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Structural Phase Transition in $K_{1-x}Cs_xDy(WO_4)_2$ Single Crystals

Single crystals of dysprosium potassium (caesium) double tungstates were grown both by typical flux growth and Top Seeded Solution Growth. $K_2W_2O_7$ was used as flux. Potassium tungstate provides broad range of growth temperatures, rather low volatility, and does not introduce additional components into the melt. $K_{1-x}Cs_xDy(WO_4)_2$ crystals belong to the monoclinic syngony (α -KY(WO_4)₂ structure) and has the space group C2/c. Dy^{3+} ions are situated on the two-fold axes (C_2) (which coincide with the crystallographic [010] directions) inside distorted octahedra of oxygen ions. $KDy(WO_4)_2$ is known to undergo a structural phase transition of Jahn-Teller type at 6.38K. The influence of caesium ions on structural phase transition was investigated. Spectroscopic studies of this compound at low temperature have revealed some peculiarities of optical absorption spectra. The ground state of the Dy^{3+} ions is split into Kramer's doublets with the first excited doublet lying closely to the ground doublet what determines the thermal behaviour of absorption spectra. The increase of the distance between the Dy^{3+} lowest doublets observed at low temperature is interpreted as the result of the cooperative Jahn-Teller effect.

Keywords: double tungstates, $K_{1-x}Cs_xDy(WO_4)_2$, TSSG, optical absorption, structural phase transition, cooperative Jahn-Teller effect

(Received October 20, 1999; Accepted October 26, 2000)

1. Introduction

The rare-earth double molybdates $MRe(MoO_4)_2$ ($M = K, Rb, Cs$) with low-dimensional structures in the form of chain-layered crystals are currently intensively studied (KUTKO, ANDERS). The similarly structured double tungstates have been studied to a far lesser degree despite their better mechanical properties than the ones of molybdates (lower mechanical anisotropy and higher binding energy between $(DyO_8)(WO_4)$ layers). Scientific interest in these compounds is mainly connected with the cooperative Jahn-Teller (CJT) structural phase transitions (SPT) which occur in them at low temperatures (above 4K) and complex magnetic ordering at temperatures below 1K (BOROWIEC, 1997; BOROWIEC, 1997; BOROWIEC, 1998). The SPTs of CJT type in double tungstates are unique because of very low symmetry of Jahn-Teller centres in paraelastic state (the SPTs in these compounds change paraelastic state to antiferroelastic ordered one). Some of double tungstates, e.g. $KGd(WO_4)_2$ or $KY(WO_4)_2$ are useful matrices for laser applications and for this reason are intensively investigated (MAJCHROWSKI).

Three representatives of rare-earth double tungstates ($KDy(WO_4)_2$ ($KDyW$), $RbDy(WO_4)_2$ ($RbDyW$) and $CsDy(WO_4)_2$ ($CsDyW$)) investigated earlier in our group belong to the monoclinic syngony C2/c (at 300K) (BOROWIEC, 1996; TRUNOV). Probably the highest temperature of SPT for double tungstates has been found in $CsDyW$ - it is equal to about

29K. Nevertheless, the crystallization of CsDyW is very difficult due to large radius of caesium ions - up till now the biggest obtained crystals of this compound do not exceed 300 μm in diameter. Due to this fact they cannot be used as optical materials. Therefore we decided to investigate mixed $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$ single crystals which could have properties suitable for optical purpose.

2. Crystal growth

Near 1300K double tungstates undergo an irreversible polymorphic transition to a high-temperature phase. For this reason growth of $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$ single crystals, like other materials of this group, has to be carried out from high temperature solutions. Use of flux enables to lower the temperature of crystallization below the temperature of phase transition. $\text{K}_2\text{W}_2\text{O}_7$ has been used as a high temperature solvent. It provides broad range of growth temperatures, has rather low volatility, and does not introduce additional components into the melt.

