Pramāṇa - J. Phys., Vol. 34, No. 2, February 1990, pp. 151-156. © Printed in India.

Indentation studies on alkaline earth fluoride crystals at elevated temperatures

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MS received 12 May 1989; revised 11 October 1989

Abstract. Indentations have been made on the (111) planes of CaF_2, SrF_2 and BaF_2 at various temperatures up to 700°C. By etching the crystals, the indentation dislocation rosettes (IDRs) have been recorded and the relative hardness is estimated from the dimensions of the IDRs. The hardness of all these crystals falls with temperature according to the equation $H = A\exp(-BT)$. Dramatic changes are observed in the shape of the IDR at elevated temperatures indicating activation of new slip systems.

Keywords. Hardness; indentation; slip; fluorite type crystals.

PACS Nos 62·20, 61·70

1. Introduction

The hardness of a crystal is generally determined by indenting its surface with a precision-cut diamond under an applied load. The hardness is calculated from the dimensions of the indentation figure. During indentation, dislocations are generated by the deformation due to indentation. When an indented crystal surface is etched, these dislocations reveal themselves in the form of an array of etch pits. Such an array is referred to as an Indentation Dislocation Rosette (IDR). It has been pointed out that the dimensions of the IDR are related to the hardness of the crystal (Gridneva *et al* 1979). Direct measurements on the indentation provides values of hardness. A study of the IDR provides the value of relative hardness i.e., hardness of a sample in terms of the hardness of a standard. Besides, the IDRs provide information about the mobility of dislocations and slip systems. The design of a simple instrument for determination of relative hardness based on measurements on IDRs was discussed in an earlier paper (Kishan Rao and Sirdeshmukh 1984, hereinafter referred as I). Using this instrument, the variation of hardness with temperature of some alkali halides was studied (Kishan Rao and Sirdeshmukh 1985 hereinafter referred as II).

These studies have now been extended to another interesting class of crystals – the alkaline earth fluorides. The alkaline earth fluorides – CaF_2, SrF_2 and BaF_2 are ionic crystals with high melting points and have the cubic fluorite structure. These crystals have applications in infrared optics, in thin film dielectric devices and they display superionic conduction at high temperatures. Because of the simplicity of structure and bonding and the varied applications, these crystals have been the subject of a large amount of experimental as well as theoretical work (Hayes 1974). However, there is very little work on hardness and much less on its temperature variation. The microhardness of CaF_2, SrF_2 and BaF_2 was determined by Kishan Rao and Sirdeshmukh (1983) by the Vickers indentation method at room temperature. The temperature variation of hardness of CaF_2 was studied by Boyarskaya *et al* (1981) and Jain and Rawat (1982a) by the Vickers indentation method up to 500°C; in both the investigations, the hardness was found to decrease with increasing temperature. In BaF_2, Liu and Li (1964) recorded the IDR at room temperature; there is no work on the temperature variation of hardness. On SrF_2, there is no work on the temperature variation of hardness nor has the IDR been observed at any temperature.

In the present investigation, a systematic study has been made of the indentation on CaF_2, SrF_2 and BaF_2 at elevated temperatures. The study has yielded information on the temperature variation of hardness and also on the slip activation process at high temperatures.

2. Experimental

The crystals used in this study were supplied by Optovac in the form of cylinders, 10 mm in diameter, from which plates 2 mm thick with (111) faces were cleaved out. The design features of the instrument for indentation at room temperature and elevated temperatures have been described in I and II. The indented surfaces were etched with nitric acid to reveal the dislocation etch pits and IDRs. For obtaining clear etch pits, the normality of nitric acid and the time of etching had to be chosen after some trials. The optimum values of the normalities and etching times were 0·2 N and 60 min for CaF_2, 0·1 N and 40 min for SrF_2 and 0·1 N and 30 s for BaF_2. The etch pits on the (111) face are in the form of equilateral triangles with their sides along the $\langle 110 \rangle$ directions.

In I, it was shown that a relation between the hardness and linear dimension of the IDR exists in crystals with diamond structure. It was assumed in I and II that the same relation exists in crystals with the NaCl structure. It is now assumed that the relation holds in the crystals with the CaF_2 structure also.

