Analysis of self-trapped hole mobility in alkali halides and metal halides

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Abstract. The small radius hole polarons (self-trapped holes (STH) known also as the V_k centres) are very common color centers observed in alkali halides and alkaline-earth halides. Their mobility controls the rate of secondary reactions between electron and hole defects and thus radiation stability/sensitivity of materials. We have analysed here the correlation between the temperatures at which hole polarons start migration in a series of alkali halides (fluorites, chlorides, bromides, iodides) and the lattice displacement around X_2^- quasi-molecule. These results are especially important for identification of the self-trapped holes, for example, in novel scintillating materials such as SrI_2, as well as in a large family of perovskite halides and more complex halide materials.

1. Introduction

The mobilities of small radius polarons affect properties of many insulating materials and thus attract considerable attention [1-3]. The self-trapped hole (STH) polarons (called V_k centres), in which a hole is shared by two nearest halogen ions, X_2^-, are very common color centers created in alkali halides, alkaline-earth halides and some other halides under various kinds of irradiation (UV light, electrons, gamma rays, neutrons, heavy swift ions) [4-28] Their mobility controls the rate of secondary reactions between electron and hole defects and thus radiation stability/sensitivity of materials.

The hole polarons start to migrate and recombine above certain onset temperatures (in the range 50-200 K). Their diffusion-controlled decay has been observed by different experimental techniques in almost all alkali halides, as well as in some other binary halides, but also in complex halides, such as perovskite halides, ammonium halides, halide sodalites etc. [8, 11, 12, 15, 23, 25, 26]

In this paper, we review and analyse the STH migration temperatures for a series of alkali halides as a function of halogen-halogen (X-X) distance in a regular crystalline lattice as well as the bond length in isolated X_2^- molecular ions.

2. Analysis of the STH migration

Due to formation of chemical bond, the equilibrium distance of a X_2^- hole polaron is smaller than the distance between two nearest host halogens in perfect crystals and very close to that in a gas-phase molecule [29] (Fig. 1). Above certain temperatures the STH migration occurs via a quasi-molecule reorientation by 60º or 90º (dependent on the f.c.c. or b.c.c. lattice), during which one of the two halogens becomes a common partner in the old and new quasi-molecule (*bond switching*). Application of the small radius polaron theory to the V_k centers [30] has shown that its hopping probability W is expected to be an exponential function of the migration energy E_a

$$W = \nu_0 \exp(-E_a/kT), \tag{1}$$

$$E_a = S\, h\omega/4, \quad S = A\, M\, \omega\, \Delta^2, \tag{2}$$

where ν_0 is a pre-factor, S the so-called Huang-Rhys factor, dependent on the displacement Δ of the halogen from the regular lattice site after formation of the chemical bond (Fig. 1), ω is the LO optical phonon frequency, M the halogen mass, and A pre-factor depending on the reorientation angle (A=0.9 for 60º). The hole delocalization/reorientation occurs when during thermal fluctuations one of halogens in the STH approaches the regular lattice site. Eqs. (1), (2) show that a decrease of displacement Δ lowers the migration energy and hence the onset temperature T_{migr} at which hole migration begins. The latter may be defined by the temperature at which STH performs one jump per second, $W = 1\ s^{-1}$

$$T_{migr} = A\, M\, \omega\, \Delta^2 / 4k \ln \nu_0 \ \sim \Delta^2 \tag{3},$$

i.e. is a quadratic function of the ionic displacement.

Tables 1 to 4 summarize the experimental migration temperatures and inter-halogen distances for different types of crystalline structures – f.c.c., b.c.c., fluorite, and some more complicated structures (wurtzite, layered maltlockite etc) corresponding to four classes of halides – fluorites, chlorides, bromides, and iodides. These literature data are used for analysing the dependence of the migration temperatures on the halogen-halogen distances in the above-mentioned four classes of halogen-containing solids (Figs. 2-5).

As one can see, the migration temperatures show a *linear* dependence on the displacement Δ, rather than the theoretically predicted quadratic one. (The first point with

0K corresponds to the equilibrium distances in free X_2^- molecules.) The reason for this is not clear at the moment. What is more striking is that this linear dependence holds for each class, e.g. fluorides, *irrespective* on the specific lattice structure, e.g. f.c.c. LiF, fluorite CaF_2, perovskite $KMgF_3$. This observation clearly demonstrates that the main factor determining the migration temperature is the lattice displacement.

 These results may be useful in the following cases:

1. Very often thermoluminescence peaks or optical absorption annealing stages are attributed to the self-trapped holes, but it remains unclear, whether it is captured by impurities or self-trapped in a regular lattice. This linear relationship certainly helps to make a more specific conclusion.

