



ELECTRICAL CONDUCTIVITY OF CuBr IN THE TEMPERATURE RANGE 30-490°C

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ABSTRACT

The electrical conductivity (d.c.) of the solid CuBr was determined employing cell configuration Cu/CuBr/Cu over an extensive range of temperature (30°C-490°C), which allowed us to obtain the detail runs of conductivity, including the phase transformations: γ -CuBr \leftrightarrow β -CuBr and β -CuBr \leftrightarrow α -CuBr. Employing the measured conductivities, activation energy and pre-exponential factors were evaluated in the wide ranges of temperature. The transport properties in respective phases were discussed. The results are compared with those reported in the literature. Though, the order of magnitude of observed conductivity is same to that of literature, however, the observed value are even greater than Wojakowska and Krzyzak, which is potentially interesting.

Key words: Conductivity, CuBr, Activation energy, Phase transformation.

INTRODUCTION

Conductivity measurement of CuBr has been an important topic of research for the decades¹⁻⁶. The electrical conductivity of cuprous bromide was first studied by Friederich and Meyer⁷, who suggested that CuBr shows metallic type conduction. Later its specific conductivity was determined by Fischer⁸ using CuBr pellet sandwiched between Pt electrodes and he supported the suggestion of Friederich⁷ and Freres⁹, who studied the electrical conductivity of CuBr across the temperature 200-330°C and concluded that between these temperatures, conductivity turns gradually from metallic to pure electrolytic.

Tubandt¹⁰ studied the electrical conductivity of CuBr with respect to temperature and concluded that CuBr follows a straight line temperature - conductivity relationship. He made a distinction between electronic and ionic conductivity of CuBr suggesting that below 300°C, CuBr behaves as an electronic conductor and above this, it acts as a mixed conductor.

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Wagner and Wagner¹¹ applied the polarization technique to estimate the contribution of electronic and ionic conductivity. They concluded that electronic contribution makes only a small contribution to the total conductivity of sample equilibrated with copper above 300°C. Thus, the total conductivity is essentially ionic. Maidonovskaya et al.¹² used e.m.f. measurements and concluded that CuBr samples showed hole conductivity at 50-350°C and ionic conductivity due to Frenkel defects¹³ > 300°C. They also studied the effect of concentration of halogen to the ionic conductivity of CuBr and found that participation of ionic conductivity increased with the decrease of halogen concentration. Wojakowska, and Krzyzak¹⁴ also studied electrical conductivity of CuBr in the temperature range of 227-773°C.

The solid state structure of CuBr is temperature dependent¹⁵. γ -CuBr has the cubic zinc-blende structure¹⁵ at low temperature, which shows a mixed ionic-electronic conductivity¹¹. However, it *fait accomplie*¹⁶ that above 573 K, the electronic conductivity is negligible. The γ -phase transforms to the β -phase at 658 K having hexagonal wurtzite structure¹⁵ with a high ionic conductivity around $100 \Omega^{-1} \text{ m}^{-1}$ ^{17,18}. α -CuBr is super-ionic phase, similar to α -AgI and is stable in temperature range 742 K-759 K¹⁹⁻²¹. Buhner and Halg¹⁵ and Kvist et al.²² reported that bromide ions form a rigid bcc sub-lattice while Cu^+ ions are distributed statistically on tetrahedral positions^{15,22}. It is interesting to note that the electrical conductivity of α -CuBr is even higher than that of α -AgI at the same temperature.

Relevant review of literature^{17,18,22-25} reveals that significant work has been done on structural and transport properties of solid and molten CuBr in order to analyze structure and ionic motion in different phases. However, some detailed experimental data are still desirable. The main objective of the present work is to carry out the conductivity measurements of CuBr in a low as well as high temperature region, including the phase transition γ -phase \leftrightarrow β -phase, β -phase \leftrightarrow α -phase. In the present work, conductivity of CuBr was determined across the wide range of temperature. Cuprous halides are interesting from both; the scientific and technological point of view. Moreover, economically reason, copper compounds might be a good alternative to the silver conductors. Since, the use of CuBr for the fast ions electrolyte, due to highly mobile cuprous ions, is getting popularity and this material also seems to possess super ionic conductivity (SIC). It has its importance both academically as well as technically.

