direction. In the situation displayed in Fig. 1, the electron charge would outflow from ions 2 and 1 (bonds 5-1 and 5-2 are lengthened), and would flow to ions 3 and 4 (bond 5-3 and 5-4 are shortened). As a result, a *negative* polarization would arise along the γ-axis. Consequently, it can be concluded that the $e^0_{\gamma i}$ value is *essentially negative* in the sphalerite-like lattices.

So, in contrast to the $Z_{\alpha\lambda}$ value, the $e_{\alpha i}$ piezoelectric constant value consists of the two *competitive* contributions presented by the two terms in the right-hand side of Equation 6. In the sphalerite-like compounds, the magnitude of the first (negative) term would increase with increasing covalency of the chemical bonds. In parallel, the increasing elasticity of the bonds would augment the phonon stiffness (ω^2_λ) thus diminishing the positive contribution of the second term. This explains why the piezoeffect being strong and positive in the mainly ionic lattices like CuCl ($e_{\gamma i} = 0.16\,\mathrm{C/m^2}$) and ZnO ($e_{\gamma i} = 0.64\,\mathrm{C/m^2}$), drops in more covalent ZnSe ($e_{\gamma i} = 0.05\,\mathrm{C/m^2}$) and CdTe ($e_{\gamma i} = 0.03\,\mathrm{C/m^2}$), and becomes negative for most (if not all) III–V structures, for example, $-0.07\,\mathrm{C/m^2}$ for InSb, and $-0.16\,\mathrm{C/m^2}$ for GaP. Since SiC is the most covalent (IV–IV!) sphalerite-type lattice with a very high-frequency T_2 phonon ($\omega = 796\ \mathrm{cm^{-1}}$), it is highly anticipated that the $e_{\gamma i}$ value is negative for this compound.

Cubic SiC is not accessible in the form of single crystal, and the piezoeffect in it is not measured. In the same time, the estimation [6] of the k^2_{31} electromechanical coefficient (9.8×10^{-4}) for the hexagonal SiC seems to be reliable. Thus one obtains $e_{31} = \pm 0.2\,\mathrm{C/m^2}$ by using Equation 10 with $C_{11} = 502$ GPa [6] and $\varepsilon^{\mathrm{st}}_{33} = 10$ [5]. Then, following Ref. [7], one can regard the cubic {111} plane as equivalent to the hexagonal {0001} plane, and thus find a correlation between the piezoelectric tensors of the cubic and hexagonal structures. In this connection, it must be noted, that a relationship $e^{\mathrm{cub}}_{14} = -2/\sqrt{3}\,e^{\mathrm{hex}}_{31}$ proposed in early work [8] is not valid, and the correct one is $e^{\mathrm{cub}}_{14} = +3/\sqrt{3}\,e^{\mathrm{hex}}_{31}$ [5]. By using the results of above considerations, one readily obtains for cubic SiC value $e_{14} = -0.35\ \mathrm{C/m^2}$ which seems to be rather reasonable in context with the values measured for other sphalerite-like lattices [4]. Treating this value jointly with $Z_{\alpha\lambda} = +2.7\,e$ within the framework of the lattice-dynamical model [5], we find charge $z(\mathrm{Si}) = 0.42\,e$ and its derivative $dz(\mathrm{Si})/dL(\mathrm{Si\text{-}C}) = 0.91\,e/\mathrm{Å}$, thus revealing that the *static ionic* charge z in SiC is almost of an order lower than the *effective dynamical* charge $Z_{\alpha\lambda}$.

The following issue thus can be made: (i) a largely covalent bonding in SiC results in a highly rigid T_2 phonon; consequently, the relaxation processes play a secondary role in the shear strains, and the piezoeffect, dominated by the intrabond electron flow, is essentially negative and the strongest one among the sphalerite-like materials and (ii) at volume expansion, the bond lengthening would *increase* the ionic charges, thus predisposing the lattice to dissociate into *charged ions*. Such an effect can occur during the sublimation of the lattice.

