Noncentrosymmetric Oxides

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Noncentrosymmetric materials are of special interest in materials chemistry owing to their technologically important properties, such as ferroelectricity and second-order nonlinear optical behavior. Over 500 noncentrosymmetric oxides have been compiled and categorized by symmetry-dependent property and crystal class. In addition, the materials are described by their transition, or main group, metal coordination environment and grouped by element. Similarities within and between groups are discussed, as are noncentrosymmetric structure−property relationships.

Contents

Introduction

Noncentrosymmetric (NCS) compounds are of particular interest because their symmetry-dependent properties such as piezoelectricity, ferroelectricity, and second-order nonlinear optical (NLO) behavior are the basis of numerous applications. The crystallographic inter-relationships between physical properties and NCS crystal classes[1] are shown in Figure 1, which is a graphical representation of a table (based on tensor rank) described by Glazer.[2] Describing a compound as simply NCS is incomplete and imprecise. NCS materials can possess some or all of the following properties: enantiomorphism, optical activity (i.e., circular dichroism), piezoelectricity, and pyroelectricity. It should be noted that second-order NLO behavior, i.e., second-harmonic generation (SHG), has the same symmetry requirements as piezoelectricity. Several interesting inter-relationships occur between the symmetry-dependent properties. For example, all pyroelectric materials have SHG behavior but the converse is not true. Of the 21 acentric crystal classes, only compounds found in class 432 (*O*) do not possess SHG behavior. Enantiomorphism occurs in compounds crystallizing in 11 classes, 1 (C_1), 2 (C_2), 3 (C_3), 4 (C_4), 6 (C_6), 422 (D_4), 222 (D_2), 622 (D_6), 32 (D_3), 23 (*T*), and 432 (*O*), and all of these materials are optically active (i.e., circular dichroism). Only compounds in crystal classes 1 (C_1), 2 (C_2), 3 (C_3), 4 (C_4), and 6 (C_6) have all of the symmetry-dependent properties.

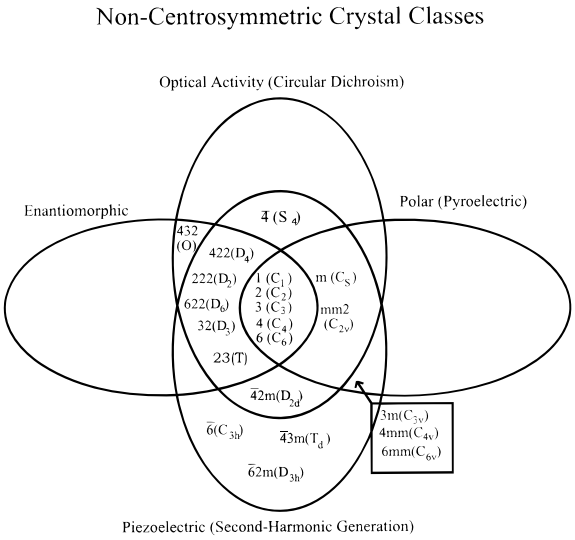

Figure 1. Interrelationships of noncentrosymmetric crystal classes in both Hermann-Mauguin and Schoenflies symbols.

A material's centricity is usually determined by single-crystal X-ray diffraction. However, the determination of centricity from single-crystal diffraction data is not always straightforward. From Friedel's law it is known that, in the diffraction process, if the incident wavelength is small compared with the absorption edge of any atom in the crystal, a center of symmetry is introduced between oppositely related reflections, $\mathbf{I}(hkl) = \mathbf{I}(-h, -k, -l)$, even in a NCS crystal. Only when the incident wavelength becomes similar to the absorption edge does Friedel's law fail. This anomalous scattering, when the imaginary part of the scattering factor becomes large, has been used to address a host of crystallographic problems.[3] For most crystallographic analyses, based on Cu Kα or Mo Kα radiation, anomalous scattering does not play a significant role, and many single-crystal diffraction laboratories do not collect Friedel pairs for comparison.

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Table 1. Symmetry-Dependent Properties

category (crystal classes)	property(ies)[a]
A (1, 2, 3, 4, 6)	I, II, III, IV
B (m, mm2)	II, III, IV
C (3m, 4 mm, 6 mm)	III IV
D (422, 222, 622, 32, 23)	I, II, IV
E (−42m, −4)	II IV
F (−6, −43m, −62m)	IV
G (432)	I II

[a] Property: I, enantiomorphism; II, optical activity; III, pyroelectricity; IV, piezoelectricity.

The intensity distribution of diffraction data also differs between a centric and acentric crystal. Statistical tests by Wilson[4] and Howells et al.[5] are useful indicators of centricity but can be incorrect if the structure contains a number of heavy atoms on special positions.[6] Marsh and co-workers have emphasized that weak reflections must be carefully scrutinized if the centricity is in question.[7,8] If these weak data are deleted, the statistical distribution tests can be strongly biased toward a NCS indication. Marsh also argues that when the diffraction data do not provide a clear choice between centric and acentric space groups, the centric space group choice is preferred even though disorder can occur.[7] Disregarding a center of symmetry results in errors in the atomic coordinates that are large compared to normal estimated standard deviations.[8] In addition, according to Dunitz it is not possible to distinguish between a centric and corresponding acentric structure through a least-squares analysis by simply expanding the parameter set over the uncertain inversion center.[9] In doing so singularities will occur during the refinement.

The purpose of this article is to review the NCS oxides and categorize them by symmetry-dependent property, crystal class, and cationic coordination environment. In an effort to elucidate common features of NCS oxides, the inter-relationships between NCS crystal classes are discussed, with respect to NCS materials properties, as well as trends within and between the above categories.

Organization

The examples used are from the 1996 version of the inorganic crystal structure database.[10] The selection criteria for acentric oxides were (1) ternary or higher oxides, (2) single-crystal studies—X-ray or neutron, and (3) $R(F) \leq 0.15$ where $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

Based on the above criteria, 578 oxides were selected. The NCS compounds can be grouped into seven distinct categories based on the symmetry-dependent properties as illustrated in Figure 1 and listed in Table 1. Categories A, B, and C constitute the 10 NCS polar crystal classes (1 (C_1), 2(C_2), 3 (C_3), 4 (C_4), 6 (C_6), m (C_s), mm2 (C_{2v}), 3m (C_{3v}), 4mm (C_{4v}), and 6mm (C_{6v})), whereas categories D, E, F, and G contain the 11 NCS nonpolar crystal classes (422 (D_4), 222 (D_2), 622 (D_6), 32 (D_3), 23 (T), −42m (D_{2d}), −4 (S_4), −6 (C_{3h}), −43m (T_d), −62m (D_{3h}), and 432 (O)).

Table 2 lists all 576 NCS oxides and is divided into two large sections, compounds in polar (i.e., pyroelectrics, materials with permanent dipole moments) and nonpolar crystal classes. Within each of the two sections, the materials are grouped by element. Additionally, within Table 2, the compounds are divided further with respect to cationic coordination environments. Underlined compounds contain second-order Jahn−Teller distorted cations, whereas italicized compounds contain tetrahedrally coordinated cations. Compounds that are both underlined and italicized have second-order Jahn−Teller distorted cations linked to tetrahedrally coordinated cations. Finally, compounds that are not underlined or italicized have neither type of cation. Each section and division will be discussed in detail.

Polar and Nonpolar Compounds

One primary division that separates NCS compounds is the polar and nonpolar crystal classes. The majority, 67% or 388, of the NCS oxides fall into categories A, B, or C that constitute the 10 NCS polar (i.e., pyroelectric, materials with permanent dipole moments) crystal classes. The remaining 190 oxides are in categories D, E, F, or G, which are the 11 NCS nonpolar crystal classes. The inter-relationship of the symmetry-dependent properties are graphically shown in Figure 1 and listed in Table 1.

Noncentrosymmetric Polar Crystal Classes

From Table 1, it is apparent that pyroelectricity is not the only symmetry-dependent property the NCS polar oxides possess. However, instead of taking each symmetry property in turn and listing the relevant materials, it is more efficient to discuss the materials with respect to the categories outlined in Table 1. With the NCS polar crystal classes, three distinct and nonoverlapping categories can be described: category A comprising crystal classes 1, 2, 3, 4, and 6; category B, crystal classes m and mm2; category C, crystal classes 3m, 4 mm, and 6 mm.

The materials that are in category A possess all four of the NCS symmetry-dependent properties, specifically enantiomorphism (chirality), optical activity (circular dichroism), pyroelectricity (polarity), and piezoelectricity (same symmetry conditions as SHG). As such, these materials are chiral, polar, optically active, and exhibit SHG behavior. The structure−property relationships between polarity and SHG as well as the relationships between chirality and optical activity will be discussed later. What has not been discussed are the structure−property relationships (if any) between chirality and polarity. Both properties are important with respect to material applications, whether as ferroelectric materials or as hosts for the intercalation of chiral guests. With respect to chiral materials, often both enantiomers are produced in a crystal growth, i.e., spontaneous resolution. The enantiomer determined is wholly dependent on the particular crystal chosen from the mixture; i.e., there is a 50% probability that one enantiomer will be chosen instead of the other. However, with materials that are also polar, a different situation occurs. If we take the same crystal mixture alluded to, with both enantiomeric isomers (α and β), and now assume the material is polar—what is the result? Only two types of crystals αp and βp, where p represent the imposed polarity, are produced. Thus, there is only "type" of polarity; i.e., there is only one "isomer" of $LiNbO_3$, and the polarity is determined by the orientation of the crystal on the diffractometer. Regardless of the crystal

Table 2. Noncentrosymmetric Oxides[a]

category (polar crystal classes)		
A (1, 2, 3, 4, 6)	B (m, mm2)	C (3m, 4 mm, 6 mm)
	Scandium	
$BaCa_2Tm_5Sc_5O_{18}$[38]	$Sc_2Cu_2O_5$[39]	$Ba_3ScB_3O_9$[40]
$BaCa_2Yb_5Sc_5O_{18}$[41]		*$LiScMo_3O_8$*[42]
	Titanium	
$La_2Ti_2O_7$[43,44]	$KTiPO_5$[13]	$BaTiO_3$[521]
$Nd_2Ti_2O_7$[45]	$CdTiO_3$[46]	$MnTiO_3$[47]
$BaTi_8O_{16}$[48]	$Ba_4Ir_{1.45}Ti_{1.55}O_{10}$[49]	$PbTiO_3$[522]
$Ba_{1.12}Ti_8O_{16}$[50]	$Fe_{0.13}Ti_{1.81}O_{1.92}$[51]	$Ba_6Ti_2Nb_8O_{30}$[52]
$Ba_{1.15}Ti_8O_{16}$[50]	$Nd_4Ca_2Ti_6O_{20}$[53]	
	$Bi_4Ti_3O_{12}$[54]	*$Ba_2TiSi_2O_8$*[55]
	$K_{0.8}Mg_{0.4}Ti_{1.6}O_4$[57]	
	$K_{0.8}Zn_{0.4}Ti_{1.6}O_4$[57]	$HgTiO_3$[58]
	$Bi_5FeTi_3O_{15}$[59]	
	$K_6Ti_2O_7$[60]	
	$K_{0.375}Cs_{0.625}TiAsO_5$[56]	
	$K_{0.39}Cs_{0.61}TiAsO_5$[56]	
	$KTiAsO_5$[56]	
	$CsTiAsO_5$[61]	
	Ba_2GeTiO_4[62]	
	Zirconium	
$Na_2Zr_3W_3O_{12}$[63]	Li_2ZrO_3[64]	*$K_5Mg_{0.5}Zr_{1.5}Mo_6O_{24}$*[65]
$Na_2ZrW_3O_{12}$[66]	$PbZrO_3$[67]	*$Na_4Si_3Zr_2O_{12}$*[68]
$K_2Si_3ZrO_9$[69]	$Ti_{1.1}Zr_{0.893}Hf_{0.007}O_4$[70]	
$CaZrSi_2O_7$[71]		
$CaBAl_9ZrO_{18}$[72]		
$Ba_2Ca_5Dy_{18}ZrO_{36}$[73]		
	Vanadium	
$V_{1.44}Mo_{0.56}O_5$[74]		$K_3V_5O_{14}$[75]
$Mn_{0.47}V_{0.94}Mo_{1.06}O_6$[76]		
		$Cs_2V_5O_{13}$[77]
ZnV_2O_6[78]	NaV_2O_5[79]	*$K_2V_3O_8$*[80]
V_2WO_7[81]	$Ag_{1.43}V_4O_{10}$[82]	*$Ca_3V_2O_8$*[83]
V_2MoO_8[84]	$Cu_{1.82}V_4O_{11}$[85]	*$SrNi_2V_2O_8$*[86]
CoV_2O_6[87]	ZnV_3O_8[88]	*RbV_3O_7*[89]
$K_{0.13}V_{0.13}Mo_{0.87}O_3$[90]	$Bi_4V_2O_{11}$[91]	*$KBa_3Ca_4Cu_3V_7O_{28}$*[92]
$Bi_2Pb_2V_2O_{10}$[93]	$Te_2V_2O_9$[94]	*$Rb_{0.5}Ca_{4.75}Ba_3Cu_3V_7O_{28}$*[95]
		$SrCo_2V_2O_8$[96]
$Pb_3V_2O_8$[97]	*ThV_2O_7*[98]	
$Zn_4V_2O_9$[99]	*$KCd_4V_3O_{12}$*[100]	$BaVO_{2.5}$[101]
$Sr_2V_2O_7$[102]	*$Na_3LaV_2O_8$*[103]	$Bi_{8.1}V_{0.9}O_{14}$[104]
$Sr_{1.58}Ca_{0.42}V_2O_7$[105]	*$Cu_2V_2O_7$*[106]	
$BiCa_4V_3O_{13}$[107]	*$NaVO_3$*[108]	
	Li_3VO_4[109]	
$As_2V_4O_{13}$[110]	*LiV_2O_5*[111]	
	$SrSi_2VO_7$[112]	
$CuVO_3$[113]	*$Na_{0.33}Cd_{1.33}VO_4$*[114]	
	$Na_3NdV_2O_8$[115]	
	NaV_2O_5[116]	
	$Cu_{0.82}V_4O_{11}$[117]	
	$Cu_{0.85}V_2O_5$[118]	
	$MgVO_3$[109]	
	Niobium	
$GaNbO_4$[119]	$Sr_5Nb_5O_{16}$[120]	$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$[121]
$LaNb_7O_{19}$[122]	$Sr_2Nb_2O_7$[123]	$Li_{4.07}K_{5.7}Nb_{10.2}O_{30}$[124]
$LaNbO_4$[125]	$Sr_2Nb_{0.24}Ta_{1.76}O_7$[126]	$Ba_6CoNb_9O_{30}$[127]
$SmNbO_4$[125]	$Zr_6Nb_2O_{17}$[128]	$Ba_6FeNb_9O_{30}$[129]
$HoNbO_4$[125]	$SbNbO_4$[130]	$K_{0.8}Ba_{5.2}Nb_{7.6}U_{2.4}O_{30}$[131]
$YbNbO_4$[125]	$Cs_2Nb_4O_{11}$[132]	$Mn_2Zn_2Nb_2O_9$[133]
UNb_6O_{16}[134]	$KCuNb_3O_9$[135]	$KNbO_3$[136]
$SmNbO_4$[125]	$K_4Nb_6O_{17}$[137]	$NaNbO_3$[138]
$HoNbO_4$[125]	$Ca_2Nb_2O_7$[139]	$LiNbO_3$[27]
	$MnFe_{.01}Sn_{.47}Nb_{.33}Ta_{2.12}O_8$[140]	$BaNb_3O_6$[141]
	$Sr_2Nb_{0.24}Ta_{1.76}O_7$[142]	$Ba_{0.27}Sr_{0.75}Nb_2O_{5.78}$[121]
	$Rb_{0.298}Nb_{0.436}W_{0.564}O_3$[143]	$Li_{4.07}K_{5.7}Nb_{10.2}O_{30}$[124]
$Ba_6Si_4Nb_{14}O_{47}$[144]	$CsNaEuNb_5O_{15}$[145]	$Ba_6CoNb_9O_{30}$[127]
	Sr_2TmNbO_6[146]	$Ba_6FeNb_9O_{30}$[129]
$Cu_{0.5}Nb_{1.5}O_{3.7}$[147]	$Na_2Ba_4Nb_{10}O_{30}$[148]	$PbNb_2O_6$[143]
		Bi_3TiNbO_9[149]
	RbB_3NbO_6[150]	$Mn_2Zn_2Nb_2O_9$[133]
	TlB_2NbO_6[151]	$BaNb_3O_6$[141]
		$K_3B_2Nb_3O_{12}$[152]
	$Ni_4Nb_2O_9$[153]	
	$K_{3.8}Ge_3Nb_5O_{20.4}$[154]	*$Mn_3ZnNb_2O_9$*[155]

