JOURNAL OF MATERIALS SCIENCE **40** (2005) 3745–3747

Twinning modes of $Er_2Si_2O_7$

M. A. CHOUDHRY, M. ISLAM
Department of Physics, Islamia University Bahawalpur, Pakistan

Theory of deformation twinning by Bilby and Crocker is applied to calculate the twinning elements for all possible twinning modes in monoclinic $Er_2Si_2O_7$ *TYPE C and TYPE D.* The magnitude of shear strain was also calculated for each twinning mode. The criteria of small shear strain and minimum shuffling is applied to predict the operative twinning mode for monoclinic $Er_2Si_2O_7$ TYPE *C and TYPE D.* These predications of the theory are compared with the available experimental information and may act as guideline for future experimental work.

1. Introduction

Compounds containing rare earth ions are of technological and research interest due to their optical, electrical and magnetic properties. The unique properties of this group of compounds are due to their $4f^n$ electronic states and general shielding of these orbital in the rare earth ion.

In recent years a significant amount of research work has been devoted to rare earth compounds. Fu and coworkers [1] by considering strong correlation of the 4f electrons of Erbium in Silicon have explained experimentally observed Erbium-induced impurity levels in Silicon. Optically clear single crystals of polymorphic $Er_2Si_2O_7$ have been produced [2]. In three-dimensional photonic crystals of $Er_2Si_2O_7$, photonic band gap properties are combined with the luminescence of Er and can serve as a model object to study the effect of the photonic band gap on the spontaneous emission of the radiating center [3, 4]. The developed components are used to guide, control, and possibly modify, light signals. Choi [5] has investigated the high temperature strength and oxidation behavior of $Er_2Si_2O_7$—Si_3N_4 ceramics. Erbium doped silica glass is used in telecommunication as an optical amplifier. Stokbro [6] discussed the case of $Er_2Si_2O_7$ and gave a pseudo-potential description of rare earths in oxides.

Despite all the interesting properties of rare earth disilicates, very little effort has been made to study the structures of defects at atomic level. These defects modify the properties of the crystals considerably. Twinning is a common mode of deformation observed in rare earth compounds. In this study an effort is made to explore the possible twinning modes in $Er_2Si_2O_7$, using the theory of deformation twinning of Bilby and Crocker [7]. Based on the criteria of small shear strain and simple shuffling of atoms required for twinning, possible operative twinning modes are predicted.

2. Crystal structure of $Er_2Si_2O_7$

Smolin and Shepelev [8] have extensively investigated the structures of rare earth disilicates. Maqsood and Haq [9] have investigated the crystal structure of $Er_2Si_2O_7$, and have shown various polymorphic forms of this disilicate. Felsche [10] and Maqsood *et al.* [9] followed the nomenclature of the polymorphs of rare-earth sesquioxides, designating the various structures by capital letters A, B, C, D, E, F, G.The identification of these phases is based upon the X-ray diffraction method. Now it is accepted that the structure of $Er_2Si_2O_7$ is monoclinic at room temperature, *TYPE C* and *TYPE D*.

The lattice parameters of monoclinic $Er_2Si_2O_7$ for *TYPE C* as determined by, Felsche [10] are;

$$a = 6.841\,\text{Å}$$
$$b = 9.135\,\text{Å}$$
$$c = 4.694\,\text{Å}$$
$$\beta = 101.70^\circ$$

The lattice parameters of monoclinic $Er_2Si_2O_7$ for *TYPE D* as determined by Felsche [10] are;

$$a = 5.588\,\text{Å}$$
$$b = 10.793\,\text{Å}$$
$$c = 4.689\,\text{Å}$$
$$\beta = 95.82^\circ$$

3. Twinning modes of $Er_2Si_2O_7$

A deformation twinning mode is completely defined by four elements, "K_1" the twinning plane, "K_2" the reflection plane, "η_1" the twinning direction in "K_1" plane and "η_2" the twinning direction in "K_2" plane. If K_1 and η_2 are known K_2 and η_1 can be calculated [11].

To determine the twinning modes, the analysis of Crocker and Bilby [7] was adopted. A direct primitive lattice basis C_i is chosen to define crystal structure. While reciprocal basis is given by C^j $(i, j = 1, 2, 3)$. The direct and reciprocal lattice matrices are denoted by C_{ij} and C^{ij} respectively. The direction η_1 and η_2 are represented by $u^i C_i$ and $v^i C_i$ and plane K_1 and K_2 by $h_i C^i$ and $K_i C^i$. The elements K_1 and η_2 are sufficient to define a twinning mode completely.

