

MAGNETIC AND MAGNETOCALORIC PROPERTIES OF SOME RARE-EARTH BASED COMPOUNDS

Thesis submitted for the degree of
Doctor of Philosophy (Science)

in
Physics

by

Arindam Midya

University of Calcutta

December, 2014

Contents

Abstract	i
Acknowledgements	iii
1 Introduction	1
1.1 General Background	1
1.2 History	2
1.3 Magnetocaloric effect	3
1.4 Thermodynamics of the magnetocaloric effect	7
1.5 Outline of the thesis	8
2 Experimental details	13
2.1 Sample preparation	13
2.1.1 The solid-state reaction route	14
2.1.2 Travelling solvent floating zone image furnace	14
2.1.2.1 Crystal growth process	15
2.2 Sample characterization	16
2.2.1 X-ray diffraction	16
2.2.2 Thermogravimetric analysis	17
2.3 Measurement technique	17

2.3.1	Four probe resistivity	17
2.3.2	Magnetic measurements	18
2.3.2.1	SQUID-VSM magnetometer	19
2.3.2.2	Vibrating sample magnetometer	21
2.3.3	Specific heat	23
2.3.3.1	Simple model	24
2.4	Measurement of the magnetocaloric effect	25
2.4.1	Direct measurement:	25
2.4.2	Indirect measurements:	25
3	Anisotropic magnetic properties and giant magnetocaloric effect in multiferroic $RMnO_3$ crystals ($R=Dy, Tb, Ho$ and Yb)	29
3.1	Introduction	29
3.1.1	$RMnO_3$ ($R=$ rare earth)	29
3.1.1.1	Crystal structure	30
3.1.1.2	Magnetic interactions	33
3.1.2	Magnetic anisotropy	34
3.1.3	Anisotropy in cubic crystals	35
3.1.4	Anisotropy in hexagonal crystals	36
3.1.5	Physical origin of crystals anisotropy	37
3.2	Experimental techniques and sample preparation	39
3.3	Orthorhombic $DyMnO_3$ and $TbMnO_3$ systems	39
3.3.1	Results and discussions	41
3.4	Hexagonal $HoMnO_3$ and $YbMnO_3$ systems	50
3.5	Conclusions	59
4	Effect of 3d-4f spin interaction on magnetic and magnetocaloric properties in zircon-type RXO_4 ($R=Dy, Ho, Gd, Lu$; $X=V, Cr$) compounds	64
4.1	Introduction	64
4.2	Experimental techniques and sample preparation	66

4.3	Results and discussions	67
4.3.1	Structural analysis	67
4.3.2	$3d$ -LuCrO ₄ and $4f$ -DyVO ₄ systems	68
4.3.3	$(3d, 4f)R$ CrO ₄ (R =Dy, Ho, Gd) systems	74
4.4	Conclusion	81
5	Enhancement of magnetocaloric effect at low temperature due to frustration in EuR₂O₄ (R= Ho, Dy) compounds	84
5.1	Introduction	84
5.1.1	Magnetic frustration:	84
5.1.2	Crystal structure of EuR ₂ O ₄ :	86
5.1.3	Magnetic interactions in EuR ₂ O ₄ :	86
5.2	Experimental techniques	88
5.3	Results and discussions	88
5.4	Conclusions	94
6	Giant magnetocaloric effect in superconducting RuSr₂GdCu₂O₈	98
6.1	Introduction	98
6.1.1	Structure and properties of rutheno-cuprates	99
6.2	Experimental techniques and sample preparation	100
6.3	Results and discussions	101
6.4	Conclusions	109
7	Summary	113
	List of Publications	116