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Inverse Database of Phase Transitions in Crystals with a Single Phase Transition

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The population (frequency of appearance) of group-subgroup symmetry descents (species) and of different combinations of ferroelastic and ferroelectric properties observed in crystals with a single phase transition have been derived from the updated Tomaszewski's database of structural phase transitions [1, 2]. A striking dominance of the full ferroelastic–non-ferroelectric phases is correlated with the pronounced preponderance of holohedral symmetries in inorganic crystals.

Keywords Structural phase transitions; phase transitions database; ferroelastic phase transitions; ferroelectric phase transitions; coexistence of ferroelectricity and ferroelasticity

Tomaszewski's database of structural phase transitions [3] and its updated version [1, 2] (containing about 6300 phase transitions in about 4300 crystals) are arranged according to

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chemical formulae of crystals. From these data we have selected crystals exhibiting just one single phase transition associated with a reduction of the space-group symmetry. To increase the reliability of data on the space-groups and lattice parameters of both phases, we have taken into account only those phase transitions for which structures of both phases have been recorded in the Inorganic Crystal Structure Database (ICSD) [4]. These conditions fulfill 221 crystals (characterized by their chemical formulae) which constitute the 'Structural Phase Transitions Database /1′ (SPTD1).

The entries of SPTD1 have been rearranged according to the point-group symmetry descents (Aizu's species) associated with each transition. The 'Inverse Structural Phase

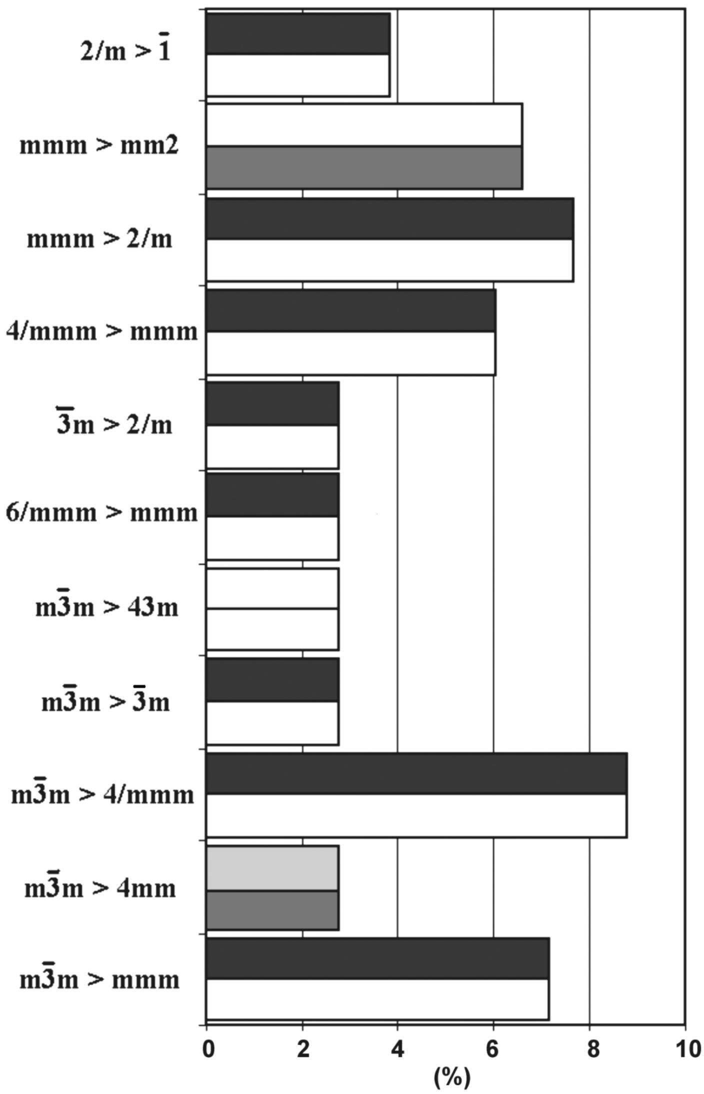

FIGURE 1 Symmetry descents—parent point-group symmetry > ferroic point-group symmetry—with the highest population rate (frequency of appearance). The dark or light blue stripe signifies the full or partial ferroelastic phases, respectively; the red one corresponds to the full ferroelectric phases. The upper or lower white stripe denotes the non-ferroelastic or the non-ferroelectric phases, respectively. (See Color Plate V)

Transitions Database /1′ (Inverse SPTD1) obtained in this way allows one to find different crystals with the same or similar characteristics and to determine the number of crystals on which each type of transition has been observed. These incidences will be called populations or frequencies.

From the 221 crystals of the Inverse SPTD1 only 39 (18%) undergo a non-ferroic phase transition, in which the change of symmetry is confined to a reduction of translational symmetry (i.e. the number of formula units per primitive unit cell is smaller in the high-symmetry parent phase than in the low-symmetry distorted phase) and both phases have the same point-group symmetry. Remaining 182 (82%) crystals are ferroic, i.e. the point-group symmetry of the distorted (ferroic) phase is a proper subgroup of the point-group symmetry of the parent phase. Our further considerations are restricted to these ferroic phase transitions and to the continuum description, in which crystal properties are expressed by property tensors and the crystal symmetry is described by a point group.