The magnitude of shear strain is

$$s = 2[(v^k h_i)^{-2} \cdot (d^{-2} C_{ij} v^p v^q - 1)]^{1/2} \tag{1}$$

$$d = (C^{ij} h_i h_j)^{-1/2} \tag{2}$$

where 'd' is the interplaner spacing of the twinning plane K_1. The elements K_2 and η_1 can be derived using the following equations:

$$K_2 = (C_{ij} v^p v^q) h_i - (v^k h_i) C_{ij} v^k \tag{3}$$

$$\eta_1 = (v^k h_i) C^{ij} h_i - (C^{ij} h_i h) v^k \tag{4}$$

The matrices C_{ij} and C^{ij} for monoclinic structure are given by

$$C_{ij} = \begin{pmatrix} a^2 & 0 & ac\cos\beta \\ 0 & b^2 & 0 \\ ac\cos\beta & 0 & c^2 \end{pmatrix}$$

Its reciprocal matrix is

$$C^{ij} = \operatorname{cosec}^2\beta \begin{pmatrix} a^{-2} & 0 & -a^{-1}c^{-1}\cos\beta \\ 0 & b^{-2}\sin^2\beta & 0 \\ -a^{-1}c^{-1}\cos\beta & 0 & C^{-2} \end{pmatrix}$$

Using Equations 1–4 and matrices C_{ij} and C^{ij} along with lattice parameters, the elements K_2 and η_1 and shear strains were calculated for all possible low shear-twinning modes.

The complexity of the atomic shuffling mechanism associated with a twinning mode is directly related to the number of lattice planes parallel to K_1 or K_2 which are intersected by a primitive lattice vector in the direction η_2 and η_1 respectively for Type-I and Type-II twinning [11]. If this number is q, a fraction q^{-1} of Bravais lattice point is sheared correctly when q is odd and a fraction $2(q)^{-1}$ when q is even, the remaining points have to shuffle. Thus for example no lattice shuffles are necessary when $q = 2$, but one half of the points must shuffle when $q = 4$. In case of $q = 3$, two third of the atoms shuffle. When a group of atoms are located at each lattice point additional shuffling is in general necessary.

The twinning modes with $q = 1, 2$ are more probable where no shuffling of atoms is required, while with $q = 4$, half of the atom need shuffling and have less chance of being operative. All possible twinning modes with low index planes were calculated. Only the twinning modes with small values of twinning shear 's' and q are being presented. Table I shows only 8 out of 32 possible twinning modes of monoclinic $Er_2Si_2O_7$ *TYPE C*, which have magnitude of shear strain less than 1.0. The shear modes with higher strain were omitted. Out of these 8 modes, one mode is with $q = 1$, three modes with $q = 2$ and four modes with $q = 4$. Table II also shows 8 possible twinning modes of monoclinic $Er_2Si_2O_7$ *TYPE D*, having shear strain magnitude less than 1.0. Out of these 8 modes, one mode is for $q = 1$, three modes for $q = 2$ and four modes for $q = 4$. These modes are listed in order of increasing shear strain. Twinning modes with $q = 3$ are omitted as they involve shuffling of two-third atoms.

TABLE I Twinning modes of $Er_2Si_2O_7$ *Type C*

Sr. No.	K_1	K_2	η_1	η_2	s	q
1	(1 0 0)	(1 0 −2)	[0 0 −1]	[2 0 1]	0.292	2
2	(1 0 0)	(0 0 1)	[0 0 1]	[1 0 0]	0.418	1
3	(1 1 0)	(1 1 −0.06)	[1 −1 −0.32]	[1 1 0]	0.710	2
4	(1 0 1)	(−1 0 1)	[−1 0 1]	[1 0 1]	0.788	2
5	(1 0 0)	(1 0 −4)	[0 0 1]	[4 0 1]	0.080	4
6	(0 0 1)	(−4 0 1)	[−1 0 0]	[1 0 4]	0.326	4
7	(1 1 0)	(4.7 −4.2 −1)	[1 −1 0.4]	[2 2 1]	0.659	4
8	(1 0 0)	(1 −4 1.2)	[0 −1 1.2]	[4 1 0]	0.800	4

TABLE II Twinning modes of $Er_2Si_2O_7$ *Type D*

Sr. No.	K_1	K_2	η_1	η_2	s	q
1	(1 0 0)	(0 0 1)	[0 0 1]	[1 0 0]	0.185	1
2	(1 0 1)	(−1 0 1)	[−1 0 1]	[1 0 1]	0.352	2
3	(1 0 0)	(1 0 −2)	[0 0 −1]	[2 0 1]	0.635	2
4	(0 0 1)	(−2 0 1)	[−1 0 0]	[1 0 2]	0.995	2
5	(1 0 0)	(1 0 −4)	[0 0 −1]	[4 0 1]	0.2	4
6	(0 0 1)	(−4 0 1)	[−1 0 0]	[1 0 4]	0.4	4
7	(1 2 1)	(1 −2.7 1.7)	[1 −2.1 3.2]	[1 1 1]	0.974	4
8	(1 0 0)	(2.7 10 1)	[0 −2.1 1]	[4 1 0]	0.98	4

Note: The twinning elements K_1, K_2, η_1 and η_2 of possible twinning modes of monoclinic $Er_2Si_2O_7$ at room temperature for $q = 1$, 2 and 4 and shear strain 's' is given for each mode. Conjugate modes can be constructed by interchanging the twinning elements.