EXPERIMENTAL

Sample preparation

Cuprous bromide was prepared by treating solutions of copper sulphate-AR (Sigma) with sodium bisulphite-AR (Sigma) and potassium bromide-AR (Sigma) with continuous

stirring. This solution was poured into a large beaker containing double distilled water. Cuprous bromide was precipitated and settled down. The solution of supernatant liquid in the beaker was decanted off. The solid mass remaining in the beaker was rinsed with water and acetone for at least 3 to 4 times to remove as much cupric bromide and other impurities from the solution till the supernatant liquid was almost colorless. Cuprous bromide was vacuum filtered with the help of Buckner funnel and washed with acetone and absolute alcohol while filtering. Cuprous bromide after the filtration was dried at 50°C in vacuum oven for 10 h and was stored in vacuum desiccator for use. Before conductivity measurements, the product obtained was probed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and electron paramagnetic resonance spectroscopy (EPR) methods.

Pellet of cuprous bromide were prepared in a KBr punch and die machine (model 341-20 Loomis Engineering and Manufacturing Co. ALDWEL, N.J., U.S.A.). The diameter of the pellet was 1.16 cm and thickness was 4 mm and the area of the pellet was 1.06 cm². The electrodes and the pellets of cuprous bromide were assembled in order to charge cell of the configuration Cu/CuBr/Cu and contacts were ensured by screwing the top electrode into the bottom part of the cell. The full cell assembly was placed in oven for heating at 200°C for 4h for annealing. The cell was kept in a resistance furnace in horizontal position. A variac was used to control the temperature. The temperature of the sample was monitored by Pt-Rh thermocouple and external thermometer. The conductivities was measured at different temperature ranging between 30 to 490°C using digital conductivity meter (Hewlett Packard HP 3457A multi meter, Voltage range 30 mV-300 V with accuracy ± 0.0005 V, current range 300 μ A-1 A with accuracy ± 0.0005 A). The circuit diagram for conductivity and current is measurement shown in Fig. 1.