As shown in II, the relative hardness is calculated from the relation:

$$H_t = H_{RT} l^2_{RT} / l_t^2 \tag{1}$$

where H_{RT} and H_t are the hardness values at room temperatures and temperature t and l_{RT} and l_t are the linear dimensions of the IDR at the respective temperatures. Values of 185, 163 and 149 (in units of kg/mm^2) obtained in the earlier work (Kishan Rao and Sirdeshmukh 1983) have been used for H_{RT} of CaF_2, SrF_2 and BaF_2 respectively.

A detailed discussion of the slip systems in the CaF_2 structure will be given in the next section. Here, it is sufficient to note that the IDR due to the primary slip system is triangular with its sides along the $\langle 110 \rangle$ directions. The length of the side of the triangle is taken as the linear dimension of the IDR. It will be mentioned later that at elevated temperatures, the secondary slip system introduces a change in the shape of the IDR but for purposes of hardness measurement, the IDR due to primary slip alone is considered.

3. Results and discussion

3.1 *Temperature variation of hardness*

The values of the relative hardness of CaF_2, SrF_2 and BaF_2 at different elevated temperatures, determined by the method described in §2 are shown in figure 1. In SrF_2 and BaF_2, the measurements were made up to 700°C; in CaF_2, the measurements could not be made above 400°C due to reasons discussed later in this section. In all the three crystals, the hardness decreases with temperature. The fall in hardness is fast up to about 200°C and thereafter, it is slow. The pattern of temperature variation of hardness is similar in the three crystals. Further, the temperature variation of hardness of CaF_2 determined in this study is close to the results obtained by Boyarskaya *et al* (1981) and Jain and Rawat (1982a) by the direct vickers indentation method. SrF_2 is harder than BaF_2 up to 250°C but at higher temperatures, it becomes relatively softer.

Neither Boyarskaya *et al* (1981) nor Jain and Rawat (1982a) have discussed their results on CaF_2 quantitatively. In II, it was shown that a good fit to experimental data was provided by the relation.

$$H = A \exp(-BT) \tag{1}$$

where A and B are constants characteristic of the crystal. It has been verified that the hardness values in figure 1 are represented well by (1). Plots of $\log H$ vs T are linear. From a least-squares fitting of the data, values of A and B have been obtained. The values of A and B for CaF_2, SrF_2 and BaF_2 are (6·58, 0·0055), (7·26, 0·0073) and (5·95, 0·0045) respectively. These values are of the same order as in the alkali halides (II).

3.2 *The shape of the indentation dislocation rosette*

A visual examination of the indentation dislocation rosette (IDR) provides consider-

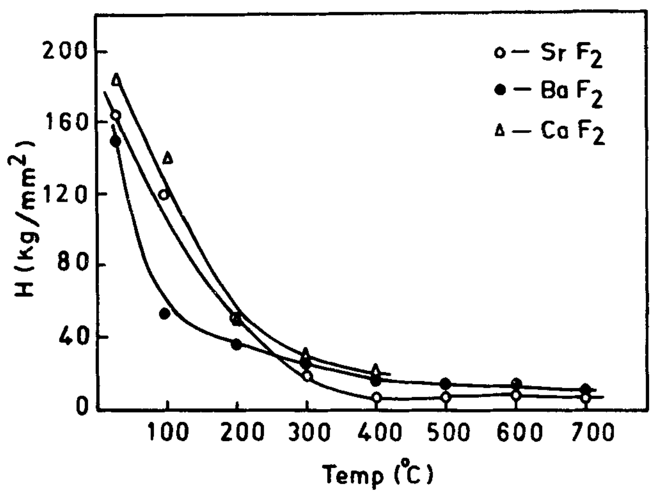

Figure 1. Variation of relative hardness (H) with temperature (T).

able information regarding the slip process. Thus, Boyarskaya *et al* (1975) observed that the IDR on the (111) face of NaCl has its arms along the ⟨110⟩ direction at room temperature and along the ⟨121⟩ directions at 160°C. A change in the mode of deformation was proposed to explain the observed change in the shape of the IDR. Similarly, Kishan Rao and Sirdeshmukh (II) observed that the IDR on the (100) face of NaCl is well-defined up to 400°C but becomes an isotropic cluster of dislocation etch pits at higher temperatures. This was attributed to the activation of new glide systems.

