Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Formability of ABX_3 (X = F, Cl, Br, I) halide perovskites

Chonghea Li,* Xionggang Lu, Weizhong Ding, Liming Feng, Yonghui Gao and Ziming Guo

Shanghai Key Laboratory of Modern Metallurgy and Materials Processingï, Shanghai University, Shanghai 200072, People's Republic of China

Correspondence e-mail: chli@staff.shu.edu.cn

Received 30 July 2008
Accepted 10 October 2008

In this study a total of 186 complex halide systems were collected; the formabilities of ABX_3 (X = F, Cl, Br and I) halide perovskites were investigated using the empirical structure map, which was constructed by Goldschmidt's tolerance factor and the octahedral factor. A model for halide perovskite formability was built up. In this model obtained, for all 186 complex halides systems, only one system (CsF–MnF_2) without perovskite structure and six systems (RbF–PbF_2, CsF–BeF_2, KCl–$FeCl_2$, TlI–MnI_2, RbI–SnI_2, TlI–PbI_2) with perovskite structure were wrongly classified, so its predicting accuracy reaches 96%. It is also indicated that both the tolerance factor and the octahedral factor are a necessary but not sufficient condition for ABX_3 halide perovskite formability, and a lowest limit of the octahedral factor exists for halide perovskite formation. This result is consistent with our previous report for ABO_3 oxide perovskite, and may be helpful to design novel halide materials with the perovskite structure.

1. Introduction

Most monovalent A^+ and divalent B^{2+} ions can form a complex halide with the stoichiometry ABX_3 (X = F, Cl, Br, I), which in turn often possess the perovskite structure (Muller & Roy, 1974). The perovskite structure is generally described as a three-dimensional arrangement of a corner-sharing octahedral BX_6 unit (which forms the ReO_3-structure type; Hagenmuller, 1985), with the A ion placed in the cuboctahedral interstices. In the ideal case, this structure is cubic (Wang & Kang, 1998), as seen in Fig. 1.

Perovskite and perovskite-related halides are important crystal structures as they possess a number of interesting properties, such as electron-acceptor behavior; a large optical transmission domain; high resistivity; antiferromagnetic; exceptional magnetic; piezoelectric; photoluminescent properties; anionic conductivity over a wide temperature range (Sarukura *et al.*, 2007; Zhang *et al.*, 2008). For example, Sarukura suggested (Sarukura *et al.*, 2007) that some of the more promising candidates of the wide-band-gap fluorides may match the need to explore new materials for deep ultraviolet (DUV) and vacuum ultraviolet (VUV) optical devices. Fluorides as well as their doped analogues have found wide applicability as components of high-density optical devices, lenses, biological labels, sensors and insulators (Bender *et al.*, 2000; Lian *et al.*, 2004; Singh *et al.*, 2005). The ternary metal fluorides, possessing cubic perovskite structures with the chemical formula $AMnF_3$ (A = K, NH_4, Rb, Tl, Cs), are antiferromagnetic, so these materials have generated considerable interest owing to their exceptional magnetic,

doi:10.1107/S0108768108032734

piezoelectric and photoluminescent properties (Laguna *et al.*, 1993; Pilla *et al.*, 1995; Zhao *et al.*, 1997; Kapusta *et al.*, 2000).

It is of interest to discover regularities governing the formation of halide perovskites and to use them to further guide the exploration of new materials. In the early 1920s, Goldschmidt (1927) proposed a 'tolerance factor'

$$t = (r_A + r_X)/(2^{1/2}[r_B + r_X]), \qquad (1),$$

where r_A, r_B and r_X are the ionic radii for the ions in the A, B and X sites, respectively, to study the stability of ABX_3 perovskites. Afterwards, Goldschmidt's tolerance factor was widely accepted as a criterion for the formation of the perovskite structure; a number of investigators have used it to discuss the perovskite stability, including oxides, fluorides and chlorides. Up to now, almost all known perovskites have t values in the range 0.75–1.00. However, it seems that t = 0.75–1.00 is not a sufficient condition for the formation of the perovskite structure, as indicated in our previous work for oxides (Li *et al.*, 2004), as for some systems with t within the most favourable range (0.8–0.9) no perovskite structure is stable.

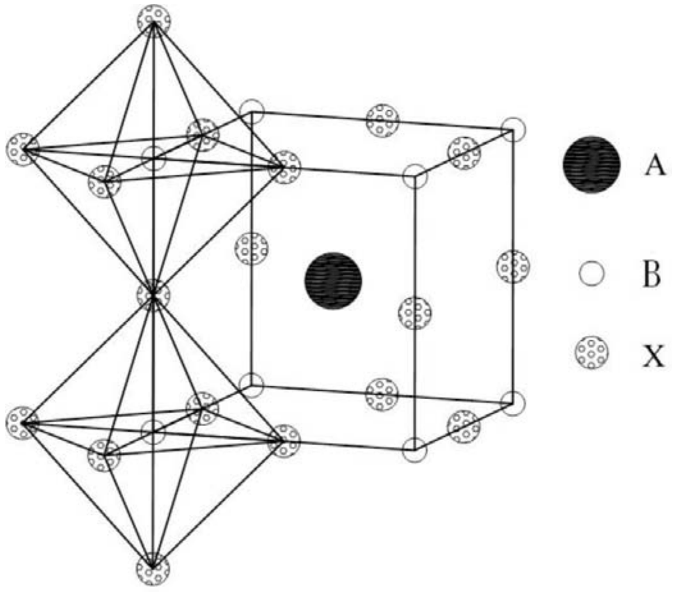

Figure 1
Cubic perovskite structure of ABX_3.