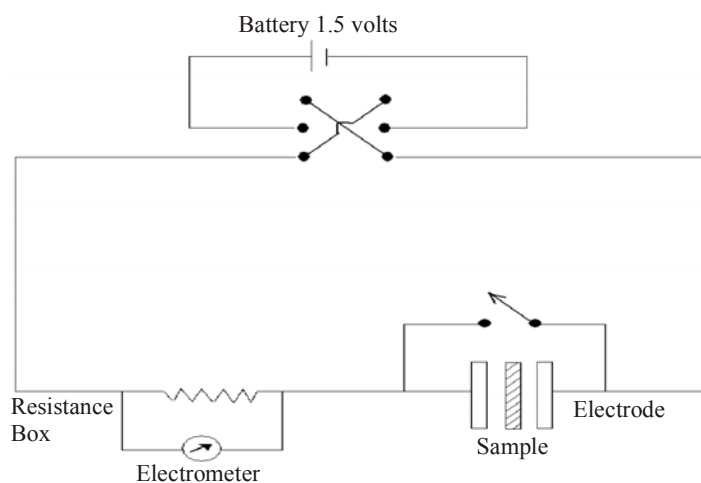


Fig. 1: Circuit diagram for conductivity and current measurement

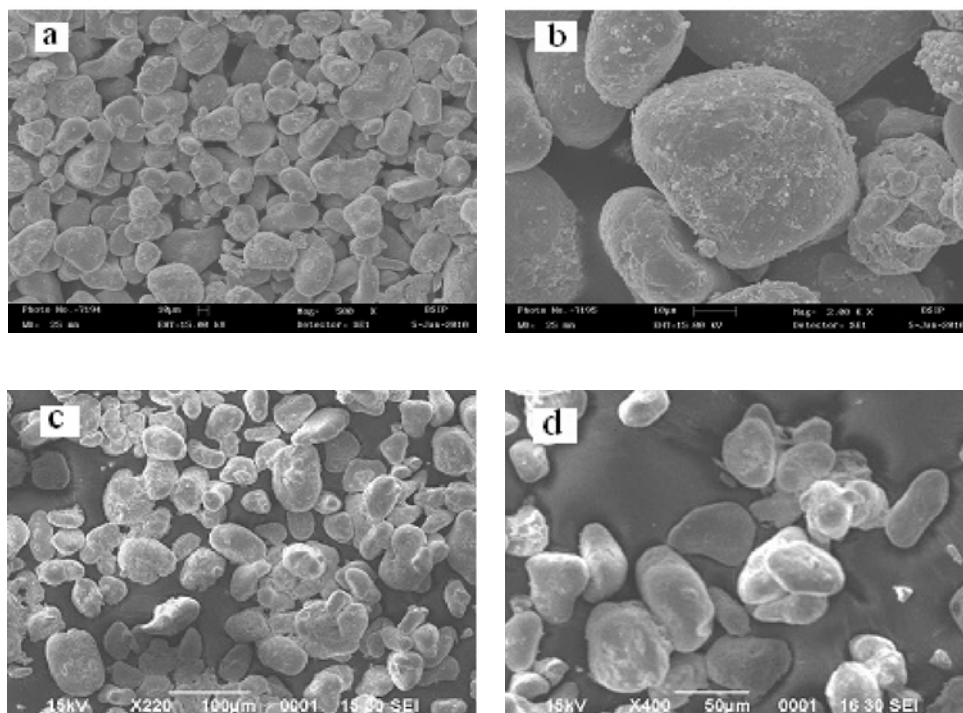
RESULTS AND DISCUSSION

Characterisation

The CuBr used in this investigation has been characterized on the basis of impurity present in it. Only Cu^{2+} impurity has been taken in account, since Cu^{2+} is only inorganic cation, which is likely to play the active role on the transport properties of CuBr. Transport property is the intrinsic property of CuBr material and effective only, when an impurity atom (bromine atom) enters into the lattice (of a given crystalline material) or produce any perturbation to the lattice by making electron deficient bond in the crystal lattice.

SEM

Fig. 2 shows the SEM images of the CuBr crystals (synthesized and standard). From the overview images, the shape of CuBr crystals can finely Core-shell sphere [Fig 2 (b) & (f)]. SEM images the sample surface by scanning it with electron beams in a raster scan pattern. The electrons interact with the sample atoms producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.



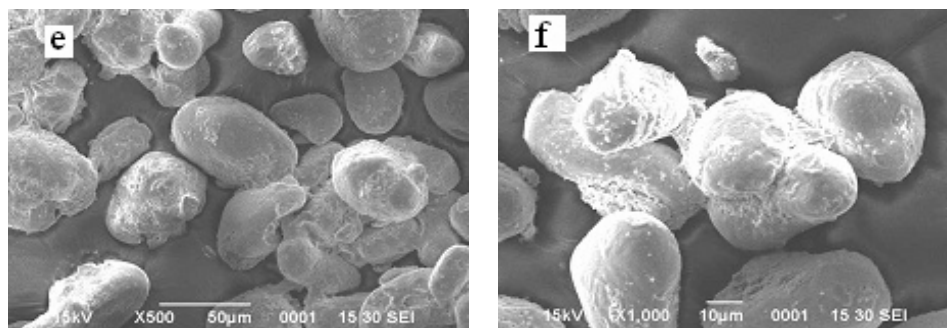


Fig. 2: SEM images of CuBr crystals: (a - b) synthesized CuBr, (c-f) are standard CuBr

A room temperature, X-ray powder diffraction pattern is shown in Fig. 3, which resembles well to that of the γ -CuBr. The XRD patterns observed are in good agreement with literature value of CuBr and the observed peaks can be attributed to the cuprous bromide γ phase^{26, 27}. The most intense peak corresponding to the centered at 27.12° , while two other relatively less intense peaks corresponding to the centered at 45.03° and 53.36° . From the literature, it is observed that X-ray diffraction pattern was found to be in good agreement with the γ -CuBr patterns, indicating that the cuprous bromide in the synthesized sample is present as the γ -phase at the room temperature.