4. Discussion

On inspection of Table I for $Er_2Si_2O_7$ *TYPE C*, it is evident that twinning mode 1 has largest probability to be operative. This is a mode with $q = 2$ which means no additional shuffling is required. For the twin structure of twinning mode 1 the magnitude of shear strain is 0.292 which is almost half of its closet rival that is twinning mode 2 with $q = 1$ in Table I for *TYPE C*. For mode with $q = 1$, also no additional shuffling is needed. This shear strain as predicted by theory in case of mode 1 is very small. In case of twinning mode 5 in Table I, the magnitude of shear strain is 0.08, which is very much smaller as compared with mode 1 and 2 and is almost negligible. If the criterion for a twinning mode to be operative is only shear strain then this mode should have priority. But twinning mode 5 is a mode with $q = 4$ which means half of the atoms must shuffle to form a twin structure. Complex shuffling may be a hindrance for this mode to be operative. Only experimental observation can confirm which mode is actually operative. Apparently on the basis of the criteria of small shear and no shuffling we may predict that twinning mode 1 may be operative with $K_1 = (1\ 0\ 0)$ and $\eta_2 = [2\ 0\ 1]$ in monoclinic $Er_2Si_2O_7$ *TYPE C*.

Similarly in case of $Er_2Si_2O_7$ *TYPE D*, the twinning mode with largest probability to be operative is mode 1 with twinning on (1 0 0), for which shear strain is also very small, with $q = 1$. In Table II, for $Er_2Si_2O_7$ *TYPE D*, we have twinning mode 5 with almost same magnitude of shear strain but with $q = 4$, it means for a twin structure half of the atoms need shuffling. Hence mode 5 of Table II is unlikely to be operative. Here we again predict that twinning mode 1 may be operative with $K_1 = (1\ 0\ 0)$ and $\eta_2 = [1\ 0\ 0]$ in monoclinic $Er_2Si_2O_7$ *TYPE D*, which is different from the twinning mode predicted for monoclinic $Er_2Si_2O_7$ *TYPE C*, having $\eta_2 = [2\ 0\ 1]$.

No experimental evidence for (1 0 0) twinning in $Er_2Si_2O_7$ could be traced out in literature. Some work on twinning modes of various rare earth disilicate compounds has been reported. For example Fleet *et al.* has observed complex twinning in $Dy_2Si_2O_7$ [12]. Hagiya *et al.* have observed twinning in commensurate phase of $Ca_2CoSi_2O_7$, dicalcium cobalt disilicate [13].

Twinning on (1 0 0) plane is common in monoclinic structure of various compounds. In monoclinic Linarite PbCu $(SO_4)(OH)_2$ twinning has been observed on (1 0 0) plane [14]. Similarly in Monoclinic Monazite, Ce $[PO_4]$, twinning is also observed on (1 0 0) plane [15].

The theory of Bilby and Crocker [7] has been successfully applied to monoclinic Zirconia [16] and BaYCuO [17]. Having confidence in this theory, we can safely conclude that the predicted modes of twinning in monoclinic $Er_2Si_2O_7$ are likely to be operative.

References

1. Y. FU, Z. HAUNG, X. WANG and L. YE, *J. Phys. Cond. Matter* **15** (2003) 1437.
2. A. MAQSOOD, *J. Mater. Sci. Lett.* **19** (2000) 711.
3. M. FUJII, M. YOSHIDA, Y. KANZAWA, S. HAYASHI and K. YAMAMOTO, *Appl. Phys. Lett.* **71** (1997) 1198.
4. A. J. KENYON, C. E. CHRYSSOU and C. W. PITT, *Appl. Phys. Lett.* **76** (2000) 688.
5. H. J CHOI, Y. W. KIM and J. G. LEE, *J. Mater. Sci. Lett.* **15**(4) (1996) 282.
6. LÆGSGAARD K. STOKBRO, *Phys. Rev.* B **63** (2001) 75108.
7. B. A. BILBY and A. G. CROCKER, *Proc. Roy. Soc.* **288** (1965) 241.
8. Y. U. SMOLIN and F. Y. SHEPLEV, *Acta Cryst.* **B26** (1970) 484.
9. A. MAQSOOD and I. HAQ, *J. Mater. Sci. Lett.* **6** (1987) 1095.
10. J. FELSCHE, *J. Less Common Metals* **21** (1970) 1.
11. J. W. CHRISTIAN and S. MAHAJAN, *Prog. Mater. Sci.* **39** (1995).
12. M. E. FLEET and X. LIU, *Acta. Crystallogr.* **56** (2000) 940.
13. K. HAGIYA, K. KUSAKA, M. OHMASA and K. IISHI, *J. Acta. Cryst.* **B57** (2001) 271.
14. GAINS, *et al.,* "Dana's New Minerology," 8th ed. (1997) p. 629.
15. R. SADANGA and M. BUNNO, *The Walkabashi Mineral Collection, Bulletin.* **7** (1974).
16. M. A. CHOUDHRY, *Adv. Ceram.* **12** (1983) 46.
17. *Idem., Ind. J. Pure Appl. Phys.* **28** (1990) 85.

Received 5 March
and accepted 6 December 2004