Therefore, lots of researchers made efforts to build up models predicting the perovskite formability. Muller & Roy (1974) proposed plotting a 'structural map' which took the ionic radii of A and B as coordinates to study the distribution of different crystal structures for $A^{\rm I}B^{\rm V}$O$_3$ and $A^{\rm II}B^{\rm IV}$O$_3$ and $A^{\rm III}B^{\rm III}$O$_3$ systems separately. Although Muller & Roy's (1974) $r_A - r_B$ structural map has proven useful for gross structural separation, the regions bordering different structural types are not well defined (Giaquinta & Loye, 1994). In order to solve this problem, Giaquinta & Loye (1994) proposed a new structural map predominantly for the A_2O$_3$–B_2O$_3$ group, which relies on the combination of ionic radii and bond ionicities. Lufaso & Woodward (2001) developed the software program *SPuDS* to predict the crystal structures of perovskites, which distorts the structure to minimize the global instability index, while maintaining rigid octahedra. In China, a group of scientists (Ye *et al.*, 2002) used the pattern recognition–atomic parameter method to study the regularities of perovskite formation. Their model contains seven atomic parameters, including the radii of ions A and B, the electronegativities of ion A and ion B, and the d electron number of ion B.

Most of the investigations mentioned above regarding the formability of perovskites are concentrated on oxides; few reports on halides can be found. In our previous works (Li *et al.*, 2004; Feng *et al.*, 2008), a newly defined octahedral factor (the radius ratio of the small cation B over the anion O for octahedral BO$_6$) is proposed and applied to construct a new and effective structural map with the tolerance factor leading to new criteria of the formability of oxide perovskites. In this study we try to use the same tolerance factor–octahedral structure-map method to explore the regularities governing the formation of halide perovskites and further build up the prediction models.

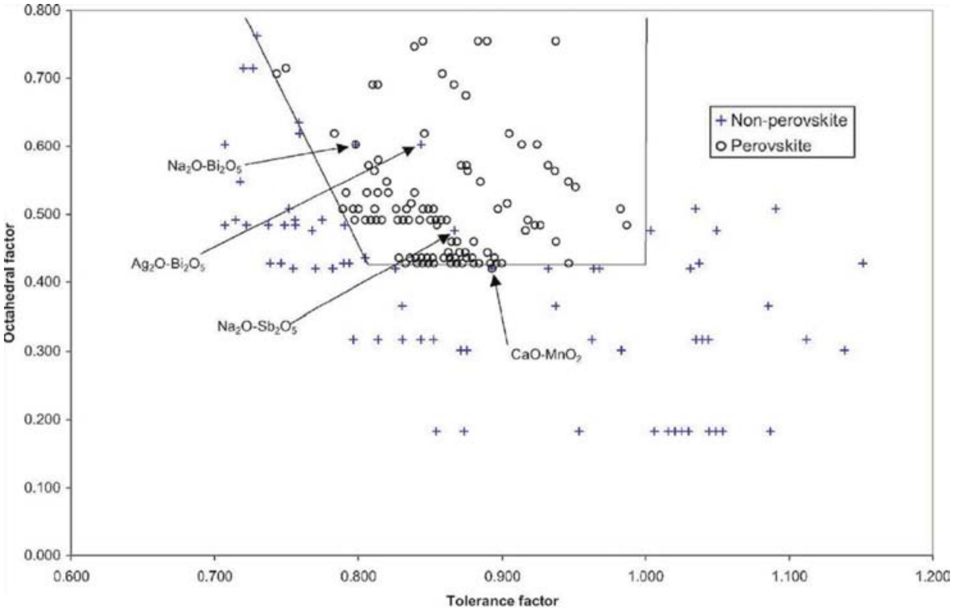

Figure 2
Classification of perovskite compounds ABO$_3$ in the t–μ structure map.

2. Tolerance factor–octahedral structure-map method

In order to understand the tolerance factor–octahedral structure-map method better, a brief introduction about this method is given here.

As detailed earlier, Goldschmidt's tolerance factor '*t*' is not by itself sufficient to predict the formation, or not, of the perovskite structure. An additional indicator is needed and the octahedra of the ReO_3 type (part of the structure) is a logical additional parameter. We use the ratio of the ionic radius of *B* and *X* atoms as an 'octahedral factor (μ)' given by

$$\mu = r_B/r_X. \qquad (2)$$

So it is natural to construct a structural map by the tolerance factor and the octahedral factor to study the perovskite formability. In previous works (Li *et al.*, 2004; Feng *et al.*, 2008), this two-dimensional structure map was used to investigate the regularities of formability for the general perovskite and cubic perovskite ABO_3, good results were obtained. As shown in Fig. 2 for the general perovskite, all perovskites and non-perovskites are located in two different regions and a clear border between the two types of compound is identified.