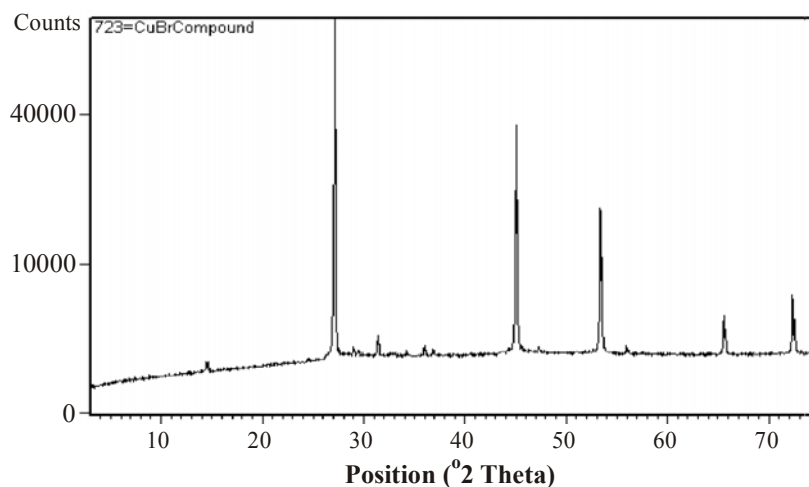


Fig. 3: Plot illustrating the XRD pattern of γ -CuBr

EPR signals were not observed in CuBr as evidenced from the EPR spectra (Fig. 4), which indicate the presences of Cu^+ in the sample. In stoichiometric cuprous bromide crystal, Cu^+ ion and Br^- ion have the configuration $3d^{10} 4s^0$ and $4s^2 4p^6$, respectively. In present sample of CuBr_x , excess bromine atoms are incorporated into cuprous bromide lattice.

Consequently, bromine atoms would interact with the electron of Cu^+ ion, as if Cu is converted to Cu^{2+} having $3d^9 4s^0$ configurations. This configuration creates an electron deficiency in copper of CuBr_x . This deficiency in copper acts as a positive hole in CuBr_x crystal, which is likely to play the active role on the transport properties of CuBr.

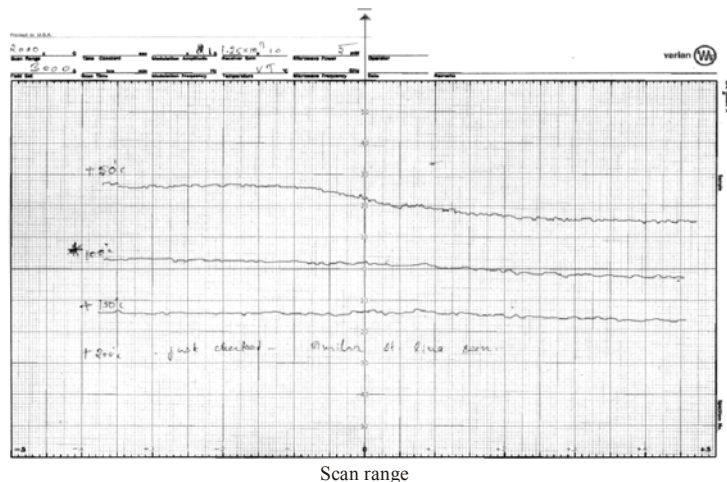


Fig. 4: EPR spectra illustrating the presence of Cu^+ ion in CuBr sample

Conductivity of CuBr as a function of temperature

Temperature relationship of the electrical conductivity of CuBr in the temperature range between 30 and 490°C is illustrated in Fig. 5 as a natural logarithm of specific conductivity $\sigma\text{-}\Omega^{-1}\text{ m}^{-1}$ versus reciprocal of absolute temperature T/K .

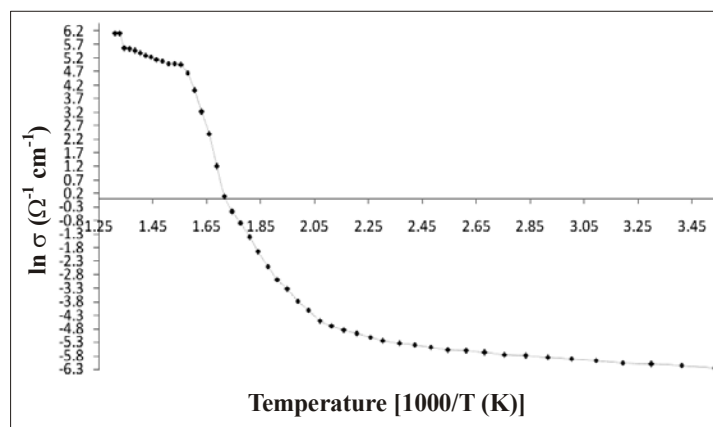


Fig. 5: Temperature dependence of the electrical conductivity of CuBr in the temperature range between 30 and 490°C