Table 2. (Continued)

category (polar crystal classes) (continued)		
A (1, 2, 3, 4, 6)	B (m, mm2)	C (3m, 4mm, 6mm)
	Niobium (continued)	
	$RbSiNbO_5$[156]	$K_2Si_4Nb_2O_{14}$[157]
	$Pb_{2.8}Nb_2O_{7.8}$[158]	
		$Pb_{17}Nb_{17}O_{59.5}$[159]
		$Pb_{2.31}Nb_2O_{7.31}$[159]
		$Pb_{2.44}Nb_2O_{7.44}$[159]
	Tantalum	
$Al_{0.33}Ta_{15}W_{0.66}O_{40}$[160]	$KCuTa_3O_9$[161]	$Cu_{1.33}Zn_{2.667}AlTaO_8$[162]
	$Ba_4FeTa_{10}O_{30}$[163]	$LiTaO_3$[538]
	$Ba_4MgTa_{10}O_{30}$[164]	
	$Ba_4NiTa_{10}O_{30}$[164]	
	$Ta_{22}W_4O_{67}$[165]	
	$Mo_{4.55}Ta_{0.35}O_{14}$[166]	
	$Ca_2La_2TaO_6$[167]	
	$Sr_2Ta_2O_7$[168]	
	$SrBi_2Ta_2O_9$[169]	
	$Ba_{0.1}Sr_{0.9}Bi_2Ta_2O_9$[170]	
	$KGeTaO_5$[171]	
	Molybdenum	
UMo_2O_8[172]	$LaMo_{7.7}O_{14}$[173]	$Na_2In_2Mo_5O_{16}$[174]
	$Sb_2Mo_{10}O_{31}$[175]	
$KMgInMo_3O_{12}$[176]	$TeMo_5O_{16}$[177]	$Fe_2Mo_3O_8$[178]
$Ag_{1.5}In_{1.5}Mo_3O_{12}$[179]	Bi_2MoO_6[180]	$Li_2ZrMo_3O_{12}$[181]
		$Cs_5BiMo_4O_{16}$[182]
$Zn_2Mo_3O_8$[183]		
$Na_{0.9}Mo_6O_{17}$[184]		
	$Cu_6La_4Mo_9O_{36}$[185]	$LiMo_8O_{10}$[186]
	$Fe_2Mo_3O_{12}$[187]	$ZnMo_8O_{10}$[188]
	$K_5InMo_4O_{16}$[189]	$LiSeMo_3O_8$[190]
	$Tb_2Mo_3O_{12}$[191]	$LiYMo_3O_8$[190]
	$RbLiMoO_4$[192]	
	$Gd_2Mo_3O_{12}$[193]	
	$Cu_3Mo_2O_9$[194]	
	$LiAsMoO_6$[195]	
	$NdMo_8O_{14}$[196]	
	Tungsten	
Ba_3WO_6[197]	$Na_2W_2O_7$[198]	$Rb_{0.28}Ga_{0.2}W_{0.8}O_3$[202]
$K_{0.26}WO_3$[423]		
$CuYW_2O_8$[200]	$Ag_8W_4O_{16}$[201]	
Cu_2WO_4[203]	$Cs_6W_{11}O_{36}$[204]	
$CuBiW_2O_8$[205]	Bi_2WO_6[206]	
Eu_3BWO_9[207]		
$CuDyW_2O_8$[207]	Sr_2CaWO_6[208]	
$CuErW_2O_8$[207]		
$LiFeW_2O_8$[209]		
$Nb_{16}W_5O_{55}$[210]		
$Nb_{12}WO_{33}$[210]		
	Rhenium	
La_3ReO_8[211]		$PbRe_2O_8$[212]
	Iron	
$Ca_4Fe_9O_{17}$[213]	$GaFeO_3$[214]	$BaNd_2Fe_4O_{15}$[215]
$CaFe_5O_{8.33}$[216]	$Ca_2Fe_{1.4}Al_{0.6}O_5$[217]	$Ba_5SrLa_2Fe_4O_{15}$[215]
	$Ca_2Fe_{1.28}Al_{0.72}O_5$[217]	$Ba_5SrNd_2Fe_4O_{15}$[215]
	Ca_2FeAlO_5[218]	$Ba_{4.5}Ca_{1.5}Nd_2Fe_4O_{15}$[219]
	$Sr_2Fe_2O_5$[220]	$Fe_{2.5}V_{7.5}O_{16}$[221]
		$Li_{4.66}Fe_4Sb_2Sn_{1.32}O_{16}$[222]
	$Sr_4Fe_6O_{13}$[223]	$Li_2Fe_3SbO_8$[224]
	$YFeO_3$[225]	$Ba_{4.975}Ca_{1.025}La_2Fe_4O_{15}$[226]
		$Ba_{4.5}Ca_{1.5}La_2Fe_4O_{15}$[227]
		$Ba_5CaEu_2Fe_4O_{15}$[227]
		$BaCaSm_2Fe_4O_{15}$[219]
		$BiFeO_3$[228]
		$YBaCuFeO_5$[229]
	Cobalt	
Na_4CoO_3[230]	$Co_2Mn_3O_8$[231]	$Ba_6La_2Co_4O_{15}$[232]
		$Ba_5CaNd_2Co_4O_{15}$[227]
	$Sr_8Co_4Bi_8O_{25}$[233]	
		$Na_{0.6}CoO_2$[234]
	Boron	
$Sm_{14}Ge_2B_6O_{34}$[235]	SrB_4O_7[236]	$BaHoB_3O_9$[237]
$Nd_{14}Ge_2B_6O_{34}$[235]	EuB_4O_7[238]	$Li_2B_4O_7$[239]
BiB_3O_6[240]	$Al_{19.2}Cr_{0.8}B_4O_{36}$[241]	$Ba_3HoB_3O_9$[242]

Table 2. (Continued)

category (polar crystal classes) (continued)		
A (1, 2, 3, 4, 6)	B (m, mm2)	C (3m, 4mm, 6mm)
	Boron (continued)	
$CeBSiO_5$[243]	Al_5BO_9[244]	$Ba_3TmB_3O_9$[242]
$LaBGeO_5$[245]	$CaAlBO_4$[246]	$Ba_3YbB_3O_9$[242]
$NaBSiO_4$[247]	$Al_{20}B_4O_{36}$[248]	$Ba_3LuB_3O_9$[242]
		BaB_2O_4[539]
$LaBSiO_5$[249]	$Zn_3B_2O_6$[250]	
	$CuTmB_5O_{10}$[251]	
$CaB_2U_2O_{10}$[252]	$Na_2Zn_2MnB_{4.86}O_{11}$[253]	
	LiB_3O_5[254]	
CsB_9O_{14}[255]	$CuLuB_5O_{10}$[251]	
K_2LiBO_3[256]		
	$Ca_2Sm_2B_6O_{20}$[257]	
	$Ca_4GdB_3O_{10}$[258]	
	$Ca_4TbB_3O_{10}$[258]	
	$Ca_4LuB_3O_{10}$[258]	
	$Er_2S_3B_4O_{12}$[259]	
	$Li_2B_6O_{10}$[260]	
	$Nd_2Sr_3B_4O_{12}$[261]	
	$La_2Sr_3B_4O_{12}$[262]	
	$Ca_4SmB_3O_{10}$[263]	
	Aluminum	
$Ba_3Fe_2Ga_2Al_2O_{12}$[264]	$Na_{17}Al_5O_{16}$[265]	$Ca_{0.95}Mg_{0.9}Al_{10.1}O_{17}$[266]
$BaAl_2O_4$[267]	$Ca_8Al_{12}W_2O_{32}$[268]	$Cd_{0.971}Mg_{0.942}Al_{10.06}O_{17}$[266]
$BaFe_{1.5}Al_{0.5}O_4$[269]	$Ca_5Al_8O_{14}$[270]	$Zn_{0.865}Mg_{0.730}Al_{10.27}O_{17}$[266]
$Sr_7Al_{12}O_{25}$[271]	$CuInAlO_4$[272]	
$SrAl_2O_4$[273]		
Ba_2NdAlO_5[274]		
$BeMg_3Al_8O_{16}$[275]		
$Ba_6La_2Al_{1.5}Fe_{2.5}O_{15}$[276]		
$AlPb_2O_4$[277]		
$Li_2Cr_2AlSbO_8$[224]		
$Li_2Cr_2FeSbO_8$[224]		
$Li_2CrAl_2SbO_8$[224]		
	Gallium	
$BaGa_2O_4$[278]	$LaSrGaCuO_5$[279]	
Ga_2PbO_4[277]	$Nd_{0.83}Sr_{0.83}GaCuO_5$[280]	
	$Ca_5Ga_6O_{14}$[281]	
$YGaO_3$[282]	$NaGaO_2$[283]	
	$Ca_3Ga_4O_9$[284]	
	$In_{0.667}Ga_{0.667}Fe_{0.667}O_3$[285]	
	$NdGaO_3$[286]	
	Indium	
$CuIn_2O_5$[287,288]	$Ba_4In_6O_{13}$[289]	$YInO_3$[290]
		$Sr_2In_2O_5$[291]
	Silicon	
$KNd_9Si_6O_{26}$[292]	$BaTiSi_3O_9$[293]	$Ba_2TiSi_2O_8$[294]
$BaSr_2Mn_2Si_4O_{14}$[295]	$KSiSbO_5$[296]	Ca_3SiO_5[297]
$La_{7.58}Si_6O_{26}$[298]	$AgSiSbO_5$[299,300]	Li_8SiO_6[301]
$La_{7.87}Si_6O_{26}$[298]	$PbZnSiO_4$[302]	
$La_{9.31}Si_6O_{26}$[298]	Bi_2SiO_5[303]	
Pb_2SiO_4[304]		
	Germanium	
$La_2Ge_2O_7$[305]	$Li_2Ge_2O_5$[306]	$Ca_3GeO_{6.45}$[307]
$Li_4Ge_9O_{20}$[308]	Nd_4GeO_8[309]	
$Rb_2Ga_2Ge_3O_{10}$[310]	$RbGeSbO_5$[311]	
$Ca_3Ga_2Ge_4O_{14}$[312]	$TlGeSbO_5$[313]	
$BaZnGeO_4$[314]	$NaGeSbO_5$[299]	
Li_8GeO_6[301]	$KGeSbO_5$[315]	
$PbGe_4O_9$[316]	Bi_2GeO_5[317]	
Pb_3GeO_5[318]		
$Pb_5Ge_3O_{11}$[319]		
	Antimony	
$Ba_3NiSb_2O_9$[144]	$Tl_{10}Sb_2O_{10}$[320]	Sr_2MnSbO_6[321]
	$K_3Sb_5O_{14}$[322]	
	$Pb_2Sb_2O_7$[323]	
	Lead/Bismuth/Tellurium	
$CuBi_2O_4$[324]	$Sr_2BiPbMnO_6$[325]	Bi_2PdO_4[326]
$CuSr_{10}Bi_{10}O_{29}$[327]		
Cs_4PbO_3[523]	$Ca_4Bi_6O_{13}$[328]	
$PbTeO_3$[329]	Bi_2TeO_5[330]	
Ag_3BiO_3[524]	Cs_2PbO_3[331]	
	Rb_2PbO_3[332]	
	$Pb_3Mn_7O_{15}$[333]	
	Hg_2TeO_3[525]	

Table 2. (Continued)

category (polar crystal classes)			
A (1, 2, 3, 4, 6)	B (m, mm2)	C (3m, 4mm, 6mm)	
	Rare Earth Cation(s)		
$Ba_3Lu_4O_9$[334]	$Sr_3La_4O_9$[335]	$LiUO_3$[336]	
$Ba_3Yb_4O_9$[337]	$Sr_3Nd_4O_9$[338]	$YbMnO_3$[339]	
$Ba_3Tm_4O_9$[340]	$Ca_{0.33}MgY_{2.67}O_6$[341]	$La_8Ru_4O_{21}$[342]	
$Ba_3Ho_4O_9$[340]	$Sr_3Pr_4O_9$[343]		
$Ba_3Dy_4O_9$[344]	$Sr_3La_2Sm_2O_9$[343]		
$Ba_3Er_4O_9$[344]	$Cu_2Y_2O_5$[345]		
$Ba_3Y_2Yb_2O_9$[344]	$Ba_3ErMn_2O_9$[346]		
$Sr_2CaYb_{10}O_{18}$[347]	$Cu_2Ho_2O_5$[348]		
$SrCa_2Lu_{10}O_{18}$[347]	Cs_2PrO_3[349]		
$BaCa_2Er_{10}O_{18}$[350]	$LaYbO_3$[351]		
$BaCa_2Yb_{10}O_{18}$[350]	$Be_4Pr_9O_{20}$[352]		
$BaCa_2Tm_{10}O_{18}$[350]	$Cu_2Lu_2O_5$[353]		
$BaCa_2Ho_5Y_5O_{18}$[41]			
$BaCa_2La_5Y_5O_{18}$[41]			
	Miscellaneous		
Na_2BeO_2[354]	*Na_2NiO_2*[355]	K_6MgO_4[356]	
$Ca_{3.5}Cu_{0.5}PtO_6$[357]		$K_2Zn_6O_7$[358]	
	$AuSe_2O_7$[359]		
	$CsCuO$[360]	$BaNiO_3$[361]	
	$Ca_{1.803}Sr_{0.197}CuO_3$[362]		

category (nonpolar crystal classes)			
D (422, 222, 622, 32, 23)	E (−42m, −4)	F (−6, −43m, −62m)	G (432)
	Titanium		
$Fe_{1.58}Mn_{0.09}Ti_{3.22}O_9$[363]		Dy_2TiO_5[364]	
$Bi_{12}TiO_{20}$[365]		*$BaTiSi_3O_9$*[293]	
	Vanadium		
$Cu_4V_{2.15}O_{9.38}$[367]	VNb_6O_{16}[368]	*$Ca_5Mg_3ZnV_6O_{24}$*[369]	
$Cr_{0.1}V_{1.9}O_9$[370]			
BaV_2O_6[371]	*$Ba_{0.5}Sr_{0.5}Cu_2V_2O_8$*[372]	NaV_6O_{11}[373]	
	$NaMg_4V_3O_{12}$[374]		
$K_5V_3O_{10}$[375]	*$BaCu_2V_2O_8$*[376]		
$SrTlVO_4$[377]			
$Sr_{1.5}Cd_{0.5}V_2O_7$[105]	*VTa_9O_{25}*[378]		
PbV_2O_6[379]	*$VNb_9O_{24.9}$*[378]		
$Bi_{12.03}V_{0.89}O_{20}$[380]			
$Bi_{25}VO_{40}$[381]			
$LiVTeO_5$[382]			
	Niobium		
$Te_3Nb_2O_{11}$[383]	$SrCa_{0.33}Nb_{0.66}O_3$[384]	*$K_6Ge_4Nb_6O_{26}$*[385]	
$BaNb_2O_6$[386]	$FeNb_2O_6$[387]	*$Ba_3Si_4Nb_6O_{26}$*[388]	
$Li_5La_3Nb_2O_{12}$[389]		*$Ba_3Ti_{1.2}Si_4Nb_{4.8}O_{25.4}$*[390]	
Li_3NbO_4[391]	*$Nb_{14}W_3O_{44}$*[392]		
$La_3Ga_{5.5}Nb_{0.5}O_{14}$[393]			
	Tantalum		
		$Cu_5Ta_{11}O_{30}$[395]	
$Na_{.06}Ca_{.94}Nb_{.13}Ta_{3.86}O_{10.97}$[396]		$LaTa_7O_{19}$[397]	
		$Ba_3SrRu_{1.2}Ta_{0.8}O_9$[394]	
		$Ba_3SrRu_{0.6}Ta_{1.4}O_9$[394]	
		$Ba_3Si_4Ta_6O_{26}$[388]	
		$Ba_3Si_4Ta_6O_{23}$[385]	
	Molybdenum		
U_2MoO_8[398]	*$AgYbMo_2O_8$*[399]	*$CsLiMoO_4$*[400]	
	KMo_4O_6[401]	*$Cs_6Zn_5Mo_8O_{32}$*[402]	
$Cu_2Zn_{1.75}Mo_3O_{12}$[403]	*$AgSmMo_2O_8$*[399]		
$K_4ZnMo_3O_{12}$[404]	*La_2MoO_6*[405]	*$ThMo_2O_8$*[406]	
$Cu_{3.85}Mo_3O_{12}$[407]			
	Tungsten		
$Nb_8W_9O_{47}$[408]	$Rb_{21.79}W_{32.74}O_{68}$[409]	*$Li_{11}FeW_7O_{28}$*[410]	
$Ba_3Fe_2WO_9$[411]	$Sn_{0.25}WO_3$[412]		
$Cs_{0.07}WO_3$[541]	$Nd_{1.2}Lu_{0.8}WO_6$[413]	$CsLiWO_4$[414]	
$Ge_{0.4}WO_3$[415]	$Sn_{0.11}WO_3$[412]		
Y_2WO_6[413,416]	$Rb_{22}W_{32}O_{107}$[417]		
Er_2WO_6[418]	$Na_{0.33}WO_3$[419]		
Gd_2WO_6[418]			
Nd_2WO_6[420]			
$Ge_{0.24}WO_3$[421]			
$Ca_4Al_6WO_{16}$[268]			
$SnWO_4$[422]			
$K_{0.26}WO_3$[199]			