3. Data collection of halides ABX_3

A total of 186 pseudo-binary halide systems (Chen, 1985; Inorganic Crystal Structure Database, 2004; The American Ceramic Society, 2005) have been studied and are listed in Table 1. We have limited our investigation to structures that are stable at ambient temperature and pressure, and that have normal ionic occupation. In the 186 systems, 78 systems (denoted 'yes') are found to have the perovskite structure, 108 systems (denoted 'no') do not have the perovskite structure and represent at least one of the following three conditions:

(1) there are no new ternary compounds;

(2) there are new ternary compounds, but they are not halides with the chemical formula ABX_3;

(3) there is at least one ABX_3 compound, but it is not a perovskite structure.

In order to list these systems systematically, we list the systems first on the radius of the *X*-site anion, then the *A*-site ion, and finally on the *B*-site cation, as seen in Table 1. With this arrangement, it can be seen that '*t*' decreases systematically for the 'Rb' compounds as the radius in the *B*-site increases and r_B/r_X increases as expected. The same is true for 'K', 'Ag' and 'Tl', respectively.

A total of 186 pseudo-binary halide systems with their formability, the radii of the *A*-, *B*- and *X*-site ions, the tolerance factor and the octahedral factor are listed in Table 1. The ionic radii used here are from the original data of Shannon (1976); values from Rohere (2001) and Lide (1999) have also been used. Based on the perovskite crystal, the values of the *A* site of the 12-coordinate structure, the *B* site of the six-coordinated structure and the *X* site of the (2 + 4)-coordinated structure are used to calculate the tolerance factor and the octahedral factor. For some *A*-site ions, whose radius of the 12-coordinated structure are absent in the Shannon scale, the values were extrapolated by Zachariasen's relationship between ionic radius and coordination number (Zachariasen, 1978).

Table 1

Formability, tolerance factor and octahedral factor of 186 pseudo-binary halide systems.

No.	Systems	Formability	r_A	r_B	r_X	t	μ
Fluoride							
1[a]	LiF–MgF$_2$	No	1.13	0.72	1.33	0.849	0.541
2[a]	LiF–ZnF$_2$	No	1.13	0.74	1.33	0.840	0.556
3[a]	LiF–MnF$_2$	No	1.13	0.83	1.33	0.805	0.624
4[a]	LiF–CaF$_2$	No	1.13	1.00	1.33	0.747	0.752
5[a]	LiF–PbF$_2$	No	1.13	1.19	1.33	0.690	0.895
6[b]	NaF–NiF$_2$	Yes	1.39	0.69	1.33	0.952	0.519
7[b]	NaF–MgF$_2$	Yes	1.39	0.72	1.33	0.938	0.541
8[b]	NaF–CuF$_2$	Yes	1.39	0.73	1.33	0.934	0.549
9[b]	NaF–ZnF$_2$	Yes	1.39	0.74	1.33	0.929	0.556
10[b]	NaF–CoF$_2$	Yes	1.39	0.745	1.33	0.927	0.560
11[b]	NaF–FeF$_2$	Yes	1.39	0.78	1.33	0.912	0.586