An Arrhenius type equation was found to follow the observed results of the measurements, in the ranges of temperature where the dependence $\ln \sigma = f(T^{-1})$ could be approximated with a linear function.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \quad \dots(1)$$

Pre-exponential factors and activation energies were evaluated using the equation (1) and the enthalpies of activation for conduction H_a was calculated using the equation (2).

$$\sigma = \frac{A}{T} \exp\left(\frac{-H_a}{RT}\right) \quad \dots(2)$$

where A is a constant. Observed values of pre-exponential factors, activation energies and enthalpy of activation are summarized in Table 1.

Table 1: Pre-exponential factors, activation energies and enthalpy of activation data for CuBr

Phase	Temperature range (°C)	$\ln \sigma_0 (\Omega^{-1} \text{ m}^{-1})$	$E_a (\text{kJ mol}^{-1})$	$H_a (\text{kJ mol}^{-1})$
γ	30-225	16.54	85.58	94.5647
	225-320	20.15	96.25	109.54
	320-380	29.08	145.35	148.35
β	400-460	8.98	22.45	28.67
α	475-486	5.74	2.38	8.78

It is interesting to note that our results on conductivity of γ -CuBr are similar to those reported recently in the literature (Wojakowska et al.¹⁴ and Biermann et al.²⁸). In the temperature range studied, the electrical conductivity of γ -CuBr increases instantaneously with temperature, from 2.51×10^{-3} at 50°C, 3.39×10^{-3} at 100°C, $9.1 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$ at 200°C, $2.26 \times 10^{-2} \Omega^{-1} \text{ m}^{-1}$ at 230°C to $16.08 \Omega^{-1} \text{ m}^{-1}$ at 400°C. A curvature of the Arrhenius plot (Fig. 5) illustrate that the activation energy for conduction in the γ -CuBr increases with temperature. Wojakowska and Krzyzak¹⁴ observed two slopes in the temperature range 500-590 K and 590-650 K whereas we observed one more slope at lower temperature range of

30-225°C in the addition to two slopes observed almost in the same temperature range of as those of Wojakowska and Krzyzak¹⁴. The activation energies corresponding to temperature range 30-225°C, 225-320°C and 320-380°C were found to be 85.58, 96.25 and 145.35 kJ mol⁻¹, respectively. However, last value is more nearer with those of Safadi et al.¹⁶ (154 kJ mol⁻¹ if 270°C < T < 385 °C) and Biermann and Oel²⁸ (151 kJ mol⁻¹ in the high temperature limit of the γ -phase). It is well established that at 320°C¹¹, the transference number of Cu⁺ ion starts to fall down considerably while electronic conductivity becomes more and more predominant. The enthalpy of activation for conduction of γ -CuBr, calculated for the whole range of temperature was estimated as 94.50 kJ mol⁻¹ (30-275°C), 109.54 kJ mol⁻¹ (225-320°C) and 140.35 kJ mol⁻¹ (320-380°C).

After the first phase transition γ -CuBr \rightarrow β -CuBr, the electrical conductivity attains value of 148 $\Omega^{-1} \text{ m}^{-1}$ and increases further with increase in temperature; however, it is relatively slower than in the γ -phase. To our knowledge, this is the highest conductivity ever reported, though Wojakowska and Krzyzak¹⁴ reported that the conductivity of β -CuBr to be about order of higher than that reported by Wagner and Wagner¹¹. The conductivity at 470°C is 260.5 $\Omega^{-1} \text{ m}^{-1}$. It was established^{11, 16} that β -CuBr is a purely ionic conductor. The energy of activation $E_a = 22.45 \text{ kJ mol}^{-1}$ (Table 1) is in a close agreement with the value of Safadi et al.¹⁶ of 26 kJ mol⁻¹¹⁸. The enthalpy of activation calculated from the $\ln \sigma$ versus T^{-1} relation was found to be 28.67 kJ mol⁻¹ which is close to 33 kJ mol⁻¹¹⁷, 30 kJ mol⁻¹¹⁸ and 31 kJ mol⁻¹¹⁴.

