mirror plane. Thus, no activity occurs along the optic axis in crystal classes $\bar{4}$ and $\bar{4}2m$. In classes *m* and *mm*2, no activity can be present along the two optic axes if these axes lie in *m*. If they are not parallel to *m*, they show optical rotation(s) of opposite sense.

3.2.2.4.3. Second-harmonic generation (SHG)

Light waves passing through a noncentrosymmetric crystal induce new waves of twice the incident frequency. This second-harmonic generation is due to the nonlinear optical susceptibility. The *second-harmonic coefficients* form a third-rank tensor, which is subject to the same symmetry constraints as the piezoelectric tensor (see Section 3.2.2.6). Thus, only 20 noncentrosymmetric crystals, except those of class 432, can show the second-harmonic effect; *cf.* Table 3.2.2.1.

Second-harmonic generation is a powerful method of testing crystalline materials for the absence of a symmetry centre. With an appropriate experimental device, very small amounts (less than 10 mg) of powder are sufficient to detect the second-harmonic signals, even for crystals with small deviations from centrosymmetry (Dougherty & Kurtz, 1976).

3.2.2.5. Pyroelectricity and ferroelectricity

In principle, *pyroelectricity* can only exist in crystals with a permanent electric dipole moment. This moment is changed by heating and cooling, thus giving rise to electric charges on certain crystal faces, which can be detected by simple experimental procedures.

An electric dipole moment can be present only along a polar direction that has no symmetry-equivalent directions.[24] Such polar directions occur in the following ten classes: 6*mm*, 4*mm*, and their subgroups 6, 4, 3*m*, 3, *mm*2, 2, *m*, 1 (*cf.* Table 3.2.2.1). In point groups with a rotation axis, the electric moment is along this axis. In class *m*, the electric moment is parallel to any direction in the mirror plane (direction [*u*0*w*]). In class 1, any direction [*uvw*] is possible. In point groups 1 and *m*, besides a change in magnitude, a directional variation of the electric moment can also occur during heating or cooling.

In practice, it is difficult to prevent strains from developing throughout the crystal as a result of temperature gradients in the sample. This gives rise to piezoelectrically induced charges superposed on the true pyroelectric effect. Consequently, when the development of electric charges by a change in temperature is observed, the only safe deduction is that the specimen must lack a centre of symmetry. Failure to detect pyroelectricity may be due to extreme weakness of the effect, although modern methods are very sensitive.

A crystal is *ferroelectric* if the direction of the permanent electric dipole moment can be changed by an electric field. Thus, ferroelectricity can only occur in the ten pyroelectric crystal classes, mentioned above.

3.2.2.6. Piezoelectricity

In piezoelectric crystals, an electric dipole moment can be induced by compressional and torsional stress. For a uniaxial compression, the induced moment may be parallel, normal or inclined to the compression axis. These cases are called longitudinal, transverse or mixed compressional piezoeffect, respectively. Correspondingly, for torsional stress, the electric moment may be parallel, normal or inclined to the torsion axis.

The *piezoelectricity* is described by a third-rank tensor, the moduli of which vanish for all centrosymmetric point groups. Additionally, in class 432, all piezoelectric moduli are zero owing to the high symmetry. Thus, piezoelectricity can only occur in 20 noncentrosymmetric crystal classes (Table 3.2.2.1).

The piezoelectric point groups 422 and 622 show the following peculiarity: there is no direction for which a longitudinal component of the electric moment is induced under uniaxial compression. Thus, no longitudinal or mixed compressional effects occur. The moment is always normal to the compression axis (pure transverse compressional effect). This means that, with the compression pistons as electrodes, no electric charges can be found, since only transverse compressional or torsional piezoeffects occur. In all other piezoelectric classes, there exist directions in which both longitudinal and transverse components of the electric dipole moment are induced under uniaxial compression.

An electric moment can also develop under hydrostatic pressure. This kind of piezoelectricity, like pyroelectricity, can be represented by a first-rank tensor (vector), whereby the hydrostatic pressure is regarded as a scalar. Thus, piezoelectricity under hydrostatic pressure is subject to the same symmetry constraints as pyroelectricity.

Like ‘second-harmonic generation’ (Section 3.2.2.4.3), the piezoelectric effect is very useful for testing crystals for the absence of a symmetry centre. There exist powerful methods for testing powder samples or even small single crystals. In the old technique of Giebe & Scheibe (*cf.* Wooster & Brenton, 1970), the absorption and emission of radio-frequency energy by electromechanical oscillations of piezoelectric particles are detected. In the more modern method of observing ‘polarization echoes’, radio-frequency pulses are applied to powder samples. By this procedure, electromechanical vibration pulses are induced in piezoelectric particles, the echoes of which can be detected (*cf.* Melcher & Shiren, 1976).

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[24] In the literature, the requirement for pyroelectricity is frequently expressed as ‘a unique (or singular) polar axis’. This term, however, is misleading for point groups 1 and *m*.