Physical Properties of Gadolinium Molybdate Crystal

at Different Phase Transition Temperatures

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Abstract

The crystal **$Gd_2(MoO_4)_3$(GMO)** which has structure of 42_1m (D_{2d} group) the prototypic point group is changed into mm2 structure (C_{2v} group) (ferroic point group) around 50k temperature, again this crystal changes it's structure into mm2 (C_{2v} group) the ferroic point group, and again the structure changes into 222 (D_2 group) ferroic point group and also it changes into 2 (C_2 group) at different temperatures. These temperatures. In this paper we found the physical properties of this crystal at different phase transition temperatures.

Keywords: Phase transitions, prototypic point group, ferroic point group, ferro electric, ferromagnetic, magneto-electric polarizability

1. INTRODUCTION

$Gd_2(MoO_4)_3$(GMO) had been prepared first by Borchardt .H.J. This material was found to be ferroelectric by Borchardt and Bierstedt P.E. The space group determination carried out Prewitt C.T (in preparation) who found orthorhombic symmetry. The space group C_{2v}^8 for the ferro electric room – Temperature modification of **$Gd_2(MoO_4)_3$(GMO).** The full structure of the ferroelectric room-temperature of **$Gd_2(MoO_4)_3$(GMO)** is determined from three dimensional single crystal x-ray counter data. The Gadolinium atoms have seven nearest Oxygen neighbors at distances ranging from 2.27 to 244 A^0. All Mo atoms have a tetrahedral oxygen environment with distances varying from 1.73 to 1.8 A^0. The structure of the tetragonal sub cell as found by Abraham and Bernstein's, corresponding to the average structure of the two ferroelectric orientations, comes very close to the high – temperature (above 160C). **$Gd_2(MoO_4)_3$** is a electrical transport in rare-earth molybdates. It reveals intrinsic conduction arises due to localized impurities. This crystal is grown in Gzochralski's method. The elastic and Piezo electric constants of **$Gd_2(MoO_4)_3$** have been measured in a

temperature 100∘C to 400∘C by means of resonance- anti resonance method. The pyroelectric detection properties of $Gd_2(MoO_4)_3$ **(GMO)** stated near 150˚C ferroelectric transition temperature. Since GMO does not exhibit a dielectric anomaly, it can be used as a threshold detector by heating through the transition temperatures from a pre-selected temperature increment below the transition. The space group of $Gd_2(MoO_4)_3$ **(GMO)** is 42_1m (D_{2d}^3 group) and its phase transitions (above 160˚C) are mm2 (C_{2v}^8 group), 222 (D_2 group) and 2(C_2 group).

2.1 SYMMETRY ELEMENTS:
A symmetry element is a geometrical entity such as a line or a plane or a point about which an operation of rotation or reflection or inversion is done.

2.2 SYMMETRY OPERATIONS:
Symmetry operations of a geometric figure can easily be enumerated. They include rotations about axes, reflections and rotations reflections (or improper rotations). An important rotation is a rotation about a symmetry axis followed by a reflection in a plane perpendicular to the axis. A simple reflection may be looked upon as being a special case of a rotation reflection where the rotation is 0 to 2π. A complete set of symmetry operations in respect of any rigid body or a geometric figure will satisfy all the group postulates under the composition rule of consecutive application. When the smallest angle of rotation, which brings the body in to complete coincidence with itself, is $2\pi/p$, the corresponding axis is called a p-fold of rotation and the corresponding symmetry operation is denoted by the symbol C_p for crystals **p** takes the values **1, 2, 3, 4** and **6.**

A plane of reflection is denoted by 'σ'. The subscript 'v' or 'h' is attached to σ according as the plane of reflection contains the symmetry axis or is perpendicular to it. The symbol **Sp** stands for an operation in which a rotation of $2\pi/p$ about an axis is followed by a reflection in a plane normal to the rotation axis. The centre of inversion is designated by the symbol 'i'. The symbol c_{2x}, c_{2y} and c_{2z} are used for diagonal rotations about the co-ordinate axes x, y and z respectively. Similarly the symbols σ_x, σ_y and σ_z are used for reflections in the co-ordinate planes yz, zx and xy respectively. Identity operation, which is a rotation 0 to 2π about any axis is a symmetry operation for all bodies and is denoted by E.