Table 2. (Continued)

category (nonpolar crystal classes) (continued)			
D (422, 222, 622, 32, 23)	E (−42m, −4)	F (−6, −43m, −62m)	G (432)
		Iron	
$BaFe_2O_4$[424]			$Li_{0.75}Fe_{4.75}Zn_{0.5}O_8$[425]
$Ca_2Fe_{15.5}O_{25}$[426]			
$Ca_2Fe_{15.6}O_2$[426]			
$Bi_{12.5}Fe_{0.5}O_{19.5}$[427]			
$Sr_{15}Fe_{10}Bi_{10}O_{46}$[428]			
$Nd_{0.5}Fe_3B_4Bi_{0.5}O_{12}$[429]			
		Rhenium/Ruthenium/Osmium/Iridium	
$La_4Re_6O_{19}$[430]		Ca_2IrO_4[431]	$LiRhO_2$[432]
$La_4Ru_6O_{19}$[433]		$Ba_3CaRu_2O_9$[394]	
$La_4Os_6O_{19}$[434]			
$Nd_4Os_6O_{19}$[435]			
		Boron	
$Ce_{0.5}La_{0.5}BSiO_5$[436]	$LiBSiO_4$[437]	$Ca_3Er_3Ge_2BO_{13}$[438]	
$BaZn_2B_2O_6$[439,440]	$LiBGeO_4$[437]	$KBSi_2O_6$[441]	
	$CsLiB_6O_{10}$[442]	$CsBe_4B_{12}Al_4O_{28}$[443]	
Ag_3BO_3[444]	CuB_2O_4[445]	$Zn_4B_6O_{13}$[446]	
$NdAl_3B_4O_{12}$[447]	PdB_2O_4[448]	$K_{0.981}B_{1.041}Si_{1.959}O_6$[449]	
$YAl_3B_4O_{12}$[450]		$NdAl_{2.07}B_4O_{10.6}$[451]	
$GdAl_3B_4O_{12}$[452,453]		$LiCdBO_3$[454]	
$Gd_{0.97}Eu_{0.03}Al_3B_4O_{12}$[453]	$Sr_{0.74}Ba_{0.27}B_2Cu_2O_6$[455]	$Be_2Sr_2B_2O_7$[456]	
$NdGa_3B_4O_{12}$[457]	$Sr_{0.66}Ca_{0.34}B_2Cu_2O_6$[455]		
$Y_{0.5}Eu_{0.5}Al_3B_4O_{12}$[441]			
		Cobalt	
KCo_2O_4[458]	$Co_3As_2O_8$[459]		
	$Ca_2CoSi_2O_7$[460]		
		Copper/Silver/Zinc	
K_3AgO_2[461]	KAgO[462]	$Ba_3In_2Zn_5O_{11}$[366]	
K_3CuO_2[463]	LiCuO[464]		
	NaAgO[465]		
	RbAgO[465]		
	CsAgO[465]		
	NaCuO[465]		
	RbCuO[465]		
	$Ba_2YCu_3O_{6.8}$[466]		
		Aluminum	
$LiAlO_2$[467]	$CaAl_{0.67}LaGa_{2.33}O_7$[468]	$Ca_{12}Al_{0.4}O_{33}$[469]	
$Na_{0.625}Ca_{8.68}Al_6O_{18}$[470]	$Sr_2Al_2SiO_7$[471]	$Ca_4Al_6O_{13}$[472]	
$Mg_{0.6}Al_{1.2}Si_{1.8}O_6$[473]	$CaAl_3LaO_7$[468]	$MgAl_2O_4$[474]	
	$CaYAl_{2.91}Cr_{0.06}B_{0.03}O_{6.07}$[475]	$Cu_2Al_4O_7$[476]	
$Al_{5.03}Ge_{0.97}Nd_{0.06}Pb_{0.15}O_{9.71}$[477]		$Ba_{1.9}Al_{21.33}Pb_{0.37}O_{35.47}$[478]	
$Al_5Ge_{0.972}Pb_{0.2}O_{9.71}$[477]		$Ba_6Rh_{2.33}Yb_2Al_{1.67}O_{15}$[479]	
		$Ba_{5.5}Ca_{0.5}Rh_2Y_2Al_2O_{15}$[479]	
		$Ba_6Rh_4Al_2O_{15}$[479]	
		$Na_{1.3}Nd_{0.9}Al_{23}O_{36.5}$[480]	
		$Ba_6Al_2Ho_2Rh_2O_{15}$[481]	
		Gallium	
Li_5GaO_4[482]	Ca_2GaGeO_7[483]		
$La_3Ga_5SiO_{14}$[484]	$Ca_2Ga_2SiO_7$[485]		
$La_3Ga_5GeO_{14}$[486]			
$Sr_3Ga_2Ge_4O_{14}$[487]			
$Bi_{12}GaO_{20}$[488]			
$Bi_{25}GaO_{39}$[489]			
		Indium	
		$Na_{24}In_5O_{15}$[490]	
		Silicon	
$Bi_{12}Si_{0.87}O_{20}$[491]			
		Germanium	
$Cs_4Ge_4Sb_4O_{20}$[492]	$Fe_{10.65}Ge_{5.33}O_{24}$[493]	$Bi_4Ge_3O_{12}$[494]	
$BaGe_4O_9$[495]	$Cd_2Ge_7O_{16}$[526]		
$Bi_{12}GeO_{20}$[496]	$Tb_{55}Ge_{12}O_{107}$[235]		
	$CsGeSbO_5$[497]		
		Antimony	
$MnSb_2O_6$[498]		$Gd_3Sb_5O_{12}$[499,500]	
		$Nd_3Sb_5O_{12}$[500]	
		$Sm_3Sb_5O_{12}$[500]	
		$Yb_3Sb_5O_{12}$[500,501]	

Table 2. (Continued)

category (nonpolar crystal classes) (continued)			
D (422, 222, 622, 32, 23)	E (−42m, −4)	F (−6, −43m, −62m)	G (432)
	Lead/Bismuth/Tellurium		
$\underline{Bi_{12}Zn_3O_{20}}$[502]	$\underline{Pb_2MnO_4}$[503]	$\underline{Na_6PbO_4}$[504]	
$\underline{Bi_{12}Cd_3O_{20}}$[502]		$\underline{Na_3BiO_3}$[505]	
$\underline{Bi_{12}MnO_{20}}$[506]		$\underline{Sr_{4.79}Cu_{0.66}Pb_{3.21}O_{11.12}}$[507]	
$\underline{Bi_{12.67}Zn_{0.33}O_{19.33}}$[427]			
$\underline{Bi_{25.33}Zn_{0.667}O_{40}}$[421]			
$\underline{K_2Pb_2O_3}$[508]			
$\underline{La_2TeO_6}$[509]			
In_2TeO_6[510]			
Yb_2TeO_6[511]			
	Rare Earth Cation(s)		
NiU_2O_6[512]	$BaPtEu_2O_5$[513]		
CoU_2O_6[512]			
	Miscellaneous		
$BaZnO_2$[514]		$Ca_{12}Be_{17}O_{29}$[515]	
$K_9Ni_2O_7$[516]			
		$Ba_3Pt_{2.07}O_{7.11}$[517]	
Rb_2SnO_2[518]		$SrBe_3O_4$[519]	
Na_2HgO_2[520]		$Li_{0.64}Pt_3O_4$[435]	
K_2HgO_2[520]			

[a] Underlined compounds contain second-order Jahn−Teller distorted cation(s). Italicized compounds contain tetrahedrally coordinated cation(s). Underlined and italicized compounds have both types of cation(s). Compounds that are not underlined or italicized have neither type of cation.

chosen in the mixture, the polarity remains unchanged. However, this is not the case with respect to chirality. If one enantiomer, α, is selected no reorientation or transformation will generate the β isomer. One question that seems relevant to materials chemistry is the structure−property relationships between chirality and polarity. Does the chirality influence the polarity? For ferroelectrics, polar materials whose dipole moment may be reoriented in an applied electric field, that are also chiral, does the enantiomorph influence the reorientation of the dipole? This seems unlikely, given that for enantiomorphic materials physical properties are identical, but to our knowledge there has been no report of ferroelectric measurements on a chiral-polar material, to confirm this assumption.

The two remaining categories within NCS polar materials are categories B, crystal classes m and mm2, and C, crystal classes 3m, 4mm, and 6mm. Materials in these categories are both pyroelectric and piezoelectric, with compounds in category B also possessing optical activity. It should be emphasized that the materials in these categories are *not* enantiomorphic. Although it is sometimes reported in the literature that for materials in these categories the enantiomorph was refined, what is actually being done is a coordinate transformation such that the polar direction is consistent with convention. Thus the two structures of opposite polarity are not different in the sense of handedness, but rather only with respect to their orientation on the diffractometer.

Pyroelectrics, or polar materials, have received a great deal of attention owing to their important technological properties.[11,12] The commonly accepted distinction between ferroelectrics and pyroelectrics is in ferroelectrics the electric dipole moment can be reoriented by an external electric field, whereas pyroelectrics include materials where this reorientation does not occur. Thus ferroelectricity may be considered a subset of pyroelectricity. One of the premier NLO materials, $KTiOPO_4$,[13] is generally termed as a ferroelectric, although owing to the high ionic conductivity no dielectric hysteresis has ever been measured.[14] With ferroelectric materials the phase transition to a polar state is accompanied by a movement of atoms, usually metal cations, from their nonpolar symmetry positions. Abrahams et al.[15] has defined this movement of atoms along the polar direction as Δz. By studying a variety of ferroelectric materials, they were able to determine a fundamental relationship between Δz and the Curie temperature, T_c. This relationship, T_c (K) $= [(2.00 \pm 0.09) \times 10^4](\Delta z)^2$, was shown to give good agreement for a variety of ferroelectric materials.

In terms of symmetry, only compounds in 10 crystal classes can show pyroelectric behavior, all of which can also have SHG behavior (see Figure 1). The NLO properties of oxygen-octahedra ferroelectrics have been studied extensively owing to their favorable materials properties, e.g., transparent in the visible, phase-matchability, and chemical inertness. The relationship between dipole moments and SHG behavior has been discussed by a number of groups,[16−21] and d_{ijk} values (i.e., second-order NLO susceptibilities) have been calculated based on the intra-octahedral distortions, since the NLO susceptibility tensor, d_{ijk}, is extremely sensitive to asymmetric chemical bonding. One of the most successful methods for describing the relationships between intraoctahedral distortions and NLO behavior is the geometric analysis of Jeggo and Boyd.[18] These authors demonstrated that the full tensoral character of d_{ijk} can be accounted for in terms of individual bond polarizabilities β. In their model, the NLO polarizability of an individual bond is assumed to have C_∞ symmetry. This assumption generates two independent tensor coefficients, $\beta^{||}$ and $\beta^{\perp}$, a parallel and perpendicular bond component. The piezoelectric matrix for C_∞, and all other point groups, has been given by Nye.[22] These matrixes immediately reveal which tensor elements are nonzero. By use of the matrix for C_∞ and the geometrical model, the NLO bond polarizability is reduced to a parallel $\beta^{||} = \beta_{33}$ and perpendicular $\beta^{\perp} = \beta_{31} = \beta_{15}$.

(A complete explanation of the subscript notation is beyond the scope of this article. The reader is referred to Nye[22] for a full derivation.) Relating β, the NLO bond polarizability, to d_{ijk}, the NLO optical coefficients, is accomplished through the use of direction cosines on the crystallographically determined bond lengths. Thus for every nonzero d_{ijk}, the ith bond has direction cosines $l_i m_i n_i$ (from the metal to the oxygen). For a particular d_{ijk}, all of the pertinent bonds in the unit cell are summed and divided by the unit cell volume.[18] The initial work of Jeggo and Boyd assumed a highly anisotropic NLO polarizability, $\beta^{\parallel} \gg \beta^{\perp}$. Thus $\beta^{\perp}$ was ignored in their calculations. Even with this approximation, they were able to demonstrate excellent agreement between theory and experiment for the d_{ijk} values of $LiNbO_3$[23] and $Ba_2NaNb_5O_{15}$.[148] The geometrical model was extended by Bergman and Crane,[24] who treated the transition metal−oxygen bond as a three-dimensional entity, and thus determined d_{ijk} by using both $\beta^{\parallel}$ and $\beta^{\perp}$. The geometrical model is analogous to bond valence arguments[25] in that both models are nonquantum mechanical and are dependent on the crystallographically determined metal−oxygen bond length. Similar to bond valence parameters, bond polarizability values, $\beta^{\parallel}$ and $\beta^{\perp}$, have been calculated for a variety of metal−oxygen bonds.[24]

A second but more quantum mechanically derived model has been developed by Levine.[26] His bond charge model describes the bond polarizability with respect to a bond charge residing in an anharmonic potential well. The size and electronegativity differences between atoms result in the anharmonicity. The nonlinearity observed in niobates and tantalates is explained through the unequal contributions of the short and long transition metal−oxygen bonds to the total NLO susceptibility. In Levine's model β is dependent on the bond length, which makes the model fully compatible with the geometrical model of Jeggo and Boyd. Similar to the geometrical model, but implicit in Levine's model, is the assumption that the perpendicular bond polarizability is negligible, e.g., $\beta^{\parallel} \gg \beta^{\perp}$.

Irrespective of model, a common factor is the inclusion of the crystallographically determined transition metal−oxygen bond lengths in the theoretical calculation of d_{ijk}. The experimental determination of d_{ijk} is done by utilizing the Maker fringe technique and SHG active crystals.[27] Necessary requirements for Maker fringe measurements are large crystals, >5 mm, that have been cut and polished to expose a specific face. Because of the above requirements, d_{ijk} values have been experimentally determined for only a few of the materials that are SHG active. It remains an ongoing challenge for chemists and material scientists not only to synthesize new SHG materials but also to grow large enough crystals for Maker fringe measurements.

Noncentrosymmetric−Nonpolar Crystal Classes

Categories D, E, F, and G comprise the NCS nonpolar crystal classes. Except for category F, which include crystal classes −6, −43m, and −62m that contain materials that are only piezoelectric; the remaining categories have compounds that possess a combination of NCS symmetry properties. Compounds in category D are enantiomorphic, optically active, and piezoelectric, whereas materials in category E are optically active and piezoelectric, and complexes in category G are enantiomorphic and optically active.

Before continuing on with the categories, it is instructive to discuss a term often associated with *all* NCS materials, especially enantiomorphic compounds, namely, "absolute". It was suggested by Jones[28] and expanded by Glazer and Stadnicka[29] that absolute should be extended to instances where an external macroscopic physical property has been related to the structure. The latter two authors argue that "the use of absolute [should] connect the crystal structure to the outside world, so that once the connection has been made, it is no longer necessary to redo the X-ray measurement when referring to the way in which the structure correlates with the property in question, i.e., the structure determination is absolute in the true sense of the word."[28] It is this definition of absolute, linking crystallography with a physical property, that should be used when the absolute structure of a material is discussed.

Returning to the categories listed in Table 1 reveals that materials in categories D and G are enantiomorphic as well as optically active. Compounds in category D are also piezoelectric, but that shall not concern us at present. The connection between enantiomorphism and optical activity is conceptually the most straightforward and has been discussed at length.[30] The determination of the structure for an enantiomorphic crystal fixes the structural chirality—the crystal is of one enantiomer or the other. Thus irrespective of the crystal's orientation on the diffractometer or the method used in obtaining the data, no transformation or reorientation will produce the other isomer. Once the structure and chirality have been determined, the observation and measurement of the optical rotation fixes the structure with regards to the sign of the rotation. That is, the chiral structure has been irrevocably linked with the sign of the optical rotation.