12[c]	NaF–VF$_2$	Yes	1.39	0.79	1.33	0.907	0.594
13[b]	NaF–CrF$_2$	Yes	1.39	0.80	1.33	0.903	0.602
14[b]	NaF–MnF$_2$	Yes	1.39	0.83	1.33	0.890	0.624
15[a]	NaF–CdF$_2$	No	1.39	0.95	1.33	0.844	0.714
16[a]	NaF–CaF$_2$	No	1.39	1.00	1.33	0.825	0.752
17[a]	NaF–PbF$_2$	No	1.39	1.19	1.33	0.763	0.895
18[a]	NaF–BaF$_2$	No	1.39	1.35	1.33	0.718	1.01
19[b]	AgF–CoF$_2$	Yes	1.49	0.65	1.33	1.007	0.489
20[b]	AgF–NiF$_2$	Yes	1.49	0.69	1.33	0.987	0.519
21[b]	AgF–MgF$_2$	Yes	1.49	0.72	1.33	0.973	0.541
22[b]	AgF–ZnF$_2$	Yes	1.49	0.74	1.33	0.963	0.556
23[b]	AgF–MnF$_2$	Yes	1.49	0.83	1.33	0.923	0.624
24[a]	AgF–PbF$_2$	No	1.49	1.19	1.33	0.791	0.895
25[b]	KF–CoF$_2$	Yes	1.64	0.65	1.33	1.061	0.489
26[b]	KF–NiF$_2$	Yes	1.64	0.69	1.33	1.040	0.519
27[b]	KF–MgF$_2$	Yes	1.64	0.72	1.33	1.024	0.541
28[b]	KF–CuF$_2$	Yes	1.64	0.73	1.33	1.019	0.549
29[b]	KF–ZnF$_2$	Yes	1.64	0.74	1.33	1.015	0.556
30[b]	KF–FeF$_2$	Yes	1.64	0.78	1.33	0.995	0.586
31[b]	KF–VF$_2$	Yes	1.64	0.79	1.33	0.991	0.594
32[b]	KF–CrF$_2$	Yes	1.64	0.80	1.33	0.986	0.602
33[b]	KF–MnF$_2$	Yes	1.64	0.83	1.33	0.972	0.624
34[b]	KF–CdF$_2$	Yes	1.64	0.95	1.33	0.921	0.714
35[b]	KF–CaF$_2$	Yes	1.64	1.00	1.33	0.901	0.752
36[b]	KF–HgF$_2$	Yes	1.64	1.02	1.33	0.894	0.767
37[a]	KF–BaF$_2$	No	1.64	1.35	1.33	0.784	1.015
38[b]	TlF–CoF$_2$	Yes	1.70	0.65	1.33	1.082	0.489
39[b]	TlF–CuF$_2$	Yes	1.70	0.73	1.33	1.040	0.549
40[b]	TlF–FeF$_2$	Yes	1.70	0.78	1.33	1.015	0.586
41[b]	TlF–CrF$_2$	Yes	1.70	0.80	1.33	1.006	0.602
42[b]	TlF–MnF$_2$	Yes	1.70	0.83	1.33	0.992	0.624
43[b]	TlF–CdF$_2$	Yes	1.70	0.95	1.33	0.940	0.714
44[c]	RbF–BeF$_2$	No	1.72	0.45	1.33	1.212	0.338
45[b]	RbF–CoF$_2$	Yes	1.72	0.65	1.33	1.089	0.489
46[b]	RbF–CuF$_2$	Yes	1.72	0.73	1.33	1.047	0.549
47[b]	AgF–CuF$_2$	Yes	1.72	0.73	1.33	1.047	0.549
48[b]	RbF–ZnF$_2$	Yes	1.72	0.74	1.33	1.042	0.556
49[b]	RbF–FeF$_2$	Yes	1.72	0.78	1.33	1.022	0.586
50[b]	RbF–VF$_2$	Yes	1.72	0.79	1.33	1.017	0.594
51[b]	RbF–CrF$_2$	Yes	1.72	0.80	1.33	1.013	0.602
52[b]	RbF–MnF$_2$	Yes	1.72	0.83	1.33	0.998	0.624
53[b]	RbF–CdF$_2$	Yes	1.72	0.95	1.33	0.946	0.714
54[b]	RbF–CaF$_2$	Yes	1.72	1.00	1.33	0.926	0.752
55[b]	RbF–HgF$_2$	Yes	1.72	1.02	1.33	0.918	0.767
56[a]	RbF–SrF$_2$	No	1.72	1.18	1.33	0.859	0.887
57[c]	RbF–PbF$_2$	Yes	1.72	1.19	1.33	0.856	0.895
58[c]	CsF–BeF$_2$	Yes	1.88	0.45	1.33	1.275	0.338
59[c]	CsF–MgF$_2$	Yes	1.88	0.72	1.33	1.107	0.541
60[c]	CsF–MnF$_2$	No	1.88	0.83	1.33	1.051	0.624
61[b]	CsF–CdF$_2$	Yes	1.88	0.95	1.33	0.996	0.714
62[b]	CsF–CaF$_2$	Yes	1.88	1.00	1.33	0.974	0.752
63[b]	CsF–HgF$_2$	Yes	1.88	1.02	1.33	0.966	0.767
64[b]	CsF–SrF$_2$	Yes	1.88	1.18	1.33	0.904	0.887
65[c]	CsF–PbF$_2$	Yes	1.88	1.19	1.33	0.901	0.895
66[a]	CsF–BaF$_2$	No	1.88	1.35	1.33	0.847	1.015
Chloride							
67[a]	LiCl–BeCl$_2$	No	1.13	0.45	1.81	0.920	0.249