Crystallization of $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$ was carried out from solution of K_2O , Cs_2O , Dy_2O_3 , and WO_3 containing 20 mol. % of $\text{K}_{0.95}\text{Cs}_{0.05}\text{Dy}(\text{WO}_4)_2$ in $\text{K}_2\text{W}_2\text{O}_7$. Two-zone resistance furnace enabled to grow $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$ single crystals under conditions of very low temperature gradients both by spontaneous crystallization and Top Seeded Solution Growth. For one hour the melt was overheated by 100K over the temperature of crystallization to remove centres of spontaneous crystallization. Then the temperature was lowered near the temperature of crystallization and in case of TSSG $\text{KDy}(\text{WO}_4)_2$ seed was dipped into the melt. The temperature of the furnace was decreased linearly at the rate of 0.1K/h. The growing crystal was rotated at a rate of 30rpm. As a result transparent, slightly yellow crystals confined with flat planes were obtained. The shape of as grown crystals depended on the orientation of used seeds. Square or hexagonal cross-sections $2 \times 2 \text{cm}^2$ were obtained. Pulling was not used and the crystals were 5-10mm thick. The crystals showed strong tendency to cracking.

3. Structural phase transition in $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$

Investigations of cooperative Jahn-Teller type structural phase transitions were made with use of optical absorption spectral technique. The optical absorption was measured with use of PAR Lock-in Amplifier Model 5209 and Zeiss GDM 1000 monochromator. The sample was placed into Oxford Instrument Cryostat CF 1104, which allowed us to make the measurements from 3.5K to 500K with stability of about 0.2K in the LHe temperature range to 25K. The investigations were limited to the spectral region 8000 cm^{-1} to 15000 cm^{-1} with two kind of detectors: PbS from 8000 cm^{-1} to 11000 cm^{-1} and EMI S20 type photomultiplier from 11000 cm^{-1} to 15000 cm^{-1} . The resolution of the spectra was on the level of $0.4/0.5 \text{ cm}^{-1}$. The samples were cut in the form of thin plates in the *ac* crystallographic plane.

The spectra of $\text{K}_{1-x}\text{Cs}_x\text{Dy}(\text{WO}_4)_2$ versus temperature were measured in the range from 3.5K to 30K. The spectra consist of several narrow lines divided into groups of spectral multiplets what is connected with the f-f transitions between the terms of Dy^{3+} ions. The Dy^{3+} ion has the electronic configuration of $4f^9$. The ground state multiplet of Dy^{3+} ion is $^6\text{H}_{15/2}$ and in low symmetry of crystal field is fully splitted into 8 Kramer's doublets. Two lowest Kramer's doublets are placed closely one to another and they are separated by the energy distance of about 11 cm^{-1} for paraelastic state. For all spectral lines belonging to the transitions from the lowest Kramer's doublet there were observed satellite lines from low energy side on the above energy distance of 11 cm^{-1} . The intensity of low energy satellite lines depends strongly on temperature.

In Fig.1 the optical absorption spectra are presented for the region from 13240 cm^{-1} to 13300 cm^{-1} (the transition from ${}^6\text{H}_{15/2}$ to ${}^6\text{H}_{1/2}$, ${}^6\text{F}_{3/2}$). One can see clearly two lines at about 13290 cm^{-1} and 13270 cm^{-1} corresponding to the transition from the lowest doublet and the line at about 13259 cm^{-1} corresponding to the transition from first excited doublet of ${}^6\text{H}_{15/2}$ multiplet. The second line from the first excited doublet is covered by other lines and it is clearly seen in the spectral analysis of the spectrum. It can be also clearly seen in Fig.1 that between the temperature of 14K and 25K lines change their position in the irregular way. An irregular shift of lines at about 19K is observed. The magnitude of this effect reaches the value of 2 cm^{-1} .

This behaviour of the spectral lines means an increase of the energy distance between two lowest Kramer's doublets and it indicates the SPT of the CJT type discussed above that was observed firstly for some double molybdates (ZVYAGIN). With decrease of the temperature the high-energy lines are shifted by 2 cm^{-1} to higher energies and low temperature thermal satellites are shifted in opposite directions by approximately the same value. It is interpreted as a result of increasing the distance between two lowest Kramer's doublets of Dy^{3+} by about 4 cm^{-1} . The temperature of the phase transition, found in this way, lies in the expected range of temperature, between the phase transition temperatures of $\text{KDy}(\text{WO}_4)_2$ (6.4 K) and $\text{CsDy}(\text{WO}_4)_2$ (29 K).