The final two categories, E and F, contain materials that are piezoelectric and, for compounds in category E, optically active. As previously stated piezoelectricity and SHG behavior have the same symmetry requirements and are described by a third-rank tensor, d_{ijk}.[22] We have already discussed that with SHG behavior the d_{ijk} values can be computed as well as experimentally determined. But what about d_{ijk} values concerning piezoelectric behavior? If an electric field is applied to a piezoelectric crystal, strains develop in the crystal. This phenomenon is the well-known converse piezoelectric effect. The strains of the crystal are attributable to the microscopic deformations in the unit cell. It has been shown[31] that in a piezoelectric crystal the Bragg angles of a given reflection will be changed in the presence of an electric field. Thus by collecting the crystal data in the presence of an electric field, one can determine the piezoelectric tensor elements. In practice, however, the measurement is nontrivial. A technique has been developed to measure very small changes in X-ray diffracted intensities upon application of an electric field.[32] They demonstrated this technique on the organic NLO material 2-methyl-4-nitroanaline and were able to determine the magnitude and sign of the

piezoelectric tensors.[32] This method should be extendable to oxides and should provide another manner in which a NCS symmetry property can be measured.

Cation Coordination Environments

The NCS oxides listed in Table 2 are also described by the coordination environment of the transition or main group metal. The table is organized as follows: Underlined compounds contain second-order Jahn−Teller distorted cations. Italicized compounds contain tetrahedrally coordinated cations. Both underlined and italicized materials have second-order Jahn−Teller distorted and tetrahedrally coordinated cations. Finally, compounds that are not underlined or italicized have neither type of cation.

The first-order Jahn−Teller effect (FOJT)[33] deals with molecular distortions attributable to degenerate electronic ground states, whereas the second-order Jahn−Teller effect (SOJT)[34] is concerned with structural changes owing to a nondegenerate ground-state interacting with a low-lying excited state. An SOJT distortion occurs when the energy gap between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital is small and there is a symmetry allowed distortion permitting the mixing of the HOMO and LUMO states.[35−37] For example, if the HOMO and LUMO have *a* and *e* orbital symmetry, respectively, and the energy difference between the two orbitals is small, then the LUMO *e* will be split to *a* and *b* orbitals and the HOMO *a* will be stabilized by mixing with the LUMO *a*. Mathematically, the SOJT effect can be understood through the use of second-order perturbation and group theory. A full mathematical treatment is beyond the scope of this article and the reader is referred to the relevant papers.[527−530] Briefly, the wave function after the distortion can be described as

$$\psi = \psi_o + \Sigma_k[(Q<\psi_o|\partial u/\partial Q|\psi_k>)/(E_o - E_k)]\psi_k$$

We are interested in the $<\psi_o|\partial u/\partial Q|\psi_k>$ and the $(E_o - E_k)$ terms. With respect to the former term, the integral will only be nonzero if the symmetry of the excited state (LUMO) matches that of the ground state (HOMO). The latter term is the energy gap between the HOMO and LUMO. We will be discussing how the SOJT effect relates to NCS oxides. For octahedrally coordinated d^0 transition metals the mixing of the HOMO and LUMO is always symmetry allowed, with the energy between the orbitals correlating with the size and charge of the cation.[531] As Goodenough and Longo[532] discussed, a d^0 transition metal cation may distort tetragonally, along the C_4 axis, orthorhombically, along the C_2 axis, or rhombohedrally, along the C_3 axis (see Figure 2). Kunz and Brown[531] recently pointed out that SOJT distortions are not the only displacive presence in d^0 materials. By using bond valence arguments[25] they were able to demonstrate that bond network stresses (i.e., the asymmetry in the bond network, including contributors from second and third bonded neighbors), lattice stresses (i.e., stresses caused by the requirement of translational symmetry), and cation−cation repulsions can also be important. Based on their model, of the four effects, only the bond network and cation−cation repulsions can direct the distortion. The lattice stresses and the electronic distortion (SOJT) do not have directional preferences. They argue for a weak electronic distortion (e.g., Sc^{3+}); no structural distortion is observed, whereas for a moderate electronic distortion (e.g., Ti^{4+}, Nb^{5+}, and Ta^{5+}) the direction of the distortion is determined by the bond network asymmetry and (if present) cation−cation repulsions. They also suggest that for V^{5+}, Mo^{6+}, and W^{6+} where the electronic distortion is large, the bond network will support and direct the distortion.

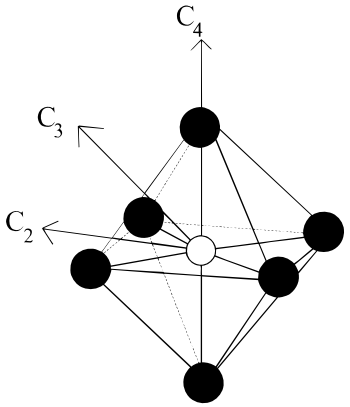

Figure 2. Possible intraoctahedral distortions for d^0 transition metal oxides.

The SOJT effect, the HOMO−LUMO interaction, can also be used to explain the distorted environments of metals with nonbonded electron pairs, Tl^+, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Se^{4+}, and Te^{4+}. An example using Te^{4+} should prove illustrative. Four-coordinate tellurium might be expected to have tetrahedral symmetry (T_d). However, in this geometry the s^2 electron pair would occupy a strongly antibonding a_1* orbital (HOMO). As such, a distortion occurs to square-pyramidal geometry (C_{4v}) which lowers the energy of the HOMO by mixing with the LUMO p-orbital, i.e., s−p mixing. Thus the HOMO is stabilized, and the lone pair becomes stereochemically active, thus resulting in the observed asymmetric coordination environment.

But how does a SOJT distortion manifest itself in the NCS oxides? An SOJT distortion is observed in 184 (47%) of the 388 NCS polar oxides, and in 70 (38%) of the 190 NCS nonpolar oxides. As previously stated, two families of cations are susceptible to an SOJT distortion, d^0 transition metals and cations with nonbonded electron pairs. Within the NCS polar group, 201 oxides contain d^0 transition metals, of which 154 (77%) have an SOJT distortion. In addition, an SOJT distortion is observed for all 43 of the polar oxides containing cations with nonbonded electron pairs. For the NCS nonpolar oxides, 71 materials contain d^0 transition metals, of which 45 (63%) have an SOJT distortion. Similar to the polar oxides, an SOJT distortion is observed for the 32 nonpolar materials containing cations with nonbonded electron pairs. It should be remembered that two factors are necessary for an SOJT distortion. There must be a symmetry allowed distortion permitting the HOMO and LUMO to interact, and the energy gap between the HOMO and LUMO must be small. From the above distribution of NCS oxides, it is clear that if an SOJT distortion occurs the material is more likely to be polar than nonpolar.

This observation may be understood by examining the symmetry changes that occur for both d^0 transition metals and cations with nonbonded electron pairs during an SOJT distortion. The undistorted symmetry for d^0 transition metal oxides is O_h, with t_{1u} (HOMO) and t_{2g} (LUMO) orbitals. It has been shown[533] that if the oxidation state of the transition metal is large, e.g., Ti^{4+}, Nb^{5+}, and Mo^{6+}, the gap between the HOMO and LUMO is reduced. The interaction between the t_{1u} and the t_{2g} results in vibrations of t_{1u} and t_{2u} symmetries. The t_{1u} vibration is a tetragonal displacement of the central metal atom along the C_4 axis of the octahedron, whereas the t_{2u} vibration changes the octahedral symmetry to trigonal prismatic, i.e., the cation distorts along the C_3 axis (see Figure 2). Thus an SOJT distortion on a d^0 transition metal with a high oxidation state changes the symmetry from centrosymmetric to NCS polar. An examination of the NCS oxides with d^0 transition metals supports this statement. For example, of the 69 NCS oxides with a SOJT distorted Nb^{5+}, 58 materials are polar, whereas only 11 are nonpolar. Similarly, for the 30 NCS oxides with a SOJT distorted Ti^{4+}, 25 are polar with only four compounds found in nonpolar crystal classes. A related situation occurs for the cations with nonbonded electron pairs, Tl^+, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Se^{4+}, and Te^{4+}. As stated earlier, the antibonding a_1* HOMO orbital is stabilized through interacting with the t_{1u} LUMO orbital. The resultant coordination environment varies depending on the size and charge of the metal cation; however, a square pyramidal geometry (C_{4v}) is not uncommon. With regards to the polar and nonpolar crystal classes, of the 75 oxides with nonbonded electron pairs 43 of the materials are polar, whereas 32 are nonpolar. The above observations concerning the SOJT effect on NCS oxides does not take into account packing forces, second- and third-bonded neighbors, or cation−cation repulsions. Nonetheless, it is clear that an SOJT distortion has a strong influence on whether a NCS compound is polar or nonpolar.

In addition to a SOJT distortion, NCS oxides often contain cations with tetrahedral coordination geometries. In oxides, tetrahedra are usually corner linked, rarely edge sharing, and never face sharing. This observation follows Pauling's third rule, that states the sharing of sides and, in particular, faces between coordination polyhedra reduces the stability of the structure.[534] Three possible structural arrangements for corner-sharing tetrahedra are shown in Figure 3. In the Figure 3a, the central atom is on a mirror plane parallel to (110); in Figure 3b the central atom is on a 2-fold axis, whereas in Figure 3c the linking atom is on an inversion center. The occupation of particular symmetry positions has been discussed in detail by Wilson,[535] who suggested that how often a space group is observed in nature depends on the extent to which its symmetry elements interfere with packing. In a given space group any unoccupied special position creates a space around itself in which another atom cannot reside owing to unfavorable interatomic interactions.[536] Around an inversion center the space is a spherical region of diameter R, for any rotation axis it is an infinite cylinder of diameter R, whereas for a mirror plane the space is an infinite sheet of thickness R. Vacant mirror planes create more forbidden space than vacant rotation axes,

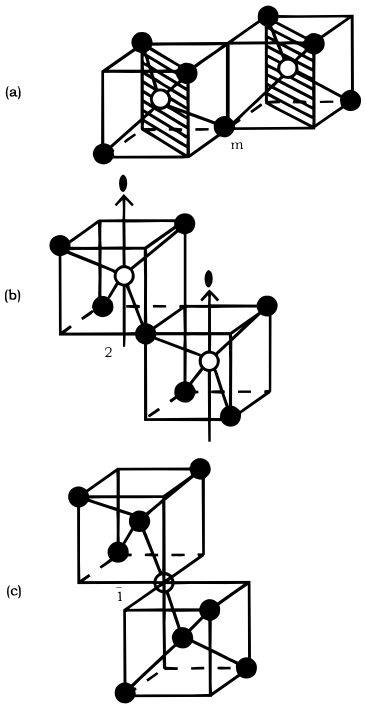

Figure 3. Three possible structural arrangements of corner-linked tetrahedra. The tetrahedrally coordinated atom is on (a) a mirror plane parallel to (110) or (b) a 2-fold special position. In (c) the bridging atom is on an inversion center.

which in turn have more forbidden space than vacant inversion centers. Based on Wilson's arguments, in a space group containing all three symmetry elements, placing an atom on a mirror plane should be more advantageous than on an inversion center. If a cell edge of "x" is assumed, the distance between the central atoms residing on a mirror plane is $x\sqrt{2}$, which is the same as when the atoms are related by a 2-fold (Figure 3b). The cation−cation distance is $x\sqrt{3}$ when the bridging atom is on an inversion center (Figure 3c). If the tetrahedra are symmetry related by a mirror plane or 2-fold, the cation−cation distance is 18% closer compared with an inversion center. For example, the Ge−Ge distance in the NCS nonpolar $Cd_2Ge_7O_{16}$[526] where the Ge^{4+} are on 2-folds is 3.171 Å, whereas in the centric $CdGe_2O_5$[537] the Ge^{4+} are on inversion centers and the Ge−Ge distance in 3.454 Å.

Conclusion

This review has compiled the NCS oxides and categorized the materials by symmetry-dependent property, crystal class, and cation coordination environment. One of the purposes of this review was to elucidate common features of NCS oxides. Based on our primary division, polar and nonpolar, and our discussion of coordination environments, a number of conclusions can be drawn from Table 2. Of the 578 NCS oxides, a majority, 388 (67%), of the materials are polar. The NCS polar oxides can be further divided into materials that have a SOJT distortion, 184 (47%), and compounds that have a tetrahedrally coordinated cation, 118 (30%). Oxides with both types of cations have been counted once and included in the former category. With regards to the NCS nonpolar materials, they comprise 190 (33%) of the 578. Similar to the NCS polar oxides, the 184

NCS nonpolar materials can be further divided with 70 (38%) having a SOJT distorted cation and 73 (40%) containing cations in tetrahedral coordination. A chart is given below that illustrates the divisions.

NCS, 576			
polar, 388 (67%)		nonpolar, 190 (33%)	
SOJT distorted	tetrahedral coord	SOJT distorted	tetrahedral coord
184 (47%)	118 (30%)	70 (38%)	73 (40%)

Within each group, polar and nonpolar, the percentage of materials with a SOJT distorted cation and a tetrahedrally coordinated cation are nearly equal and opposite. This suggests that if an oxide contains a cation susceptible to a SOJT distortion and is NCS, the material is more likely to be polar that nonpolar. An SOJT distortion on d^0 transition metals and cations with nonbonded electron pairs changes the site symmetry of the cations from centrosymmetric to NCS polar. This symmetry change often, but not always, manifests itself through the material crystallizing in a polar space group.

This review has also discussed the host structure−property relationships that are found for NCS materials, as well as describing the techniques available to measure the symmetry-dependent properties. What has not been discussed is the synthesis of new NCS materials. Based on this review can any strategies be put forward concerning the rational synthesis of new NCS materials? From our compilation, nearly 80% of the 578 oxides have either a SOJT distorted cation or a tetrahedrally coordinated cation. It would seem reasonable that to increase the incidence of NCS in any new material, one would combine metals that are susceptible to an SOJT distortion and found in tetrahedral coordination environments. Of course, these two factors are not solely responsible for all NCS oxides, as there are numerous examples of materials with both types of cations that are centrosymmetric. Nonetheless, we feel that by combining these types of cations the highest probability exists for synthesizing new NCS materials.

