

Identification and synthesis of nonlinear optical materials for practical applications

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ABSTRACT

Organic materials for optical applications have received considerable attention in recent years. A particularly large effort has been placed on organic materials for nonlinear optical applications. Organic materials are of special interest because they have the potential to provide unusually large nonlinear optical effects compared to inorganic materials and they can be designed by molecular modeling techniques. We currently know much about the type of materials that make good NLO materials, but useful materials for optical components have been difficult to find because of light absorption at the wavelengths of interest, symmetric crystal formation, and poor physical properties. For long term space applications, an additional concern is the need for the materials to withstand ionizing radiation. The net effect is that most of the materials that are synthesized are not generally useful. We have involved molecular modeling techniques (quantum mechanics and molecular mechanics) as well as crystal engineering in order to reduce the number of materials that must be synthesized. We have had good success with molecular modeling techniques, but crystal modeling methods still need improvement. In our synthetic work we have put a great deal of emphasis on compounds related to dicyanovinylbenzene because of their processability.

Keywords: nonlinear optics, nitroanilines, dicyanovinylbenzenes, polymorphism.

1. INTRODUCTION

Nonlinear optical materials are of interest because of their potential use in telecommunication and other areas. Organic materials are of special interest because they have the potential to provide unusually large nonlinear optical effects compared to inorganic materials and they can be designed by molecular modeling techniques.

For the purposes of this paper, we will concentrate on some of the materials that have been prepared as part of the project conducted by the Alliance for Nonlinear Optics. The Alliance for Nonlinear Optics is a group, sponsored by NASA, which is working on nonlinear optical phenomena. The group consists of faculty from Alabama A&M University, Grambling State University, New Mexico Highlands University, Spelman College, the University of Alabama in Huntsville, the University of Puerto Rico at Mayaguez, and the University of Texas at El Paso.

2. NITROANILINES

Initially, the group was concerned about prediction of NLO properties. Two members of the group, Beatriz Cardelino and Craig Moore developed an improved calculation procedure for predicting second order NLO responses that they called HYPER¹. At that time, we were concerned about how well the procedure worked on a series of compounds. As a consequence, we initially synthesized a group of substituted nitroanilines, some of which are shown in Table I.

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Table I. Second harmonic generation in 2 and 3 substituted-N,N-dimethylamino-4-nitrobenzenes.

Position		Beta x 10 ⁻⁵¹ SI (Cm ³ V ⁻²)	
2	3	Theoretical ^a	Experimental ^a
-NH ₂		81.6	75.0
	-NH ₂	117.8	80.9
-Cl		94.7	90.7
-CN		101.6	83.5
	-CN	85.2	86.1
-CH ₃		92.5	90.9
	-CH ₃	99.6	84.6
-OCH ₃		74.4	***
	-OCH ₃	118.5	93.0
-NO ₂		72.2	76.6
	-NO ₂	96.1	***

Both experimental and calculated beta values are given in Table I. The theoretical values were calculated by Cardelino and Moore using the HYPER program, and generally, but not always, came within 10% of the experimental values, suggesting that the procedure was good enough to be a useful tool. The EFISH measurements were carried out using an apparatus developed by Dr. Mohan Sanghadasa from our group.

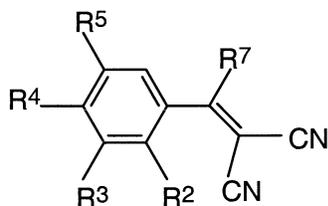
3. DICYANOVINYLBENZENES

Early in our investigations, we concluded that it would be more useful to concentrate on materials with intermediate levels of nonlinearity rather than seek materials with ever-igher beta values. Basically, it was felt that compounds with beta values in the 200 x 10⁻⁵¹ Cm³V⁻² range with superior processability and thermal stability would be more valuable for practical devices than better materials that could not be easily made into devices. Thermal stability under processing conditions was considered to be a key property. Since CVD is the most common procedure for preparation of optical and electronic devices, the materials should be volatile enough to be useful in a vapor deposition process, yet not so volatile that they would sublime away on standing.