Point-group symmetry descents with the highest population in the Inverse SPTD1 are displayed in Fig. 1. The horizontal stripes express the percentage of population of the point-group symmetry descents given on the left side. The dark or light blue upper stripe signifies full or partial ferroelastic phases, respectively, and the red lower stripe represents proper ferroelectric phases. The white upper or lower stripe denotes non-ferroelastic or non-ferroelectric phases, respectively. We recall that, according to Aizu [5], in a full (partial) ferroelectric phase all (at least two but not all) domain states differ in direction of spontaneous polarization and a non-ferroelectric phase is either non-polar or possesses only one direction of spontaneous polarization. Similarly, in a full (partial) ferroelastic phase all (at least two but not all) domain states differ in spontaneous strain and in a non-ferroelastic phase all domain states exhibit the same strain. This classification is available for all species or point-group symmetry descents [5, 6].

One can infer from Fig. 1 that the full ferroelasticity is a prevailing feature of ferroic phases, whereas the full ferroelectricity is less frequent. This assessment is confirmed by Fig. 2, which displays the population of both phenomena. A high (nearly 80%) occurrence of ferroelastics contrasts to a relatively low appearance of ferroelectrics (less than 30%). Partial ferroelastics have been observed only in about 13% of crystals and partial ferroelectrics are even scarcer (less than 5%).

Nine possible combinations of Aizu's full-partial-non- classification of ferroelastics and ferroelectrics are displayed in Fig. 3. All these combinations have representative crystals in the Inverse SPTD1. Obvious is a clear superiority of the full ferroelastic–non-ferroelectric combination, which covers nearly 60% of all crystals in the SPTD1. Ferroelectricity appears less frequently but in all combinations with ferroelasticity. The lowest population exhibits the combination full ferroelastic–partial ferroelectric.

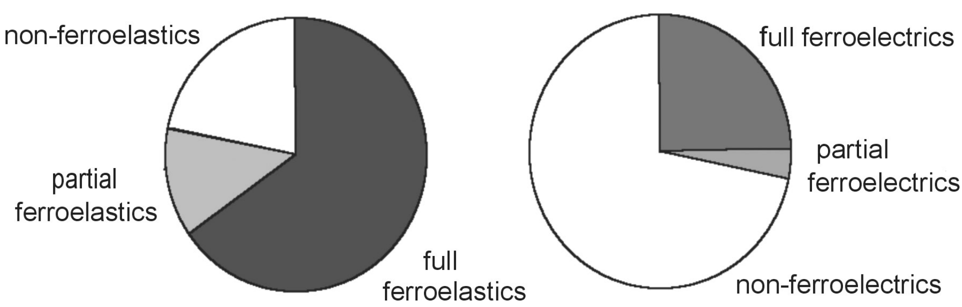

FIGURE 2 Population of the full, partial and non-ferroelastic phases and of the full, partial and non-ferroelectric phases. (See Color Plate VI)