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References

(1) Hahn, T. *International Tables for Crystallography*; D. Reidel Publishing Company: Dordrecht, 1983.
(2) Glazer, A. M.; Stadnicka, K. *Acta Crystallogr.* **1989**, *A45*, 234.
(3) Abrahams, S. C.: Absolute Configuration and Tensoral Properties. In Anomalous Scattering; Ramaseshan, S., Abrahams, S. C., Eds.; Munksgaard: Copenhagen, 1975; pp 197−221.
(4) Wilson, A. J. C. *Acta Crystallogr.* **1949**, *2*, 318.
(5) Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.
(6) Baur, W. H.; Kassner, D. *Acta Crystallogr.* **1992**, *B48*, 356.
(7) Marsh, R. E. *Acta Crystallogr.* **1986**, *B42*, 193.
(8) Marsh, R. E. *Acta Crystallogr.* **1995**, *B51*, 897.
(9) Ermer, O.; Dunitz, J. *Acta Crystallogr.* **1970**, *A26*, 163.
(10) Bergerhoff, G.; Hundt, R.; Sievers, R.; Brown, I. D. *J. Chem. Inf. Comput. Sci.* **1983**, *23*, 66.
(11) Landolt-Bornstein *Ferroelectrics and Related Substances. Oxides*; Springer-Verlag: Berlin, 1990.
(12) Landolt-Bornstein *Ferroelectrics and Related Substances. Non-oxides*; Springer-Verlag: Berlin, 1990.
(13) Tordjman, I.; Masse, R.; Guitel, J. C. *Z. Kristallogr.* **1974**, *139*, 103.
(14) Hagerman, M. E.; Poeppelmeier, K. R. *Chem. Mater.* **1995**, *7*, 602.
(15) Abrahams, S. C.; Kurtz, S. K.; Jamieson, P. B. *Phys. Rev.* **1968**, *172*, 551.
(16) DiDomenico, M.; Wemple, S. H. *J. App. Phys.* **1969**, *20*, 720.
(17) Jeggo, C. R. *Opt. Commun.* **1970**, *1*, 375.
(18) Jeggo, C. R.; Boyd, G. D. *J. App. Phys.* **1970**, *41*, 2741.
(19) Kurtz, S. K.; Robinson, F. N. H. *App. Phys. Lett.* **1967**, *10*, 62.
(20) Miller, R. C. *App. Phys. Lett.* **1964**, *5*, 17.
(21) Levine, B. F. *Phys. Rev. B* **1973**, *7*, 2600.
(22) Nye, J. F. *Physical Properties of Crystals*; Clarendon Press: Oxford, 1985.
(23) Abrahams, S. C.; Reddy, J. M.; Bernstein, J. L. *J. Phys. Chem. Solids* **1966**, *27*, 997.
(24) Bergman, J. G.; Crane, G. R. *J. Solid State Chem.* **1975**, *12*, *172*.
(25) Brown, I. D. *Acta Crystallogr.* **1977**, *B33*, 1305.
(26) Levine, B. F. *Phys. Rev. B* **1973**, *7*, 2600.
(27) Maker, P. D.; Terhune, R. W.; Nisenoff, M.; Savage, C. M. *Phys. Rev. Lett.* **1962**, *8*, 21.
(28) Jones, P. G. *Acta Crystallogr.* **1984**, *A40*, 660.
(29) Glazer, A. M.; Stadnicka, K. *Acta Crystallogr.* **1989**, *A45*, 234.
(30) Glazer, A. M.; Stadnicka, K. *J. Appl. Crystallogr.* **1986**, *19*, 108.
(31) Barsch, G. R. *Acta Crystallogr.* **1976**, *A32*, 575.
(32) Paturle, A.; Graafsma, H.; Sheu, H.-S.; Coppens, P.; Becker, P. *Phys. Rev. B* **1991**, *43*, 14683.
(33) Jahn, H. A.; Teller, E. *Proc. R. Soc.* (*London*) **1937**, *A161*, 220.
(34) Opik, U.; Pryce, M. H. L. *Proc. R. Soc.* (*London*) **1957**, *A238*, 425.
(35) Wheeler, R. A.; Whangbo, M. H.; Hughbanks, T.; Hoffman, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222.
(36) Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971.
(37) Cohen, R. E. *Nature* **1992**, *358*, 136.
(38) Mueller-Buschbaum, H. K.; Lenz, A. *J. Less-Common Met.* **1989**, *156*, 173.
(39) Freund, H. R.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1977**, *B32*, 1123.
(40) Cox, J. R.; Kesler, D. A.; Huang, J. F. *Chem. Mater.* **1994**, *6*, 2008.
(41) Mueller-Buschbaum, H. K.; Vogt, R. *Z. Anorg. Allg. Chem.* **1990**, *589*, 89.
(42) Benedittis, J. de; Katz, L. *Inorg. Chem.* **1965**, *4*, 1836.
(43) Gasperin, M. *Acta Crystallogr.* **1975**, *B31*, 2129.
(44) Scheunemann, K.; Mueller-Buschbaum, H. K. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1879.
(45) Scheunemann, K.; Mueller-Buschbaum, H. K. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2261.
(46) Sasaki, S.; Prewitt, C. T.; Bass, J. D.; Schulze, W. A. *Acta Crystallogr.* **1987**, *C43*, 1668.
(47) Ko, J.; Prewitt, C. T. *Phys. Chem. Miner.* **1988**, *15*, 355.
(48) Schmachtel, J.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1980**, *B35*, 332.
(49) Mueller-Buschbaum, H. K.; Neubacher, M. *Z. Anorg. Allg. Chem.* **1990**, *586*, 87.
(50) Bolotina, N. B.; Dmitrieva, M. T.; Rastsvetaeva, R. K. *Kristallografiya* **1992**, *37*, 598 (311).
(51) Bursill, L.; Grey, I. E.; Lloyd, D. J. *J. Solid State Chem.* **1976**, *16*, 331.
(52) Jamieson, P. B.; Abrahams, S. C. *Acta Crystallogr.* **1968**, *B24*, 984.
(53) Nanot, M.; Queyroux, F.; Gilles, J.; Chevalier, R. *Acta Crystallogr.* **1976**, *B32*, 1115.
(54) Dorrian, J. F.; Newnham, R. E.; Smith, D. K.; Kay, M. I. *Ferroelectrics* **1971**, *3*, 17.
(55) Moore, P. B.; Louisnathan, J. *Science* **1967**, *156*, 1361.
(56) Northrup, P. A.; Parise, J. B.; Cheng, L. K.; Cheng, L. T.; McCarron, E. M. *Chem. Mater.* **1994**, *6*, 434.
(57) Groult, D.; Mercey, C.; Raveau, B. *J. Solid State Chem.* **1980**, *32*, 289.
(58) Sleight, A. W.; Prewitt, C. T. *J. Solid State Chem.* **1973**, *6*, 509.
(59) Kubel, F.; Schmid, H. *Ferroelectrics* **1992**, *129*, 101.
(60) Kissel, J.; Hoppe, R. *J. Less-Common Met.* **1990**, *158*, 327.
(61) Protas, J.; Marnier, G.; Boulanger, B.; Menaert, B. *Acta Crystallogr.* **1989**, *C45*, 1123.
(62) Iijuma, K.; Marumo, F.; Kimura, M.; Kawamure, T. *J. Chem. Soc. Jpn.* **1981**, *10*, 1557.
(63) Klevtsova, R. F.; Bakakin, V. V.; Solodovnokov, S. F.; Glinskaya, L. A. *Zh. Strukt. Khim.* **1981**, *22*, 6 (807).
(64) Dittrich, G.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1969**, *371*, 306.
(65) Klevtsova, R. F.; Bazarova, Z. G.; Glinskaya, L. A.; Alekseev, V.; Arkhincheeva, S.; Bazarov, B. G.; Klevtsov, P. V.; Fedorov, K. N. *Zh. Strukt. Khim.* **1994**, *35*, 11.
(66) Klevtsova, R. F.; Bakakin, V. V.; Solodovnikov, S. F.; Glinskaya, L. A. *Zh. Strukt. Khim.* **1981**, *22*, 6 (807).
(67) Glazer, A. M.; Roleder, K.; Dec, J. *Acta Crystallogr.* **1993**, *B49*, 846.

(68) Sizova, R. G.; Blinov, V. A.; Voronkov, A. A.; Ilyukhin, V. V.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1981**, *205*, 90.
(69) Blinov, V. A.; Shumyatskaya, N. G.; Voronkov, A. A.; Ilyukhin, V. V.; Belov, N. V. *Kristallografiya* **1977**, *22*, 59 (31).
(70) Yamamoto, A.; Yamada, T.; Ikawa, H.; Fukunga, O.; Tanaka, K.; Marumo, F. *Acta Crystallogr.* **1991**, *C47*, 1588.
(71) Roelofsen Ahl, J. N.; Peterson, R. C. *Can. Miner.* **1989**, *27*, 703.
(72) Moore, P. B.; Araki, T. *Am. Miner.* **1976**, *61*, 88.
(73) Mueller-Buschbaum, H. K.; Vogt, R. *J. Less-Common Met.* **1990**, *163*, 347.
(74) Kihlborg, L. *Acta Chem. Scand.* **1967**, *21*, 2495.
(75) Evans, H. T.; Brusewitz, A. M. *Acta Chem. Scand.* **1994**, *48*, 533.
(76) Kozloski, R.; Stadnicka, K. *J. Solid State Chem.* **1981**, *39*, 271.
(77) Waltersson, R.; Forslund, B. *Acta Crystallogr.* **1977**, *B33*, 784.
(78) Angenault, J.; Rimsky, A. *C. R. Acad. Sci. Paris* **1968**, *267*, 227.
(79) Carpy, A.; Galy, J. *Acta Crystallogr.* **1975**, *B31*, 1481.
(80) Galy, J.; Carpy, A. *Acta Crystallogr.* **1975**, *B31*, 1794.
(81) Mondet, S.; Rimsky, A.; Borene, J.; Freundich, W. *C. R. Acad. Sci. Paris* **1968**, *266*, 1145.
(82) Drozdov, Y. N.; Kuz′min, E. A.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1973**, *210*, 339.
(83) Gopal, R.; Calvo, C. *Z. Kristallogr.* **1973**, *137*, 67.
(84) Eick, H. A.; Kihlborg, L. *Acta Chem. Scand.* **1966**, *20*, 1658.
(85) Galy, J.; Lavaud, D. *Acta Crystallogr.* **1971**, *B27*, 1005.
(86) Wichmann, R.; Mueller-Buschbaum, H. *Rev. Chim. Miner.* **1986**, *23*, 1.
(87) Jasper-Toennies, B.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1984**, *508*, 7.
(88) Lloyd, D. J.; Galy, J. *Cryst. Struct. Commun.* **1973**, *2*, 209.
(89) He-Eierdanz, M. L.; Mueller, U. *Z. Anorg. Allg. Chem.* **1992**, *613*, 63.
(90) Darriet, B.; Galy, J. *J. Solid State Chem.* **1974**, *8*, 189.
(91) Touboul, M.; Lokaj, J.; Tessier, L.; Kettman, V.; Vrabel, V. *Acta Crystallogr.* **1992**, *C48*, 1176.
(92) Postel, M.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 123.
(93) Wang, P. L.; Li, D. Y. *Acta Phys. Sin.* **1985**, *34*, 235.
(94) Darriet, J.; Galy, J. *Cryst. Struct. Commun.* **1973**, *2*, 1973.
(95) Postel, M.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1993**, *200*, 165.
(96) Osterloh, D.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1994**, *B49*, 923.
(97) Kasatani, H.; Umeki, T.; Terauchi, H. *J. Phys. Soc. Jpn.* **1992**, *61*, 2309.
(98) Launay, S.; Mahe, P.; Quarton, M.; Robert, F. *J. Solid State Chem.* **1992**, *97*, 305.
(99) Waburg, M.; Mueller-Buschbaum, H. *Monatsh. Chem.* **1986**, *117*, 131.
(100) Holt, E.; Drai, S.; Olazcuaga, R.; Vlasse, M. *Acta Crystallogr.* **1977**, *B33*, 95.
(101) Beaulieu, D. C. de; Mueller-Buschbaum, H. K. *Monatsh. Chem.* **1082**, *113*, 415.
(102) Baglio, J. A.; Dann, J. N. *J. Solid State Chem.* **1972**, *4*, 87.
(103) Vlasse, M.; Salmon, R.; Parent, C. *Inorg. Chem.* **1976**, *15*, 1440.
(104) Kashida, S.; Hori, T.; Nakamura, K. *J. Phys. Soc. Jpn.* **1994**, *63*, 4422.
(105) Murashova, E. V.; Velikodnyi, Y.; Ilyukhin, A. B.; Zhuravlev, V. D. *Zh. Neorg. Khim.* **1993**, *38*, 428 (401).[540]
(106) Calvo, C.; Faggiani, R. *Acta Crystallogr.* **1975**, *B31*, 603.
(107) Huang, J. F.; Sleight, A. W. *J. Solid State Chem.* **1993**, *104*, 52.
(108) Ramani, K.; Shaikh, A. M.; Reddy, B. S.; Viswamitra, M. A. *Ferroelectrics* **1975**, *9*, 49.
(109) Bouloux, J.; Milosevic. I.; Galy, J. *J. Solid State Chem.* **1976**, *16*, 393.
(110) Enjalbert, R.; Lecante, P.; Galy, J. *Acta Crystallogr.* **1986**, *C42*, 1465.
(111) Galy, J.; Hardy, A. *Acta Crystallogr.* **1965**, *19*, 432.
(112) Takeuchi, Y.; Joswig, W. *Miner. J.* (*Jpn.*) **1967**, *5*, 98.
(113) Rea, J. R.; Bless, P. W.; Kostiner, E. *J. Solid State Chem.* **1972**, *5*, 446.
(114) Ben Amara, M.; Vlasse, M.; Olazcuaga, R.; Flem, G. le *Acta Crystallogr.* **1979**, *B35*, 50.
(115) Parent, C.; Fava, J.; Salmon, R.; Vlasse, M.; Flem, G. le; Hagenmueller, P.; Antic-Fidancev, E.; Lemaitre-Blaise, M.; Caro, P. *Nouv. J. Chem.* **1979**, *3*, 523.
(116) Galy, J.; Cassalot, A.; Pouchard, M.; Hagenmuller, P. *C. R. Acad. Sci. Paris* **1966**, *262*, 1055.
(117) Galy, J.; Lavaud, D. *Acta Crystallogr.* **1971**, *B27*, 1005.
(118) Galy, J.; Lavaud, D.; Casalot, A.; Hagenmuller, P. *J. Solid State Chem.* **1970**, *2*, 531.
(119) Morosin, B.; Rosenzweig, A. *Acta Crystallogr.* **1965**, *18*, 874.
(120) Schuekel, K.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1985**, *528*, 91.
(121) Jamieson, P. B.; Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1968**, *48*, 5048.
(122) Hofmann, R.; Gruehn, R. *Z. Anorg. Allg. Chem.* **1991**, *602*, 105.
(123) Ishizawa, N.; Maruma, F.; Kawamura, T.; Kimura, M. *Acta Crystallogr.* **1975**, *B31*, 1912.
(124) Jamieson, P. B.; Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1971**, *54*, 2355.
(125) Kinzhibalo, L. N.; Trunov, V. K.; Evdokimov, A. A.; Krongauz, V. G. *Kristallografiya* **1982**, *27*, 43 (22).[540]
(126) Ishizawa, N.; Moruma, F.; Iwai, S. I. *Acta Crystallogr.* **1981**, *B37*, 26.
(127) Lehmann, V.; Meuller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1981**, *481*, 7.
(128) Galy, J.; Roth, R. S. *J. Solid State Chem.* **1973**, *7*, 277.
(129) Brandt, R.; Mueller-Buschbaum, H. K. *Monatsh. Chem.* **1986**, *117*, 1239.
(130) Ponomorev, V. I.; Filipenko, O. S.; Atovmyan, L. O.; Rannev, N. V.; Ivanov, S. A.; Venevtsev, Y. N. *Kristallografiya* **1981**, *26*, 341 (194).[540]
(131) Saine, M. *J. Less-Common Met.* **1988**, *139*, 315.
(132) Gasperin, M. *Acta Crystallogr.* **1981**, *B37*, 641.
(133) Rohweder, W.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1988**, *142*, 75.
(134) Busch, J.; Hoffmann, G.; Greuhn, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1056.
(135) Groult, D.; Hervieu, M.; Raveau, B. *J. Solid State Chem.* **1984**, *53*, 184.
(136) Hewat, A. W. *J. Phys. C* **1973**, *6*, 1074.
(137) Gasperin, M.; Bihan, M. T. *J. Solid State Chem.* **1982**, *43*, 346.
(138) Seidel, P.; Hoffmann, W. *Z. Kristallogr.* **1976**, *143*, 444.
(139) Scheunemann, K.; Mueller-Buschbaum, H. K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1965.
(140) Graham, J.; Thorber, M. R. *Am. Min.* **1974**, *59*, 1040.
(141) Moehr, S.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1994**, *B49*, 915.
(142) Ishizawa, N.; Marumo, F.; Iwai, S. I. *Acta Crystallogr.* **1981**, *B37*, 26.
(143) Mattes, L.; Leimkuehler, M.; Nagel, A. *Z. Anorg. Allg. Chem.* **1990**, *582*, 131.
(144) Koehl, P.; Reinen, D. *Z. Anorg. Allg. Chem.* **1977**, *433*, 81.
(145) Dion, M.; Ganne, M.; Tournoux, M.; Ravez, J. *J. Solid State Chem.* **1984**, *53*, 422.
(146) Sirotinkin, V. P.; Efremov, V. A.; Trunov, V. K. *Zh. Neorg. Khim.* **1985**, *30*, 1727 (981).[540]
(147) Schweizer, M.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1979**, *B34*, 774.
(148) Labbe, P.; Leligny, H.; Raveau, B.; Schneck, J.; Toledano, J. C. *J. Phys.: Condens. Matter* **1989**, *2*, 25.
(149) Thompson, J. G.; Rae, A. D.; Withers, R. L.; Craig, D. C. *Acta Crystallogr.* **1991**, *B47*, 174.
(150) Baucher, A.; Gasperin, M.; Cervelle, B. *Acta Crystallogr.* **1976**, *B32*, 2211.
(151) Gasperin, M. *Acta Crystallogr.* **1974**, *B30*, 1181.
(152) Choisnet, J.; Groult, D.; Raveau, B.; Gasperin, M. *Acta Crystallogr.* **1977**, *B33*, 1841.
(153) Wichmann, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1985**, *525*, 135.
(154) Belokoneva, E. L.; Mill′, B. V.; Butashin, A. V. *Zh. Neorg. Khim.* **1993**, *38*, 1455 (1356).[540]
(155) Rohweder, U.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1988**, *142*, 75.
(156) Genkina, E. A.; Belokoneva, E. L.; Mill′, B. V.; Butashin, A. V.; Makisimov, B. A. *Kristallografiya* **1992**, *37*, 606 (316).[540]
(157) Crosnier, M. P.; Guyomard, D.; Verbaere, A.; Piffard, Y.; Tournoux, M. *J. Solid State Chem.* **1992**, *98*, 128.
(158) Bernotat-Wulf, H.; Hoffmann, W. *Z. Kristallogr.* **1983**, *164*, 129.
(159) Bernotat-Wulf, H.; Hoffmann, W. *Z. Kristallogr.* **1982**, *158*, 101.
(160) Stephenson, N. C.; Roth, R. S. *Acta Crystallogr.* **1971**, *B27*, 1025.
(161) Harneit, O.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1992**, *184*, L21.
(162) Harneit, O.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1992**, *184*, 323.
(163) Brandt, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1986**, *542*, 18.
(164) Brandt, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1987**, *551*, 13.
(165) Stephenson, N. C.; Roth, R. S. *Acta Crystallogr.* **1971**, *B27*, 1010.
(166) Yamazoe, N.; Kihlborg, L. *Acta Crystallogr.* **1975**, *B31*, 1666.
(167) Rajaomera, P. *Rev. Chim. Miner.* **1976**, *13*, 249.
(168) Ishizawa, N.; Moruma, F.; Iwai, S. I. *Acta Crystallogr.* **1981**, *B37*, 26.
(169) Rae, D. A.; Thompson, J. G.; Withers, R. L. *Acta Crystallogr.* **1992**, *B48*, 418.
(170) Newnham, R. E.; Wolfe, R. W.; Horsey, R. S.; Diaz-Colon, F. A.; Kay, M. I. *Mater. Res. Bull.* **1973**, *8*, 1183.
(171) Belokoneva, E. L.; Mill′, B. V. *Zh. Neorg. Khim.* **1992**, *37*, 998 (502).[540]
(172) Serezhkin, V. N.; Kovba, L. M.; Trunov, V. K. *Kristallografiya* **1973**, *18*, 514 (323).[540]
(173) Leligny, H.; Ledesert, M.; Labbe, P.; Raveau, B.; McCarroll, W. H. *J. Solid State Chem.* **1990**, *87*, 35.

