

Lattice Thermal Expansion of Sodium Metaperiodate, NaIO₄

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The lattice parameters and the principal coefficients of thermal expansion of sodium metaperiodate have been determined at different temperatures. The temperature dependence of the two coefficients, α_a along the a axis and α_c along the c axis, could be expressed in the following forms:

$$\begin{aligned}\alpha_a &= 36.57 \times 10^{-6} + 4.89 \times 10^{-8} t + 14.19 \times 10^{-11} t^2 \\ \alpha_c &= 49.43 \times 10^{-6} + 18.42 \times 10^{-8} t - 9.22 \times 10^{-11} t^2.\end{aligned}$$

Here t is the temperature ($^{\circ}\text{C}$). The results have been compared with authors' earlier data on potassium metaperiodate. It is pointed out that the difference in the behaviour of the two isotopic crystals is due to the small but significant structural changes produced by the different sizes of the two metal ions.

In a recent communication we have reported the results of an X-ray study of the temperature variation of the lattice parameters and the principal coefficients of thermal expansion of potassium metaperiodate, KIO₄ (Deshpande, Pawar & Suryanarayana, 1967). This note gives similar results obtained for sodium metaperiodate, NaIO₄. The aim of these studies and the details of the experimental techniques have already been described in the earlier papers (Deshpande, Pawar & Suryanarayana, 1967; Deshpande & Pawar, 1962). Table 1 gives the values of the lattice parameters of sodium metaperiodate at different temperatures along with the standard errors evaluated by the method of Jette & Foote (1935).

Table 1. Values of the lattice parameters of sodium metaperiodate at different temperatures

Temperature	a	c
28.5 $^{\circ}\text{C}$	5.3387 \pm 0.0002 Å	11.9556 \pm 0.0008 Å
40.0	5.3419 \pm 0.0004	11.9637 \pm 0.0027
50.0	5.3442 \pm 0.0009	11.9660 \pm 0.0027
77.0	5.3486 \pm 0.0004	11.9909 \pm 0.0012
96.0	5.3534 \pm 0.0003	12.0042 \pm 0.0009
127.0	5.3607 \pm 0.0003	12.0267 \pm 0.0009

The values of the principal coefficients of thermal expansion at different temperatures were determined by the procedure suggested by Deshpande & Mudholker (1961) and the following expressions were obtained by the usual method of statistical treatment:

$$\alpha_a = 36.57 \times 10^{-6} + 4.89 \times 10^{-8} t + 14.19 \times 10^{-11} t^2$$

and

$$\alpha_c = 49.43 \times 10^{-6} + 18.42 \times 10^{-8} t - 9.22 \times 10^{-11} t^2.$$

Here α_a and α_c are the coefficients of expansion at $t^{\circ}\text{C}$, parallel to the a axis and the c axis respectively.

Fig. 1 gives a comparison of the temperature variation of the principal coefficients of NaIO₄ and KIO₄. It brings out prominently the similarities and differ-

ences in behaviour between the two crystals. In both the crystals the coefficient of expansion along the c axis is larger than that along any perpendicular direction, throughout the ranges of temperature covered. Such behaviour is also exhibited by calcium tungstate, CaWO₄, the only other crystal belonging to the Scheelite group for which thermal expansion data are available (Nassau & Broyer, 1962). However, the rates of the temperature variation of the two coefficients of KIO₄ are much greater than those of the coefficients of NaIO₄, suggesting that, in a general way, the

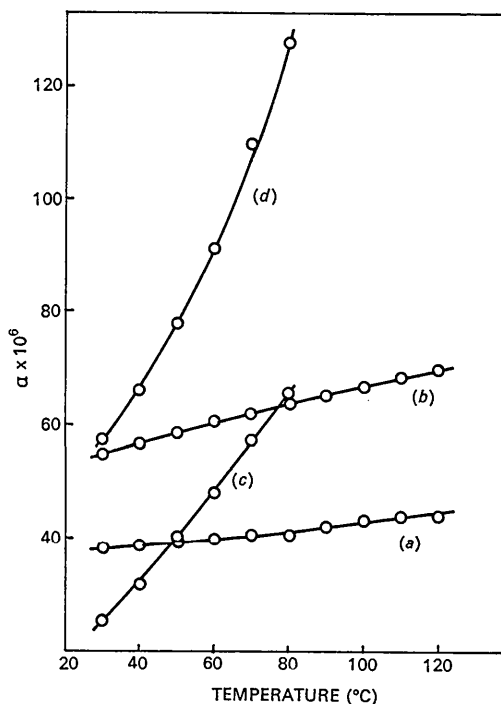


Fig. 1. Comparison of the temperature variation of the principal coefficients of thermal expansion of NaIO₄ and KIO₄. (a) α_a of NaIO₄, (b) α_c of NaIO₄, (c) α_a of KIO₄, (d) α_c of KIO₄.

weakening of the binding forces with rise of temperature is more significant in KIO_4 than in NaIO_4 .