2.3 PROTOTYPIC POINT GROUP:
Every time symmetric point group is a prototypic point group.

2.4 FERROIC POINT GROUP:
Let H be a point group of an orientation state "s" and a subgroup of prototypic point group $G1^1$. Then H is called the ferroic point group. .

2.5 PHYSICAL PROPERTY:
Physical properties of substances generally express the relation between two quantities. These may be scalars, vectors, second or higher order tensors. In crystals with symmetry elements, the maximum number of coefficients will be reduced.
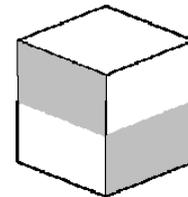
2.6 FERROIC SPEICES:

All different ways in which the elements of the ferroic point group correspond to the elements of the prototypic point group gives so many possible species and they are denoted as **G1^{1}FH.**

3. SPACE GROUP OF Gd$_2$(MoO$_4$)$_3$(GMO):
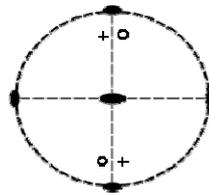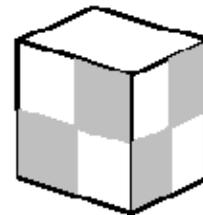
Tetragonal 42$_1$m(D$_{2d}$) form
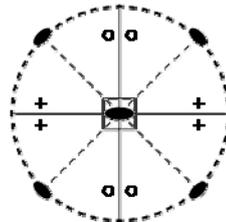
Stereograph   3D object

P42$_1$m(D$_{2d}$) product table

D$_{2d}$	E	C$_2$	2S$_4$	2C$_2$'	2σ_d		
A$_1$	1	1	1	1	1		x^2+y^2, z^2
A$_2$	1	1	1	-1	-1	I$_z$	
B$_1$	1	1	-1	1	-1		x^2-y^2
B$_2$	1	1	-1	-1	1	Z	xy

Stereograph

3D object

E	2	-2	0	0	0	(x, y), (I$_x$, I$_y$)	(xz, yz)

1.1 Orthorhombic 222(D2) form

222(D$_2$) product table

D$_2$	E	C$_2$(x)	C$_2$(y)	C$_2$(z)		
A	1	1	1	1		x^2, y^2, z^2
B$_1$	1	-1	-1	1	z, I$_z$	xy
B$_2$	1	-1	1	-1	y, I$_y$	xz
B$_3$	1	1	-1	-1	x, I$_x$	yz

1.1 Orthorhombic mm2 (C$_{2V}$)
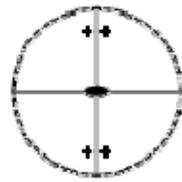
Stereograph
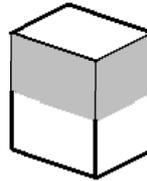
3D object

mm2 (C$_{2v}$) product table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	I_z	xy
B_1	1	-1	1	-1	x, I_y	xz
B_2	1	-1	-1	1	y, I_x	yz

1.2 Monoclinic: 2 (C$_2$)
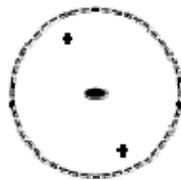
Stereograph
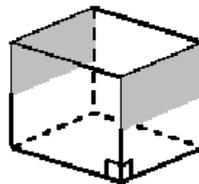
3D object

2 (C$_2$) product table

C_2	E	C_2		
A	1	1	z, I_z	x^2, y^2, z^2, xy
B	1	-1	x, y, I_x, I_y	xz, yz

2. FERRO - ELECTRICS

The materials exhibit interesting electrical properties, the binding forces in many solid materials are largely electric and ferro electrics may show up these forces in exaggerated fashion. Ferro electrics are most simply studied when the material is in crystal form. Most ferro electrics cease to be ferro electric above a temperature known as the "transition temperature". The significant characteristic of ferro electrics is dielectric non-linearity. It is represented by the polar vector with the character $\chi_\rho(R_\varphi)$; corresponding to a symmetry element R_φ in this representation, is

$$\chi_\rho(R_\varphi) = 2\cos\varphi \pm 1$$

Where the +ve and −ve signs are to be taken accordingly as the symmetry operation R is a pure rotation or a rotation reflection (Bhagavantham S. and Venkata Rayudu. T.V., 1962).