Table 1 (continued)

No.	Systems	Formability	r_A	r_B	r_X	t	μ
68[a]	LiCl–NiCl$_2$	No	1.13	0.69	1.81	0.832	0.381
69[a]	LiCl–MgCl$_2$	No	1.13	0.72	1.81	0.822	0.398
70[a]	CuCl–ZnCl$_2$	No	1.13	0.74	1.81	0.815	0.409
71[a]	LiCl–VCl$_2$	No	1.13	0.79	1.81	0.800	0.436
72[a]	LiCl–CrCl$_2$	No	1.13	0.80	1.81	0.797	0.442
73[a]	CuCl–CdCl$_2$	No	1.13	0.95	1.81	0.753	0.525
74[a]	CuCl–CaCl$_2$	No	1.13	1.00	1.81	0.740	0.552
75[a]	LiCl–CaCl$_2$	No	1.13	1.00	1.81	0.740	0.552
76[a]	LiCl–PbCl$_2$	No	1.13	1.19	1.81	0.693	0.657
77[a]	LiCl–BaCl$_2$	No	1.13	1.35	1.81	0.658	0.746
78[a]	NaCl–BeCl$_2$	No	1.39	0.45	1.81	1.001	0.249
79[a]	NaCl–NiCl$_2$	No	1.39	0.69	1.81	0.905	0.381
80[a]	NaCl–ZrCl$_2$	No	1.39	0.72	1.81	0.894	0.398
81[a]	NaCl–ZnCl$_2$	No	1.39	0.74	1.81	0.887	0.409
82[a]	NaCl–CrCl$_2$	No	1.39	0.80	1.81	0.867	0.442
83[a]	NaCl–MnCl$_2$	No	1.39	0.83	1.81	0.857	0.459
84[a]	NaCl–CdCl$_2$	No	1.39	0.95	1.81	0.820	0.525
85[a]	NaCl–CaCl$_2$	No	1.39	1.00	1.81	0.805	0.552
86[a]	NaCl–SnCl$_2$	No	1.39	1.10	1.81	0.778	0.608
87[a]	NaCl–SrCl$_2$	No	1.39	1.18	1.81	0.757	0.652
88[a]	NaCl–PbCl$_2$	No	1.39	1.19	1.81	0.754	0.657
89[a]	NaCl–BaCl$_2$	No	1.39	1.35	1.81	0.716	0.746
90[a]	AgCl–MgCl$_2$	No	1.49	0.72	1.81	0.922	0.398
91[a]	AgCl–CaCl$_2$	No	1.49	1.00	1.81	0.830	0.552
92[a]	AgCl–SnCl$_2$	No	1.49	1.10	1.81	0.802	0.608
93[a]	KCl–BeCl$_2$	No	1.64	0.45	1.81	1.079	0.249
94[b]	KCl–NiCl$_2$	No	1.64	0.69	1.81	0.976	0.381
95[a]	KCl–ZrCl$_2$	No	1.64	0.72	1.81	0.964	0.398
96[c]	KCl–MgCl$_2$	No	1.64	0.72	1.81	0.964	0.398
97[c]	KCl–FeCl$_2$	Yes	1.64	0.78	1.81	0.942	0.431
98[b]	KCl–MnCl$_2$	Yes	1.64	0.83	1.81	0.924	0.459
99[c]	KCl–CdCl$_2$	Yes	1.64	0.95	1.81	0.884	0.525
100[b]	KCl–CaCl$_2$	Yes	1.64	1.00	1.81	0.868	0.552
101[a]	KCl–SrCl$_2$	No	1.64	1.18	1.81	0.816	0.652
102[a]	KCl–SmCl$_2$	No	1.64	1.22	1.81	0.805	0.674
103[a]	KCl–BaCl$_2$	No	1.64	1.35	1.81	0.772	0.746
104[a]	TlCl–BeCl$_2$	No	1.70	0.45	1.81	1.098	0.249
105[a]	TlCl–MgCl$_2$	No	1.70	0.72	1.81	0.981	0.398
106[a]	TlCl–ZnCl$_2$	No	1.70	0.74	1.81	0.973	0.409
107[b]	TlCl–MnCl$_2$	Yes	1.70	0.83	1.81	0.940	0.459
108[c]	TlCl–CdCl$_2$	Yes	1.70	0.95	1.81	0.899	0.525
109[a]	TlCl–EuCl$_2$	No	1.70	1.17	1.81	0.833	0.646
110[a]	TlCl–SrCl$_2$	No	1.70	1.18	1.81	0.830	0.652
111[a]	TlCl–PbCl$_2$	No	1.70	1.19	1.81	0.827	0.657
112[a]	RbCl–BeCl$_2$	No	1.72	0.45	1.81	1.104	0.249
113[c]	RbCl–MgCl$_2$	No	1.72	0.72	1.81	0.987	0.398
114[a]	RbCl–ZnCl$_2$	No	1.72	0.74	1.81	0.979	0.409
115[c]	RbCl–CoCl$_2$	No	1.72	0.745	1.81	0.977	0.412
116[a]	RbCl–FeCl$_2$	No	1.72	0.78	1.81	0.964	0.431
117[c]	RbCl–CrCl$_2$	Yes	1.72	0.80	1.81	0.956	0.442
118[c]	RbCl–MnCl$_2$	Yes	1.72	0.83	1.81	0.945	0.459
119[c]	RbCl–CdCl$_2$	Yes	1.72	0.95	1.81	0.904	0.525
120[b]	RbCl–CaCl$_2$	Yes	1.72	1.00	1.81	0.888	0.552
121[a]	RbCl–EuCl$_2$	No	1.72	1.17	1.81	0.838	0.646
122[a]	RbCl–SrCl$_2$	No	1.72	1.18	1.81	0.835	0.652
123[b]	CsCl–NiCl$_2$	No	1.88	0.69	1.81	1.044	0.381
124[b]	CsCl–MgCl$_2$	No	1.88	0.72	1.81	1.031	0.398
125[c]	CsCl–GeCl$_2$	No	1.88	0.73	1.81	1.027	0.403
126[a]	CsCl–ZnCl$_2$	No	1.88	0.74	1.81	1.023	0.409
