Supporting Information

Exploring the Influence of Cationic Skeletons on the Arrangement of Isolated BO_3 Groups Based on $RbMgBO_3$, $CsZn_4(BO_3)_3$ and $Cs_4Mg_4(BO_3)_4$

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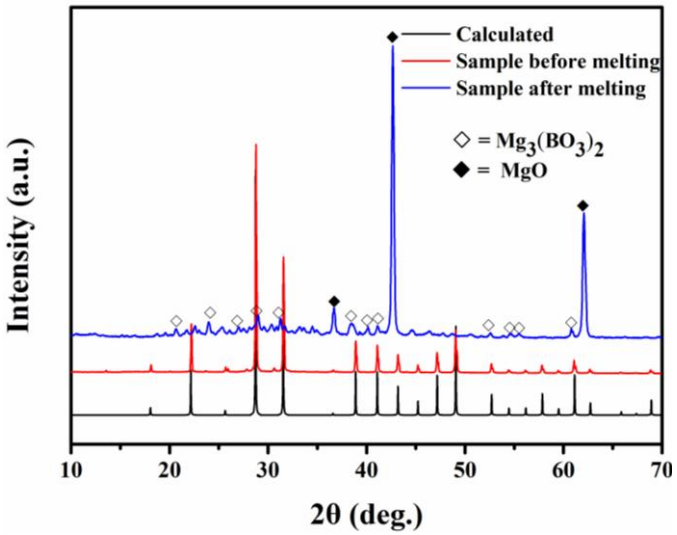
Table S1. Atomic coordinates, equivalent isotropic displacement parameters (Å^2) and bond valence sum (BVS) for RMBO, CZBO and CMB4. *U*(*eq*) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff positions	*x*	*y*	*z*	*U*(*eq*)	BVS
			RMBO			
Rb(1)	4a	0.6086(1)	0.3914(1)	0.8914(1)	0.016(1)	1.29
Mg(1)	4a	0.3904(1)	0.3904(1)	0.3904(1)	0.011(1)	1.79
B(1)	4a	0.6471(4)	0.1471(4)	0.3529(4)	0.011(1)	3.02
O(1)	12b	0.6532(3)	0.2794(2)	0.4989(3)	0.014(1)	2.03
			CZBO			
Cs(1)	2e	1.0000	0.2645(1)	0.2500	0.018(1)	1.07
Zn(1)	4g	0.2116(1)	0.1674(1)	0.5610(1)	0.010(1)	2.08
Zn(2)	4g	0.5126(1)	0.3517(1)	0.3737(1)	0.009(1)	2.00
B(1)	4g	0.8066(9)	0.3421(12)	0.5418(5)	0.009(1)	2.92
B(2)	2f	0.5000	-0.1518(17)	0.2500	0.009(2)	2.98
O(1)	4g	0.7220(6)	0.1979(8)	0.4600(3)	0.014(1)	2.18
O(2)	2f	0.5000	0.1209(11)	0.2500	0.011(1)	1.60
O(3)	4g	0.2700(5)	0.4002(8)	0.4428(3)	0.010(1)	2.19
O(4)	4g	0.5953(6)	0.7109(8)	0.3292(3)	0.013(1)	1.90
O(5)	4g	0. 9543(6)	0. 2441(8)	0. 6020(3)	0.014(1)	2.08
			CMBO			
Cs(1)	4e	0.4428(1)	0.7773(1)	0.9009(1)	0.019(1)	0.99
Cs(2)	4e	0.2716(1)	0.7638(1)	0.6417(1)	0.017(1)	0.98
Cs(3)	4e	0.0572(1)	0.7746(1)	0.4583(1)	0.019(1)	1.02
Cs(4)	4e	0.2283(1)	0.7463(1)	0.8703(1)	0.017(1)	0.91
Mg(1)	4e	0.0591(1)	0.2269(3)	0.7805(2)	0.008(1)	2.04
Mg(2)	4e	0.6551(1)	0.7648(3)	0.9900(2)	0.009(1)	2.06
Mg(3)	4e	0.4415(1)	0.2812(3)	0.7223(2)	0.010(1)	2.01
Mg(4)	4e	0.1553(2)	0.2436(3)	0.6646(2)	0.010(1)	2.03
B(1)	4e	0.8230(5)	0.7674(9)	0.0132(6)	0.008(2)	2.92
B(2)	4e	0.5799(4)	0.2829(10)	0.8841(5)	0.008(1)	2.99