(174) Collins, B. T.; Fine, S. M.; Potenza, J. A.; Tsai, P. P.; Greenblatt, M. *Inorg. Chem.* **1989**, *28*, 2444.
(175) Parmentier, M.; Gleitzer, C.; Courtois, A.; Protas, J. *Acta Crystallogr.* **1979**, *B35*, 1963.
(176) Khazheeva, Z. I.; Simonov, V. I.; Mokhosoev, M. V.; Smirnyagina, N. N.; Kozhevnikova, N. M.; Alekseev, F. P. *Kristallografiya* **1987**, *32*, 79 (43).[540]
(177) Foresteier, P.; Goreavd, M. *C. R. Acad. Sci. Paris* **1991**, *312*, 1141.
(178) Lepage, Y.; Strobel, P. *Acta Crystallogr.* **1982**, *B38*, 1265.
(179) Klevtsov, P. V.; Solodovnokov, S. F.; Perepelitsa, A. P.; Klevtsova, R. F. *Kristallografiya* **1984**, *29*, 701 (415).[540]
(180) Elzen, A. F. van den; Gieck, G. D. *Acta Crystallogr.* **1973**, *B29*, 2436.
(181) Klevtsova, R. F.; Antonova, A. A.; Glinskaya, L. A. *Kristallografiya* **1979**, *24*, 1043 (596).[540]
(182) Efremov, V. A.; Klevtsova, R. F.; Lazoryak, B. I.; Glinskaya, L. A.; Matsichek, I.; Solodovnikov, S. F. *Kristallografiya* **1982**, *27*, 461 (281).[540]
(183) Ansell, G. B.; Katz, L. *Acta Crystallogr.* **1966**, *21*, 482.
(184) Onoda, M.; Masuda, Y.; Sato, M. *J. Solid State Chem.* **1987**, *69*, 67.
(185) Krueger, T. F.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1992**, *614*, 35.
(186) Lii, K. H.; McCarley, R. E.; Kim, S.; Jacobson, R. A. *J. Solid State Chem.* **1986**, *64*, 347.
(187) Rapposch, M. H.; Anderson, J. B.; Kostiner, E. *Inorg. Chem.* **1980**, *19*, 3531.
(188) Lii, K. H.; McCarley, R. E.; Kim, S.; Jacobson, R. A. *J. Solid State Chem.* **1986**, *64*, 347.
(189) Kudin, O. V.; Efremov, V. A.; Trunov, V. K.; Velikodyni, Y. A. *Zh. Neorg. Khim.* **1981**, *26*, 2734 (1464).[540]
(190) Beneditte, J. de; Katz, L. *Inorg. Chem.* **1965**, *4*, 1836.
(191) Svensson, C.; Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1979**, *71*, 5191.
(192) Kruglik, A. I.; Klevtsova, R. F.; Aleksandrov, K. S. *Dokl. Akad. Nauk SSSR* **1983**, *271*, 1388.
(193) Jeitschko, W. *Naturwissenschaften* **1970**, *57*, 544.
(194) Kihnborg, L.; Norrestam, R.; Olivecrona, B. *Acta Crystallogr.* **1971**, *B27*, 2066.
(195) Linnros, B. *Acta Chem. Scan.* **1970**, *24*, 3711.
(196) Gougeon, P.; McCarley, R. E. *Acta Crystallogr.* **1991**, *C47*, 241.
(197) Balashov, V. L.; Khorlanov, A. A.; Kondratov, O. I.; Fomichev, U. V. *Zh. Neorg. Khim.* **1991**, *36*, 456 (254).[540]
(198) Range, K. J.; Hasse, H. *Acta Crystallogr.* **1990**, *C46*, 317.
(199) Pye, M. F.; Dickens, P. G. *Mater. Res. Bull.* **1979**, *14*, 1397.
(200) Mueller-Buschbaum, H. K.; Kruger, T. *Z. Anorg. Allg. Chem.* **1992**, *607*, 52.
(201) Skarstad, P. M.; Geller, S. *Mater. Res. Bull.* **1975**, *10*, 791.
(202) Mattes, R.; Leimkuehler, M.; Nagel, A. *Z. Anorg. Allg. Chem.* **1990**, *582*, 131.
(203) Mumm, H. C.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1988**, *142*, 85.
(204) Okada, K.; Marumo, F.; Iwai, S. I. *Acta Crystallogr.* **1978**, *B34*, 50.
(205) Krueger, T. F.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1992**, *190*, L1.
(206) Rae, A. D.; Thompson, J. G.; Withers, R. L. *Acta Crystallogr.* **1991**, *B47*, 870.
(207) Mueller-Buschbaum, H. K.; Gressling. T *J. Alloys Compd.* **1993**, *202*, 63.
(208) Zhenngmin, F.; Wenxiu, L.; Dongcai, L. *Sci. Sin., Ser. A* **1983**, *26*, 835.
(209) Klevtsova, R. F.; Borisov, S. V. *Kristallografiya* **1969**, *14*, 610 (515).[540]
(210) Roth, R. S.; Wadsley, A. D. *Acta Crystallogr.* **1965**, *19*, 32.
(211) Baud, G.; Besse, J.; Chevalier, R.; Gasperin, M. *J. Solid State Chem.* **1979**, *29*, 267.
(212) Picard, J. P.; Baud, G.; Besse, J. P.; Chevalier, R.; Gasperin, M. *J. Less-Common Met.* **1984**, *96*, 171.
(213) Malaman, B.; Alebouyeh, H.; Courtois, A.; Gerardin, R.; Evrard, O. *Mater. Res. Bull.* **1982**, *17*, 795.
(214) Abrahams, S. C.; Reddy, J. M.; Bernstein, J. L. *J. Chem. Phys.* **1965**, *42*, 3957.
(215) Mevs, H.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1990**, *158*, 147.
(216) Millon, E.; Malaman, B.; Bonazebi, A.; Brice, J. F.; Gerardin, R.; Evrard, O. *Mater. Res. Bull.* **1986**, *21*, 985.
(217) Colville, A. A.; Geller, S. *Acta Crystallogr.* **1972**, *B28*, 3196.
(218) Colville, A. A.; Geller, S. *Acta Crystallogr.* **1971**, *B27*, 2311.
(219) Reuter, I.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1990**, *162*, 175.
(220) Harder, M.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1980**, *464*, 169.
(221) Hanson, A. W. *Acta Crystallogr.* **1958**, *11*, 703.
(222) Lacorre, P.; Hervieu, M.; Choisnet, J.; Raveau, B. *J. Solid State Chem.* **1984**, *51*, 44.
(223) Yoshiasa, A.; Uena, K.; Kanamarv, F. *Mater. Res. Bull.* **1986**, *24*, 175.
(224) Tarte, P.; Cahay, R.; Preudhomme, J.; Hervieu, J.; Choisnet, J.; Raveau, B. *J. Solid State Chem.* **1982**, *44*, 282.
(225) Coppens, P.; Eibschutz, M. *Acta Crystallogr.* **1965**, *19*, 524.
(226) Reuter, I.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1990**, *585*, 82.
(227) Mueller-Buschbaum, H. K.; Martin, F. D. *Z. Anorg. Allg. Chem.* **1992**, *617*, 84.
(228) Michel, C.; Moreau, J. M.; Achenbach, G. D.; Gerson, R.; James, W. J. *J. Solid State Commun.* **1969**, *7*, 701.
(229) Vaughey, J. T.; Poeppelemeier, K. R. *NIST Spec. Publ.* **1991**, *804*, 419.
(230) Barker, M. G.; Fourhall, G. A. *J. Chem. Res.* **1979**, *1979*, 371.
(231) Riou, A.; Lecerf, A. *Acta Crystallogr.* **1975**, *B31*, 2487.
(232) Mevs, H.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1990**, *584*, 114.
(233) Tarascon, J. M.; Miceli, P. F.; Barboux, P.; Hwang, D. M.; Hull, G. W.; Giroud, M.; Greene, L. H.; Lepage, Y.; McKinnon, W. R.; Tselepis, E.; Pleizier, M.; Eibscutz, M.; Neumann, D. A.; Rhyne, J. J. *Phys. Rev. B* **1989**, *39*, 11587.
(234) Foussaier, C.; Matejka, G.; Reau, J. M.; Hagenmuller, P. *J. Solid State Chem.* **1973**, *6*, 532.
(235) Ilyukhin, A. B.; Dzhurinskii, B. F. *Zh. Neorg. Khim.* **1994**, *39*, 556 (530).[540]
(236) Perloff, A.; Block, S. *Acta Crystallogr.* **1966**, *20*, 274.
(237) Ilyukhin, A. B.; Dzhurnskii, B. F. *Zh. Neorg. Khim.* **1993**, *38*, 1625 (1516).[540]
(238) Machida, K. I.; Adachi, G. Y.; Shiokawa, J. *Acta Crystallogr.* **1980**, *B36*, 2008.
(239) Krogh-Moe, J. *Acta Crystallogr.* **1962**, *15*, 190.
(240) Froehlich, R.; Bohaty, L.; Liebertz, J. *Acta Crystallogr.* **1984**, *C40*, 343.
(241) Garsche, H.; Kupah, V.; Tillmans, E.; Alman, H.; Schnieder, H. *European J. Miner.* **1991**, *3*, 1991.
(242) Ilyukhin, A. B.; Dzhurinskii, B. F. *Zh. Neorg. Khim.* **1993**, *38*, 1625 (1516).[540]
(243) Voronkov, A. A.; Pyatenko, Y. A. *Kristallografiya* **1967**, *12*, 258 (214).[540]
(244) Sokolova, E. V.; Azizov, A. V.; Simonov, N. A.; Leonyuk, N. I.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1978**, *243*, 655.
(245) Kaminskii, A. A.; Mill′, B. V.; Belokoneva, E. L.; Butashin, A. V. *Neorg. Mater.* **1990**, *26*, 1105.
(246) Schuckmann, W. *Nues Jahrb. Miner.* **1968**, *1968*, 80.
(247) Sokolova, E. V.; Khomyakov, A. P. *Dokl. Akad. Nauk SSSR* **1991**, *319*, 879.
(248) Ihara, M.; Imai, K.; Fukunaga, J.; Yoshida, N. *J. Ceram. Soc. Jpn.* **1980**, *88*, 877.
(249) Samygina, V. R.; Genkina, E. A.; Maksimov, B. A.; Leonyuk, N. I. *Kristallografiya* **1993**, *38*, 61 (744).[540]
(250) Garcia-Blanco, S.; Fayos, J. *Z. Kristallogr.* **1968**, *127*, 145.
(251) Schaefer, J.; Bluhm, K. *Z. Naturforsch.* **1995**, *B50*, 762.
(252) Gasperin, M. *Acta Crystallogr.* **1987**, *C43*, 1247.
(253) Bondareva, O. S.; Malinovskii, Y. A.; Belov, N. V. *Kristallografiya* **1980**, *25*, 944.
(254) Koenig, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1978**, *439*, 71.
(255) Krogh-Moe, J.; Ihara, M. *Acta Crystallogr.* **1967**, *23*, 427.
(256) Meissen, M.; Hoppe, R. *Phys. Chem. Miner.* **1985**, *22*, 331.
(257) Khamagonova, T. N.; Trunov, V. K.; Dzhurinskii, B. F. *Zh. Neorg. Khim.* **1991**, *36*, 855 (484).[540]
(258) Khamagonova, T. N.; Trunov, V. K.; Ilyikhin, A. B. *Zh. Neorg. Khim.* **1993**, *38*, 917 (1674).[540]
(259) Abdullaev, G.; Mamedov, C. *Zh. Strukt. Khim.* **1976**, *17*, 188 (166).[540]
(260) Ihara, M.; Yuge, M.; Krogh-Moe, J. *J. Ceram. Soc. Jpn.* **1980**, *88*, 179.
(261) Abdullaev, G. K.; Mamedov, K. S. *Zh. Strukt. Khim.* **1974**, *15*, 157 (145).[540]
(262) Abdullaev, G. K.; Mamedov, K. S.; Amirov, S. T. *Kristallografiya* **1973**, *18*, 1075 (675).[540]
(263) Norrestam, R.; Nygren, M.; Bovin, J. O. *Chem. Mater.* **1992**, *4*, 737.
(264) Rath, M.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1992**, *189*, L15.
(265) Barker, M. G.; Gadd, P. G.; Wallwork, S. C. *J. Chem. Soc., Chem. Commun.* **1982**, 516.
(266) Thomas, J. O.; Alden, M.; Farrington, G. C. *J. Phys. Chem.* **1969**, *73*, 1774.
(267) Hoerkner, W.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1979**, *451*, 40.
(268) Depmeier, W. *Acta Crystallogr.* **1984**, *C40*, 226.
(269) Harder, M.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1979**, *448*, 135.
(270) Vincent, M. G.; Jeffery, J. W. *Acta Crystallogr.* **1978**, *B34*, 1412.
(271) Nyevsky, V. N. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 821.
(272) Kutoglu, A.; Roesler, A.; Reinen, D. *Z. Anorg. Allg. Chem.* **1979**, *456*, 130.
(273) Schulze, A. R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1981**, *475*, 205.
(274) Antipov, E. V.; Lykova, L. N.; Kovba, L. M. *Coordination Chemsitry* (*USSR*) **1985**, *11*, 1151.