127[c]	CsCl–CoCl$_2$	No	1.88	0.745	1.81	1.021	0.412
128[b]	CsCl–FeCl$_2$	No	1.88	0.78	1.81	1.007	0.431
129[b]	CsCl–VCl$_2$	No	1.88	0.79	1.81	1.004	0.436
130[b]	CsCl–CrCl$_2$	No	1.88	0.80	1.81	1.000	0.442
131[b]	CsCl–MnCl$_2$	Yes	1.88	0.83	1.81	0.988	0.459
132[b]	CsCl–CdCl$_2$	Yes	1.88	0.95	1.81	0.945	0.525
133[b]	CsCl–CaCl$_2$	Yes	1.88	1.00	1.81	0.929	0.552
134[b]	CsCl–HgCl$_2$	Yes	1.88	1.02	1.81	0.922	0.564
135[c]	CsCl–SnCl$_2$	Yes	1.88	1.10	1.81	0.897	0.608
136[c]	CsCl–EuCl$_2$	Yes	1.88	1.17	1.81	0.876	0.646
137[b]	CsCl–SrCl$_2$	Yes	1.88	1.18	1.81	0.873	0.652
138[b]	CsCl–PbCl$_2$	Yes	1.88	1.19	1.81	0.870	0.657
139[a]	CsCl–BaCl$_2$	No	1.88	1.35	1.81	0.826	0.746
Bromide							
140[a]	LiBr–MgBr$_2$	No	1.13	0.72	1.96	0.815	0.367
141[a]	LiBr–CoBr$_2$	No	1.13	0.745	1.96	0.808	0.380
142[a]	LiBr–CaBr$_2$	No	1.13	1.00	1.96	0.738	0.510
143[a]	LiBr–SrBr$_2$	No	1.13	1.18	1.96	0.696	0.602
144[a]	LiBr–PbBr$_2$	No	1.13	1.19	1.96	0.694	0.607
145[a]	LiBr–BaBr$_2$	No	1.13	1.35	1.96	0.660	0.689
146[a]	NaBr–MgBr$_2$	No	1.39	0.72	1.96	0.884	0.367
147[a]	NaBr–CdBr$_2$	No	1.39	0.95	1.96	0.814	0.485
148[a]	NaBr–CaBr$_2$	No	1.39	1.00	1.96	0.800	0.510
149[a]	NaBr–SrBr$_2$	No	1.39	1.18	1.96	0.754	0.602
150[a]	NaBr–BaBr$_2$	No	1.39	1.35	1.96	0.716	0.689
151[a]	AgBr–CdBr$_2$	No	1.49	0.95	1.96	0.838	0.485
152[a]	AgBr–PbBr$_2$	No	1.49	1.19	1.96	0.774	0.607
153[a]	KBr–CoBr$_2$	No	1.64	0.745	1.96	0.941	0.380
154[a]	KBr–BaBr$_2$	No	1.64	1.35	1.96	0.769	0.689
155[b]	RbBr–NiBr$_2$	No	1.72	0.69	1.96	0.982	0.352
156[c]	RbBr–MnBr$_2$	No	1.72	0.83	1.96	0.933	0.423
157[c]	RbBr–CdBr$_2$	Yes	1.72	0.95	1.96	0.894	0.485
158[a]	RbBr–BaBr$_2$	No	1.72	1.35	1.96	0.786	0.689
159[b]	CsBr–NiBr$_2$	No	1.88	0.69	1.96	1.025	0.352
160[c]	CsBr–MnBr$_2$	No	1.88	0.83	1.96	0.973	0.423
161[c]	CsBr–TiBr$_2$	No	1.88	0.86	1.96	0.963	0.439
162[b]	CsBr–CdBr$_2$	Yes	1.88	0.95	1.96	0.933	0.485
163[b]	CsBr–HgBr$_2$	Yes	1.88	1.02	1.96	0.911	0.520
164[b]	CsBr–SnBr$_2$	Yes	1.88	1.10	1.96	0.887	0.561
165[b]	CsBr–PbBr$_2$	Yes	1.88	1.19	1.96	0.862	0.607
166[a]	CsBr–BaBr$_2$	No	1.88	1.35	1.96	0.820	0.689
Iodide							
167[a]	CuI–CdI$_2$	No	1.10	0.95	2.2	0.741	0.432
168[a]	LiI–MgI$_2$	No	1.13	0.72	2.2	0.806	0.327
169[a]	LiI–MnI$_2$	No	1.13	0.83	2.2	0.777	0.377
170[a]	NaI–MgI$_2$	No	1.39	0.72	2.2	0.869	0.327
171[a]	NaI–CdI$_2$	No	1.39	0.95	2.2	0.806	0.432
172[a]	NaI–CaI$_2$	No	1.39	1.00	2.2	0.793	0.455
173[a]	NaI–HgI$_2$	No	1.39	1.02	2.2	0.788	0.464
174[a]	KI–MgI$_2$	No	1.64	0.72	2.2	0.930	0.327
175[a]	KI–CoI$_2$	No	1.64	0.745	2.2	0.922	0.339
176[a]	KI–MnI$_2$	No	1.64	0.83	2.2	0.896	0.377
177[a]	KI–CdI$_2$	No	1.64	0.95	2.2	0.862	0.432
178[a]	KI–HgI$_2$	No	1.64	1.02	2.2	0.843	0.464
179[c]	TlI–MnI$_2$	Yes	1.70	0.83	2.2	0.910	0.377
180[c]	TlI–PbI$_2$	Yes	1.70	1.19	2.2	0.813	0.541
181[a]	RbI–MgI$_2$	No	1.72	0.72	2.2	0.949	0.327
182[a]	RbI–MnI$_2$	No	1.72	0.83	2.2	0.915	0.377
183[c]	RbI–SnI$_2$	Yes	1.72	1.10	2.2	0.840	0.500
184[a]	CsI–MgI$_2$	No	1.88	0.72	2.2	0.988	0.327
185[c]	CsI–MnI$_2$	No	1.88	0.83	2.2	0.952	0.377
186[b]	CsI–SnI$_2$	Yes	1.88	1.10	2.2	0.874	0.500