4. Tetragonal zirconia ZrO_2

One of the most technologically important materials zirconium dioxide ZrO_2 has three polymorph forms at ambient pressure. On cooling from the melting point (≈3100 K), it crystallizes into a fluorite-like structure, and then undergoes a succession of structural phase transitions, cubic ($\mathrm{O^5_h}$) → tetragonal ($\mathrm{D^{15}_{4h}}$) → monoclinic ($\mathrm{C^5_{2h}}$), each time with doubling the primitive unit cell volume. The presence of impurities like Y_2O_3, CaO, MgO etc. stabilizes the high-symmetry phases of zirconia which thus can occur at room temperature. The existence (and co-existence) of various modifications of ZrO_2 at ambient conditions makes the identification of the structure an important and actual problem to which vibrational spectroscopy is frequently employed, since the longwave spectra of the zirconia

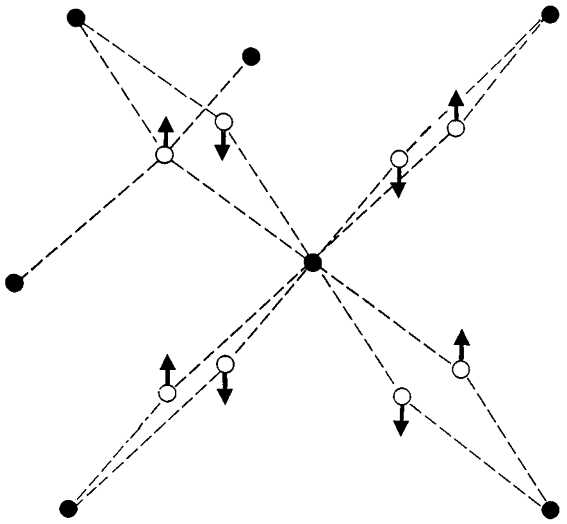

Figure 2 The fragment of a cubic ZrO_2 displaying the first coordination spheres of zirconium (black circles) and oxygen (white circles). The arrows represent the displacement pattern corresponding to the cubic-tetragonal transformation.

polymorphs differ markedly. Although those spectra are the objects of extensive studies, many points of their interpretations remain debatable. This paper concerns the points related to the assignments of the lines in the Raman spectra of t-zirconia. We shall discuss them jointly with the structural and elastic properties of the c- and t-phases. For this, the system of the cubic axes will be kept for t-phase.

The piezoeffect is forbidden in zirconia by symmetry, and the V value (see Equation 1) can be rewritten as:

$$V = 1/2U_i C^0_{ik} U_k + 1/2 Q_\lambda \omega^2_\lambda Q_\lambda + U_i F_{\lambda i} Q_\lambda \quad (14)$$

Equation 4 describing the "mechanical" bulk elasticity remains valid; Equation 11 reduces to view

$$\Delta Q_\lambda = -\left(F_{\lambda i}\big/\omega^2_\lambda\right)\Delta U_i \quad (15)$$

The set of atomic shifts distorting the c-lattice into the t-lattice is shown in Fig. 2: the oxygen atoms move along a cubic axis, whereas the metals are immobile. This displacement pattern is equal to that which would be induced by a condensation of a so-called X_2^- mode which belongs to the triply degenerate X-point of the cubic Brillouin zone. In line with this, the results of the formal theory-group analysis [9], the lattice-dynamical treatments [10–13] and some experimental evidence [13] strongly argue for the X_2^- soft-mode mechanism of the c-t inversion. The discussion which follows is based on this position.

In the cubic phase, the ZrO_2 lattice does not contain totally symmetric vibrations. Therefore, the U_i strains with $i = 1, 2, 3$ are not accompanied by internal relaxation processes. In the t-phase, the soft mode (which will be labelled sm hereafter) becomes a single mode of the totally symmetric A_{1g} representation. Let us discuss the consequences of this effect. Note first that the tetragonal distortion of ZrO_2 is driven by the amplitude ΔQ_{sm} of the "frosen" (totally symmetric) soft mode, i.e. by magnitudes of oxygen shifts δ shown in Fig. 2. These destroy the cubic symmetry of the initial structure, and give rise to the optic-acoustic coupling between the A_{1g} mode and the U_i $(i = 1, 2, 3)$ macroscopic strains. Therefore, spontaneous internal displacements δ (i.e., ΔQ_{sm}) associated with the phase transition would induce those strains whose values are given by equilibrium conditions $dV/dU_i = 0$ (see Equation 14),

$$\Delta U_i = -\left(F_{k\ \mathrm{sm}}\big/C^0_{ik}\right)\Delta Q_{\mathrm{sm}} \quad (16)$$