(275) Nuber, B.; Schechtur, K. *Nues Jahrb. Miner.* **1983**, *1983*, 393.
(276) Reuter, I.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1990**, *588*, 97.
(277) Plotz, K. B.; Mueller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1982**, *488*, 38.
(278) Deiseroth, H. J.; Mueller-Buschbaum, H. K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3177.
(279) Vaughey, J. T.; Wiley, J. B.; Poeppelmeier, K. R. *Z. Anorg. Allg. Chem.* **1991**, *598*, 327.
(280) Roth, G.; Adelman, O.; Knitter, R.; Massing, S.; Wolf, T. *J. Solid State Chem.* **1992**, *99*, 376.
(281) Bilyi, A. I.; Bruskov, V. A.; Grin′, Y.; Zavalii, P.; Kravchishin, V. V.; Nosenko, A. E. *Kristallografiya* **1986**, *31*, 1217 (719).[540]
(282) Geller, S.; Jeffries, J. B.; Curlander, P. J. *Acta Crystallogr.* **1975**, *B31*, 2770.
(283) Vielhaber, E.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1964**, *369*, 14.
(284) Schutze, A. R.; Mueller-Buschbaum, H. K. *Monatsh. Chem.* **1981**, *112*, 149.
(285) Nodari, I.; Malaman, B.; Evrard, O. *Mater. Res. Bull.* **1985**, *20*, 687.
(286) Brusset, H.; Giller-Paudraud, H.; Budot, J. L. *Bull. Soc. Chim. Fr.* **1967**, *1967*, 2886.
(287) Bergerhoff, G.; Kasper, H. *Acta Crystallogr.* **1968**, *B24*, 388.
(288) Freund, H. R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1978**, *441*, 103.
(289) Yoshiasa, A.; Takeno, S.; Iishi, K. *Miner. J.* **1992**, *16*, 40.
(290) Pistorius, C. W. F. T.; Kruger, G. J. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1471.
(291) Schenck, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1973**, *395*, 280.
(292) Pushcharovskii, D. Y. *Dokl. Akad. Nauk SSSR* **1978**, *242*, 1978.
(293) Fischer, K. *Z. Kristallogr.* **1969**, *129*, 222.
(294) Masse, R.; Grenier, J. C.; Durif, A. *Bull. Soc. Fr. Mineral. Cristallogr.* **1967**, *90*, 20.
(295) Yamnova, N. A.; Kalacheva, L. V.; Pushcharovskii, D. Y.; Kolinin, V. V. *Kristallografiya* **1992**, *37*, 613 (319).[540]
(296) Crosnier, M. P.; Gugomard, D.; Verbaere, A.; Piffard, Y. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 845.
(297) Ilinetz, A. M.; Malinowskii, Y. A.; Newskii, N. N. *Dokl. Akad. Nauk SSSR* **1985**, *281*, 332.
(298) Kalsbeck, N.; Larsen, S.; Ronsbo, J. G. *Z. Kristallogr.* **1990**, *191*, 249.
(299) Belokoneva, E. L.; Mill′, B. V. *Zh. Neorg. Khim.* **1994**, *39*, 355 (341).[540]
(300) Belokoneva, E. L.; Mill′, B. V. *Zh. Neorg. Khim.* **1994**, *39*, 363 (349).[540]
(301) Hofmann, R.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1987**, *555*, 118.
(302) Prewitt, C. T.; Kirchner, E.; Preisinger, A. *Z. Kristallogr.* **1967**, *124*, 115.
(303) Ketterer, J.; Kraemer, V. *Nues Jahrb. Miner.* **1986**, *1986*, 13.
(304) Glasser, L. S.; Howie, R. A.; Smart, R. M. *Acta Crystallogr.* **1981**, *B37*, 303.
(305) Vetter, G.; Queyroux, F. *J. Solid State Chem.* **1988**, *73*, 287.
(306) Voellenkle, H.; Wittman, A. *Monatsh. Chem.* **1968**, *99*, 251.
(307) Nishi, F.; Takeuchi, Y. *Z. Kristallogr.* **1986**, *176*, 303.
(308) Voellenkle, H.; Wittman, A.; Nowotny, H. *Monatsh. Chem.* **1971**, *102*, 361.
(309) Merinov, B. V.; Maksimov, B. A.; Dem′yants, D. V.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 353.
(310) Klaska, K. H.; Jarchow, O. *Z. Kristallogr.* **1985**, *172*, 167.
(311) Belokoneva, E. L.; Mill′, B. V. *Zh. Neorg. Khim.* **1992**, *37*, 998 (502).
(312) Belokoneva, E. L.; Simonov, M. A.; Batushin, A. V.; Mill′, A. V.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1980**, *255*, 1099.
(313) Belokoneva, E.; Dolguishin, F. M.; Antipov, Y.; Mill′, B. V.; Struchkov, Y. U. *Zh. Neorg. Khim.* **1993**, *38*, 631 (584).[540]
(314) Iijima, J.; Marumo, F.; Taker, H. *J. Ceram. Soc. Jpn.* **1983**, *91*, 67.
(315) Belokoneva, E. L.; Mill′, B. V.; Butashin, A. V. *Neorg. Mater.* **1991**, *27*, 1708.
(316) Shashkov, A. Y.; Rannev, N. V.; Venevtsev, Y. V. *Zh. Neorg. Khim.* **1981**, *26*, 2926 (1565).[540]
(317) Aurivillus, B.; Lindblom, C. I.; Stenson, P. *Acta Chem. Scand.* **1969**, *18*, 1555.
(318) Ivanov, S. A.; Rannev, N. V.; Schedrin, B. M.; Venevtsev, Y. N. *Dokl. Akad. Nauk SSSR* **1978**, *239*, 586.
(319) Kay, M. I.; Newnham, R. E.; Wolfe, R. W. *Ferroelectrics* **1975**, *9*, 1.
(320) Bouchama, M.; Tournoux, M. *Rev. Chim. Miner.* **1975**, *12*, 93.
(321) Politova, E. D.; Kaleva, G. M.; Danilenko, I. N.; Chupralov, V. F.; Ivanov, S. A.; Venevtsev, Y. *Neorg. Mater.* **1990**, *26*, 2352.
(322) Aurivillius, B. *Arkiv. Kemi* **1966**, *25*, 505.
(323) Ivanov, S. A.; Zavodnik, V. E. *Kristallografiya* **1990**, *35*, 842 (494).
(324) Arpe, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1976**, *426*, 1.
(325) Tselepis, E.; Wang, E.; Huil, G. W.; Tarascor, J. M.; Lepage, Y.; McKinnon, W. R.; Ramesh, R.; Eibschutz, M. *Phys. C* **1990**, *167*, 20.
(326) Arpe, R.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1976**, *B31*, 1708.
(327) Onoda, M.; Sato, M. *Solid State Commun.* **1988**, *67*, 799.
(328) Parise, J. B.; Torardi, C. C.; Whangbo, M. H.; Rawn, C. J.; Roth, R. S.; Burton, B. P. *Chem. Mater.* **1990**, *2*, 454.
(329) Sciau, P.; Lapasset, J.; Moret, T. *Acta Crystallogr.* **1986**, *C42*, 1688.
(330) Mercurro, D.; El Faussi, M.; Frit, B.; Goursat, P. *Mater. Chem. Phys.* **1983**, *9*, 467.
(331) Panek, P.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1972**, *393*, 13.
(332) Hoppe, R.; Stoever, H. D. *Z. Anorg. Allg. Chem.* **1977**, *437*, 123.
(333) Darriet, B.; Devalette, M.; Latourrette, B. *Acta Crystallogr.* **1978**, *B34*, 3528.
(334) Kruger, J.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1984**, *512*, 59.
(335) Schulze, A. R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1980**, *471*, 59.
(336) Kemmler, S. *Z. Anorg. Allg. Chem.* **1965**, *338*, 9.
(337) Kruger, J.; Mueller-Buschbaum, H. K. *Rev. Chim. Miner.* **1983**, *20*, 456.
(338) Schulze, A. R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1980**, *461*, 48.
(339) Isobe, M.; Kimizuka, N.; Nakamura, M.; Mohri, T. *Acta Crystallogr.* **1991**, *C47*, 423.
(340) Mueller-Buschbaum, H. K.; Scheikowski, M. *Z. Anorg. Allg. Chem.* **1990**, *591*, 181.
(341) Schroeder, F.; Mueller-Buschbaum, H. K. *J. Less-Common Met.* **1986**, *553*, 212.
(342) Cotton, F. A.; Rice, C. E. *J. Solid State Chem.* **1978**, *24*, 359.
(343) Mueller-Buschbaum, H. K.; Boehlke, A. *Z. Anorg. Allg. Chem.* **1987**, *553*, 212.
(344) Mueller-Buschbaum, H. K.; Schrandt, O. *J. Alloys Compd.* **1993**, *191*, 151.
(345) Fameny, R.; Queyroux, F. *Mater. Res. Bull.* **1989**, *24*, 275.
(346) Rabbow, C. H.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1994**, *B49*, 1277.
(347) Muschick, M.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1976**, *31*, 1064.
(348) Freund, H. R.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1977**, *B32*, 609.
(349) Brunn, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1977**, *433*, 189.
(350) Mueller-Buschbaum, H. K.; Mevs, H. *J. Less-Common Met.* **1987**, *136*, 193.
(351) Mueller-Buschbaum, H. K.; Teske, C. L. *Z. Anorg. Allg. Chem.* **1969**, *369*, 255.
(352) Schweizer, M.; Muller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1981**, *482*, 173.
(353) Freund, H. R.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1977**, *B32*, 1123.
(354) Schuldt, D.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1989**, *578*, 119.
(355) Zentgraf, H. *Z. Anorg. Allg. Chem.* **1980**, *462*, 71.
(356) Dariet, B.; Devalette, M.; Roulleau, F.; Avallet, M *Acta Crystallogr.* **1974**, *B30*, 2667.
(357) Tomaszewska, A.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1992**, *617*, 23.
(358) Wambach, K. R.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1978**, *445*, 91.
(359) Jones, P. G.; Sheldrick, G. M.; Schwarzmann, E.; Vielmaeder, A. *Z. Naturforsch.* **1983**, *38*, 10.
(360) Klassen, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1983**, *497*, 70.
(361) Krichner, H.; Kolbesen, B. O.; Torkor, K. *J. Solid State Chem.* **1971**, *3*, 349.
(362) Kiosse, G. A.; Petrenko, P. A.; Banaga, M. P.; Mazus, M. D.; Malinovskii, T. I. *Izv. Akad. Nauk Mold. SSR* **1989**, *3*, 26.
(363) Grey, I. E.; Reid, A. F. *Am. Miner.* **1975**, *60*, 898.
(364) Tiedemann, P.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1985**, *520*, 71.
(365) Swindels, D. C. N.; Gontaks, J. L. *Acta Crystallogr.* **1988**, *B44*, 12.
(366) Scheikowski, M.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 559.
(367) Christian, H. P.; Mueller-Buschbaum, H. K. *Z. Naturforsch.* **1975**, *B30*, 175.
(368) Busch, J.; Hoffmann, G.; Greuhn, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1056.
(369) Mueller-Buschbaum, H. K.; Postel, M. *Z. Anorg. Allg. Chem.* **1992**, *615*, 101.
(370) Pierce, J. W.; Goodenough, J. B. *Phys. Rev. B* **1972**, *5*, 4104.
(371) Launay, S.; Thoret, J. *C. R. Acad. Sci. Paris* **1973**, *277*, 1973.
(372) Vogt, R.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1991**, *602*, 149.
(373) Deoy, M. E.; Besse, J. P.; Chevalier, R.; Gasperin, M. *J. Solid State Chem.* **1987**, *67*, 185.
(374) Murashova, E. V.; Velikodynyj, Y. A.; Trunov, V. K. *Zh. Strukt. Khim.* **1988**, *29*, 182.
(375) Kato, K.; Takayama-Muromachi, E. *Acta Crystallogr.* **1985**, *C41*, 647.
(376) Vogt, R.; Mueller-Buschbaum, H. *Z. Anorg. Allg. Chem.* **1990**, *591*, 167.