References: (*a*) The American Ceramic Society (2005); (*b*) Chen (1985); (*c*) Inorganic Crystal Structure Database (2004).

4. Results and discussion

A structure map for ABX_3 complex halides is illustrated in Fig. 3. The distribution of perovskites and non-perovskites can be seen in this figure. The perovskites and non-perovskites are located in different areas: compounds with perovskite structure are in the central zone, compounds without perovskite structure are in the outer zone, and a clear boundary exists between the two types of compound.

Out of all the 186 complex halides systems, only one system (CsF–MnF$_2$), which cannot form a perovskite structure, is wrongly classified into the perovskite area; six systems (RbF–PbF_2, CsF–BeF_2, KCl–$FeCl_2$, TlI–MnI_2, RbI–SnI_2, TlI–PbI_2), which have the perovskite structure, are located outside the indicated perovskite region. As seen in Fig. 3, approximately 96% of the perovskites studied are included in our models. Although RbF–PbF_2 and KCl–$FeCl_2$ are wrongly distributed into the non-perovskite area, they are close to the border. $TlMnI_3$ possesses a very low value for the octahedral factor μ (0.377); it is a perovskite, but is wrongly classified into the non-perovskite zone. This may be traced back to the large polarizability of the I^- cation (Rohere, 2001). The I^- ion may change shape into an ellipsoid because of the attraction of the cation. The 'real' radius then becomes small and the value of μ increases. It is not clear why $CsBeF_3$ adopts a perovskite structure, with a value of μ (0.338) which is also small.

It is interesting to discuss the effect of tolerance factor and octahedral factor on the formability of perovskites of complex halides. It is well known (Hagenmuller, 1985) that the tolerance factor is a key factor governing the formability of perovskites of ternary halides, and its value varies in the range 0.76–1.13. The tolerance factors of the ABX_3 perovskites in this study are in the range 0.813–1.107 (excluding the abnormal $CsBeF_3$). As seen in Table 1 and Fig. 3, the two ranges are almost same. It can also be seen from Fig. 3 that a system with a tolerance factor which is too low (< 0.85) or two high (> 1.11) can never form a perovskite structure. However, this does not mean that the system with a suitable tolerance factor definitely has a perovskite structure; in fact, many systems exist with tolerance factors values in this range which cannot form perovskites, as seen in Table 1 and Fig. 3. From the discussion above, it seems that the tolerance factor is a necessary but not sufficient condition for the formation of the perovskite structure in AX–BX_2 complex halide systems.

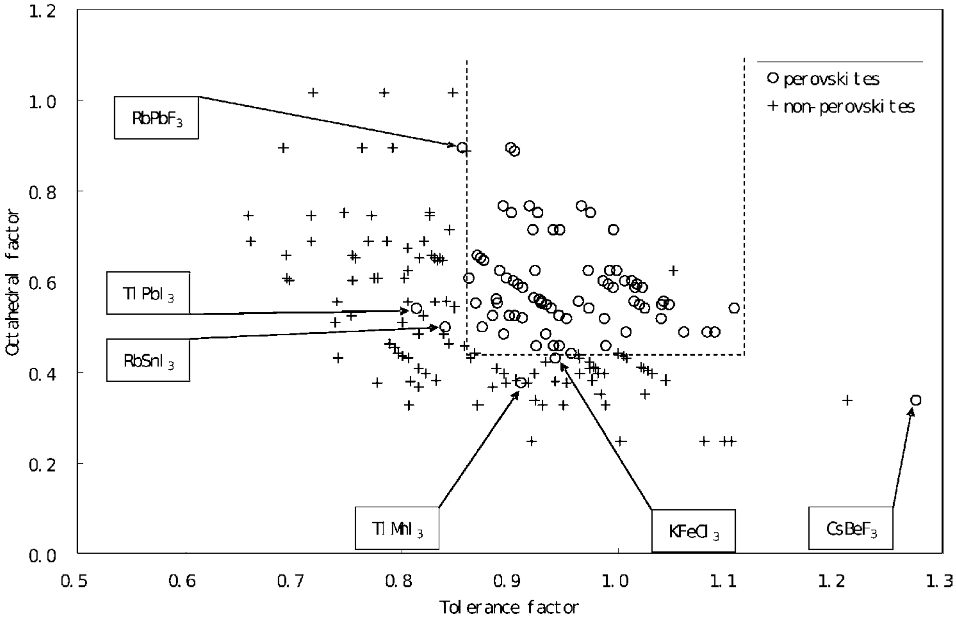

Figure 3
Classification of perovskite compounds ABX_3 in the t–μ structure map.

Next, the focus moves to the octahedral factor. According to the simple model for the ionic bond (Rohere, 2001), if anion X and cation B can form the sixfold coordination octahedral structure BX_6, the radius ratio r_B/r_X should range between 0.414 and 0.732. In fact, the radius ratio value for perovskite halides is between 0.377 and 0.895. If we exclude the two abnormal systems ($TlMnI_3$ and $CsBeI_3$), the ratio varies between 0.442 and 0.895; the two ranges are very similar, as seen in Table 1 and Fig. 3. Similarly, many systems exist in which the values are between 0.414 and 0.732, but they cannot form perovskites. As indicated in Fig. 3, a lowest value of the octahedral factor μ (0.442), if μ < 0.442, actually exists so a stable perovskite cannot be expected even though this system has a very favourable tolerance factor. This may be explained as follows: in perovskites, the BX_6 octahedron is the basic unit; if μ is too small, this unit may become unstable, as does the perovskite. The reported lowest limit of μ for the octahedron (Rohere, 2001) is 0.414, whereas the actual lowest limit of the octahedral factor for halide perovskite formation is 0.442, so these two values agree well. The discussion mentioned above may imply that the octahedral factor μ is also a necessary but not sufficient condition for the formation of the perovskite structure in AX–BX_2 complex halide systems. If one uses these two factors to build the two-dimensional structural map, an efficient predictive model of formability can be obtained, as seen in Fig. 3.