While nitroanilines tend to have the best nonlinear optical response, they also tend to be unstable at melt temperatures. Methoxy groups are also strong donor groups and their compounds tend to be more thermally stable than amino groups. Thus they can frequently be used in place of amino groups with only a modest loss in nonlinearity. We have also found that the dicyanovinyl group is often a suitable substitute for the nitro group. While the dicyanovinyl group is not as good as an acceptor group, it has much better thermal stability. As a consequence, we have prepared a large number of compounds containing methoxy and dicyanovinyl groups because of their exceptional stability. Compound II is a well known NLO material². Table II gives a list of some of the molecules containing the dicyanovinyl group that we have prepared. Table III gives a list of some of some similar compounds with an added double bond in the system.

Results of optical measurements on some of these molecules are summarized in Table IV. The experimental results were obtained using an EFISH apparatus developed by Dr. Mohan Sanghadasa from our group. In most cases, the calculated beta values were close to the experimental values. Crystal or powder studies, however, suggest that all of the compounds except the ortho compound are totally inactive because they crystallize in a centrosymmetric manner. Addition of a double bond to the system produces materials that have higher beta values, and that have a greater tendency to crystallize in a more useful manner.

Table II. List of compounds studied in the series of substituted dicyanovinylbenzene and its analogs



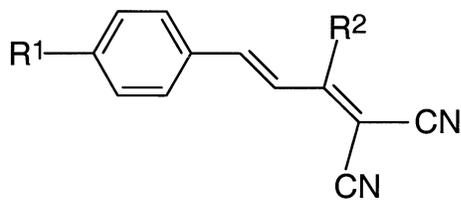
Molecules I-XVII

Molecule	R ²	R ³	R ⁴	R ⁵	R ⁷
I ^a	H	H	H	H	H
II ^a (DIVA)	OMe	H	H	H	H
III ^a	H	OMe	H	H	H
IV ^a	H	H	OMe	H	H
V ^a	OMe	H	OMe	H	H
VI ^a	H	OMe	OMe	H	H
VII ^a	H	OMe	OMe	OMe	H
VIII ^a	H	H	H	H	Ph
IX ^a	OMe	H	H	H	Ph
X	H	H	OMe	H	Ph
XI	NMe ₂	H	H	H	H
XII ^a	H	H	NMe ₂	H	H
XIII ^a	H	H	NEt ₂	H	H
XIV ^a	NO ₂	H	H	H	H
XV ^a	F	H	H	H	H
XVI ^a	Cl	H	H	H	H
XVII ^a	H	H	Cl	H	H

Table III. Dicyanovinyl benzene compounds containing an extra double bond.

Molecules XXVIII-XXIV

Molecule	R ¹	R ²
XVIII ^a	OMe	H
XIX ^a	NMe ₂	H
XX	NEt ₂	H
XXI	OMe	CN
XXII	NMe ₂	CN
XXIII	NEt ₂	CN
XXIV	H	H



^aX-ray structures were studied³⁻⁵

Table IV. Calculated dipole moments (μ , D), second order polarizabilities (β , 10^{-51} Cm³ V⁻²), and crystal space groups with Z for molecules I-XXIV

Molecule	μ (calc)	β (calc)	β (exp)	Sp. Group	Z
I	4.88	16.1	22.75	P2 ₁ /c	4
II	6.81	12.4	18.71	P2 ₁	2
III	5.70	19.4		P2 ₁ ;P-1	6; 4
IV	4.96	42.0	56.49	P2 ₁ /c	4
V	6.56	35.7	76.27	P2 ₁ /n	4
VI	4.87	51.1	78.6		2
VII	3.98	37.9		P2 ₁ /c	4
VIII	4.77	6.5		P2 ₁ /c	4
IX	5.99	7.6		P2 ₁ /n	4
X	5.83	18.5			
XI	5.16	8.5			
XII	7.21	88.6	145.5	P2 ₁	2
XIII	7.65	98.7		P2 ₁ /n	4
XIV	5.86	1.4		P2 ₁ /n	4
XV	4.54	11.3		Pc	2
XVI	5.18	15.2		P2 ₁ /c	4
XVII	3.36	20.5	46.4	P2 ₁	2
XVIII	7.43	103.5	90.9	Pc	2
XIX	7.18	136.5		P2 ₁ /n; P2 ₁ /c	4; 4
XX	8.46	198.7			
XXI	6.02	106.9			
XXII	8.44	256.7			
XXIII	8.52	275.4			
XXIV	5.11	40.9		Pn; P-1	4; 2

Compounds II, III, XII, XV, XVII and XVIII of this series form acentric crystals and among them XII, XVII and XVIII have rather large values of the molecular hyperpolarizabilities and were found to be active in the second harmonic generation of the laser light in solutions and the solid state.