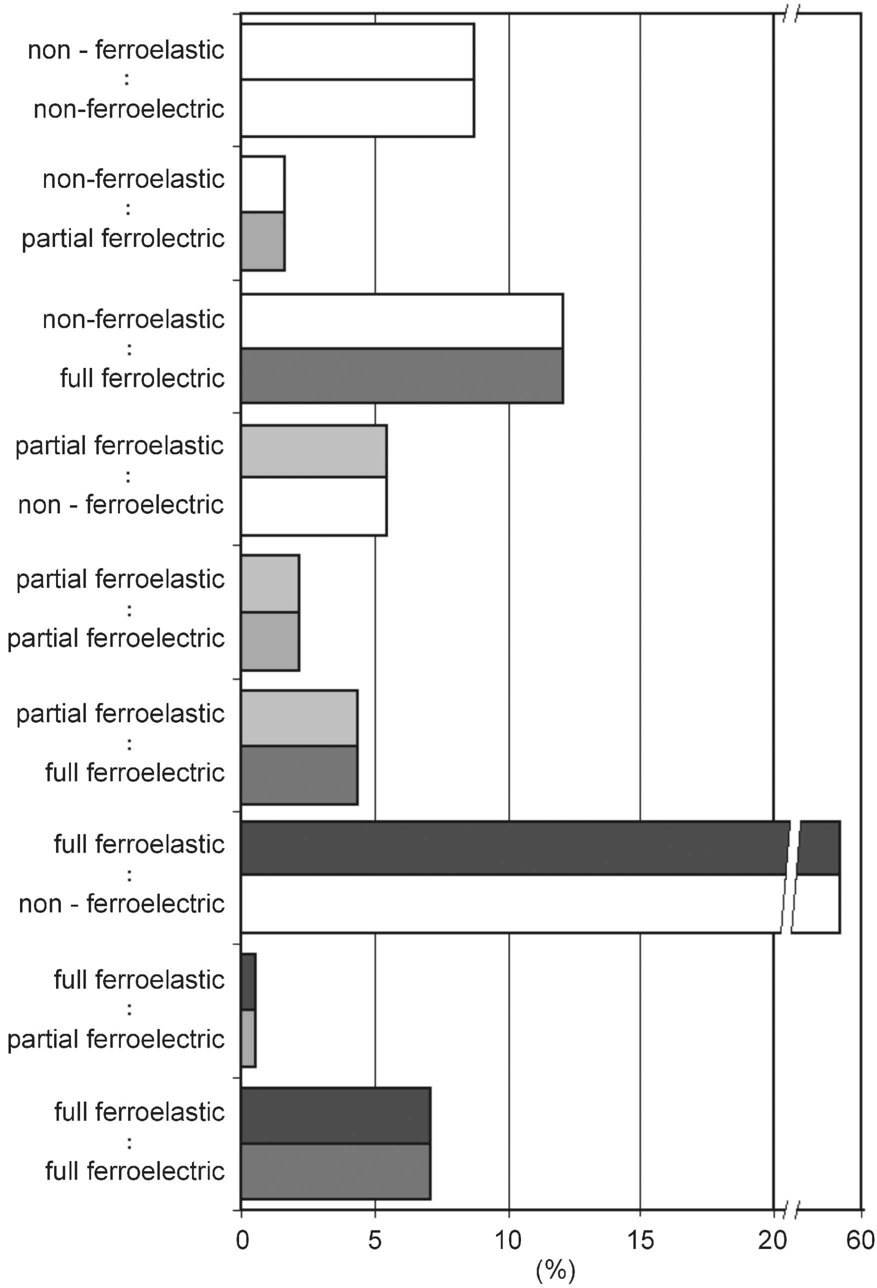

FIGURE 3 Population of nine possible combinations of coexisting ferroelastic and ferroelectric phases. Colors have the same meaning as in Figs. 1 and 2. (See Color Plate VII)

There is a striking correlation between these results and the population of the point groups (crystal classes) in the realm of inorganic crystals, not necessarily exhibiting phase transitions. As the Tomaszewski's databases indicate, most of structural phase transitions appear in inorganic crystals [1–3]. Figure 4 displays the population of point groups (crystal classes) in the inorganic crystals that are recorded in the Inorganic Crystal Structure Database (ICSD) with about 70 000 entries [4]. Seven point groups with the highest population

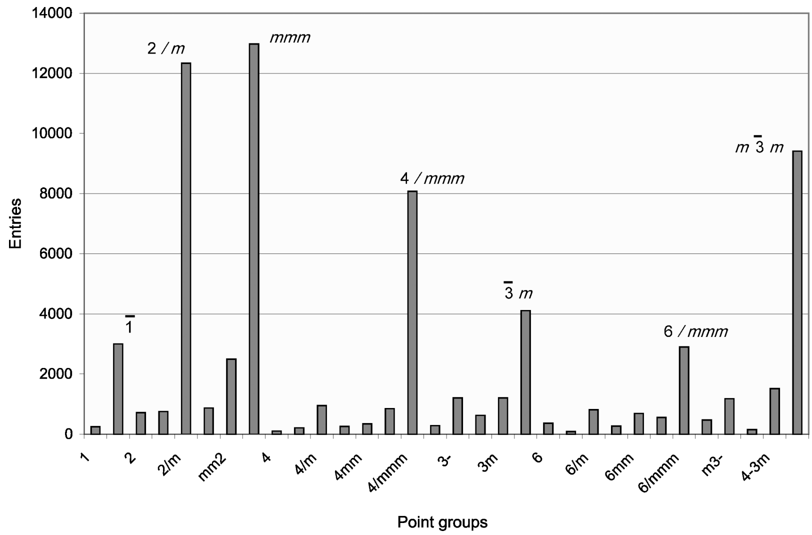

FIGURE 4 Population of 32 crystallographic point groups (crystal classes) in inorganic crystals recorded in the Inorganic Crystal Structure Database [4]. No corrections for multiple occurrences has been made, several entries may, therefore, correspond to one particular structure. (See Color Plate VIII)

correspond exactly to the holohedral point groups of the seven crystal systems. These holohedral groups express the point-group symmetry of the corresponding lattices and are non-polar since they contain inversion.

Correlations of this result with Figs. 1 and 3 are conspicuous. The high population of the holohedral crystal classes in Fig. 4 can be decisive in interpreting the predominant population of full ferroelastic–non-ferroelectric phase transitions. On the other hand, a relatively low appearance of the ferroelectric crystals can be attributed to the fact that spontaneous polarization can exist only in less populated non-holohedral crystal classes.

Although our conclusions have been obtained on the limited statistical sample (crystals with a single phase transition and with both phases recorded in the ICSD database) one can expect that similar features would also appear on larger sets of structural phase transitions.

Acknowledgements

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