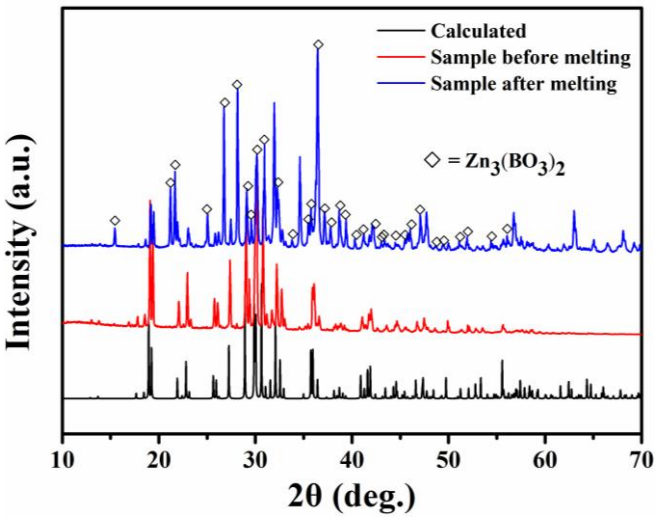
B(3)	4e	0.6769(5)	0.7261(10)	0.1931(6)	0.011(2)	3.05
B(4)	4e	0.0811(4)	0.7245(10)	0.6959(5)	0..10(1)	2.95
O(1)	4e	0.7496(3)	0.7434(6)	0.9928(4)	0.018(1)	1.99
O(2)	4e	0.3700(3)	0.2710(7)	0.7676(4)	0.020(1)	2.05
O(3)	4e	0.2509(3)	0.2708(7)	0.7581(4)	0.019(1)	2.05
O(4)	4e	0.1508(3)	0.2941(8)	0.5488(4)	0.019(1)	2.13
O(5)	4e	0.6503(3)	0.7124(7)	0.1017(3)	0.013(1)	1.99
O(6)	4e	0.4162(2)	0.651(6)	0.6138(2)	0.011(1)	2.10
O(7)	4e	0.6188(2)	0.1371(7)	0.9575(2)	0.018(1)	1.91
O(8)	4e	0.1193(2)	0.8720(7)	0.6614(2)	0.017(1)	1.94
O(9)	4e	0.0835(2)	0.4420(6)	0.6970(2)	0.011(1)	2.10
O(10)	4e	0.0379(2)	0.8514(7)	0.7334(2)	0.013(1)	1.97
O(11)	4e	0.8741(3)	0.7646(7)	0.1018(4)	0.019(1)	1.94
O(12)	4e	0.4616(2)	0.6572(7)	0.6954(2)	0.014(1)	2.04

Table S2. Selected bond lengths (Å) for RMBO, CZBO and CMBO[a].