3.1. 4-aryl-1,1-dicyano-(Z)-1,3-butadienes and their derivatives

Variations on the basic dicyanovinyl structure have also been prepared. For example, after preliminary calculations of molecular hyperpolarizability characteristics of a large series of 4-aryl-1,1-dicyano-(Z)-1,3-butadienes (**3a-h**) and their derivatives (**4a-f**) with cyclic oxazole- and thiazole-substituents were synthesized (scheme on the next page). Compounds **4a-f** were obtained from the corresponding compounds **3** by an acylation reaction using halogen substituted ketones with formation of five-membered heterocycles. Molecular and crystal structure of the compounds marked with an asterisk have been investigated by X-ray analysis. EFISH and further X-ray investigations of this series of compounds are still in progress.

4. CRYSTAL ENGINEERING

A major problem in all of the synthetic work is that most molecules tend to crystallize in a centrosymmetric manner. This tendency becomes greater when the molecule is made more polar in order to produce higher beta values. Clearly, in order to make the synthesis process more efficient it will be

necessary to include crystal structure predictions in the original theoretical work done in predicting which molecules to prepare.

Prediction methods for crystal structure are not nearly as well developed as single molecule techniques. One of the problems is that in trying to find the configuration with minimum energy, there are many false minima. Nevertheless, we have had some success by looking at dimer configurations using both a quantum mechanical and a molecular mechanics approach. For example, for several dicyanovinyl derivatives we minimized the energy of the dimers with different molecular orientations. The relative energies of these dimers (kcal/mol) are shown in Table V.

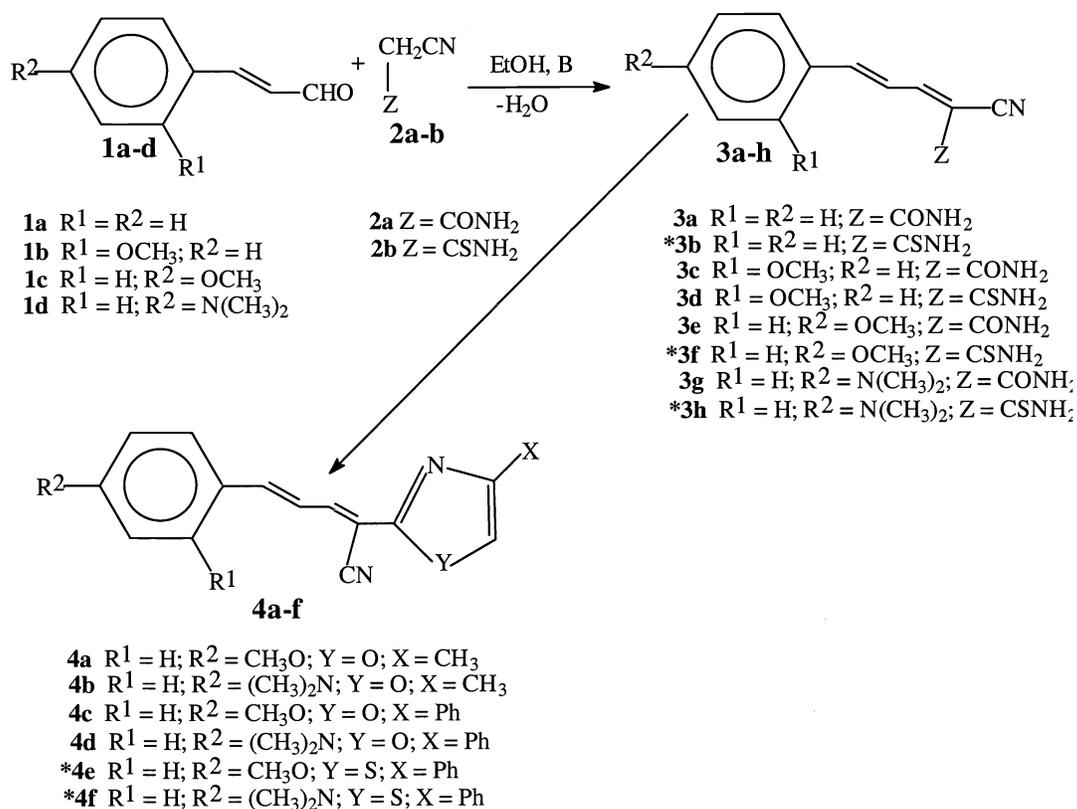


Table V. Relative energies of molecular dimers (kcal/mol)

