СТРУКТУРНАЯ СЛОЖНОСТЬ И ПОЛИМОРФИЗМ В ЩЕЛОЧНЫХ И ЩЕЛОЧНО-ЗЕМЕЛЬНЫХ БОРАТАХ

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STRUCTURAL COMPLEXITY AND POLYMORPHISM IN ALKALI- AND ALKALINE-EARTH-METAL BORATES

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Nowadays complexity theory is a well-developed field of computer science with interdisciplinary applications in many areas of theoretical and applied sciences (Sanjeev, 2009). Until recently, it was considered that crystal structures may possess different degrees of complexity, but the complexity of crystal structures escaped a quantitative definition.

Different approaches to structural complexity were suggested by many researches, however, all of them had its own disadvantages. More advanced method to evaluate the complexity of structures was proposed by Krivovichev (Krivovichev, 2013; Krivovichev, 2014). It was based upon the relatively simple application of Shannon information theory and allowed both size- and symmetry-dependent properties of complex structures to be quantitatively evaluated.

According to the proposed concepts the formula to calculate the structural information content (I_G) of a crystal structure is:

$$I_G = -\sum_{i=1}^{k} pi \log 2\ pi \quad \text{[bits/atom]},$$

where k – number of crystallographic orbits; p_i ($p_i = m_i/v$) – the probability of occurrence of the atom of the ith crystallographic orbit; m_i – the multiplicity of the crystallographic orbit relative to the reduced unit cell; v – the number of atoms in the reduced unit-cell.

The total information content of a crystal structure is determined by:

$I_{G,\text{total}} = \text{v} \times I_G$ [bits/unit cell].

All inorganic crystal structures can be classified according to their complexity into very simple (<20 bits/u.c.), simple (20-100 bits/u.c), intermediate (100-500 bits/u.c), complex (500-1000 bits/u.c), and very complex (>1000 bits/u.c).

The information-based complexity measures allowed introducing the concept of information density:

$\rho_{inf} = I_{G,\text{total}} / V$ [bits/Å^3].

Information density also can be used as a measure of complexity for the crystal structures of solids with similar composition. It is an important parameter

for the investigation of behavior of structural information in the course of phase transitions induced by temperature and pressure. For two structures with similar unit cells but different symmetry, information density will be higher for the structure with lower symmetry (and higher complexity).

Identification of structural complexity and its density allows to quantitatively examined the relations between information and kinetics and thermodynamic parameters in crystalline materials.

In our work, we systematically investigated and analyzed the complexity of inorganic structures in the case of borate compounds especially alkali- and alkaline-earth-metal borates. Furthermore, a very interesting problem, considered in our research, is the behavior of information along the path of phase transitions induced by changing pressure and temperature.

At the moment, more than 1000 borate crystal structures are listed in the Inorganic Crystal Structure Database (ICSD). These compounds show an exceptionally large number of structural phase transitions. We have taken into account only those phase transitions for which structures of all phases have been recorded in the ICSD. These conditions fulfill 38 structures with different amount of polymorphic modifications. Complexity parameters have been calculated using the TOPOS software (Blatov, 2000). Some examples of investigated polymorphic borate structures and their complexity parameters are presented in Table.

Table 1

Crystallographic and structural complexity parameters for polymorphic modifications of alkali- and alkaline-earth-metal borates

Structure	**Polymorph Identification**	**Sp. gr.**	**I_G, bits/a.**	**$I_{G,total}$, bits/u.c.**	**ρ_{inf}, bit/Å^3**
$LiBO_2$	α, Ht	$P2_1/c$	2.000	32.000	0.215
	γ, Hp	I-42d	1.500	12.000	0.105
LiB_3O_5		$Pna2_1$	3.170	114.117	0.356
	HP	*Pnma*	4.448	640.469	0.588
CsB_5O_8	α(IV), Ht	$P2_1/c$	3.807	213.212	0.304
	β(III), Lt	*Pbca*	3.807	426.424	0.302
	γ(II), Lt	*Pbca*	3.807	426.424	0.272
	δ	*Pccn*	4.843	1084.848	0.373
$Na_2B_4O_7$	α	*P*-1	4.700	244.423	0.415
	HP	$P3_221$	4.362	510.392	0.469
	γ	*P*-1	5.285	412.261	0.522
CaB_2O_4	I	*Pbcn*	1.950	54.606	0.177
	II, Hp	*Pccn*	2.807	157.212	0.271
	III, Hp	$Pna2_1$	4.392	368.955	0.449
	IV, Hp	*Pa*3-	2.081	174.837	0.239
BaB_4O_7	α	$P2_1/c$	4.585	440.156	0.404
	β, Hp	*Pmnb*	2.752	132.078	0.309

The fact that complexity is a function of information content and unit-cell volume makes it dependent upon size of atoms and ions that make up the respective crystal, as well as upon temperature and pressure. The increase in temperature

usually results in simplification of mineral structures. In contrast, the effect of pressure upon structural complexity is non-linear. The influence of high-temperature/high-pressure (Ht/Hp) conditions on the formation of borates is not studied fundamentally. The relations between temperature, pressure and structural complexity in processes that involve transformations of crystalline phases require further exploration, which should necessarily combine thermodynamic and information-based approaches.

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