2. For STH in complex structures with several halogen-halogen distances, the linear law allows us to estimate the range of lattice sites where the STH could exist. For example, in there are 12 symmetrically distinct I–I ion pairs a novel efficient scintillator SrI_2 [31-33], with a broad range of the distances, 3.9–5.0 Å [32]. From our analysis for the iodides (Fig.5), we expect that migration temperatures of V_k centers in SrI_2 fall into range 50 - 100 K, respectively. Indeed, Yang et al [33] have recently reported thermoluminescence of X-rayed SrI_2:Eu consisting of 9 peaks, between LHeT and RT, including three peaks below 100 K. It is important, however, that the peak at 50 K dominates the thermoluminescence glow curve, which is more than an order of magnitude stronger than any other peak, which is typical for Vk centers in ionic solids. The position of this peak corresponds to the lowest distance among all I–I pairs where the V_k center could be localized.

This analysis indicates how to interpret the thermoluminescence peaks in this and similar complex materials, but also allows conclusions about stable local atomic configurations, in terms of the carrier self-trapping. Moreover, it allows us to understand how to use impurity doping of the material for controling the channels of the electronic excitation relaxation.

   Another example of complex materials is the family of metal fluorohalides, which are important media for X –ray and neutron imaging [35-38]. In BaFCl layered matlockite crystals, only Cl_2^- in-plane configuration was found (see Table 4). Simple analysis of Fig.3 allows one to conclude that V_k in-plane configuration with T_{mig} ~ 130 K [35] fits well the proposed linear relation, and to predict that the V_k migration for out-of-plane configuration (with the distance of 2.72 A close to 2.71 Å in free molecule) could begin at very low temperatures. This is why such Vk centers have not been observed in

commonly used experiments performed above LHeT. We suggest that only experiments at temperatures below LHeT could help to observe this type of defects.

From the viewpoint of scintillator engineering, materials are required with fast hole diffusion (and thus recombination) at room temperatures, which holds for STH with small lattice displacements and thus low delocalization temperatures, e.g. NaI.

3. It is established that V_k centers are produced and well studied in all fluoroperovskites ($KMgF_3$ (Fig. 2), $BaLiF_3$, $KZnF_3$). We have demonstrated here that their thermal stability/ migration follow the same pattern as simple binary halides. This makes it possible to straightforwardly assess the thermal stability of the STH for a wide range of AMX_3 materials. In forthcoming paper we plan to discuss the behavior of V_k centers in more details.

3. Conclusions

A simple linear dependence of the migration temperatures of self-trapped holes in several classes of ionic solids was established as a function of the two halogen atom relaxation constituting the X_2^- quasi-molecule from the regular lattice sites. As demonstrated in the paper, this correlation allows us to identify the STH and their structural configuration in various cases, including the promising scintillating material SrI_2.

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Table 1. Compilation of migration temperature of Vk centers in some metal halides, obtained via thermal annealing of optical absorption, EPR as well as TSL measurements. Alkali halides with NaCl-type lattice Cl-Cl distance = $a/\sqrt{2}=0.707a$, a is the Me-X distance.

Material	Type	Lattice constant	Halogen-halogen distance	T_{migr} (V_k)
LiF	NaCl	4.028	2.8482	125; 150
NaF	NaCl	4.634	3.2767	160; 180
KF	NaCl	5.348	3.7816	175; 210
RbF	NaCl	5.63	3.9810	216
F_2^-			1.90	
LiCl	NaCl	5.14	3.6345	115, 120, 123
NaCl	NaCl	5.64	3.9881	150; 165; 168
KCl	NaCl	6.294	4.4505	205; 208; 210
RbCl	NaCl	6.582	4.6542	220;240
Cl_2^-			2.71	
LiBr	NaCl	5.502	3.8905	122
NaBr	NaCl	5.978	4.2271	115; 134
KBr	NaCl	6.596	4.6641	160; 170;175
RbBr	NaCl	6.89	4.8720	170; 206
Br_2^-			2.90	
LiI	NaCl	6.00	4.2426	
NaI	NaCl	6.474	4.5778	58; 60
KI	NaCl	7.066	4.9964	105;110
RbI	NaCl	7.342	5.192	125
I_2^-			3.28	

Table 2. The same as Table 1 for alkali halides with CsCl-type lattice, Cl-Cl distance = a