Molecules	Dimer symmetry			Space group
	C_i	C_2	Parallel	
I $C_6H_5-CH=C(CN)_2$	0.00	0.44	2.47	$P2_1/c$
II $2-(CH_3O)-C_6H_4-CH=C(CN)_2$	0.11	0.00	2.68	$P2_1$
IV $4-(CH_3O)-C_6H_4-CH=C(CN)_2$	0.00	0.01	2.36	$P2_1/c$
V $2,4-(CH_3O)_2-C_6H_3-CH=C(CN)_2$	0.00	0.22	3.24	$P2_1/n$
VI $3,4-(CH_3O)_2-C_6H_3-CH=C(CN)_2$	0.00	0.23	1.03	P-1
VII $3,4,5-(CH_3O)_3-C_6H_2-CH=C(CN)_2$	0.00	0.25	3.49	$P2_1/c$
XIX $4-(CH_3)_2NC_6H_4-CH=CH-CH=C(CN)_2$	0.03	0.00	2.81	Pc

A slight energy preference of non-centrosymmetric dimers was found for acentric structures. On the other hand the energy difference in many cases is too small to make a firm prediction.

5. POLYMORPHISM

As a consequence of our efforts to predict crystal structure and the prominence of false minima, we have been led to look for polymorphism in many of our molecules. We have observed several examples of this phenomenon. Some of these are summarized in Table VI. As early as the 1960's it was suggested that if you can find the right conditions, most molecules will crystallize in more than one configuration⁶.

Table VI. Pairs of polymorph modifications found for NLO compounds

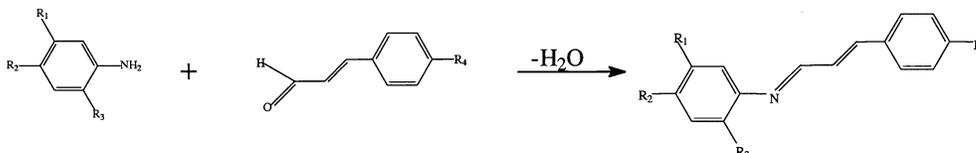
Compound	Space group	Z	Color
III 3-(CH ₃ O)-C ₆ H ₄ -CH=C(CN) ₂	P2 ₁ /c	4	red
	P2 ₁ /n	4	dark
XIX 4-(CH ₃) ₂ NC ₆ H ₄ -CH=CH-CH=C(CN) ₂	P2 ₁	6	yellow
	P-1	4	colorless
XXIV C ₆ H ₅ -CH=CH-CH=C(CN) ₂	Pn	4	colorless
	P-1	2	colorless
NO ₂ -C ₅ NH ₄ -NH-C ₈ H ₁₃	Pna2 ₁	4	yellow
2-adamantylamino-5-nitro-pyridine	Pca2 ₁	4	yellow

On one hand this phenomenon complicates modeling of potential NLO crystalline materials, and to some extent experimental investigations of such materials. For instance for compounds III, XIX and XXIV both polymorph modifications mentioned in Table VI were obtained from the same solvent. For compound XIX it was possible to separate modifications with different color manually, for compounds III and XXIV where both modifications have almost the same color, identification and separation of modifications was possible only with powder and single crystal diffraction methods.

On the other hand, modification of crystal structure by different crystallization conditions might be used as a tool in crystal engineering of NLO materials. For instance for 2-adamantylamino-5-nitro-pyridine (Table VI) the second acentric modification was found when this material was sublimed.