To minimize the volume variation, those strains obey the relations $\Delta U_1 = \Delta U_2 \approx -1/2\Delta U_3$, which corresponds to

$$F_{1\ \mathrm{sm}} = F_{2\ \mathrm{sm}} \approx -1/2 F_{3\ \mathrm{sm}}. \quad (17)$$

Consequently, the variations of the unit cell dimensions $\Delta a = \Delta b \approx -1/2\Delta c$ take place. The model considerations [10, 11] inambiguously show that $F_{3\,\mathrm{sm}} < 0$. This explains why the initial cubic unit cell transforms into a tetragonal prism with $c > a$ (see Equation 16).

Thus, the tetragonality of the D_{4h} zirconia can be described by two parameters: by the primary (internal) parameter δ; and by the secondary (external) parameter $k = c/a$. For the pure t-zirconia, $\delta = \delta_{\max} = 0.065$ (in c units), and $k = k_{\max} = 1.024$ [13]. For the stabilized zirconia, the values of these parameters depend on the quantity of dopants, and lie in the following limits: $0 < \delta \leq \delta_{\max}$, and $1 \leq k \leq k_{\max}$. The case when $\delta > 0, k = 1$ occurs in reality [14] and means that internal deformations δ are not followed by the external ones. From the lattice-dynamical point of view such a situation would imply that, despite the occurrence of the internal strain ΔQ_{sm}, the external structural parameters do not relaxe (i.e., condition (16) is not satisfied), and the lattice is anisotropically stressed.

So it can be said that the A_{1g} normal coordinate of the tetragonal zirconia is an effective spring which provides a coupling between the various effects: the microscopic internal deformations, the external stresses, and macroscopic strains of this lattice. In fact it dominates the behavior of the t-structure. So, the knowledge of its elasticity (ω^2) is a key to understand the behavior of the t-ZrO_2 structure.

Because of the absence of the pure single crystals and the disorder in the doped structures, the objective difficulties occur for the reliable determination of the symmetry properties of the lattice vibrations in t-zirconia. However, a conventionally accepted assignment of the Raman-active modes of t-ZrO_2 can be found in literature [15, 16]. According to this, the A_{1g} mode corresponds to a weak line near 600 cm^{-1}, in the vicinity of the principal (former cubic T_{2g}) band in the Raman spectra. It was originally proposed in Ref. [15], and since then is frequently cited (see e.g. [16]). To our belief, some points of that assignment are worth another look.

Note first that the above frequency of the *soft mode* is surprisingly high, and seems to be an exceptional case in the spectroscopy of the displacive-type structural phase transitions. None of the lattice-dynamical treatments of the cubic zirconia [10–12, 17] extrapolated to the tetragonal structure can explain that effect. Actually, during the *c*-*t* inversion of zirconia, there are no dramatic structural changes accounting for such a huge hardening of the condensed phonon (which vanishes at the *c*-*t* transition point). Besides, it appears that strong doubts in the validity of the above assignment of the A_{1g} mode come from the comparative analysis of the elastic constants C_{ik} $(i, k = 1, 2, 3)$ of the cubic and tetragonal ZrO_2. The experimental values for c-ZrO_2 are $C_{11} = 417$ and $C_{12} = 82$ GPa [17]. The C_{ik} values for the *t*-phase are not measured (to our knowledge), whereas those for *m*-phase were investigated as a function of temperature [18]. By extrapolating them to the point of the *m*-*t* transition, we can estimate the values for t-ZrO_2 as $C_{11} = 340$, $C_{33} = 325$, $C_{12} = 33$, and $C_{13} = 160$ GPa. They markedly differ from the cubic ones. Let us examine the origin of this difference. In the cubic phase, the C_{ik} $(i, k = 1, 2, 3)$ elastic constants consist of the first terms in the right-hand side of Equation 4 only. Due to the *c*-*t* distortion, the crystal geometry changes slightly. Consequently, there would be no a considerable difference between the "instant" elastic response of the *t*-lattice and that of the *c*-lattice. In other words, it can be accepted that