(377) Boje, J.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem*. **1992**, *611*, 137.
(378) Casaics, M. T.; Gutierrez-Puebla, E.; Monge, M. A.; Rasines, I.; Ruiz-Valero, C. *J. Solid State Chem*. **1993**, *102*, 261.
(379) Celestani, G.; Andreetti, G. D.; Montenero, A.; Bettinelli, M.; Rebizant, J. *Acta Crystallogr*. **1985**, *C41*, 179.
(380) Radaev, S. F.; Muradyan, L. A.; Sarin, V. A.; Kanepit, V. N.; Yudin, A. N.; Mar′in, A. A.; Simonov, V. I. *Dokl. Akad. Nauk SSSR* **1989**, *34*, 585.
(381) Yudin, A. N.; Pobedimskaya, E. A.; Terent′eva, L. E.; Petrova, I. V.; Kaplinnik, L. N.; Malakhova, G. V. *Neorg. Mater*. **1989**, *25*, 1715.
(382) Darriet, J. *Bull. Soc. Fr. Mineral. Cristallogr*. **1973**, *96*, 97.
(383) Galy, J.; Lindqvist, O. *J. Solid State Chem*. **1979**, *27*, 279.
(384) Hervieu, M.; Raveau, B. *J. Solid State Chem*. **1979**, *28*, 209.
(385) Shannon, J.; Katz, L. *J. Solid State Chem*. **1970**, *1*, 399.
(386) Sirotinkin, V. P.; Sirotinkin, S. P. *Zh. Neorg. Khim*. **1990**, *35*, 2189.
(387) Aruga, A.; Tokizaki, E.; Nakai, I.; Sugitani, Y. *Acta Crystallogr*. **1985**, *C41*, 663.
(388) Shannon, J.; Katz, L. *Acta Crystallogr*. **1970**, *B26*, 105.
(389) Hyooma, H.; Hayashi, K. *Mater. Res. Bull*. **1988**, *23*, 1399.
(390) Yamnova, N. A.; Pushcharovsky, D. Y.; Voloshin, A. V. *Kristallografiya* **1990**, *35*, 346 (195).[540]
(391) Grener, J. C.; Bassi, G. *Bull. Soc. chim. Fr*. **1965**, *88*, 345.
(392) Roth, R. S.; Wadsley, A. D. *Acta Crystallogr*. **1965**, *19*, 38.
(393) Kaminskii, A. A.; Mill, B. V.; Belokoneva, E. L.; Sarkisov, S. E.; Pastukhova, T. Y.; Khadzhabagyan, G. G. *Neorg. Mater*. **1984**, *20*, 2058.
(394) Wilkens, J.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem*. **1993**, *619*, 517.
(395) Jahnberg, L. *J. Solid State Chem*. **1982**, *41*, 286.
(396) Yamnova, N. A.; Pushcharovskii, D. Y.; Voloshin, A. V. *Kristallografiya* **1988**, *33*, 845 (498).[540]
(397) Langenbach-Kuttert, B.; Sturm, J.; Gruehn, R. *Z. Anorg. Allg. Chem*. **1986**, *543*, 117.
(398) Serezhkin, V.; Kovba, L. M.; Trunov, V. K. *Kristallografiya* **1973**, *18*, 514 (323).[540]
(399) Rath, M.; Mueller-Buschbaum, H. K. *J. Alloys Compd*. **1993**, *198*, 193.
(400) Klevtsova, R. F.; Klevtsov, P. V.; Aleksandrov, K. S. *Dokl. Akad. Nauk SSSR* **1980**, *255*, 1379.
(401) Ramanujachary, K. V.; Greenblatt, M.; Jones, E. B.; McCarroll, W. H. *J. Solid State Chem*. **1993**, *102*, 69.
(402) Mueller, M.; Hildmann, B. O.; Hahn, T. *Acta Crystallogr*. **1987**, *C43*, 184.
(403) Szillat, H.; Mueller-Buschbaum, H. K. *Z. Naturforsch*. **1995**, *B50*, 247.
(404) Gicquel-Mayer, C.; Mater, M.; Perez, G. *C. R. Acad. Sci. Paris* **1976**, *283*, 533.
(405) Efremav, V. A.; Tyulin, A. V.; Trunov, V. K. *Coord. Chem*. (*USSR*) **1987**, *13*, 1276.
(406) Thoret, J. *Rev. Chim. Miner*. **1974**, *11*, 237.
(407) Katz, L.; Kasenally, A.; Kihlborg, L. *Acta Crystallogr*. **1971**, *B27*, 2071.
(408) Craig, D. C.; Stephenson, N. C. *Acta Crystallogr*. **1969**, *B25*, 2071.
(409) Goreaud, M.; Desgardin, G.; Raveau, B. *J. Solid State Chem*. **1979**, *27*, 145.
(410) Borisov, S. V.; Klevtsova, R. F.; Belov, N. V. *Kristallografiya* **1968**, *13*, 980.
(411) Hagulin, V. V.; Fadeeva, N. V.; Belous, A. G.; Titon, A. V.; Mitrofanov, K. P.; Plotnikova, M. V.; Solov′ev, S. P.; Venevtsev, Y. N. *Phys. Status Solidi A* **1978**, *48*, 183.
(412) Steadman, R. *Mater. Res. Bull*. **1972**, *7*, 1143.
(413) Tyulin, A. V.; Efremov, V. A.; Trunov, V. K. *Kristallografiya* **1989**, *34*, 531 (46).[540]
(414) Perticek, V.; Fabri, J.; Golubev, A. M.; Simonov, V. I.; Aleksandrov, K. S. *Dokl. Akad. Nauk SSSR* **1987**, *293*, 358.
(415) Plies, V. *Z. Anorg. Allg. Chem*. **1985**, *521*, 191.
(416) Beaury, O.; Faucher, M.; Teste, G. de S. *Acta Crystallogr*. **1981**, *B37*, 1166.
(417) Okada, K.; Marumo, F.; Iwai, S. I. *Acta Crystallogr*. **1977**, *B33*, 3345.
(418) Tyulin, A. V.; Efremov, V. A. *Kristallografiya* **1987**, *32*, 371 (215).[540]
(419) Takusagawa, F.; Jacobson, R. A. *J. Solid State Chem*. **1976**, *18*, 163.
(420) Efremov, V. A.; Tyulin, A. V.; Trunov, V. K. *Kristallografiya* **1984**, *29*, 673 (398).[540]
(421) Craig, D. C.; Stephenson, N. C. *J. Solid State Chem*. **1975**, *15*, 1.
(422) Jeitschko, W.; Sleight, A. W. *Acta Crystallogr*. **1972**, *B28*, 3174.
(423) Schultz, A. J.; Horiuchi, H.; Krause, H. B. *Acta Crystallogr*. **1986**, *C42*, 641.
(424) Mitsuda, H.; Mori, S.; Okuzaki, C. *Acta Crystallogr*. **1971**, *B27*, 1263.
(425) Vincent, H.; Nicopoulos, S. *J. Solid State Chem*. **1992**, *98*, 386.
(426) Kapinskii, O. G.; Arakcheeva, A. V. *Kristallografiya* **1987**, *32*, 55 (28).[540]
(427) Radaev, S. F.; Muradyan, L.; Simonov, V. I. *Acta Crystallogr*. **1991**, *B47*, 1.
(428) LePage, Y.; McKinnon, W. R.; Tarascon, J. M.; Barboux, P. *Phys. Rev. B* **1989**, *40*, 6810.
(429) Belokoneva, E. L.; Al'shinskaya, L. I.; Simonov, M. A.; Leonyuk, N. I.; Timchenko, T. I.; Belov, N. V. *Zh. Strukt. Khim*. **1979**, *20*, 542 (461).[540]
(430) Morrow, N. L.; Katz, L. *Acta Crystallogr*. **1968**, *B24*, 1466.
(431) Babel, D.; Ruedorff, W.; Tschopp, R. *Z. Anorg. Allg. Chem*. **1966**, *347*, 282.
(432) Hobbie, K.; Hoppe, R. *Z. Anorg. Allg. Chem*. **1986**, *535*, 20.
(433) Abraham, F.; Trehoux, J.; Thomas, D. *Mater. Res. Bull*. **1977**, *12*, 43.
(434) Abraham, F.; Trehoux, J.; Thomas, D. *J. Less-Common Met*. **1981**, *77*, *P*23.
(435) Schwatrz, K. B.; Parise, J. B.; Prewitt, C. T.; Shannon, R. D. *Acta Crystallogr*. **1982**, *B38*, 2109.
(436) Burns, P. C.; Howthorne, F. C.; MacDonald, D. J.; Ventura, G.; Parodi, G. C. *Can. Miner*. **1993**, *31*, 147.
(437) Parise, J. B.; Gier, T. E. *Chem. Mater*. **1992**, *4*, 1065.
(438) Chenavas, J.; Grey, I. E.; Guitel, J. C.; Joubert, J. C.; Marezio, M.; Remeika, J. P.; Cooper, A. S. *Acta Crystallogr*. **1981**, *B37*, 1343.
(439) Smith, R. W.; Keszler, D. A. *J. Solid State Chem*. **1992**, *100*, 325.
(440) Smith, R. W.; Koliha, L. J. *Mater. Res. Bull*. **1994**, *29*, 1203.
(441) Ihara, M.; Kamei, F. *J. Ceram. Soc. Jpn*. **1980**, *88*, 32.
(442) Tu, J. M.; Kezler, D. A. *Mater. Res. Bull*. **1995**, *30*, 209.
(443) Buerger, M. J.; Taxer, K. *Science* **1966**, *152*, 500.
(444) Jansen, M.; Scheld, W. *Z. Anorg. Allg. Chem*. **1981**, *477*, 85.
(445) Martinez-Ripoll, M.; Marrinez-Carrera, S.; Garcia-Blanco, S. *Acta Crystallogr*. **1971**, *B27*, 677.
(446) Smith, P.; Garcia-Blanco, S.; Rivoir, L. *Z. Kristallogr*. **1964**, *119*, 375.
(447) Hong, H. Y. P.; Dwight, K. *Mater. Res. Bull*. **1974**, *9*, 1661.
(448) Depmeier, W.; Schmid, H. *Acta Crystallogr*. **1982**, *B38*, 605.
(449) Miklos, D.; Smrcok, L.; Durovic, S.; Gyepesova, D.; Handlovic, M. *Acta Crystallogr*. **1992**, *C48*, 1831.
(450) Belokoneva, E.; Azizov, A. V.; Leonyuk, N. I.; Simonov, M. A.; Belov, N. V. *Zh. Strukt. Khim*. **1981**, *22*, 196 (476).[540]
(451) Pushcharovskii, D. Y.; Karpov, O. G.; Leonyuk, N. I.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 91.
(452) Belokoneva, E.; Pashkova, A. V.; Timchenko, T. I.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1981**, *261*, 361.
(453) Kuroda, R.; Mason, S. F.; Rosini, C. *J. Chem. Soc. Faraday Trans. 2* **1981**, *77*, 2125.
(454) Kasanskaja, E. V.; Sandomirskii, P. A.; Simonov, M. A.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1340.
(455) Norrestam, R.; Carlson, S.; Sjoedin, A. *Acta Crystallogr*. **1994**, *C50*, 1847.
(456) Chem, C. T.; Wang, Y. B.; Wu, B. C.; Wu, K. C.; Zeng, W. I.; Yu, L. H. *Nature* **1995**, *373*, 322.
(457) Belokoneva, E.; Alshinskaya, L. I.; Simonov, M. A.; Leonyuk, N. I.; Timchenko, T.; Belov, N. V. *Zh. Strukt. Khim*. **1978**, *19*, 382 (332).[540]
(458) Jansen, M.; Hoppe, R. *Z. Anorg. Allg. Chem*. **1974**, *408*, 97.
(459) Gopal, R.; Rutherford, J. S.; Robertson, B. E. *J. Solid State Chem*. **1980**, *32*, 29.
(460) Kimata, M. *Naturwissenschaften* **1982**, *69*, 40.
(461) Durriet, B.; Devalette, M.; Lacart, B. *Rev. Chim. Miner*. **1977**, *14*, 423.
(462) Sabrowsky, H.; Hoppe, R. *Z. Anorg. Allg. Chem*. **1968**, *358*, 241.
(463) Hoppe, R.; Losert, W. *Z. Anorg. Allg. Chem*. **1985**, *521*, 69.
(464) Migeon, H.; Zanne, M.; Gleitzer, C.; Courtois, A. *J. Solid State Chem*. **1976**, *16*, 325.
(465) Losert, T.; Hoppe, R. *Z. Anorg. Allg. Chem*. **1985**, *524*, 7.
(466) Garbauskas, M. F.; Arendt, R. H.; Kasper, J. S. *Inorg. Chem*. **1987**, *26*, 3191.
(467) Marezio, M. *Acta Crystallogr*. **1965**, *19*, 396.
(468) Antipov, E.; Luzikova, A. V. *Z. Anorg. Allg. Chem*. **1993**, *619*, 889.
(469) Bartl, H.; Scheller, T. *Nues Jahrb. Miner*. **1970**, *1970*, 547.
(470) Takeachi, Y.; Nishi, F.; Moki, I. *Z. Kristallogr*. **1980**, *152*, 299 (259).[540]
(471) Kimata, M. *Z. Kristallogr*. **1984**, *167*, 103.
(472) Ponomanev, V. I.; Kheiker, D. M.; Belov, N. V. *Kristallografiya* **1970**, *15*, 918 (799).[540]
(473) Schulz, H. *Z. Kristallogr*. **1971**, *134*, 253.
(474) Grimes, N.; Thompson, P.; Kay, H. F. *Proc. R. Acad. London* **1983**, *A386*, 333.
(475) Kuz′micheva, G. M.; Mukhin, B. V.; Rybakov, V. B.; Denisov, A. L.; Zharikov, E. V.; Smirnov, V. A. *Zh. Neorg. Khim*. **1995**, *40*, 569 (548).[540]
(476) Meyer, H.; Mueller-Buschbaum, H. K. *Monatsh. Chem*. **1981**, *112*, 51.
(477) Saalfeld, H.; Klaska, K. H. *Z. Kristallogr*. **1985**, *172*, 129.

(478) Iyi, N.; Inoue, Z.; Takekawa, S.; Kimura, S. *J. Solid State Chem.* **1985**, *60*, 41.
(479) Schlueter, D.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1993**, *197*, 51.
(480) Kahn, A.; Thery, J. *J. Solid State Chem.* **1986**, *64*, 102.
(481) Schlueter, D.; Mueller-Buschbaum, H. K. *J. Alloys Compd.* **1993**, *191*, 305.
(482) Stewner, F.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1971**, *381*, 140.
(483) Belekoneva, E. L.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **191**, *260*, 1363.
(484) Mill′, B. V.; Batushin, A. V.; Holzhabajan, K. V.; Belokoneva, E. L.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1982**, *264*, 1385.
(485) Korczak, P.; Reiaz, F. *Anz. Oesterr. Akad. Wiss. Math.—Naturwiss. Kl.* **1967**, *104*, 383.
(486) Kaminskii, A. A.; Mill′, B. V.; Belokonova, E. L.; Khodzhabagyan, G. G. *Neorg. Mater.* **1983**, *19*, 1762.
(487) Kaminskii, A. A.; Belokoneva, E. L.; Mill, B. V.; Pisarevskii, Y. V.; Sarkisov, S. E.; Silvestrova, I. M.; Butashin, A. V.; Khoszhabagyan, G. G. *Phys. Status Solidi A* **1984**, *86*, 345.
(488) Yudin, A. N.; Pobedinskaya, E. A.; Terent′eva, L. E.; Petrova, I. V.; Kaplunnik, L. N.; Malakhava, G. V. *Neorg. Mater.* **1989**, *25*, 1715.
(489) Radaev, S. F.; Muradyan, L. A.; Kargin, Y. F.; Sarin, V. A.; Rider, E. E.; Simonov, V. I. *Dokl. Akad. Nauk SSSR* **1989**, *34*, 407.
(490) Wagner, K.; Hoppe, R. *J. Less-Common Met.* **1986**, *116*, 129.
(491) Abrahams, S. C.; Bernstein, J. L.; Svensson, C. *J. Chem. Phys.* **1979**, *71*, 788.
(492) Pagnoux, C.; Verbaere, A.; Kanno, Y.; Piffard, Y.; Tournoux, M. *J. Solid State Chem.* **1992**, *99*, 173.
(493) Modaressi, A.; Gerardin, R.; Malaman, B.; Gleitzer, M. *J. Solid State Chem.* **1984**, *53*, 22.
(494) Radaev, S. F.; Muradyan, L. A.; Kargin, Y. F.; Sarin, V. A.; Kanepit, V. N.; Simonov, V. I. *Kristallografiya* **1990**, *35*, 361 (204).
(495) Smolin, Y. I. *Dokl. Akad. Nauk SSSR* **1968**, *181*, 595.
(496) Svensson, C.; Abrahams, S. C.; Bernstein, J. L. *Acta Crystallogr.* **1979**, *B35*, 2687.
(497) Belokoneva, E. L.; Mill′, B. V.; Butashin, A. V. *Zh. Neorg. Khim.* **1992**, *37*, 2435 (1256).[540]
(498) Vincent, H.; Turrillas, X.; Rasines, I. *Mater. Res. Bull.* **1987**, *22*, 1369.
(499) Marcano, C. M.; Rasines, I.; Vegas, A.; Otero-Diaz, L. C. *Z. Anorg. Allg. Chem.* **1987**, *555*, 176.
(500) Cascales, C.; Marcano, M.; Rasines, I.; Fernandez, F.; Saez-Puche, L. *J. Less-Common Met.* **1989**, *149*, 63.
(501) Rannev, N. V. *Kristallografiya* **1984**, *29*, 790.
(502) Kirik, S. D.; Kutuitski, V. A.; Kuryagini, T. I. *Zh. Strukt. Khim.* **1985**, *26*, 90 (569).[540]
(503) Teichert, A.; Mueller-Buschbaum, H. K. *Z. Anorg. Allg. Chem.* **1991**, *598*, 319.
(504) Panek, P.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1973**, *400*, 224.
(505) Stoever, H. D.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1980**, *468*, 137.
(506) Delicat, U.; Radaev, S. F.; Troemel, M.; Behrens, P.; Kargin, Y. F.; Marin, A. A. *J. Solid State Chem.* **1994**, *110*, 66.
(507) Kim, J. S.; Tang, X. X.; Manthiram, A.; Swinnea, J. S.; Steinfink, H. *J. Solid State Chem.* **1990**, *85*, 44.
(508) Martens, K. P. *Z. Anorg. Allg. Chem.* **1977**, *437*, 116.
(509) Troemel, M.; Huetzler, F. W.; Burckhardt, H. G.; Platte, C.; Muench, E. *Z. Anorg. Allg. Chem.* **1987**, *551*, 95.
(510) Frit, B. *C. R. Acad. Sci. Paris* **1975**, *281*, 769.
(511) Troeml, M.; Huetzler, F. W.; Burkhardt, H. G.; Platt, C.; Muench, E. *Z. Anorg. Allg. Chem.* **1987**, *551*, 95.
(512) Kemmler-Sack, S. *Z. Anorg. Allg. Chem.* **1968**, *358*, 226.
(513) Mueller-Buschbaum, H. K.; Lang, C. *J. Less-Common Met.* **1988**, *142*, L1.
(514) Schnering, H. G. von; Hoppe, R.; Zemann, J. *Z. Anorg. Allg. Chem.* **1960**, *305*, 241.
(515) Harris, L. A.; Yakel, H. L. *Acta Crystallogr.* **1966**, *20*, 295.
(516) Zentgraf, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1980**, *462*, 80.
(517) Haradem, P. S.; Chamberland, B. L.; Katz, L.; Gleizes, A. *J. Solid State Chem.* **1977**, *21*, 217.
(518) Braun, R. M.; Hoppe, R. *Z. Naturforsch.* **1982**, *37*, 688.
(519) Harris, L. A.; Yakel, H. L. *Acta Crystallogr.* **1969**, *B25*, 1647.
(520) Hoppe, R.; Roehrborn, H. J. *Naturwissenschaften* **1962**, *49*, 419.
(521) Evans, H. T. *Acta Crystallogr.* **1951**, *4*, 377.
(522) Shirane, G.; Pepinsky, R.; Frazier, B. C. *Acta Crystallogr.* **1956**, *9*, 131.
(523) Stoll, H.; Brazel, B.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1988**, *564*, 45.
(524) Bortz, M.; Jansen, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1446.
(525) Grice, J. D. *Can. Miner.* **1989**, *27*, 133.
(526) Plattner, E.; Voellenkle, H. *Monatsh. Chem.* **1977**, *108*, 443.
(527) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137.
(528) den Boer, D. H. W.; Longuet-Higgens, H. C. *Mol. Phys.* **1962**, *5*, 387.
(529) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 1252.
(530) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947.
(531) Kunz, M.; Brown, I. D. *J. Solid State Chem.* **1995**, *115*, 395.
(532) Goodenough, J. B.; Longo, J. M.: Crystallographic and magnetic properties of perovskite and perovskite-related compounds. In *Landolt-Bornstein*; Hellwege, K. H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1970; Vol. 4, pp 126—314.
(533) Orgel, L. E. *Trans. Faraday Soc.* **1958**, *26*, 138.
(534) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.
(535) Wilson, A. J. C. *Z. Kristallogr.* **1991**, *197*, 85.
(536) Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118.
(537) Belokoneva, E. L.; Arakcheeva, A. V.; Simonov, M. A.; Belov, N. V. *Kristallografiya* **1976**, *21*, 303 (163).[540]
(538) Abrahams, S. C.; Bernstein, J. C. *J. Phys. Chem. Solids* **1967**, *28*, 1685.
(539) Froehlich, R. *Z. Kristallogr.* **1984**, *168*, 109.
(540) For Russian journals, the page number of the English translation (if known) is given in parentheses.
(541) Hussain, A. *Chem. Scr.* **1977**, *11*, 224.

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