6. COMBINATORIAL SYNTHESIS

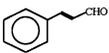
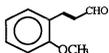
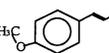
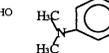
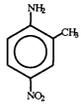
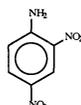
Combinatorial techniques have proven to be useful for drug synthesis, and in principle might be useful for NLO materials. Therefore, we have looked into the use of combinatorial techniques to find useful molecules for NLO materials^{7,8}. As a test group we selected a small group of Schiff's bases with potentially useful structures for NLO applications. This group proved to be an excellent choice to



demonstrate the specific advantages and disadvantages of the method. The specific compounds selected are shown in Table VII. Calculated beta values are also shown in Table VII. These values indicate that of the molecules in this series, the compounds in columns 1 and 2 are not expected to be useful materials. These compounds were not synthesized. Based on theoretical calculations, several of the compounds in columns 3 and 4 of Table VII (compounds 9-16) are expected to be potentially useful materials. A straightforward synthesis procedure was then devised that was common to all materials shown in Table VII. The conditions chosen were to combine 0.01 M of each starting material in 25ml of absolute ethanol and heat for three minutes with a catalytic amount of acetic acid.

Table VII.

Calculated magnitudes of β , $10^{-51}\text{Cm}^3\text{V}^{-2}$ for the Schiff's bases expected from condensation of amines (vertical column) and aldehydes (horizontal column)

				
	1	5	9	13
	42	49	77	134
	66	78	107	173
	59	67	101	172
	79	90	143	217

The synthesis of the Schiff's bases **9-16** was carried out and their structure was investigated by single crystal X-ray analysis. It was found that under equal conditions Schiff's bases **9-11** and **13-15** were formed as expected. In figure 1, the molecular crystal structure of one of the Schiff's bases is shown. Compounds **12** and **16**, however, did not form as expected. Compound **12** formed a complex that is shown in figure 2. Compound **16** did not form at all, and starting material was recovered. While both compounds could probably have been formed under more rigorous conditions, this observation illustrates the problem of assuming that the product formed, and proceeding, without further structural analysis. Unfortunately, all of the molecules formed in this series were found to be centrosymmetric^{7,8}, and thus their crystals are not useful for direct NLO applications.

7. MATERIAL STABILITY UNDER IRRADIATION

Finally, the question that must be asked is how stable are the materials in question to random events. Photochemical reactions and the influence of ionizing radiation are two areas to consider. For photochemical reactions, the applied radiation that is used for NLO work is generally too low in energy to be a problem. On the other hand, these materials have been optimized for second harmonic radiation, and may produce some third order radiation. These shorter wavelengths may be of high enough energy to produce photochemical reactions in susceptible molecules.

Photochemical dimerization is one of the more obvious reaction types to be considered. A 2 + 2 cyclization reaction is a well known reaction. This reaction is believed to be responsible for the photochemical condensation of A-T base pairs possibly leading to skin cancer. Orbital symmetry rules require this reaction to proceed via photochemistry rather than via a thermal route. In the crystal phase, the two groups might be lined up so as to make this an easy reaction, or they might be lined up in such a manner as to prevent the reaction from taking place.

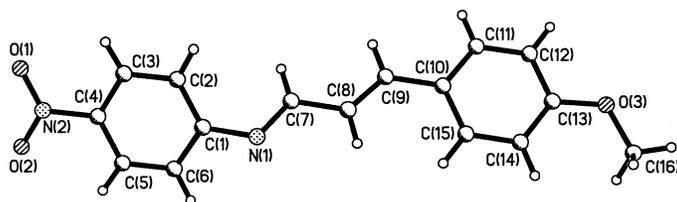


Figure 1. Molecular crystal structure of compound **10**

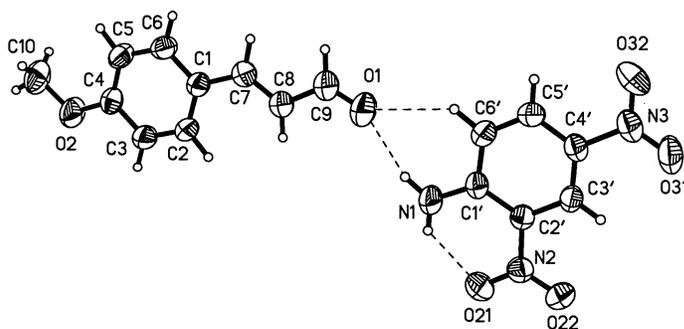
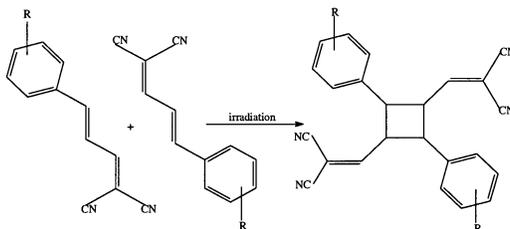
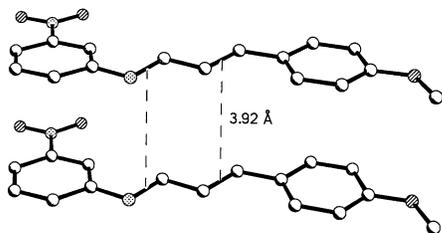