Material	Type	Lattice constant	Halogen-halogen distance	T_{migr} (V_k)
CsCl	CsCl	4.123	4.123	202
CsBr	CsCl	4.286	4.286	122; 130
CsI	CsCl	4.5667	4.5667	60 (linear); 85 (jump)
NH$_4$Cl	CsCl	3.8756	3.8756	180
NH$_4$Br	CsCl	4.0594	4.0594	120
TlCl	CsCl	3.8340	3.8340	Not found
TlBr	CsCl	3.97	3.97	Not found
TlI	CsCl	4.108	4.108	Not found

Table 3. The same as table 1 for metal halides with fluorite lattice, F-F distance = a/2=0.5a

Material	Type	Lattice constant	Halogen-halogen distance	T_{migr} (V_k)
CaF_2	CaF_2	5.4626	2.7313	126 K
SrF2	CaF_2	5.800	2.900	110; 120
$SrCl_2$	CaF_2	6.9767	3.488	105
CdF_2	CaF_2	5.3895	2.695	95

Table 4. The same as Table 1 for several other halides with crystalline structures different from those in Tables 1-3.

Material	Type	Lattice constant	Halogen-halogen distance	T_{migr} (V_k)
AgI	wurtzite	a=4.580; c=7.494	a=4.580	Not found
NH_4F	wurtzite	a=4.390; c=7.02	a=4.390	Not found
$KMgF_3$	perovskite	a=3.93	$a/\sqrt{2}=0.707a = 2.78$	110
BaFCl (only Cl_2^-)	layered matlockite		4.11 (in-plane) 2.72 (out-of_plane)	130

Fig.1. Schematic view of the STH in f.c.c. structure, Δ is halogen displacement from the perfect lattice site as a result of the STH formation
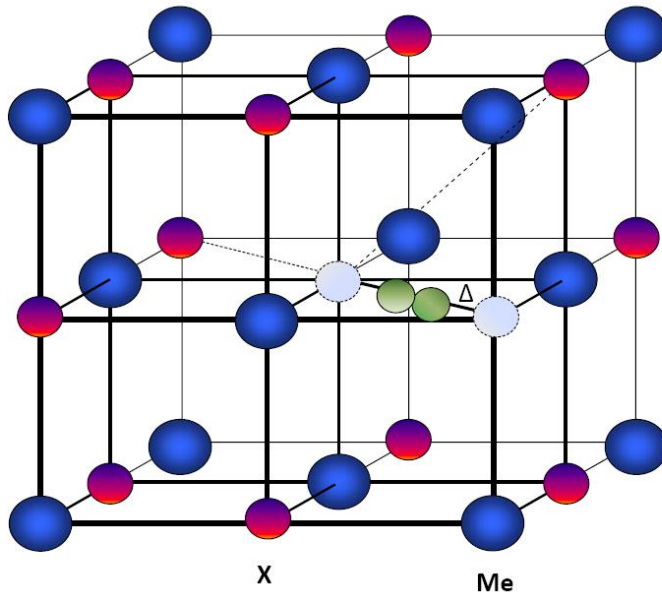