The slip systems for the CaF_2 structure are discussed by Chin (1975). The primary slip system is {001} ⟨$\bar{1}$10⟩; the glide traces of this system on the (111) face are along ⟨0$\bar{1}$1⟩. There is also a secondary slip system {110} ⟨$\bar{1}$10⟩; the corresponding glide traces on the (111) plane are along the ⟨$\bar{1}$10⟩ and ⟨$\bar{1}\bar{1}$2⟩ directions. Evans *et al* (1966) have suggested that in CaF_2 in addition to the primary slip system, the secondary slip also gets activated at 200°C. Boyarskaya *et al* (1981) do not make any comment except that the dislocation mobility in CaF_2 increases sharply at a temperature of 0·35 T_m, where T_m is the melting point. Jain and Rawat (1982b) observed a transition at 200°C in the surface distortion features on (111) faces of CaF_2 studied with Fizeau fringe pattern technique. Some interesting observations made in the present study are discussed below.

The IDRs on the (111) planes of the alkaline earth fluorides at some select temperatures are shown in figure 2. For convenience, we shall discuss the observations on SrF_2 and BaF_2 first and take up CaF_2 in the end. From figure 2a, it can be seen that the IDR on SrF_2 at room temperature is essentially triangular with its sides along the ⟨110⟩ directions. These three ⟨110⟩ directions are identified with the ⟨0$\bar{1}$1⟩ glide traces of the primary slip planes. There is a feeble protrusion (figure 2a) in the sides of the IDR due to the secondary slip system. These protrusions become clear at about 300°C indicating that the secondary slip system is fully activated. These protrusions form a second triangle with sides along the ⟨$\bar{1}$10⟩ glide traces of the secondary slip system. There is no dislocation motion along the ⟨$\bar{1}\bar{1}$2⟩ directions. As the temperature increases, both the slip systems contribute to the deformation and the IDR has the shape of a well-formed six-cornered star. This is seen in the IDR at 500°C in figure 2a. From the dimensions of the two sets of triangles, it is seen that the contribution of the primary slip system to the deformation is greater than that of the secondary slip system. These features are observed up to 700°C, the maximum temperature of observation in the present investigation. It may be mentioned that for the relative hardness results discussed in §3.1, measurements were made only on the triangular IDR due to the primary slip system. The results on BaF_2 are very similar to those on SrF_2. The activation of the secondary slip system takes place at 200°C itself (although in figure 2b the IDR at 300°C is shown for the sake of uniformity in presentation). A well-defined six-cornered IDR persists up to 700°C, the maximum temperature in this study.

In CaF_2, the protrusions in the sides of the triangle due to secondary slip are clearly seen at room temperature itself (figure 2c). Patel and Desai (1969) refer to IDRs on CaF_2 which are approximately triangular or hexagonal. The IDRs recorded at room temperature by Patel and Desai (1969) and in the present work reveal that the secondary slip system is already participating in deformation at room temperature. At relatively elevated temperatures, the IDRs are triangular with some distortion due to the secondary slip contribution. But surprisingly, this lasts only up to 400°C. At