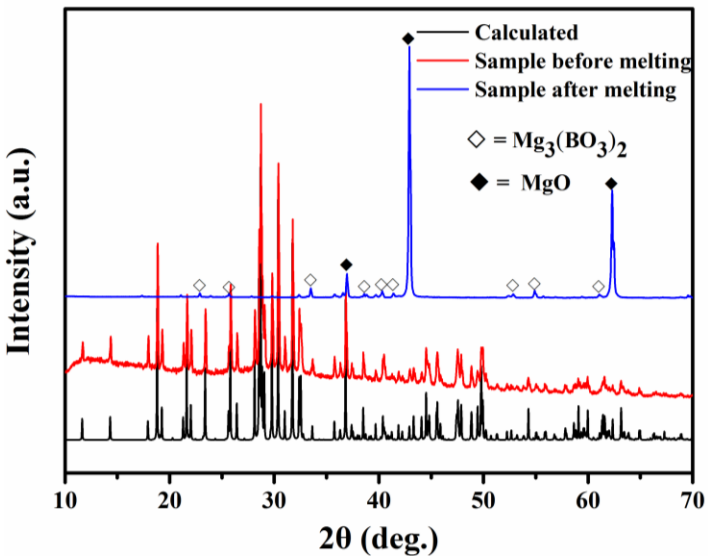
RMBO			
Mg(1)-O(1)#1	2.118(2)	Mg(1)-O(1)#5	2.166(2)
Mg(1)-O(1)	2.118(2	B(1)-O(1)#5	1.3687(18)
Mg(1)-O(1)#2	2.118(2	B(1)-O(1)	1.3687(18)
Mg(1)-O(1)#3	2.166(2)	B(1)-O(1)#18	1.3687(18)
Mg(1)-O(1)#4	2.166(2)		
CZBO			
Zn(1)-O(5)	1.906(5)	Zn(2)-O(4)	1.984(4)
Zn(1)-O(1)#6	1.913(4)	B(1)-O(1)	1.389(7)
Zn(1)-O(3)#1	1.979(4)	B(1)-O(5)	1.345(7)
Zn(1)-O(4)#3	1.998(4)	B(1)-O(3)#11	1.414(7)
Zn(2)-O(3)	1.939(4)	B(2)-O(2)	1.369(10)
Zn(2)-O(1)	1.944(4)	B(2)-O(4)#9	1.378(6)
Zn(2)-O(2)	1.974(3)	B(2)-O(4)#10	1.378(6)
CMBO			
Mg(1)-O(11)#1	1.871(7)	Mg(4)-O(8)	1.946(4)
Mg(1)-O(9)	1.963(4)	Mg(4)-O(9)	1.995(4)
Mg(1)-O(10)	1.970(4)	B(1)-O(4)#2	1.349(10)
Mg(1)-O(10)#9	1.973(4)	B(1)-O(1)	1.384(10)
Mg(2)-O(1)	1.894(6)	B(1)-O(11)	1.412(10)
Mg(2)-O(5)	1.922(6)	B(2)-O(7)	1.353(8)
Mg(2)-O(7)	1.951(4)	B(2)-O(6)#13	1.379(6)
Mg(2)-O(6)#3	1.993(4)	B(2)-O(12)#3	1.387(8)
Mg(3)-O(2)	1.887(6)	B(3)-O(3)#1	1.346(11)
Mg(3)-O(12)#2	1.969(4)	B(3)-O(2)#4	1.358(10)
Mg(3)-O(12)	1.971(4)	B(3)-O(5)	1.394(10)
Mg(3)-O(6)	1.972(4)	B(4)-O(8)	1.345(8)
Mg(4)-O(4)	1.911(6)	B(4)-O(9)#5	1.379(6)
Mg(4)-O(3)	1.926(7)	B(4)-O(10)	1.410(8)



(a)

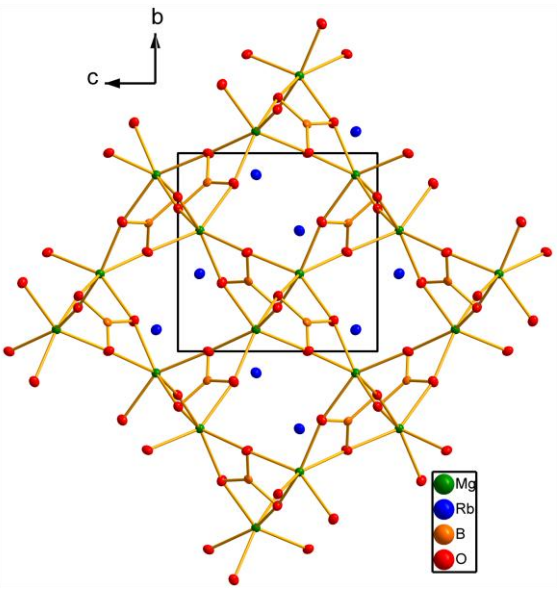


(b)

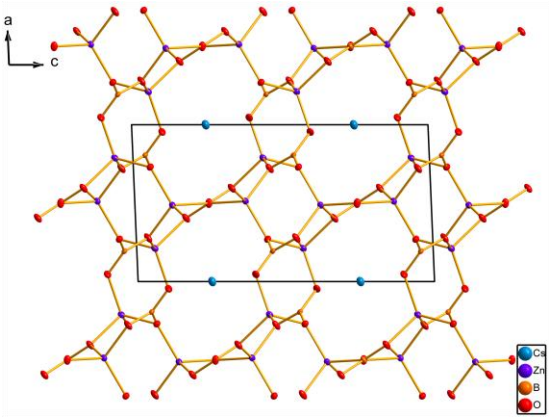


(c)