Fig. 2. Dependence of the STH delocalization and migration temperature for a series of fluorides as a function of halogen-halogen distances in the perfect crystal (see table 1)
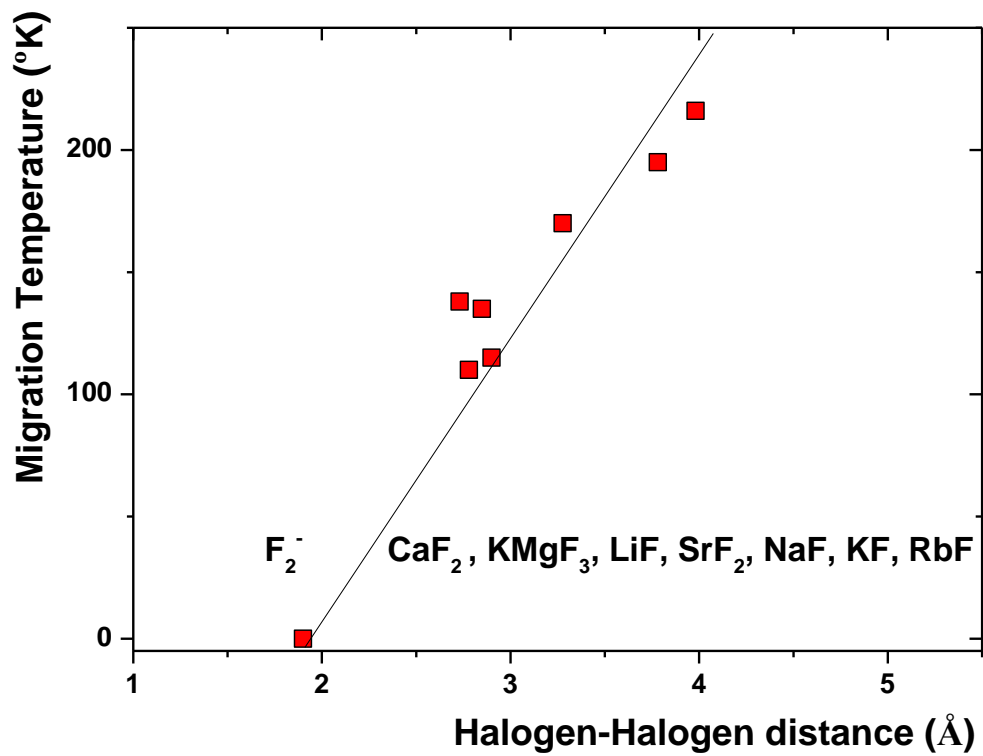
Fig.3. The same as Fig.2 for chlorides,
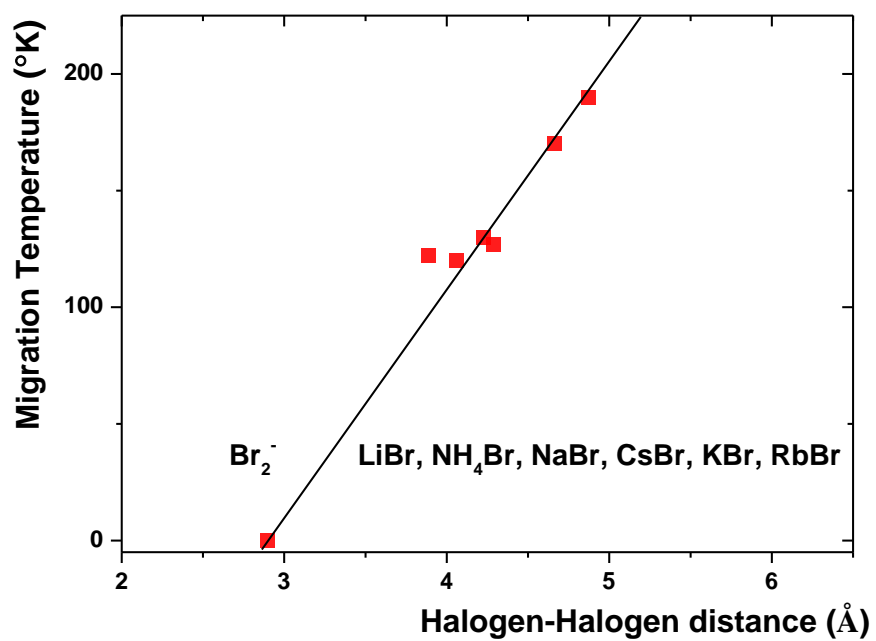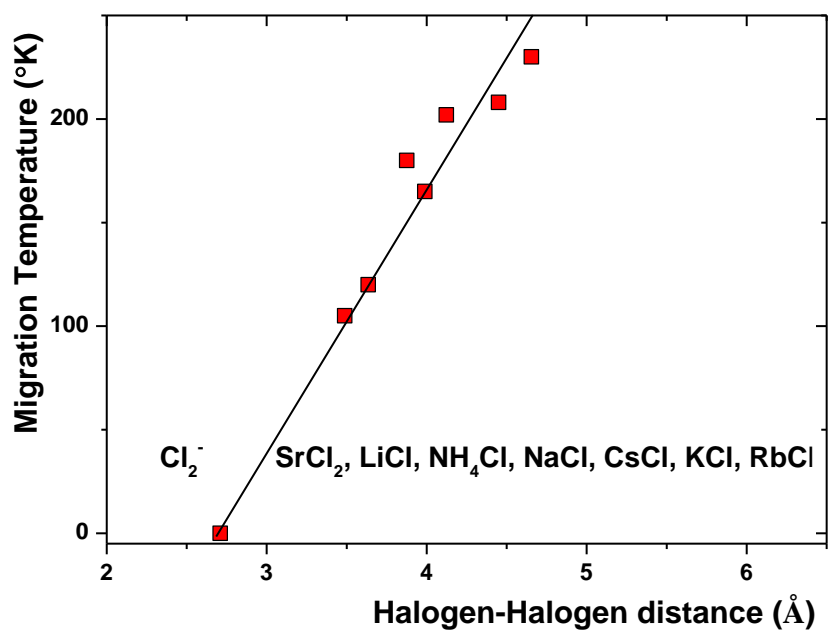**Fig.4**. The same as Fig. 1 for bromides

Fig.5. The same as Fig. 1 for iodides