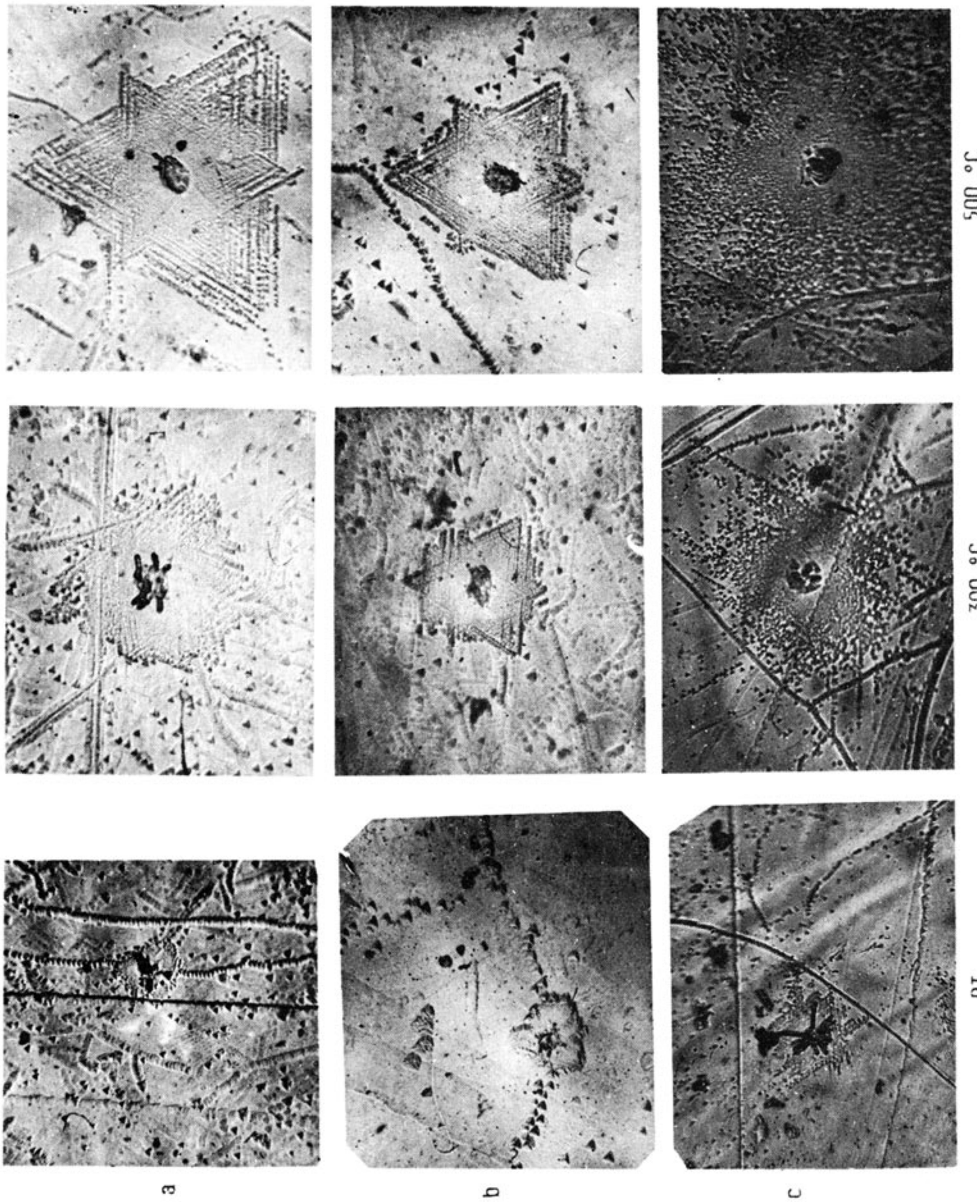

Figure 2. IDR patterns for **(a)** SrF_2, **(b)** BaF_2 and **(c)** CaF_2 crystals at different temperatures, X200.

higher temperatures the IDR is neither triangular nor six-cornered but is a mere cluster of etch pits as seen from the IDR at 500°C (figure 2c). The motion of dislocations is no longer restricted to the glide traces of either slip systems. Apparently there is cross slip and activation of a number of new, as yet, unidentified, slip systems. A similar effect was observed in NaCl (II).

Thus, the present results show that activation of the secondary slip system takes place at 300°C in SrF_2 at 200°C in BaF_2 and at about the room temperature in CaF_2. Further there is evidence that a very large number of slip systems are getting activated in CaF_2 at a temperature of about 400°C resulting in dislocation motion almost in all directions. Such an effect could not be observed in SrF_2 and BaF_2 up to 700°C but may take place at higher temperatures.

Acknowledgements

Thanks are due to the referees for numerous useful suggestions. One of the authors (KKR) is thankful to UGC, New Delhi for financial support.

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