Figure S1. XRD patterns of (a) RMBO, (b) CZBO and (c) CMBO.



a



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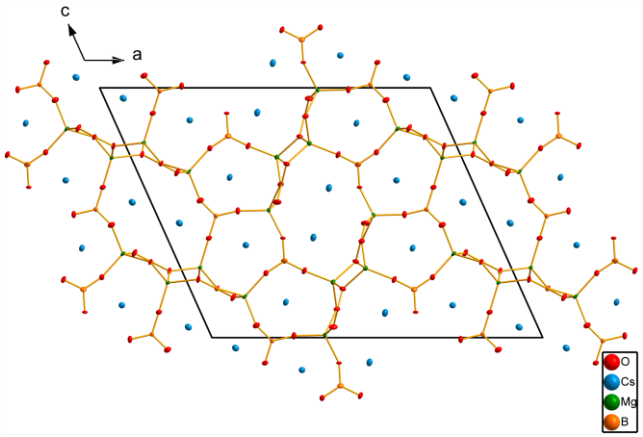

c

Figure S2. The skeletons and the distribution of BO_3 groups in (a)RMBO, (b)CZBO and (c)CMBO. Displacement ellipsoids are drawn at the 50% probability level.

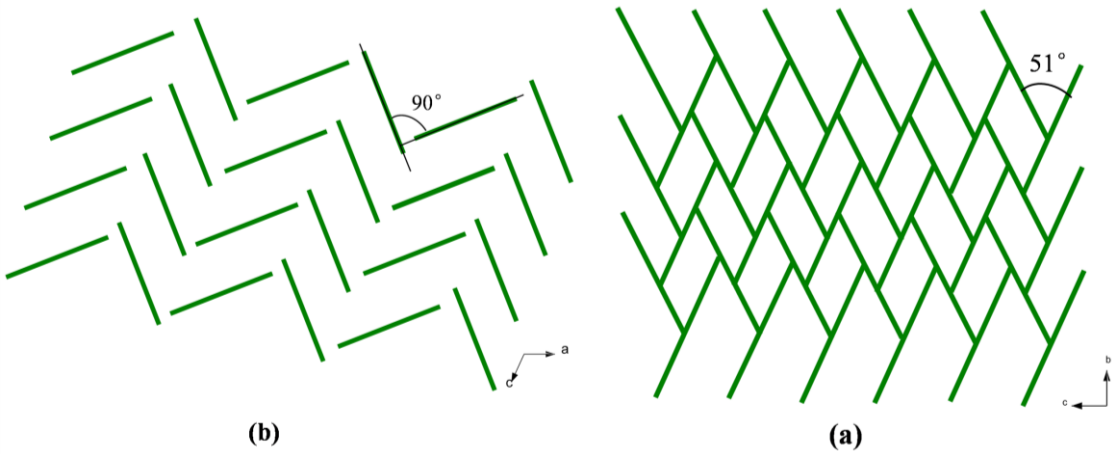

Figure S3. The angles of adjacent chains: (a) CMBO , (b) $Li_{0.8}Mg_{2.1}B_2O_5F$.