6. FERRO-MAGNETICS:

Ferromagnetic materials exhibit a long-range ordering phenomenon at the atomic level which causes the unpaired electron spins to line up parallel with each other in a region called a domain. Within the domain, the magnetic field is intense, but in a bulk sample the material will usually be unmagnetized because the many domains will themselves be randomly oriented with respect to one another. Ferromagnetism manifests itself in the fact that a small externally imposed magnetic field, say from a solenoid, can cause the magnetic domains to line up with each other and the material is said to be magnetized. The driving magnetic field will then be increased by a large factor which is usually expressed as a relative permeability for the material. There are many practical applications of ferromagnetic materials, such as the electromagnet. Ferro magnets will tend to stay magnetized to some extent after being subjected to an external magnetic field. This tendency to "remember their magnetic history" is called hysteresis. The fraction of the saturation magnetization which is retained when the driving field is removed is called the remanence of the material, and is an important factor in permanent magnets.

All ferro magnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation. This temperature is called the Curie temperature. Ferromagnetic materials will respond mechanically to an impressed magnetic field.Ferromagnetic properties are most commonly studied when the material in the crystal form. The characteristics of ferro magnetic represented by polar vector with the character $\chi_\rho(R_\varphi)$; corresponding to a symmetry element R_φ in this representation, is

$$\chi_\rho(R_\varphi) = \mathbf{1 \pm 2\cos\varphi}$$

Where +ve and −ve signs are to be taken accordingly as the symmetry operation R is a pure rotation or rotation followed by reflection. (Bhagavantham. S. and Venkata Rayudu, T.V., 1962).

7. FERRO-ELASTICS:

A ferroic crystal is said to be Ferro elastic if all or some of whose orientation states are different in spontaneous strain tensor. A Ferro elastic material has spontaneous strain and the concomitant domain structure. Ferro elasticity was first discussed by physical metallurgists in the early 1950s.

In physics, a formal description of Ferro elasticity has an independent property in its own right. We can understand Ferro elastic behaviour in a simple way by going back to the case of spontaneous distortion of a square to a rectangle. We say that the rectangle has spontaneous strain (i.e. strain occurring without the application of any mechanical stress) with respect to the square. Ferro elastic property is represented by a symmetrised stress tensor with the character $\chi_\rho(R_\varphi)$; corresponding to a symmetry element R_φ in this representation, is

$$\chi_\rho(R_\varphi) = 4\cos^2\varphi \pm 2\cos\phi$$

Where the +ve and −ve signs are to be taken accordingly as the symmetry operation R is a pure rotation or a rotation reflection (Bhagavantham, S. and Venkata Rayudu, T.V., 1962).

8. THE MAGNETO-ELECTRIC POLARIZABILITY (MEP):

The phenomenon of magneto electric polarizability is the production of a magnetic field $\hat{H}$ (or $\bar{E}$) on the application of an electric field $\bar{E}$ (or $\hat{H}$) in a direction normal to it. Following a suggestion of Landau and Lifshitz (1960) had shown that this effect is likely to appear in crystals possessing magnetic structures. Its actual occurrence has been Verified in the trioxides of chromium (Astrov, 1960) and Titanium (AL'Shin and Astrov, 1963) in their anti-ferromagnetic state. $\bar{E}$ and $\hat{H}$ connected by the relation

$$H_i = \Sigma_j \chi_{ij} E_j \ (i, j = 1, 2, 3)$$

Where χ_{ij} is represents a magneto electric polarizability tensor.

Since $\bar{E}$ is polar vector and $\hat{H}$ is an axial vector, χ is a second rank tensor whose transformation law is the same as the product of the representations of $\bar{E}$ and $\hat{H}$. Thus, the character χ_ρ (R_φ); corresponding to a symmetry element R_φ in this representation, is

$$\chi_\rho (R_\varphi) = (1 \pm 2\cos\varphi)(2\cos\varphi \pm 1)$$

Where the +ve and –ve signs are to be taken accordingly as the symmetry operation R is a pure rotation or a rotation reflection.