The conductivity increases by about 30% on β -phase \rightarrow α -phase transition. For α -CuBr, we found the maximum value of the electrical conductivity as 377.60 $\Omega^{-1} \text{ m}^{-1}$ at 487°C, whereas Wojakowska and Krzyzak¹⁴ reported as 348 $\Omega^{-1} \text{ m}^{-1}$ at 480°C. Energy of activation and enthalpy of activation were evaluated from $\ln \sigma T$ versus T^{-1} plot and these values were found (Table 1) as 2.38 kJ mol⁻¹ and 8.78 kJ mol⁻¹, respectively.

CONCLUSION

The conductivity of CuBr in its different phases has been determined using cell configuration Cu/pellet/Cu over a wide range of temperature. The conductivity in β -phase was found to be the highest ever reported; even higher than those reported by Wojakowska and Krzyzak¹⁴, Safadi et al.¹⁶, and Biermann and Oel²⁸ and are more than an order of magnitude higher than that of Wagner and Wagner¹¹. However, present results in γ -phase are in close agreement with the literature.

REFERENCES

1. C. Tabandt, Handbuck Der Experimental Physik, **12**, 385 (1932).
2. V. H. Vine and R. J. Mourer, Z. Physi., **198**, 147 (1951).
3. I. A. Kirovskaya, L. G. Maidanovskaya and V. L. Zhukova, Zh. Neorgan. Material, **3**, 291 (1967).
4. G. Wagner and C. Wagner, J. Chem. Phys., **18**, 68 (1950).
5. V. M. Glazov and S. N. Chizhevskaya, Zh. Neorgan. Khimii, **9**, 796 (1964).
6. E. Koch and C. Wagner, Z. Phys. Chem. (B), **38**, 295 (1937).
7. E. Friederich and W. Z. Meyer, Elektro. Chem., **32**, 566 (1926).
8. P. Z. Fiseher, Elektrochem. Angew. Physik Chem., **33**, 170 (1927).
9. J. N. Freres, Ber. Dent. Chem Ges., **61B**, 377 (1928).
10. C. Tubandt, Z. Elektrochem., **39**, 500 (1933).
11. J. B. Wagner and C. Wagner, J. Chem. Phys., **26**, 1597 (1957).
12. L. G. Maidanovskaya, I. A. Kirovskaya and G. L. Labanova, Izvest. Akad. Nauk SSSR Neorg. Mater., **3**, 936 (1967).
13. N. H. Hannay, Solid Stale Chemistry, Practice Hall, The New Jersey (1967)
14. A. Wojakowska and E. Krzyzak, Solis State Ionics, **176**, 2711 (2005).
15. W. Buhner and W. Halg, Electrochim. Acta, **22**, 701 (1977).
16. R. Safadi, I. Riess and H. L. Tuller, Solid State Ionics, **57**, 125 (1992).
17. S. Vallain, M. A. Desvals, G. Clugnet and P. Knauth, Solid State Ionics, **83**, 191 (1996).
18. M. J. Ferrante and R. R. Brown, Rep. Inveat-U.S., Bur. Mines, 8917 (1984).
19. A. Wojakowska, J. Therm. Anal., **35**, 91 (1989).
20. J. B. Boyce, T. M. Hayes and J. C. Mikkelsen Jr., Phys. Rev. B, **23**, 2876 (1981).
21. V. M. Nield, R. L. McGreevy, D. A. Keen and W. Hayes, Physica B, **202**, 159 (1994).
22. A. Kvist and A. M. Josefson, Z. Naturt Forsch, J. Phys. Sci., **23**, 625 (1968).
23. J. Trullas, A. Giro and M. Silbert, J. Phys. Condens. Matter, **2**, 6643 (1990).
24. L. G. Harrison and M. Prasad, J. Chem. Soc. Faraday Trans., **170**, 471 (1974).

25. M. Prasad, Thesis, University of British Columbia (1973).
26. Powder Diffraction File, Alphabetical Indexes for Experimental Patterns, Inorganic Phases, Sets 1-51, page 239, File No. 6-292.
27. G. Suyal, Ph.D. Thesis, INM Saarbrücken, Germany, (2002).
28. W. Biermann and H. J. Oel, *Z. Phys. Chem. (N.F.)*, **17**, 163 (1958).

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