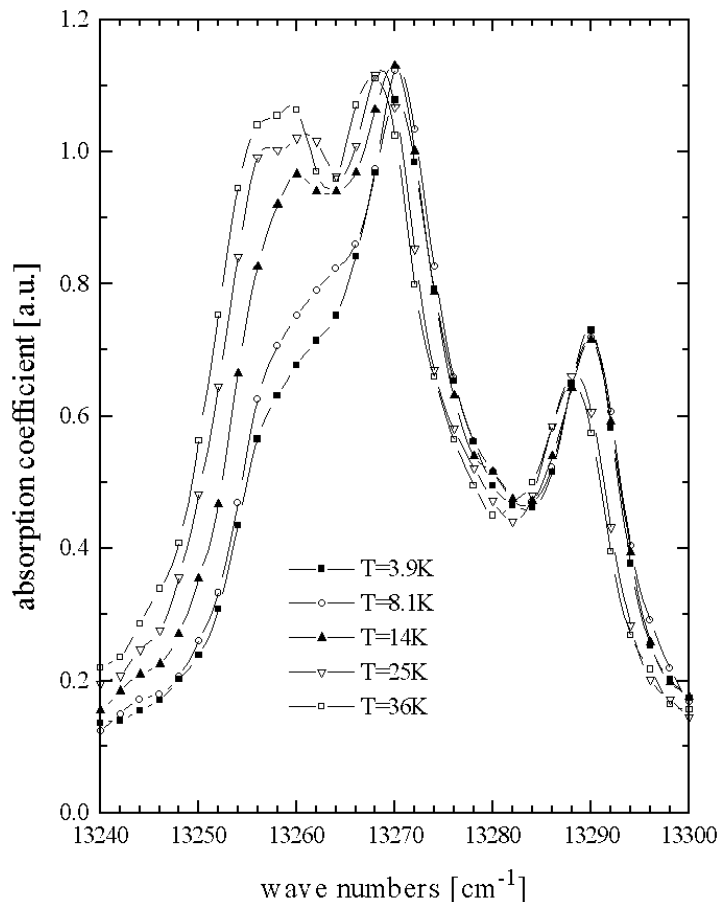


Fig. 1: Spectra of transition from ${}^6\text{H}_{15/2}$ to ${}^6\text{H}_{1/2}$, ${}^6\text{F}_{3/2}$ vs. temperature near SPT.

4. Conclusions

$K_{1-x}Cs_xDy(WO_4)_2$ single crystals have been obtained both by spontaneous crystallization and Top Seeded Solution Growth. $K_2W_2O_7$ has been used as high temperature solvent. The spectra of $K_{1-x}Cs_xDy(WO_4)_2$ versus temperature were measured in the range 3.5K to 30K. The structural phase transition occurring in this material has been found at 19K.

Acknowledgements

This work was partially supported by Polish State Committee on Science (KBN) (projects No. 2P03B 071 08 and No. 0T 00A 013 17).

References

- ANDERS E.E., KUDRYAVTSEV I.N., NEMCHENKO K.E.: Sov. Phys. Sol. State 34 (1992) 1106
BOROWIEC M.T., JEDRZEJCZAK A., SZYMCZAK H., DYAKONOV V.P., MARKOVICH V.I., PAVLYUK A.A.: Phys. Sol. State 38(7)(1996) 1229
BOROWIEC M.T., DYAKONOV V., JEDRZEJCZAK A., MARKOVICH V., NABIALEK A., PAVLYUK A., PIECHOTA S., PROKHOROV A., SZYMCZAK H.: Solid State Commun. 102(1997) 627
BOROWIEC M.T., DYAKONOV V., ZUBOV E., KHATSKO E., SZYMCZAK H.: J. de Physique I 7 (1997) 1639
BOROWIEC M.T., DYAKONOV V.P., JEDRZEJCZAK A., MARKOVICH V.I., PAVLYUK A.A., SZYMCZAK H., ZUBOV E.E., ZALESKI M.: J. Low Temp. Physics 110 (5/6) (1998) 779
KUTKO V.I., KOBETS M.I., PASHCHENKO V.A., KHATSKO E.N.: Low Temp.Phys. 21 (1995) 345
MAJCHROWSKI A., MIERCZYK Z., ZMIJA J., KOPCZYNSKI K., MICHALSKI E., CEREMUGA M.: The European Materials Conference Spring Meeting 1-4 June 1999, Strasbourg, France, CD-ROM Proceedings J-IV.2
STEFANYJ P., FEHER A.: Physica B 165/166 (1990) 465
TRUNOV V.K., RYBAKOV V.K.: J. Inorg. Chem. 19 (1974) 636
ZVYAGIN A.I., STETSENKO T.S., YURKO V.G., VAISHNORAS P.A.: PZhETF 17 (1973) 190

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