A ferroic crystal contains two or more equally stable domains of the same structure but of different spatial orientation. These domains can coexist in a crystal and may be distinguished by the values of components of certain macroscopic tensorial physical properties of the domains (Aizu, 1973; Newnham, 1974; Newham and Cross, 1974; Wadhamwan 1982).

9. PROPERTIES OF GADOLINIUM MOLYBDATE AT DIFFERENT PHASE TRANSITIONS:

9.1 When Crystal is in 222(D_2) Phase Transition:

The elements of P222(D_2) are E, $C_2(x)$, $C_2(y)$, $C_2(z)$.

Character Table for D_2

D_2	E	$3C_2$
$2\cos\varphi \pm 1$	3	-1
$1 \pm 2\cos\varphi$	3	-1
$4\cos^2\varphi \pm 2\cos\phi$	6	2
$(1 \pm 2\cos\varphi)(2\cos\varphi \pm 1)$	9	1

χ_ρ (Electric) = 0
χ_ρ(Magnetic) = 0
χ_ρ (Elastic) = 3
χ_ρ(Magnetoelectric polarizability) = 3
Hence Gadolinium Molybdate exhibits only elastic property with constant 3 and magnetoelectric polarizability with constant 3 in D_2 phase transition

9.2 When Crystal is in Pmm2 (C_{2V}) Phase Transition

The elements of Pmm2 (C_{2V}) are E, C_2, σ_x, σ_y

Character Table for C_{2v}

C_{2v}	E	C_2	2σ
$2\cos\varphi \pm 1$	3	-1	1
$1 \pm 2\cos\varphi$	3	-1	-1
$4\cos^2\varphi \pm 2\cos\phi$	6	2	2
$(1\pm2\cos\varphi)(2\cos\varphi\pm1)$	9	1	-1

χ_ρ (Electric) = 1
χ_ρ(Magnetic) = 0
χ_ρ (Elastic) = 3
χ_ρ(Magneto-electric polarizability) = 2
Hence $Gd_2(MoO_4)_3$(GMO) crystal exhibits electric, elastic and magneto-electric polarizability in C_{2v} phase transition but does not magnetic properties

9.3 When Crystal is in C_2 Phase transition:
The elements of C_2 are E, C_2

Character Table for C_2

C_2	E	C_2
$2\cos\varphi \pm 1$	3	-1
$1 \pm 2\cos\varphi$	3	-1
$4\cos^2\varphi \pm 2\cos\phi$	6	2
$(1\pm2\cos\varphi)(2\cos\varphi\pm1)$	9	1

χ_ρ (Electric) = 1
χ_ρ(Magnetic) = 1
χ_ρ (Elastic) = 2
χ_ρ(Magneto-electric polarizability) = 5
In C_2 phase transition $Gd_2(MoO_4)_3$(GMO) exhibits all electric, magnetic, elastic and magneto-electric polarizability.

10. CONCLUSION
These crystals $Gd_2(MoO_4)_3$**(GMO)** under different phase transitions exhibit Pseudo cubic direction rhombohedral, orthorhombic or monoclinic and this crystal exhibit "piezo-electric coefficients" and high electromechanical coupling factors.These properties make them very attractive for next generation Sensors and actuators. So these properties can be useful in under water "hydrophones" and "projectors", and in "ultrasonic transducers" for medical applications. Due to the phase transitions of the crystals Gd_2 $(MoO_4)_3$(GMO) cubic structure 42_1m (D_{2d}^3 group) (prototypic point group) is changed at around 160˚C temperature as Ortho rhombic mm2 (C_{2v} group) (ferroic point group) or tetragonal structures (222 (D_2 group) ferroic point group) and cubic structure 2(C_2 group) with different temperatures. The pyroelectric properties stated near 150˚C ferroelectric transition temperature. Because of its pyroelectric and piezoelectric properties this crystal exhibits ferro-electric, ferro-elastic, ferro-magnetic and magneto-electric polarizability (MEP) properties.

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