Figure 2. Molecular complex formed between dinitroaniline and methoxycinnamaldehyde

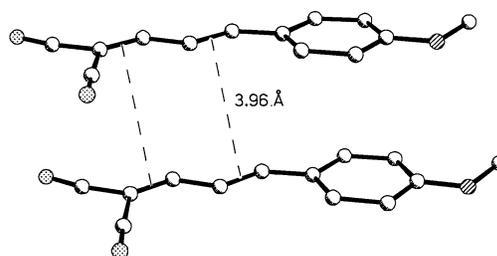
For instance solid-state photodimerisation of olefins can occur when the distances between double bonds of the neighboring molecules are $\sim 4\text{\AA}$ [see in 9]. We can suggest that in the compounds we are dealing with the reaction presented at the scheme shown below may take place in cases when molecular packing is favorable for such reaction.



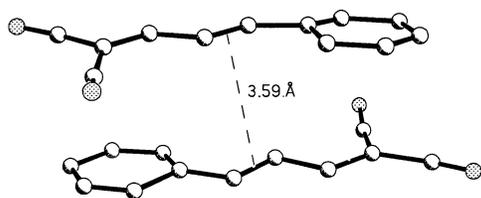
We analyzed molecular packing in two groups of the compounds described here (dicyanovinyl derivatives and Schiff's bases) and applied the above mentioned criteria for dimerization to evaluate the probability of such a process taking place. Several examples where dimerization quite is possible are shown below.



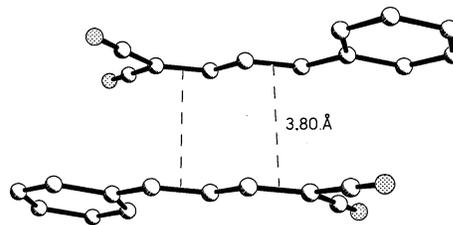
Schiff's base **9**



Dicyanovinyl derivative **XVII**



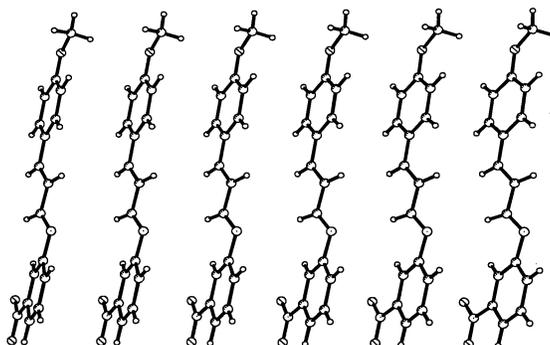
Dicyanovinyl derivative **XXIV**, form A



Dicyanovinyl derivative **XXIV**, form B

Ionizing radiation is relatively rare in practice, but in a small device, it could present a problem if the molecules are subject to reaction under those conditions. Polymerization is one of the most probable reactions. As with the photochemical reactions, it will be necessary for the molecules to be lined up properly and with the correct distances between groups for the reaction to take place. This can sometimes occur in crystals. Crystals can also keep groups apart so as to prevent reaction.

An example where molecular positions in a crystal might be favorable for solid state polymerization (Schiff's base **9**) is presented below. Intermolecular distances between double bonds in this molecular chain are less than 4.0 Å which makes solid state polymerization possible in the presence of ionizing radiation.



In most cases a side effect of a reaction taking place in a single crystal is that the crystal tends to turn to powder after the reaction is complete. In an operating device, this would be a source of failure of the device. Thus structural analysis of molecular packing may be very useful for evaluation of crystal stability under irradiation.

CONCLUSIONS

Efforts to develop improved methods of identifying candidate materials using the HYPER program and improved crystal engineering techniques are continuing.

ACKNOWLEDGEMENTS

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