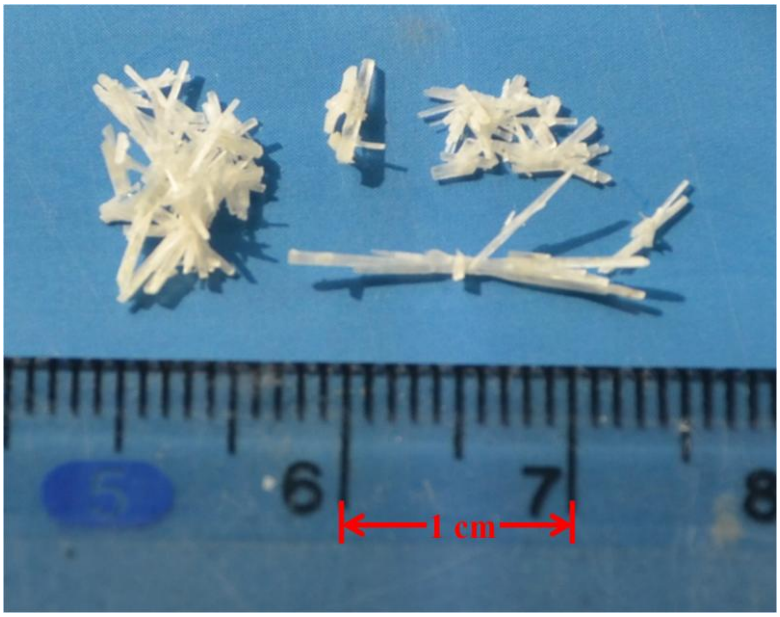

Figure S4. The picture of needlike single crystals of CMBO.

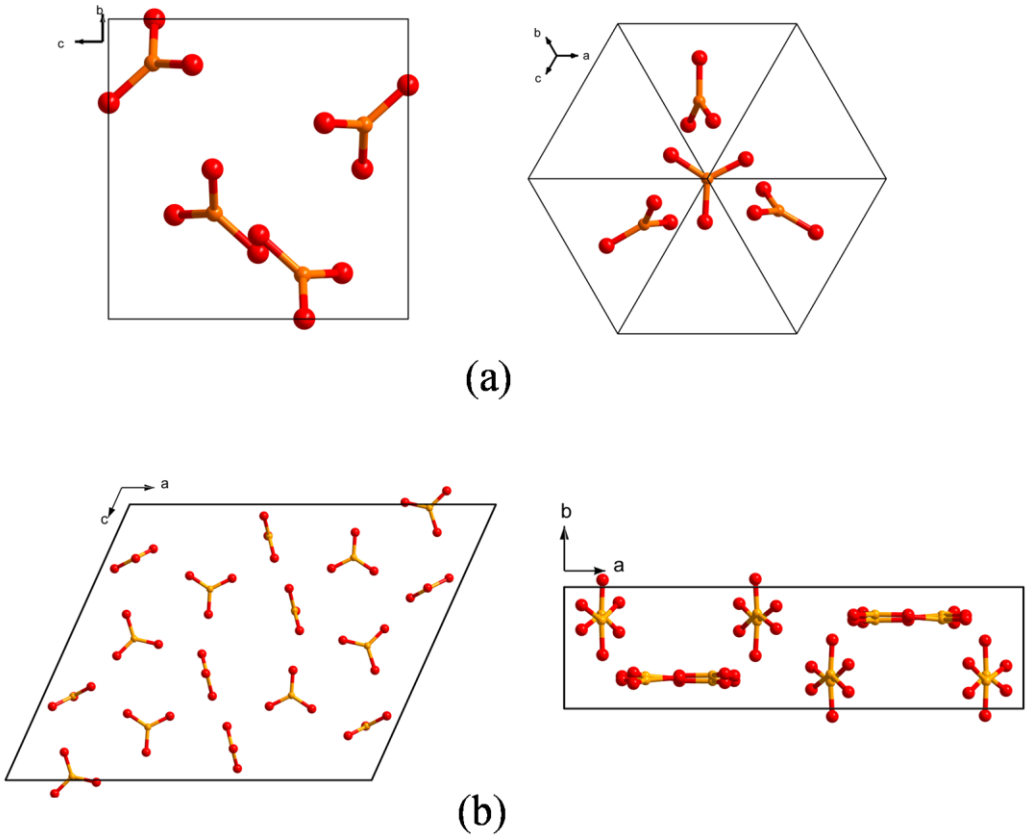

Figure S5. The orientation of isolated BO_3 groups in (a) RMBO and (b) CMBO.