Although there are lots of reports on the formability of perovskites (Muller & Roy, 1974; Goldschmidt, 1927; Li *et al.*, 2004; Giaquinta & Loye, 1994; Lufaso & Woodward, 2001; Ye *et al.*, 2002), most are focused on the oxides, which means that their study only involves the formability of a perovskite with the same anion. The recent research not only extends the scope from oxide to halide, but also deals with the formability of halide perovskites with different anions, including F^-, Cl^-, Br^- and I^- ions. Compared with the previous works, the two parameters used in our model (tolerance factor and octahedral factor) are physically meaningful, and our model gives a simple and effective prediction criterion for the formability of halide perovskites with normal ionic occupation, which may be adopted easily in the design of advanced materials with perovskite structure.

5. Conclusions

In this study, 186 AX–BX_2 pseudo-binary complex halide systems, where A is the monovalent cation, B is the divalent metallic ion and X is a halide ion (F^-, Cl^-, Br^- and I^-), are collected to determine the regularity governing the formability of halide perovskites. Two parameters with physical meaning (tolerance factor and octahedral factor) were used to span the two-dimensional structure map to obtain the criteria of formability of halide perovskites. It was found that both tolerance factor and octahedral factor are necessary but not sufficient conditions for ABX_3 halide perovskite formability; using these two factors to build up a two-dimensional structure map, this formability can be reliably predicted. Approximately 96% of the perovskites studied are included in our model's area for perovskite. The BX_6 octahedron is the basic unit for the perovskite structure. If the octahedral factor μ is too small, this mosaic may become unstable and therefore a lowest limit of the octahedral factor exists for halide perovskite formation.

This research was supported by the Science and Technology Commission of Shanghai Municipality (06XD14032), The National Basic Research Program (973 Program, 2007CB613606), The National High Technology Research and Development Program of China (863 Program, 2006 AA06Z12 and 2006 AA11A189) and The National Funding of Nature Science (NSFC50774052).

References

Bender, C. M., Burlitch, J. M., Barber, D. & Pollock, C. (2000). *Chem. Mater.* **12**, 1969–1976.

Chen, H. C. (1985). *Crystal Chemistry.* Jinan: Shandong Education Press.

Feng, L. M., Jiang, L. Q., Zhu, M., Liu, H. B., Zhou, X. & Li, C. H. (2008). *J. Phys. Chem. Solids*, **69**, 967–974.

Giaquinta, D. M. & Loye, H. C. (1994). *Chem. Mater.* **6**, 365–372.

Goldschmidt, V. M. (1927). *Ber. Dtsch. Chem. Ges.* **60**, 1263–1268.

Hagenmuller, P. (1985). *Inorganic Solid Fluorides.* London: Academic Press, Inc.

Inorganic Crystal Structure Database (2004). CD-ROM, Version 2004. Fiz Karlsruhe, Germany.

Kapusta, J., Daniel, P. & Ratuszna, A. (2000). *Phase Transitions*, **72**, 165–181.

Laguna, M. A., Sanjuán, M. L., Orera, V. M., Rubín, J., Palacios, E., Piqué, M. C., Bartolomé, J. & Berar, J. F. (1993). *J. Phys. Condens. Matter*, **5**, 283–300.

Li, C. H., Soh, K. C. K. & Wu, P. (2004). *J. Alloys Compd*, **372**, 40–48.

Lian, H., Liu, J., Ye, Z. & Shi, C. (2004). *Chem. Phys. Lett.* **395**, 362–365.

Lide, D. R. (1999). *Handbook of Chemistry and Physics*, Electronic Resource. Boca Raton: CRC Press.

Lufaso, M. W. & Woodward, P. M. (2001). *Acta Cryst.* B**57**, 725–738.

Muller, O. & Roy, R. (1974). *The Major Ternary Structural Families.* New York: Springer.

Pilla, O., Freire, P. T. C. & Lemos, V. (1995). *Phys. Rev. B*, **52**, 177–180.

Rohere, G. S. (2001). *Structure and Bonding in Crystalline Materials.* New York: Cambridge University Press.

Sarukura, N., Murakami, H., Estacio, E., Ono, S. G., El Ouenzerfi, R., Cadatal, M., Nishimatsu, T., Terakubo, N., Mizuseki, H., Kawazoe, Y., Yoshikawa, A. & Fukuda, T. (2007). *Opt. Mater.* **30**, 15–17.

Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

Singh, R., Sinha, R. D. P., Kaur, A. & Kumar, J. (2005). *Ferroelectrics*, **329**, 995–1003.

The American Ceramic Society (2005). ACerS-NIST Phase Equilibria Diagrams CD-ROM Database, Version 3.1. The American Ceramic Society, Ohio, USA.

Wang, Z. L. & Kang, Z. C. (1998). *Functional and Smart Materials.* New York: Plenum Press.

Ye, C. Z., Yang, J., Yao, L. X. & Chen, N. Y. (2002). *Chin. Sci. Bull.* **47**, 458–461.

Zachariasen, W. H. (1978). *J. Less-Common Met.* **62**, 1–7.

Zhang, F., Mao, Y., Park, T.-J. & Wong, S. S. (2008). *Adv. Funct. Mater.* **18**, 103–112.

Zhao, C., Feng, S., Xu, R., Shi, C. & Ni, J. (1997). *Chem. Commun.* **10**, 945–946.