The Scheelite group of crystals (ABO_4 type) can be said to have a complex layer structure, the layers being perpendicular to the tetragonal axis and having a two-dimensional CsCl-type arrangement of A and BO_4 ions (Arbel & Stokes, 1965). Each ion in the crystal is surrounded by eight ions of opposite sign, four lying in the layer to which this ion belongs and the other four arranged tetrahedrally around it, two from each of the two layers on either side. This structural feature offers a ready explanation for the characteristic thermal expansion behaviour of the Scheelite type crystals, namely that $\alpha_c > \alpha_a$ at all temperatures, since the ionic interactions of any ion with its neighbours of opposite sign give rise to binding forces essentially stronger along the layers than in a direction perpendicular to these (Deshpande, Pawar & Suryanarayana, 1967).

However, the structural origin of the differences in behaviour between KIO_4 and NaIO_4 mentioned above, can apparently lie in the effects produced by the different sizes of the K^+ and Na^+ ions. X-ray structural studies on KIO_4 by Hylleraas (1926) and on NaIO_4 by Hazlewood (1938) have revealed that the IO_4^- tetrahedra are not regular in these crystals. In KIO_4 the deformation is large and the tetrahedra are flat with respect to the c axis, the O-I-O angles being $121^\circ 15'$ and $103^\circ 55'$. On the other hand these tetrahedra in NaIO_4 are steep with a small departure from regularity, the angles being $107^\circ 27'$ and $110^\circ 30'$. Obviously the interionic interactions are such that the IO_4 groups do not remain and behave like rigid structures. Presumably the interionic attractions have their origin in the interactions between the metal ions and the oxygen atoms of the IO_4 groups. The flatness and the large deformation of the IO_4 groups in KIO_4 would, therefore, indicate that the attractions between a K^+ ion and the oxygen atoms from the same layer are stronger than those between this metal ion and the oxygen atoms from adjacent layers. This, in turn, would mean that the layers in KIO_4 would be strongly bound and the forces between layers would be comparatively weak. In NaIO_4 the steepness of the IO_4 tetrahedra indicates just the opposite of this but since the deformations of the IO_4 tetrahedra are small the difference between the interlayer and intralayer binding forces is not likely to be large.

This picture of the structures appears to be in good accord with the data on the thermal expansion also. The larger radius of the K^+ ions may be said to be responsible for the relatively weak electrostatic attractions in KIO_4 and hence for the pronounced tempera-

ture variation of the coefficients of its thermal expansion. The small rate of the temperature variation of the coefficients of NaIO_4 may likewise be attributed to the comparatively stronger electrostatic interactions produced by the small size of the Na^+ ions. The fact that α_a of KIO_4 at room temperature is smaller than the corresponding value of α_a of NaIO_4 may also be understood in terms of the stronger intralayer binding in KIO_4 , referred to above.

Detailed calculations of the interatomic distances in the two crystals have been made from the atomic parameters reported by Hylleraas (1926) and Hazlewood (1938). It is found that in NaIO_4 each Na^+ ion has as neighbours four oxygen atoms from the layer to which it belongs, with a tetrahedral coordination and an Na-O distance of 2.58 \AA , and four more oxygen atoms, from adjacent layers, with another tetrahedral coordination of 2.57 \AA distance. This near equality of the intralayer and the interlayer Na---O distances is in perfect agreement with the almost regular nature of the IO_4 tetrahedra in this crystal and also with its thermal expansion behaviour. Similar calculations made for KIO_4 , however, reveal that the four intralayer K-O distances are equal to 2.81 \AA and those pertaining to adjacent layers are equal to 2.76 \AA . These results agree neither with the character and magnitude of the deformations of the IO_4^- ions nor with the thermal expansion behaviour. It is possible that the position parameters of oxygen in this crystal reported by Hylleraas (1926) are in some error, resulting in an internal inconsistency of his results. A complete re-determination of the structure of KIO_4 , therefore, seems to be necessary and has been undertaken by the authors.

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