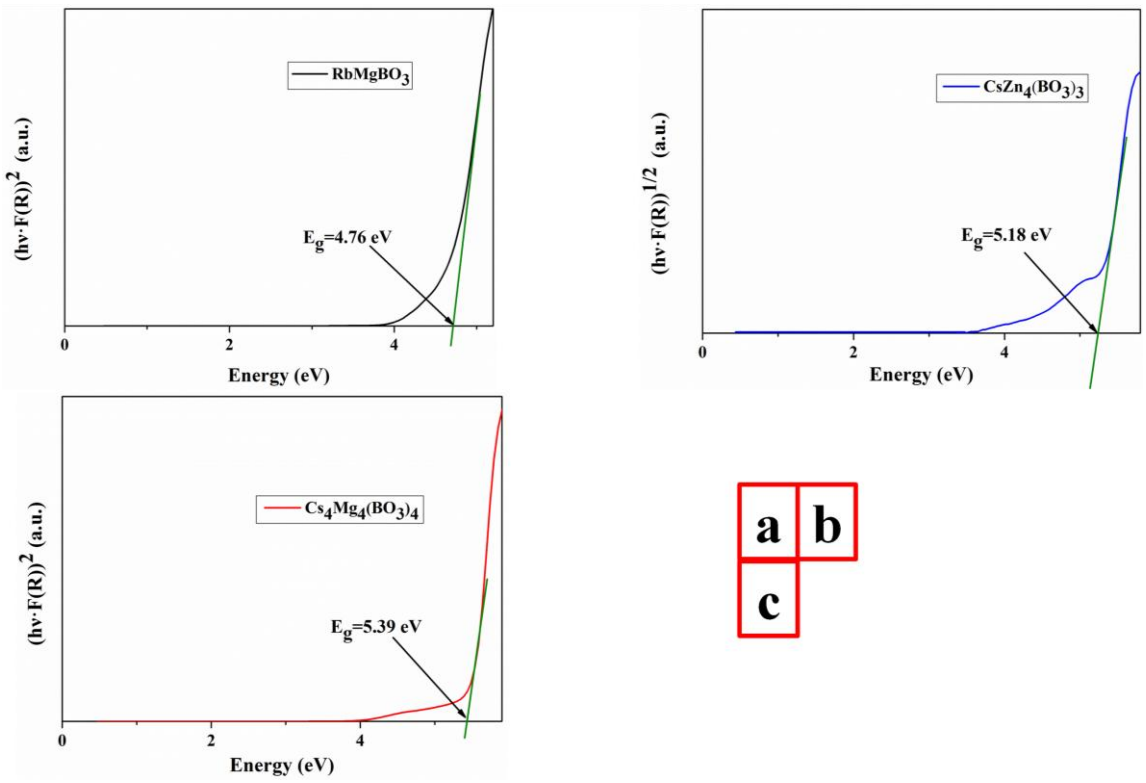

Figure S6. UV-Vis-NIR diffuse reflectance spectra of (a) RMBO, (b) CZBO and (c) CMBO.

SHG Measurements

The SHG test was performed on the powder sample of RMBO by the Kurtz-Perry method[1] on Q-switched Nd:YAG laser. For comparisons, well known SHG materials, KH_2PO_4 (KDP) samples, were used as reference.

RMBO crystallizes in the space group $P2_13$, which belongs to isotropic cubic system and the refractive index of n_x, n_y and n_z is complete equal, so it is non-phasematchable. The SHG measurements on sieved powder samples with 1064 nm radiation reveal that RMBO possesses a SHG response of about 0.5 × KDP (KH_2PO_4) (105-150 μm particle size range) (Figure S7 in the Supporting Information).

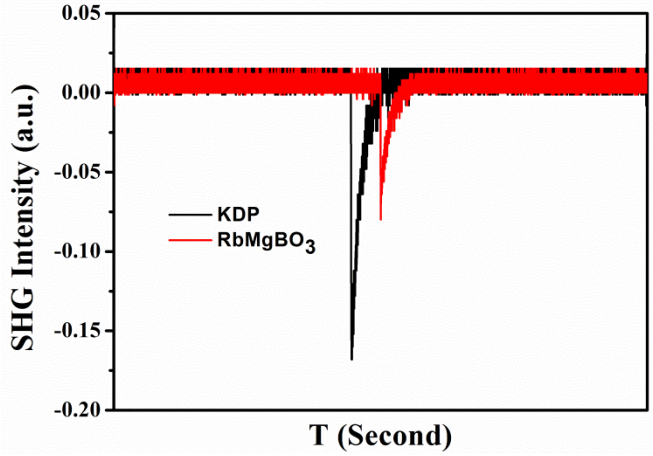

Figure S7. Oscilloscope traces of the SHG signals for the powder (105−150 μm particle size range) of KDP and RMBO.

Reference: 1. S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* 1968, **39**, 3798.