$$C^0_{ik}(\text{tetr}) \approx C_{ik}(\text{cub}) \tag{18}$$

(the model calculations [10, 11] lead to the same issue). Therefore, the changes of elastic properties due to the *c*-*t* distortion, namely, the decrease of the diagonal values C_{11} and C_{33}, and a huge splitting of the non-diagonal ones C_{12} and C_{13} (see above) must be attributed to the appearance of the totally symmetric *soft mode* in the *t*-lattice, which gives rise to the relaxation terms in Equation 4. According to relations (17), these terms would diminish the tetragonal elastic constant C_{11}, C_{33}, C_{12}, and increase C_{13}, thus accounting for the effects in question.

In jointly considering the measured magnitudes of ΔQ_{sm} (i.e., atomic shifts δ), of ΔU_i (i.e., the variations of the unit cell parameters), and of the elastic constants along with Equations 4 and 16–18, one can evaluate elasticity ω^2 of the A_{1g} mode. This results in the value of more than an order lower than that following from Ref. [15], and localizes the A_{1g} mode frequency below 300 cm^{-1}, which is in line with the lattice-dynamical model treatment [Ref. 11]. In fact, the above consideration shows that if that mode had a frequency of 600 cm^{-1}, the relaxation processes in the *t*-lattice would lose their significance and, in particular, the C_{12}-C_{13} splitting would practically disappear. In other words, the assignment of the A_{1g} mode in Refs. [15, 16] seems to be not compatible with the behavior of the elastic properties of zirconia at the *c*-*t* transformation.

5. Concluding remarks

The main point of this paper is that the vibrational spectroscopy provides a quantitative information on the main parameters of the theory of the macroscopic homogeneous strains of crystals. Therefore, together with other experimental data and lattice-dynamical model considerations, they can serve the indirect estimation of the crystal bulk properties related to those strains, when the direct methods are not effective. The last situation is typical for many ceramics-forming materials. To exemplify this point, the properties of such materials. SiC and ZrO_2 (for which the single-crystal data are not accessible), were considered along with the relevant spectroscopic data. The sign of the effective dynamical charge $Z_{\alpha\beta}$ and the value of the piezoelectric constant $e_{\gamma i}$ thus were deduced for cubic SiC which is the most covalent among the sphalerite-like structures having heterogeneous interatomic bonds.

These results allow us to accomplish and self-consistently arrange the information on the polarization properties for the series of the sphalerite-like compounds ranging (with increasing covalency of bonding) from I–VII to IV–IV ones. This explains why, in this series, the dynamic charge $Z_{\alpha\beta}$ is positive and monotonically increases from $+1.12\,e$ (for CuCl) up to $+2.7\,e$ (for SiC), whereas the piezoelectric constant $e_{\gamma i}$ first increases from $+0.16$ C/m^2 (CuCl) to $+0.64$ C/m^2 (ZnO) and then monotonically decreases down to -0.35 C/m^2 (SiC). This series includes the information on the extremely ionic (I–VII) and the extremely covalent (IV–IV) members of the sphalerite family. So it can be extrapolated to those compounds which occupy the intermediate positions and whose properties remain unknown.

The joint analysis of structural, elastic and vibrational properties of tetragonal zirconia reveals a contradiction between the parameters of structural relaxation, the *c*-*t* variation of the elastic constants, and a position of the A_{1g} mode near 600 cm^{-1}. The above considerations localize this mode below 300 cm^{-1}. In such a case, it appears that the reliable interpretation of the Raman-active lines in *t*-zirconia remains an open question.

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